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CONTENTS

Editorial

Special issue papers

Environmental Engineering and Management Journal August 2017, Vol.16, No. 8, 1649-1650
http://omicron.ch.tuiasi.ro/EEMJ/

"Gheorghe Asachi" Technical University of Iasi, Romania

EDITORIAL

Material & Energy Recovery and Sustainable Development ECOMONDO 2016

20th International Trade Fair of Material & Energy Recovery and Sustainable Development

The papers collected in this Special Issue of *Environmental Engineering and Management Journal* were presented as lectures or posters at the scientific and technical conferences hosted by *Ecomondo 2016* held in Rimini, Italy, 8–11 November, 2016 (http://en.ecomondo.com).

Ecomondo is the second largest European exhibition in the field of *Green and Circular Economy*, with over than 105,000 delegates from 45 different nations and 1200 companies exhibiting their products and processes in a 103,000 square meters. It is hosting over than 100 conferences and workshops, ensuring a weighted and rewarding balance between sales dimension and technical-scientific dimension, with extensive room dedicated to research and innovation, education and training.

As with the previous editions, the aim of Ecomondo 2016 was to explore recent industrial advances and opportunities in waste production reduction, waste collection, fractionation, recycling, exploitation; biomass and biowaste exploitation via integrated biorefinery scheme, with the production of bioplastics, biobased chemicals and biofuels, including methane; industrial eco-design; renewable and critical resources; agri-food and forestry sustainable production and residue valorization; water resources monitoring and protection; wastewater treatment and valorization with nutrients recovery and marine resources protection; sustainable remediation of contaminated sites and marine ecosystems; indoor and outdoor air monitoring and clean up; the state of the art and perspectives of the environmental footprint and the Industrial Symbiosis; circular and smart Cities.

Ecomondo 2016 hosted over than 120 conferences, more than 800 oral communications and almost 120 papers. This special issue provides some of the key information presented and discussed in the frame of some of such conferences.

We believe that this collection of papers will be useful to people who could not participate in the Ecomondo 2016 directly. It is primarily towards those individuals that it is directed, but it also aspires to provide permanent records in process of turning environmental problems and challenges into new opportunities for a green economy with a bright future.

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Fabio Fava, born in 1963, is Full Professor of "Industrial & Environmental Biotechnology" at the School of Engineering of University of Bologna since 2005. He has about 130 papers on medium/high IF peer-reviewed international journals of industrial and environmental biotechnology, sectors in which he coordinated the FP7 projects NAMASTE and BIOCLEAN and participated in other 7 FP7 collaborative projects. He is vice-chairman of the "Environmental Biotechnology" section of the European Federation of Biotechnology (EFB). He is the Representative of the Italian Ministry of Education, University and Research in the "Working Party on Biotechnology, Nanotechnology and Converging Technologies" at OECD (Organisation for Economic Co-operation and Development), Paris, in the "European Strategy for the Adriatic and Ionian Region" (EUSAIR) and in the "Western Mediterranean Initiative" (WEST MED). He is member of the "Expert Group on Biobased Products" (DG GROW, European Commission, EC) and is the Italian Representative in the a) H2020 Programming Committee "European Bioeconomy Challenges: Food Security, Sustainable Agriculture and Forestry, Marine, Maritime and Inland Water Research" (SC2, DG RTD, EC), b) "States Representatives Group" of the "Public Private Partnership BioBased Industry" (BBI JU)(DG RTD, EC) and c) BLUEMED Strategic Board (DG RTD and DG MARE, EC). Finally, he is the scientific coordinator of the International Exhibition on green and circular economy ECOMONDO held yearly in Rimini (Italy).

Grazia Totaro, born in 1976, has a degree in Chemistry (University of Ferrara), a Master's Degree in Science, Technology & Management with a specialization in Environmental Chemistry (University of Ferrara) and a PhD in Materials Engineering (University of Bologna).

She worked at the R&D Centre of Basell Polyolefins in Ferrara for 2 years in the frame of a project addressed to the development of a novel methodology for qualitative and quantitative analysis of additives in polymers. She also worked at ARPA, Regional Agency for Environment in Ferrara, division Water Analysis. Then she started working at the school of Engineering of the University of Bologna for a Ph.D. in Materials Engineering (2007-2010). After that, she had a scholarship "Spinner 2013" in cooperation with Reagens spa (San Giorgio di Piano) on novel PVC nanocomposites. Now she is post doc fellow at the same school on new polymer-based nanocomposites from renewable sources and inorganic fillers. She also worked at the laboratoire de Chimie et Biochimie Pharmacologique et Toxicologique (Université Réné Descartes) in Paris in 2001 and was visiting professor at the Ecole Nationale Superieure de Chimie (Université Blaise Pascal, Clermont Ferrand, FR) in 2012 and 2015. Dr. Totaro has about 25 scientific papers and several participations at conferences and scientific schools. She collaborates on Ecomondo from 2013.

Maria Gavrilescu (born in 1956) is Full Professor at the Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection - *Gheorghe Asachi* Technical University of Iasi, Romania. Her research and teaching interests include: chemical and biological process engineering, biotechnology/ environmental biotechnology, environmental risk assessment and management/ industrial safety, integrated pollution prevention and control/ sustainable industrial production/ cleaner production and waste management, eco-innovation/ eco-design/ eco-technologies, environmental and sustainability evaluations. Professor Gavrilescu is PhD Supervisor in *Chemical Engineering* (since 2002) and *Environmental Engineering* (since 2009). She is author/co-author of more than 650 titles, including 46 books/chapters, 151 papers published in ISI ranked journals, ISI Proceedings and book chapters (13), other peer-reviewed journals and conference proceedings (over 140), 12 patents, keynotes, oral presentations, posters etc. Prof. Gavrilescu coordinated or worked as researcher in over 60 national and international research projects. Also, she is a founder of the *National Society of Environmental Science and Engineering*, being also member of: Editorial Advisory Board of *international journals*; *Romanian Society of Chemistry*; *European Federation of Biotechnology* (member of Experts Board of *Environmental Biotechnology* Section) etc. The scientific visibility is illustrated by over 2800 citations (H-index 25) (WOS and Scopus).

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EVALUATION OF DIFFERENT STRATEGIES FOR END-OF-LIFE LIQUID CRYSTAL DISPLAYS (LCD) MANAGEMENT

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Abstract

End-of-life liquid crystal displays (LCD) represent a potential source of secondary raw materials for their relevant content of valuable materials, like plastics and metals. Furthermore, the combination of traditional and innovative recycling processes allows the recovery of indium, defined as critical raw material by European Commission. In this context, we have evaluated the environmental impacts of different management scenarios: incineration, the current recycling strategies and more innovative options addressed at indium recovery. Currently, end-of-life monitors are recycled through two different approaches: either manual dismantling, that allows the processing of homogeneous LCD flows, or mechanical treatment, where heterogeneous flows of monitor are processed, to guarantee the continuous operation of the high capacity plant. Such difference does not allow a direct comparison among the two current recycling approaches; however, the three scenarios (incineration vs. current recycling vs. innovative strategies) were assessed for each one of the two recycling approaches. The advantage of the materials recovery was confirmed in both the cases by a life cycle assessment, which showed a whole environmental credit in the range 60-130 kg CO_2-equiv., mainly due to the avoided primary production of recovered fractions. Nevertheless, the low indium concentration and the impacts of its recovery make the innovative recycling disadvantageous, if compared to the traditional one. A metal upgrading in the panel, feasible through physical treatments, can overcome this criticality, in the case of manual dismantling. The present study confirmed the life cycle assessment as support tool for the definition of the best option of waste management.

Key words: End-of-life LCD, indium, life cycle assessment, management strategies, recycling

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1. Introduction

Nowadays, the management of waste from electric and electronic equipment (WEEE) represents a very critical issue. Indeed, such waste combines the presence of hazardous components (e.g. heavy metals, polychlorinated biphenyls, brominated flame retardants) with a significant content of valuable materials (Hense et al., 2015; Salhofer et al., 2015). The interest for WEEE is mainly due to the huge quantity placed on the market, caused by the growing production of technological equipment with a short lifespan (Yang et al., 2008). Several metals that are contained in the electronic waste were classified as critical raw materials by the European Commission, on the basis of their economic importance and their high supply risk (Brunori et al., 2015; European Commission, Enterprise and Industry, 2014). Indium is included in this list, since its production is concentrated in non-European countries, with China as the largest producer (Yang et al., 2013). This metal is mainly used, combined with tin, in liquid crystal displays (LCD), for the production of a thin film of indium–tin oxide (ITO), an optoelectronic material with the characteristics of transparency to visible light, electric conduction and thermal reflection (Li et al., 2011).

Indium concentration in LCD, in the range 100-400 ppm according to different brands and generations, makes the end-of-life equipment an interesting secondary source (Rocchetti et al., 2015). Furthermore, this kind of WEEE shows several

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recoverable fractions, mainly metals and plastic (48% and 25% of the total waste, respectively), that currently are the main recovery target of the LCD recycling processes (Amato et al., 2016). In these cases, a first treatment, carried out by either a manual or a mechanical approach, is necessary for the separation of the different fractions and the removal of hazardous components (Silveira et al., 2015). Manual dismantling is the slowest way, nevertheless, it combines a low request of energy with a satisfactory separation, that simplifies the subsequent recovery steps (Shiraishi et al., 2015).

On the other hand, the mechanical treatment has higher capacities, and several types of displays are fed to the plant to guarantee the continuity of the operation, increasing the variability of the treated flows. Usually, this process includes a series of shredding and grinding steps with the consequent production of heterogenous fractions, with different dimension and composition. Further operations allow the separation of metals, by a magnetic separator, and plastics, by density separators in wet conditions. In addition, the process produces a sludge, with a significant content of valuable materials, including indium and tin of the ITO film, managed in landfilling sites for hazardous waste. In the case of manual dismantling, the panel, containing the ITO layer, is disposed of as not-hazardous waste, after the removal of lighting system. The recent literature reports different indium recovery processes from end-of-life LCD, as that developed by Rocchetti et al. (2015), performed by an acid leaching and a cementation with zinc powder. The high efficiency of this treatment is combined with the simple design; this is considered an important advantage in the perspective of new recycling facilities located near the waste producer, that should be able to treat different typologies of waste in the same plant (Amato et al., 2016). Considering the described technologies, the present work aims at the evaluation of the environmental loads of different management strategies of the waste, that combine the current end-of-life monitor recycling (either manual or mechanical) with the indium recovery process. With this purpose, the innovative technology was compared with the baseline scenario of incineration and with the traditional recycling for the recovery of the main fractions (metals, plastics, etc.), in order to assess the sustainability of indium recovery after the traditional recycling. Considering the goal of the work and the different composition of the input flow, the three scenarios of interest were analyzed in parallel for both options (manual and mechanical recycling), without a direct comparison between manual and mechanical approach.

2. Material and methods

2.1. Strategies for LCD end-of-life management

The different strategies for the management of end-of-life displays, are shown in Fig. 1: incineration without material recovery (Scenario 1), current recycling (Scenario 2), innovative recycling with indium recovery (Scenario 3). Considering the European recovery target of 80% for informatics and communication equipment (WEEE Directive), incineration represents a baseline scenario, to highlight the positive effect of the recycling approaches. More in detail, we considered a dataset relative to an average European waste-to-energy plant for the thermal treatment with a typical technology used to meet the legal requirements. Information about waste collection, transport or any pre-treatment of the waste are not included in the data set. As concerns the starting waste, it changes its characteristics on the basis of the recycling technology: indeed, a manual dismantling allows the treatment of a homogeneous flow of LCD monitors, whereas, the high capacity mechanical treatment has a mixture of different monitors (LCD, LED, O-LED, plasma) as feed. Consequently, the two treatments show different quality and quantity of the recovered materials (e.g. plastics, steel, see Table 1) and of the disposed wastes. More specifically, the indium bearing waste is the panel (6% of the input), in the case of manual dismantling, and an indium-rich sludge (2% of the input) in the case of the mechanical treatment, currently disposed of in landfilling sites for not hazardous (the panel) and hazardous (the sludge) waste. The data related to the material balance of the mechanical plant were provided by an Italian recycler, which confirmed their accuracy as average values and also confirmed such high variability of the feed.

The innovative recycling addressed at indium recovery (scenario 3 in Fig. 1) has such indium bearing waste as feed. The technology includes a cross-current leaching by sulfuric acid and an indium recovery by zinc cementation at pH 3, achieved in the presence of sodium hydroxide (Amato et al., 2016; Rocchetti et al., 2016, 2015). In the case of the panel, it is firstly ground and washed with water, for the liquid crystal removal (Rocchetti et al., 2015). The resulting wastewater is characterized by high COD, and it needs a decontamination through a Fenton treatment, carried out using ferrous sulphate and hydrogen peroxide (Kang and Hwang, 2000). The indium-rich sludge, resulting from the mechanical treatment, does not need such washing, since it comes from a wet operation based on density separation.

2.2. Goal and scope of LCA analysis

The main goal of the LCA analysis was the evaluation of the impacts due to different strategies of end-of-life monitors management, with a focus on the innovative technology for indium recovery. As showed in Fig. 1, the system boundaries include all energy and material flows, after waste collection. On the other hand, according to PAS 2050, the production of capital goods (e.g. building of site, infrastructure and equipment, their maintenance and decommissioning) and the transport of workers, waste and products are excluded from the system boundary (BSI, 2011). The scenarios in Fig. 1a are relative to a homogeneous flow composed of only LCD, whereas, those in Fig. 1b consider a mix of LCD, OLED, LED and plasma.

For the assessment, the positive effect of secondary raw materials recovery was quantified as avoided environmental load for the primary production and reported as negative value.

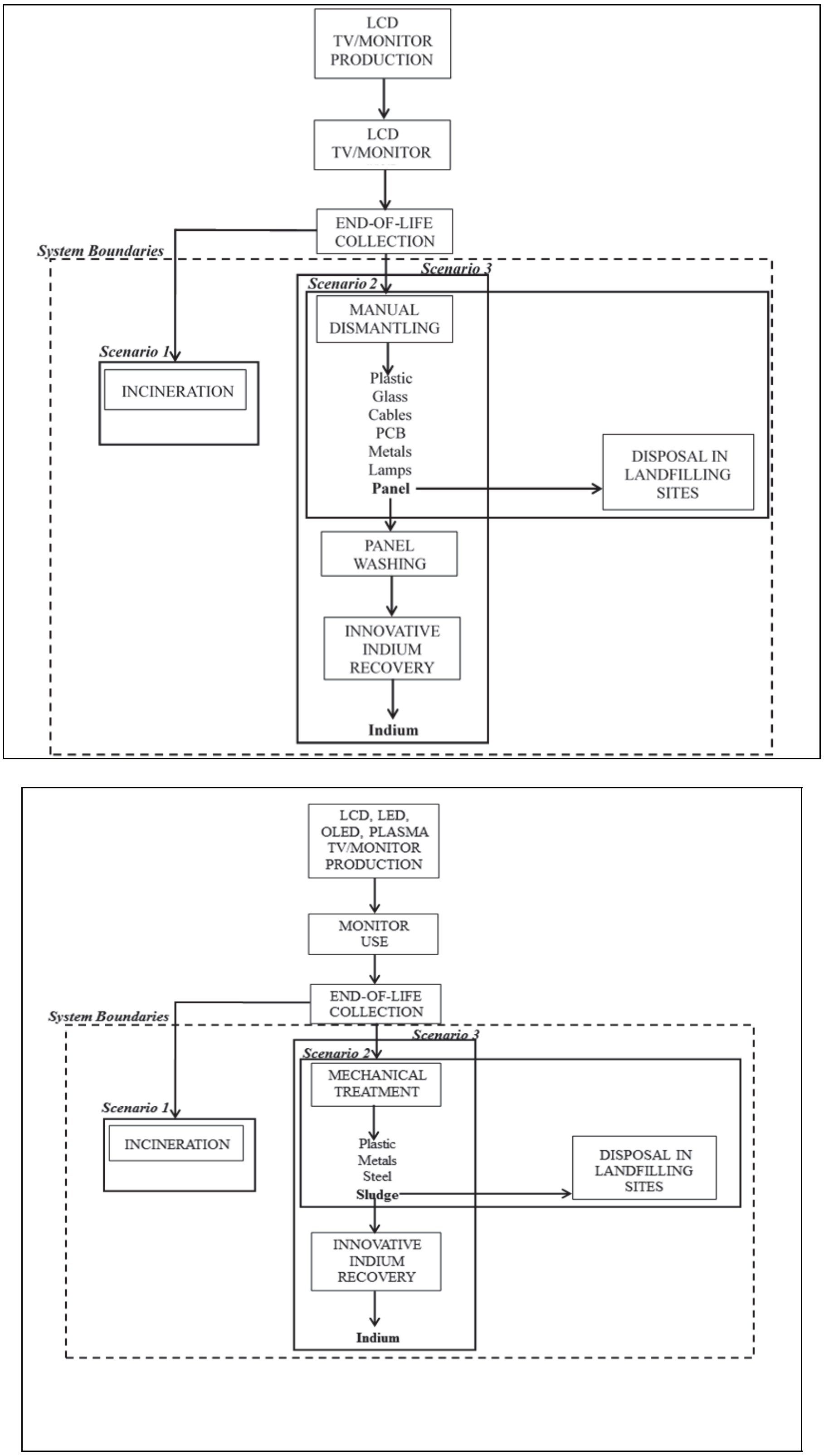


Fig. 1. System boundaries for LCA analysis in the three scenarios of interest: incineration, current recycling and innovative recycling with indium recovery in the case of a) manual dismantling and b) mechanical treatment

Table 1. Inventory data relative to 100 kg of starting waste.

Stage	*Input*	*Recovered materials*
	Manual dismantling	
Dismantling	-	Steel 23 kg, Aluminium 24 kg, Plastic 25 kg, Cables 2 kg, Printed circuit boards 8 kg, Lamps 1 kg, Glass 7 kg, Waste 4 kg, Panel 6 kg
Washing	Electricity 0.14 kWh Water 25 Ferrous sulphate 12.25 Hydrogen peroxide 8.25	-
Leaching	Electricity 0.65 kWh Sulfuric acid (98%) 2.63 Water 11.57	-
Cementation	Electricity 0.65 kWh Sodium hydroxide 1.4 Zinc 0.105	Indium 750mg
	Mechanical treatment	
Treatment	Electricity 1.19 kWh	Steel 42 kg, Aluminium 3 kg, Plastic 28 kg, Copper 12 kg, Waste 15 kg,
Leaching	Electricity 0.22 kWh Sulfuric acid (98%) 0.88 Water 3.88	-
Cementation	Electricity 0.22 kWh Sodium hydroxide 0.46 Zinc 0.035	Indium 230mg

For the attribution of the benefits, we hypothesized that the secondary raw materials are comparable, for quality and function, to the primary raw materials (Noon et al., 2011).

2.3. Methods for the LCA

The evaluation of the potential environmental loads was carried out by GaBi 6 software (thinkstep) integrated with the EcoInvent 2.2 database. The considered processes are based on European average, except electricity that uses the Italian power mix. The functional unit was 100 kg of end-of-life monitors, LCD for the first assessment and a mix of LCD, OLED, LED and plasma for the second one. The midpoint impacts of the waste management processes were evaluated according to the International Reference Life Cycle Data System (ILCD) recommendation for the life cycle impact assessment (LCIA) (ILCD, 2010).

All the results were referred to the impact category of climate change, evaluated with the Baseline model of 100 years of the IPCC, with the indicator of global warming potential (GWP100) expressed in terms of CO_2-equiv. The choice is due to the relevance of climate change issue (Dalby, 2015).

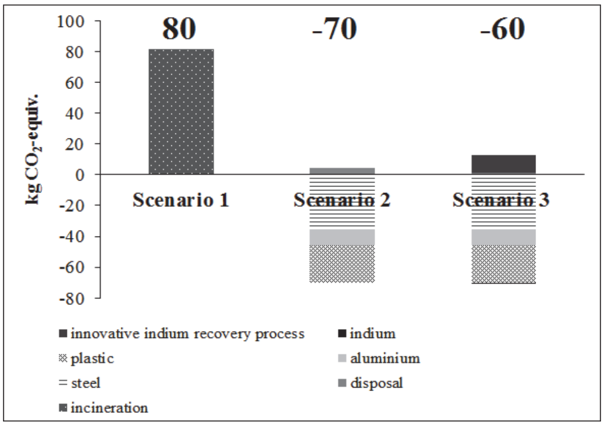
3. Results and discussion

3.1. Assessment of the different management strategies after manual dismantling

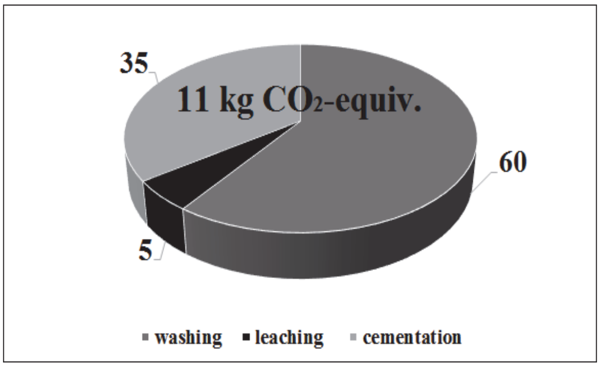
The first discussed case is the manual dismantling of end-of-life LCD. Fig. 2a shows that Scenario 1, relative to the incineration, causes the highest environmental load, with an impact of 80 kg CO_2-equiv., despite the enery recovery. This can be ascribed to a double reason: the absence of materials recovery and the emission of greenhouse gases during the combustion.

The benefit of recycling options is evident, with a small advantage of the traditional one (Scenario 2), quantified as -70 kg CO_2-equiv., versus -60 kg CO_2-equiv. of the innovative treatment (Scenario 3). In both cases, the highest positive effect is due to the recovery of steel and plastic, that represent the most abundant fractions of the total amount. In this regard, the recycling of polymeric material is a very complex issue since several types of material, with different recovery potential, can be found in LCD (Peeters et al., 2014). Furthermore, considering the composition variability connected with the equipment brand and technology, it was not possible identify a standard recycling efficiency. For this reason, we assumed a complete plastic recovery that does not modify the overall conclusion of this work. The low difference between the two scenarios (traditional recycling vs. indium recovery) can be ascribed to the low indium concentration, about 150 ppm, in LCD that can not balance the emissions of recovery treatment (Rocchetti et al., 2015). Nevertheless, as confirmed by Amato et al. (2016), this limit can be overcome by a metal upgrading in the starting waste, by a physical pretreatment.

More in details, to better understand the impacts connected with the metal recovery process, Fig. 2b shows a whole emission of 11.0 kg CO_2-equiv., with the highest contribution of about 60%, due to washing stage, in particular for hydrogen peroxide use.



(a)



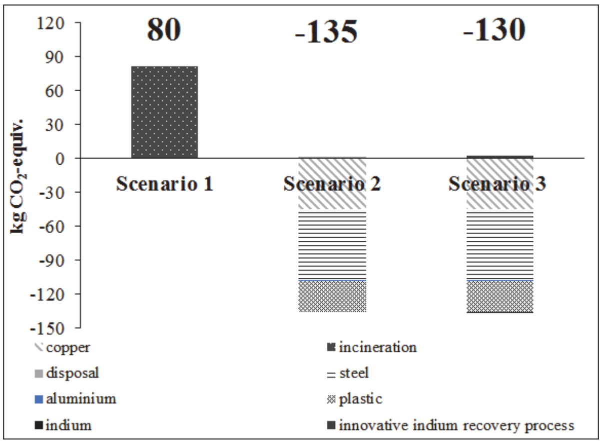
(b)

Fig. 2. Environmental loads in the impact category of global warming, a) of three considered scenarios: incineration, current recycling and innovative recycling b) with a focus on innovative indium recovery (Functional unit: 100 kg of end-of-life LCD; current recycling through manual dismantling)

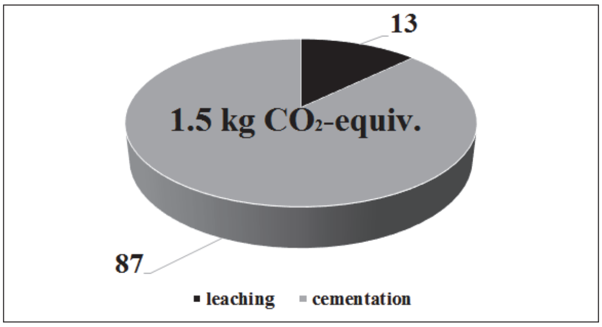
3.2. Assessment of the different management strategies after mechanical treatment

In the case of the mechanical treatment, the trend observed for the carbon dioxide emissions, is similar to the one observed for the manual dismantling, with a distinct disadvantage of the incineration strategy (Fig. 3a). As concerns Scenarios 2 and 3, the obtained results are comparable, with a whole credit around 130 kg CO_2-equiv. The highest contributions are due to the avoided primary production of: steel, plastic and copper.

As concerns indium, it is about one third of that recovered in the case of manual dismantling: indeed, the heterogeneous composition of the waste decreases the initial concentration of the metal. In addition, starting from a sludge, there is not the possibility of indium upgrading, in this case. On the other hand, the indium recovery process has an impact significantly lower in this case (about 1.5 kg CO_2-equiv) than the one observed for the treatment of the panel from manual dismantling, because the wet separation included in the mechanical treatment, makes the washing step unnecessary (Fig. 3b). Considering the avoided impact of this step, the cementation causes the highest percentage of emissions, about 87%, mainly due to the production process of sodium hydroxide.



(a)



(b)

Fig. 3. Environmental loads, in the impact category of global warming, a) of three considered scenarios: incineration, current recycling and innovative recycling b) with a focus on innovative indium recovery (Functional unit: 100 kg of end-of-life monitor, including: LCD, OLED, LED, plasma; current recycling through mechanical treatment)

3.3. Economic sustainability of indium recovery

The environmental aspect has to be considered as a priority in the modern context: indeed, the resources conservation and the decrease of emissions represent two hot topics. However, without the economic assessment of the costs and benefits associated with indium recovery, the study cannot be used for operational decisions that the responsible parties have to take in this context. In this regard, Table 2 summarizes a draft estimation of costs of raw materials and revenues, in the case of indium recovery after both the “state of the art” recycling treatments: manual dismantling and mechanical treatment.

The investment cost was omitted, in the perspective of the implementation of the technology in a flexible mobile facility, designed for the treatment of different typologies of metal bearing residues (Rocchetti et al., 2013). An average value on the market was chosen for both the costs and the revenues of the process and they refer to 1 ton of feed material to the plant (either the panel or the sludge).

It is evident that in both cases the main contribution to revenues is given by the avoided disposal of the residue rather than to the indium product, due to the low indium content.

Moreover, in the case of manual dismantling, the use of raw materials for the wastewater treatment (i.e. hydrogen peroxide and ferrous iron) have a high contribution to the total costs (around 75%) that are not balanced by the revenues. On the other hand, in the case of the mechanical treatment, the process cost considerably decrease, due to the absence of the washing step (and the consequent wastewater treatment), making the whole balance positive.

4. Conclusions

The evaluation of different strategies of end-of-life monitors management confirmed that recycling is always the best option, avoiding the primary production of materials, like steel and plastic. On the other hand, the convenience of indium recovery needs a critical analysis, due to its low concentration inside the monitors.

Indeed, in the case of a manual dismantling of the monitor, the low indium concentration in the starting waste does not balance the impacts due to the raw materials for the metal recovery process.

Table 2. Assessment of costs and revenues of indium recovery process after manual/mechanical pre-treatment

Manual dismantling			
Costs			
Input material	Unit Cost (€/kg)	Cost per ton of panel (€)	% on the total
H_2SO_4 (98%)	0.19	76	11
Zn	0.35	5	1
NaOH (30%)	0.18	36	5
H_2O	0.001	5	1
$Fe_2(SO_4)_3$	0.13	269	40
H_2O_2	0.35	240	35
Electricity	0.17 (€/kWh)	48	7
Total costs		680 €/ton of panel (40.8 €/ton of end-of-life LCD)	
Revenues			
Revenue	Unit Cost (€/kg)	Revenue per ton of panel (€)	% on the total
Indium sludge (1% In, 90% Zn)	2.60	39	19
Avoided disposal (not hazardous)	0.17	170	81
Total revenues		209 €/ton of panel (12.5 €/ton of end-of-life LCD)	
Mechanical treatment			
Costs			
Input material	Unit Cost (€/kg)	Cost per ton of sludge (€)	% on the total
H_2SO_4 (98%)	0.19	76	46
Zn	0.35	5	3
NaOH (30%)	0.18	36	22
H_2O	0.001	2	1
Electricity	0.17 (€/kWh)	47	28
Total costs		166 €/ton of sludge (3.3 €/ton of end-of-life monitor)	
Revenues			
Revenue	Unit Cost (€/kg)	Revenue per ton of sludge (€)	% on the total
Indium sludge (1% In, 90% Zn)	2.60	39	12
Avoided disposal (hazardous waste)	0.30	170	88
Total revenues		339 €/ton of sludge (6.8 €/ton of end-of-life monitor)	

This is confirmed both by the life cycle analysis and by the economic assessment, that evidence the management of wastewater as the most critical step in the indium recovery process. In the case of the mechanical treatment, it seems that traditional and innovative recycling approaches produce the same environmental credit. Nevertheless, in this case, we observed a low amount of recovered indium due to the variable waste composition. In this case, probably not only indium but also other valuable elements should be addressed; further work is needed in this direction.

The economic analysis seems to confirm an advantage of indium recovery from the sludge residue of the mechanical treatment of monitors. However, such advantage is mainly in the avoided disposal of the LCD panel. Considering the obtained results and criticality of WEEE management, the combination of traditional and innovative approaches for the end-of-life LCD exploitation represents a promising strategy in the perspective of an urban mining, where the waste become a source of secondary raw materials.

In this context, an LCA, combined with an economic assessment, was an excellent tool to evaluate the benefit of different strategies of waste management to be applied in a real context.

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PREPARATION AND CHARACTERIZATION OF NATURAL GLUES WITH CARBON NANOTUBES

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Abstract

The data presented in this work has been obtained from experimental research aiming towards the usage of natural resources of the National Park of Sila in Calabria, Southern Italy. Such resources are: "Laricio" pine resin, beeswax, mineral inert and charcoal to make natural glues. Furthermore, research has been done to find out if by using small quantities of carbon nanotubes, the strength of adhesion of prepared glues improves. Raw materials were characterized by physico–chemical techniques. In particular, the "Laricio" pine resin was characterized through the NMR techinique.
The data obtained have shown that each utilized component plays a specific role: the pine resin on the fundamental binding properties, the beeswax on the plasticity of the material, the coal and the mineral inert on raising the melting temperature, the carbon nanotubes on improvement of the adhesion resistance.

Key words: carbon nanotubes, glue, green building, pine resin

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1. Introduction

Today, about 40% of materials currently used in construction are potentially aggressive and can release volatile organic compounds (Missia et al., 2010). For this reason, it is necessary the creation of non-toxic materials, all of which must come from renewable sources and also be recyclable (Sumin et al., 2010).

Nowadays, human activities are characterized by growing dependence on enclosed spaces: in the economically advanced areas the men on average spend 90% of their lives at home, at work, at school, etc. Homes have always been played an extremely important role amongst the primary needs of mankind and even more so today, and it is obvious that their quality, including several key elements, such as air and food can radically change the quality of human life.

In order to create a house compatible with the environment, building technologies and others similar should take into account many aspects, including the usage of materials (for both production or further disposal as waste) that should be as natural as possible (Franzoni, 2001; Migliore et al., 2015; Scofieldet al. 2000; Warren and Peter, 2008). It has been proven that the environment inside homes, in particular indoor pollution is sometimes much more vital than outdoor pollution for human health. The sources of indoor pollution can be tremendously numerous and with different intensities. In the United States for example, certain human diseases are now called "Sick Building Syndrome" (Norhidayah et al., 2013; Stolwijik, 1991).

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The World Health Organization suggests that about one third of the buildings constructed in the last 30 years in industrialized countries display, from various reasons, problems that can produce disturbances to the occupants. The great development which occured in an uncontrolled manner over the past fifty years in the construction sector has led to an extensive use of synthetic materials for furniture, upholstery, flooring and building components. These materials can emit chemical substances in the air of the buildings that may generate significant negative effects on human health or on the comfort level (Apter et al., 1994; Cooley et al., 1998; de Genaro et al., 2015). For example, the emission of volatile organic compounds (VOCs) is higher at the beginning of the life of these product and tends to decrease significantly in a relatively short time (from one week for the wet products, such as paints and adhesives, to six months for other chemical compounds) (Chuck and Jeong, 2010; Hodgson et al., 1994).

A fundamental role in the construction of a healthy and safe indoor environment for ensuring a good health of the inhabitants is played by the nature of the adhesives used. Adhesives can be classified into two main groups: natural (called "glues") and synthetic (commonly called "adhesives"). The natural glues can be of plant origin, based on starch of flour and of animal origin or of proteic nature (Mathias et al., 2016). The synthetic glues (adhesives or polymers) are formed mainly from a base of real glue (the polymer) and a solvent which gives a fluid form (Packham, 2009).

The main purpose of this research was to exploit the local natural resources of the National Park of Sila in Calabria, Southern Italy, such as Laricio pine resin, charcoal, beeswax and mineral inert materials, for the preparation of natural glues. Generally, the synthetic glues have a greater glueng power than the natural ones, but have the disadvantage of being able to release potentially harmful substances such as formaldehyde, acrylates, volatile organic compounds (VOCs). For this reason, our research also considered the possibility of using a small amount of carbon nanotubes added to natural mixtures in order to improve the adhesion strength of the glues.

The carbon nanotubes (Iijima, 1991; Radushkevich et al., 1952) are carbon allotropic form and are potentially useful materials with wide variety of applications in nanotechnology, electronics, optics and other fields of materials science as reinforcing fibers. Due to their chemical composition and structure, carbon nanotubes do not release volatile substances into the environment, although nanometric materials should always be used with caution to avoid their dispersion (Lopez de Ipina et al., 2015; Maynardet al., 2006; Pacheco-Blandino and Vanner, 2012). Therefore, the possibility of finding a compromise between the use of a small amount of carbon nanotubes to prepare glues consisting mainly of natural compounds but having a better adhesion strength, has been explored. The glues without carbon nanotubes could be applied, for example, in the preparation of woody multi-layered panels for green building, while the glues containing carbon nanotubes could be used for the preparation of woody layered panels with usual destinations. In the end, in both cases, there is the advantage to use local resources to prepare glues composed of natural components. It is also important to underline that the quantities of carbon nanotubes used are very low and also these are incorporated into the resin matrix and therefore without any possibility of dispersion.

Currently, the costs of the carbon nanotubes are highly variable and depend very much on the degree of purity. It is possible, however, to predict that when production would be industrialized, the costs will not be as high, while raw materials and technology for their preparation are not very expensive.

2. Material and methods

The work was carried out in several steps. Initially, the raw materials were chosen and characterized. The raw materials used were: pine resin, beeswax, vegetable carbon and a natural mineral inert. In addition, carbon nanotubes were used as additives for some blends. For the characterization of the raw materials, physico-chemical instrumentation as: nuclear magnetic resonance (NMR), X-ray diffraction (XRD), thermal analysis (TGA; DTA) and scanning electron microscopy (SEM) were used. Subsequently, different mixtures were prepared by varying the nature and quantities of the components. On each of the systems prepared, three properties that are important for the use and implementation of the glue were evaluated: the melting temperature ranges using a pyrometer (Gallenkamp), the compressive strength of the cold mixtures using a compressive tester (Vanderkamp VK 200), and the strength of adhesion of the glues on wood test specimens using tear-off-adhesive tester.

2.1. Characterization of raw materials

The preliminary characterization of the raw materials was essential for a complete analysis and preparation of the glue.

2.1.1. Laricio pine resin

Particular attention has been given to the characterization of pine resin using different physico-chemical techniques, including even nuclear magnetic resonance (NMR) of which, to date there are few studies.

The resin used in this research has been extracted from the pine "Pinus nigra" which is an arboreal subspecies of "Laricio pine", which lives on the plateau silane of the Calabria region of Southern Italy. It is a species that belongs to the largest species of the black pine, commonly referred to as “The

Calabrian pine", "Silane pine" and "Laricio Silane pine". The exact name is "Laricio Calabrian black pine" (Cannac et al., 2009; Muscolo et al., 2007; Picchio et al., 2011). The resins are a heterogeneous set of organic substances that can change depending on the tree species, the place and the seasonality. Variability of natural resources are well-known. However, if we take into consideration some restricted areas of origin of these resources, variation decreases. The resins were collected in the highland of the Sila, basically from 20 trees, thus to be homogenized. The resin used was preliminarily characterized (Fig. 1a).

The XRD spectra of the pine resin (Fig. 1b) do not show significant peaks, confirming the amorphous nature of the substance. The thermal analyses were carried out on the resin up to a temperature of 130 °C. The thermal TG and DTG curves (Fig. 1c) showed a steady loss of weight up to 130°C of about 6.5%, to be charged to desorption of molecule of low molecular weight. The slope of the quite sharp curves shows that the losses are very fast. The DTG curve, presents a peak at about 27°C. The DTA curve (Fig. 1d) has three endothermic peaks: the first one at about 31°C due to the evaporation of residual moisture and small molecules, the second one at 75 °C and the third one, the more marked one, at a temperature above 120°C, due to removal of heavier molecules.

Nowadays, NMR spectroscopy is a robust, rapid and reliable analytical technique useful to determine chemical profiles of complex natural matrices used as raw materials for industrial scopes and of final products destined to markets (Leggio et al., 2012; Siciliano et al., 2013). In this work routine one-dimensional 1D high-resolution ^{1}H-NMR spectroscopy was applied to investigate the chemical composition of the resin case of study obtained from *Pinus nigra* ssp. *laricio* (Poir) living in Calabria, Southern Italy. Pine resins are widely used as natural materials to produce polymers, elastomers, paints, and glues. It is known that the physico-chemical characteristics of these industrially manufactured products strongly depend on the chemical composition of the starting resin (de Carvalho et al., 2008). The target of our instrumental analysis was the qualitative identification of the principal and most abundant chemical components present in the resin.

There are not many cases for ^{1}H-NMR spectroscopy application to the analysis of pine resin acids. ^{13}C-NMR spectra have been recorded for individual resin acids and their mixtures, as well as for some types of whole pine resins (Skakovskii et al., 2008). Numerous 20-carbon bicyclic, tricyclic, and macrocyclic diterpenoids of differently functionalized skeletal types (abietanes, pimaranes, labdanes, podocarpanes) are reported to be the principal chemical components of pine resins (Yang et al., 2010), and several chemical profiles supported by gas-chromatography coupled to mass spectrometry have already been reported in the literature for a restricted number of pine species of different geographical origins, e.g. pine resin from of *Pinus nigra* ssp. *laricio* from Corsica (Rezzi et al., 2005).

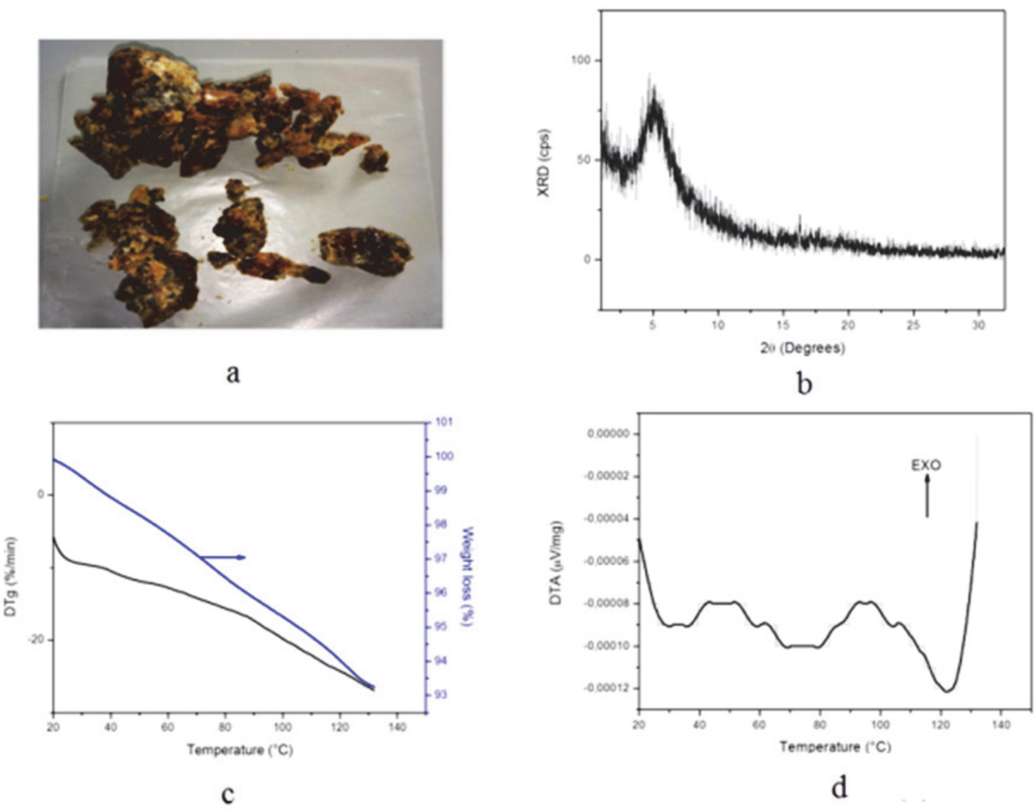


Fig. 1. (a) Laricio pine resin; (b) X-ray diffraction spectrum of the pine resin; (c) Differential thermogravimetric curve (DTg) and %weight loss (TG) of pine resin; (d) Differential thermal analysis curve (DTA) of pine resin

Literature confirms that conifers generally produce pimaric, isopimaric, levopimaric, sandaracopimaric, abietic, dehydroabietic, neoabietic, and palustric acids. In some cases, agathic, isocupressic, and (Z)-communic acids were also found to be minor resin components (Hovelstad et al., 2005).

We pointed our attention to 1D proton NMR investigation of the raw resin, being aware that more complete information for complex mixtures could be achieved only by an extensive application of two-dimensional 2D homo- and heteronuclear NMR techniques. In view of the fact that these types of instrumental investigation require very long acquisition times, this was not done rather preferring to perform a rapid analysis of the matrix. A typical high-resolution ^{1}H-NMR spectrum of a sample of *Pinus nigra* ssp. *laricio* (Poir.) resin showed a rather complicated series of signals (Fig. 2a), mostly generated by protons of terpenoid structures.

A sample (30 mg) of dried raw resin from Pinus nigra ssp. laricio (Poir.) - Calabria, Southern Italy, was dissolved in $CDCl_3$ (0.6 mL) and analyzed without further chemical manipulation. Spectroscopic analysis was immediately carried out after sample preparation to avoid acid-induced isomerization in solution of cycle structures (Di Gioia et al., 2005; Minuti et al., 2013). One-dimensional 1D high-resolution NMR analysis was performed at 25±0.1 °C under temperature control. A Bruker Avance 300 Ultrashield spectrometer equipped with a 5-mm probe with Z-axis gradient coils was used. Proton spectra were recorded at the ^{1}H frequence of 300.132 MHz, by applying a standard zg90 pulse sequence, with the lock on the deuterium resonance of the solvent. Chemical shift values were reported in ppm and referred to the line of the signal appearing at 7.251 ppm due to the residual unlabelled solvent. For acquisition, a sweep width (SW) of 4194.631 Hz, 128 K data points (TD), with a recycle delay (D1) of 5.0 s were used, resulting in an acquisition time (AQ) of 15.624 s. Two prior dummy scans (DS) were applied for each scan, and the best S/N ratio was obtained with 64 scans (NS). The total time of analysis was 22.46 min. After acquisition, the FID was zero-filled up to 512 K data points. A line broadening (LB) of 0.1 Hz was applied prior the Fourier transformation. The zero and first order phase-correction was carried outmanually. Further noise reduction and signal resolution were obtained by applying a Whittaker smoothing filter.

In the high-resolution ^{1}H NMR spectrum signals were distributed along three principal spectral regions, displaying resonances for protons of (b) methyl groups, (c) carbon-carbon double bonds, and (d) aromatic rings, in the chemical shift intervals between 0.70 and 1.40 ppm, 4.60 and 6.10 ppm, 6.50 and 7.50 ppm, respectively (Fig. 2). For determination of the principal resin acids non-overlapping and significantly resolved signals belonging to these three spectral windows were selected. Signals appearing in the spectrum as multiplet of very low intensities were not helpful and were not used for component identification. The total spectrum also showed several signals that were thought generated by protons in flavonoid structures. The modest intensities of these signals did not allow for their unequivocally assignments. ^{1}H NMR spectral resonances were determined, whenever possible, by correlation with the corresponding chemical shift values already reported in the literature. Thus, for each resin acid a representative resonance signal was assigned and confirmed by literature data. The main acid constituents of the whole resin were identified by comparing the experimental chemical shift values with those reported in the literature for the same compounds individually analyzed or as components of raw complex mixtures, under the same acquisition conditions used for the present investigation. Identification and qualitative determination of diterpenoid acids in the resin sample subjected to the analysis agreed the chemical profiles obtained by GC-MS and/or calculated by ^{13}C NMR for other different raw pine resins, as elsewhere published.

The ^{1}H-NMR spectrum recorded at room temperature for a sample of the resin case of study, dissolved in deuterated chloroform, was characterized by a series of intense signals that were assigned to the chemical structures of some known resin acids. Based on the spectroscopic results, seven resin acids (abietic **1**, dehydroabietic **2**, neoabietic **3**, palustric **4**, pimaric **5**, levopimaric **6**, and isopimaric **7**) were recognized. The structures of compounds identified in the resin are depicted in Fig. 2e (Olate et al., 2011). Although sandaracopimaric acid (**8**) is commonly reported to be another component of pine resins, this compound was not identified in the sample analyzed. Abietic, dehydroabietic, pimaric, and isopimaric acids were found to be the most abundant products, in analogy to other types of pine resins (de Carvalho et al., 2008). The analysis of the spectal region (c) showed olefinic proton signals mainly distributed in three well-distinguishable groups. All these signals appeared in form of doublets of doublets, as expected for the typical proton pattern of mono-substituted olefinic residues.

Unfortunately, not all signal lines were well-resolved, often showing complex overlapping. On the basis of the calculation of the corresponding coupling constants, the distinguishable doublets of doublets (dd) in the window between 5.643 and 5.850 ppm were attributed to the H-14 of **5** (5.712 ppm) and **7** (5.812 ppm), and to the H-8 of **1** (unresolved multiplet centered at 5.752 ppm). The complex multiplet centered at 5.335 ppm was generated by the overlapping of signals due to the H-8 of **4**, the H-9 of **1**, and the H-8 of **7**. Multiplets at 5.172 and 5.128 ppm were signals due to the H-8 of **5** and the H-6 of **6**.

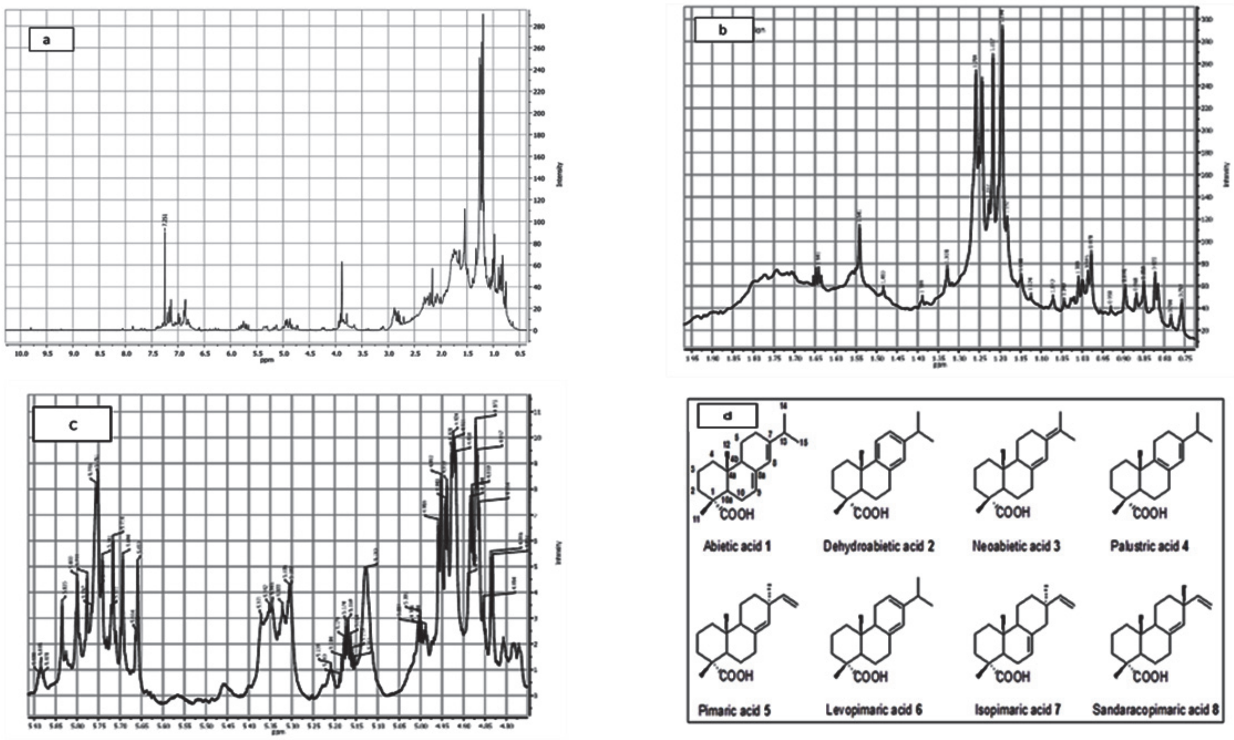


Fig. 2. (a) One-dimensional 1D high-resolution ^{1}H-NMR spectrum at 25 °C of a sample of Pinus nigra ssp. laricio (Poir.) resin dissolved in deuterated chloroform. The signal at 7.251 ppm is due to the residual unlabelled NMR solvent used for the analysis; Spectral regions of (b) methyl, (c) olefin, and (d) structures of the most abundant resin acids identified

A more complex pattern of lines was observed for the series of signals in the interval between 4.818 and 4.979 ppm. These resonances can be attributed to the H-14 and H-15 of **5** and **7**. The spectrum did not reveal signals for the structure of neoabietic acid (**3**). This evidence was supported by comparing the experimental data with those already reported for the same compound. Nevertheless, due to the sensitivity limits of the spectroscopic method, the presence of **3** as a minor component of the resin cannot definitively be excluded. The spectral window (d) featured signals of strong intensity at 6.863 (d, J=1.8 Hz), 6.977 (dd, J=8.1 and 1.8 Hz), and 7.147 (d, J= 8.1 Hz).

These resonances were attributed to the aromatic protons H-8, H-6, and H-5, respectively, of dehydroabietic acid (**2**), confirming this compound to be one of the most abundant component of the resin. Other low signals present at higher chemical shift values could be attributable to diterpenoid aldehydes present in the resin. These compounds were present in moderate amounts or, presumably, in traces, and consequently they cannot unequivocally be confirmed in the sample under analysis, lacking pure standards and due also to the sensitivity limits of the NMR techniques as used in this work.

The strong overlapping of signals appearing in the methyl region (b) of the spectrum made more difficult their attribution, consequently not all peaks were assigned. Nevertheless lines at 1.217, 1.243, 1.251, 1.259, and 1.328 ppm were attributed to the H-11 of **3** and **5**, the H-12 of **2**, the H-11 of **1**, and the H-11 of **2**, respectively. Spectral data agreed with the literature and further corroborated the presence of these acids in the resin. Signals not sufficiently intense and resolved, corresponding to very low abundant components, were not assigned and further investigated

2.1.2. Natural mineral inert and charcoal

A natural mineral and wood charcoal and were used, to make the system less fragile and less glassy and therefore to facilitate the application of glue. The natural mineral used is characterized by the presence of a clayey fraction and appears as a red soil for the presence of iron oxides (Fig. 3a). The chemical analysis averages, for red soil is about 50% silica, 16 to 25% alumina, 7 to 15% ferric oxide.

It was taken from quarries of Calabria, region of south Italy, and before being used was characterized by X diffraction and thermal analysis TG and DTA. The diffractive X-ray spectrum (Fig. 3a) shows the presence of quartz, attributable to the peak at 26.7 °2θ. Other low intensity peaks, in the range 40-70 °2θ, are visible, due to the presence of iron oxides, as also confirmed by the color of the sample. In addition, low intensity peaks are observed between 19 and 25 °2θ due to the presence of silicates in the clay matrix.

Before being used the charcoal was pulverized in a mortar (Fig. 3d). The amount of coal and natural mineral was varied within the systems to study the role played by each single component on the properties of the glue.

2.1.3. Beeswax

The beeswax was chosen to facilitate the workability of the glue. If used alone, the resin becomes glassy. The beeswax used was offered by companies in beekeeping (Fig. 3c). As known, it consists mainly of esters of linear alcohols (from C24 to C36) and of linear fatty acids (from C18 to C36). These esters are in a mixture with linear hydrocarbons (from C20 to C33) (Rivenc et al., 2008; Tsunenori, 2005; Tulloch, 1971). Waxes are chemically very stable, resistant to hydrolysis and oxidation. Virgin beeswax, not chemically treated was used. Presents itself as a colored mass, dull, oily to the touch, soft, plasticy, with a pleasant smell.

Its melting temperature was measured with a pyrometer (Gallenkamp), resulting a range between 62-66°C.

2.1.4. Carbon nanotubes

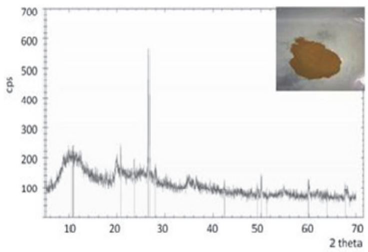
The nanotubes used were synthesized by the technique (CCVD-Catalytic Chemical Vapor Deposition) (Teo et al., 2013; Sinnott and Andrews, 2001), where the carbon source was ethylene and the catalyst used was composed of wt5% of iron and of wt5% cobalt on a support of zeolite NaY type (Fig. 3e). The zeolite is a microporous material of aluminosilicate nature. There are different types of microporous materials of the zeolitic type (De Luca et al., 2009; De Luca et al., 2014). In particular, the zeolite used in the preparation of carbon nanotubes has been the NaY. The synthesized nanotubes are MWCNT type (Multi-Walled Carbon Nanotube) (Policicchio et al., 2015). The nanotubes were observed by the electron microscope (SEM).

It was possible to observe their good quality since well formed without the presence of amorphous carbon (Fig. 3).

2.2. Preparation of mixtures

The following components were used to prepare mixtures to obtain the glues: pine resin, beeswax, coal, inert and carbon nanotubes. Initially, nineteen systems were prepared without carbon nanotubes, of which nine obtained with a percentage weight ratio pine resin / beeswax equal to 3 and with varying percentages of inert and coal and other ten systems with a percentage weight ratio pine resin / inert or coal equal to 3 and percentages of beeswax variables. The choice of this ratio was determined by preliminary tests. The systems in percentage by weight are reported in Table 1. The components, after being weighed, were mixed in a container placed on a heating plate at a temperature of 150 °C, and were added in the following order: resin - beeswax - coal and/or inert and mixed vigorously.

Mixtures referred to in Table 1 are homogenous-colour varying from brown to black depending on the quantity of carbon or mineral inert used. Any non homogeneous mixtures were discarded beforehand.



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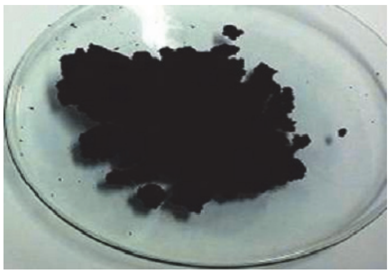

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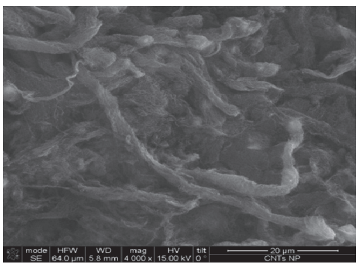


e

Fig. 3. (a) Inert pulverized and its X-ray diffraction spectrum, (b) Beeswax, (c) Charcoal, (d) Carbon nanotubes, (e) SEM image of carbon nanotubes

3. Results and discussion

The data on the characterization of the blends were analyzed taking in to consideration the variation of melting range temperatures, the compressive strength (on the cold glue) and the adhesive resistance (on wood test specimens) as a function of the quantities and nature of the components.

3.1. Variation of melting temperature of mixtures as function of components

The evaluation of melting temperature for systems intended to play the role of adhesives is important, both for the final characteristics and their application. Glues studied in this research may be classified as "hot" glues, since they are in a solid form when cold, but that must be melted for application use. For this reason, start and end fusion points were measured for each mixture to assess the role played by each component on this parameter.

The graphs reported in Figs. 4 a, b show that the melting temperature increases by increasing the amount of coal and mineral inert. The increase due to mineral inert is lower than that generated by coal. A decrease in melting temperatures is generated by increasing the amount of beeswax (Figs. 4c, d). In general, the beeswax causes a double combined effect: on one side it increases the malleability and on the other, it forms new products that softens at a higher temperature. If we add a third component to the previous two "resin and wax", i.e. coal, it appears as a filler comparable to a sponge that absorbs in its small cavity, fatty basic components of the mixture, so as to make it more plastic. Mixtures that contain more coal are those that have higher temperatures.

3.2. Variation of mechanical resistance of systems

Compression resistance of cold mixtures was measured inasmuch as future fruition in the form of a "stick" for hot glues could be possible.

To measure the mechanical resistance to compression of the cold glue, pellets were prepared using a pelletizer, by melting the mixture at 120°C. Subsequently, the pellets were cooled for 24 hours (Fig. 5a). Finally, the compressive strength was measured with a Vanderkamp VK 200 meters (Fig. 5b) on the so-prepared pellets.

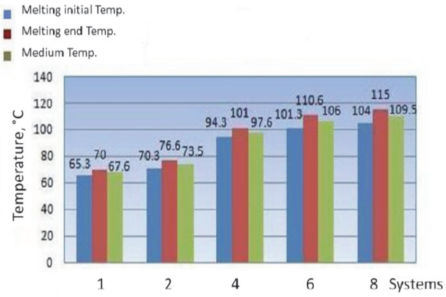
If we compare graphs 5c and 5d, it is evident that by increasing the amount of coal and maintaining constant the ratio of amounts resin/ wax at 3, the resistance to compression increases,. The same pattern was seen in the presence of inert, eventhough in this case, its effect was less important than with coal.

3.3. Adhesion strength tests on wood specimens

The best prepared systems, which have shown a certain uniformity and a homogeneous color have been selected to undergo the tests of adherence to tear. In particular the systems: 2, 4, 6, 10, 12, 14 have been chosen. The test was carried out using a base of wood length dimension 300 mm x 300 mm, on which support of size 50 mm x 50 mm was pasted, both with flat surface and with milled (at 45°) surface (Fig. 6a).

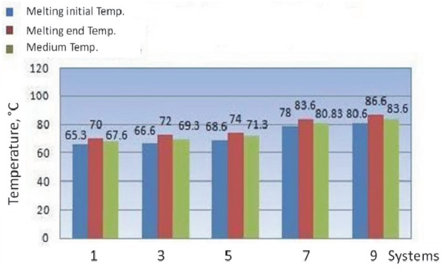
Table 1. Weight percentages of the components used for preparing the glues without carbon nanotubes

System	***(wt%)Resin / (wt%)beeswax= 3 and variable amounts of coal and inert***			
	Resin, wt%	***Beeswax, wt%***	***Coal, wt%***	***Inert, wt%***
1	75.00	25.00	0.00	0.00
2	66.67	22.23	11.10	0.00
3	66.67	22.23	0.00	11.10
4	60.00	20.00	20.00	0.00
5	60.00	20.00	0.00	20.00
6	54.54	18.18	27.27	0.00
7	54.54	18.18	0.00	27.27
8	50.00	16.66	33.34	0.00
9	50.00	16.66	0.00	33.34
	(wt%)Resin / (wt%)coal or inert=3 and variable amounts of beeswax			
10	75.00	0.00	25.00	0.00
11	75.00	0.00	0.00	25.00
12	66.67	11.10	22.23	0.00
13	66.67	11.10	0.00	22.23
14	60.00	20.00	20.00	0.00
15	60.00	20.00	0.00	20.00
16	54.54	27.27	18.18	0.00
17	54.54	27.27	0.00	18.18
18	50.00	33.34	16.66	0.00
19	50.00	33.34	0.00	16.66



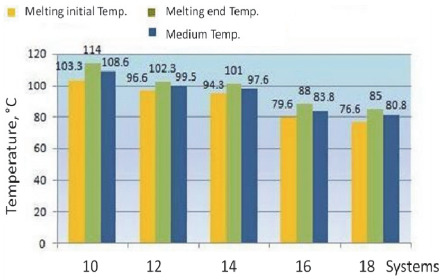
Systems	Resin, wt% / Beeswax, wt%	Coal, wt%	Inert,wt%
1	3	0	0
2	3	11.10	0
4	3	20.00	0
6	3	27.27	0
8	3	33.34	0

a



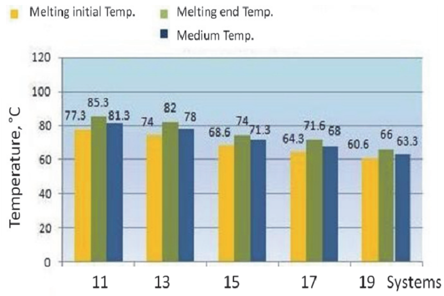
Systems	Resin, wt% / Beeswax, wt%	Coal, wt%	Inert,wt%
1	3	0	0
3	3	0	11.10
5	3	0	20.00
7	3	0	27.27
9	3	0	33.34

b



Systems	Resin, wt% / Coal wt%	Beeswax, wt%	Inert,wt%
10	3	0	0
12	3	11.10	0
14	3	20.00	0
16	3	27.27	0
18	3	33.34	0

c



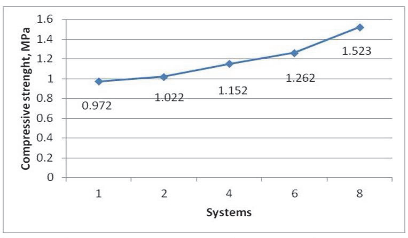
Systems	Resin, wt% / Inert wt%	Beeswax, wt%	Coal ,wt%
11	3	0	0
13	3	11.10	0
15	3	20.00	0
17	3	27.27	0
19	3	33.34	0

d

Fig. 4. Melting range temperatures of different systems obtained as a function on component amounts

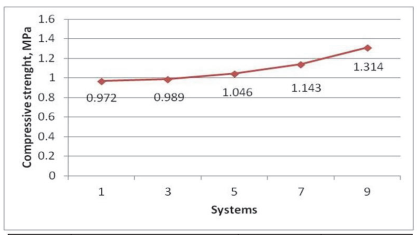
a

b



Systems	Resin, wt%/Beeswax, wt%	Coal, wt%	Inert, wt%
1	3	0	0
2	3	11.10	0
4	3	20.00	0
6	3	27.27	0
8	3	33.34	0

c



Systems	Resin, wt%/Beeswax, wt%	Coal, wt%	Inert, wt%
1	3	0	0
3	3	0	11.10
5	3	0	20.00
7	3	0	27.27
9	3	0	33.34

d

Fig. 5. (a) Pellet of a generic mixuters, (b) Hardness tester Vanderkamp VK 200, (c, d) Compressive strength of different prepared systems as a function of component amount

The six choices of mixtures were heated on a plate at a temperature of 120 °C and the molten glue obtained was used for paste the support on the basis of wood. The test specimens were put under pressure in the oven for 1 hour at a temperature of 120 °C to give to the glue a change to distribute itself in a uniform manner. The specimens, once removed from the oven were left for 24 hours at room temperature and subsequently used for the tear-off-adhesive tests. On various substrates of wood, stainless steel cylinders were glued by a very specific resistant adhesives (Fig. 6b). Finally, these steel cylinders were connected to the instrument for the measurement of the adhesion strength (Fig. 6b).

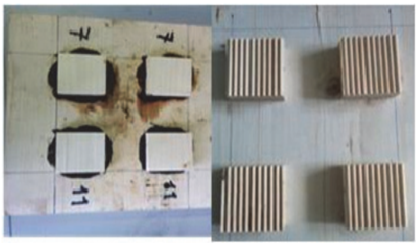
The results of tear-off-adhesive tests with specimens with flat surface and with the milled surface are shown. The results obtained by the tear-off adhesion tests show that, by increasing the amount of coal, the strength of adhesion increases too, thus increasing the quantity of wax that occurs in a lowering of the adhesion force. By using a milled surface, an increase of the forces of adhesion is expected.

3.4. Systems with carbon nanotubes

The system 12 was found to be the best one as far as adhesion strength, homogeneity and staining. Therefore, this system was taken as a reference to design new systems with carbon nanotubes. If we take system 12 as a reference we can keep the ratio of the percentages costant by weight resin/beeswax equal to 6.07 and varying amounts of carbon nanotubes and coal.

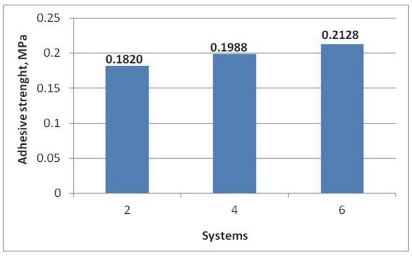
The purpose was to evaluate to what extent the substitution of coal with carbon nanotubes is possible and what is the contribution made by the carbon nanotubes to improving of the glue. The new systems formulated with carbon nanotubes are reported in Table 2. They were characterized to study the variations of the properties as a function of amounts of carbon nanotubes as was done in previous systems. By increasing the quantity of carbon nano-tubes, the melting temperatures are increased. In systems obtained both with coal and with carbon nanotubes (Fig. 7b, c) the increase of the melting temperatures (as a function of the increasing quantities of carbon nanotubes) is less evident, probably due to the predominant action of the coal.

Compression strength of these systems was measured to evaluate the role of carbon nanotubes, as done on previous systems (paragraph 3.2). The results reported in Fig. 7d show that the carbon nanotubes produce an improvements on compressive strengths. By increasing the amount of carbon nanotubes mechanical resistance increases (Figs. 7e, f). In this case, the carbon nanotubes react exactly as the reinforced fibres by increasing compression resistance.



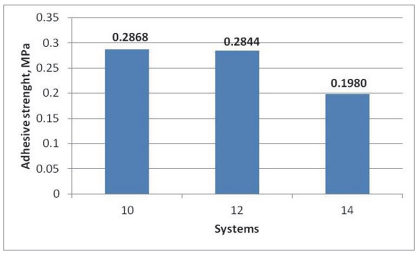
a

b



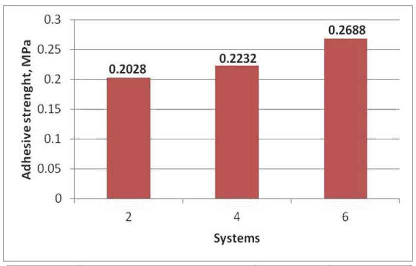
Systems	Resin, wt%/Beeswax,wt%	Coal, wt%	Inert, wt%
2	3	11.10	0
4	3	20.00	0
6	3	27.27	0

c



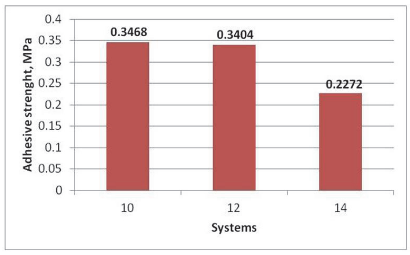
Systems	Resin, wt%/Coal, wt%	Beeswax, wt%	Inert,wt%
10	3	0	0
12	3	11.10	0
14	3	20.00	0

d



Systems	Resin, wt%/Beeswax, wt%	Coal, wt%	Inert, wt%
2	3	11.10	0
4	3	20.00	0
6	3	27.27	0

e



Systems	Resin, wt%/Coal, wt%	Beeswax, wt%	Inert, wt%
10	3	0	0
12	3	11.10	0
14	3	20.00	0

f

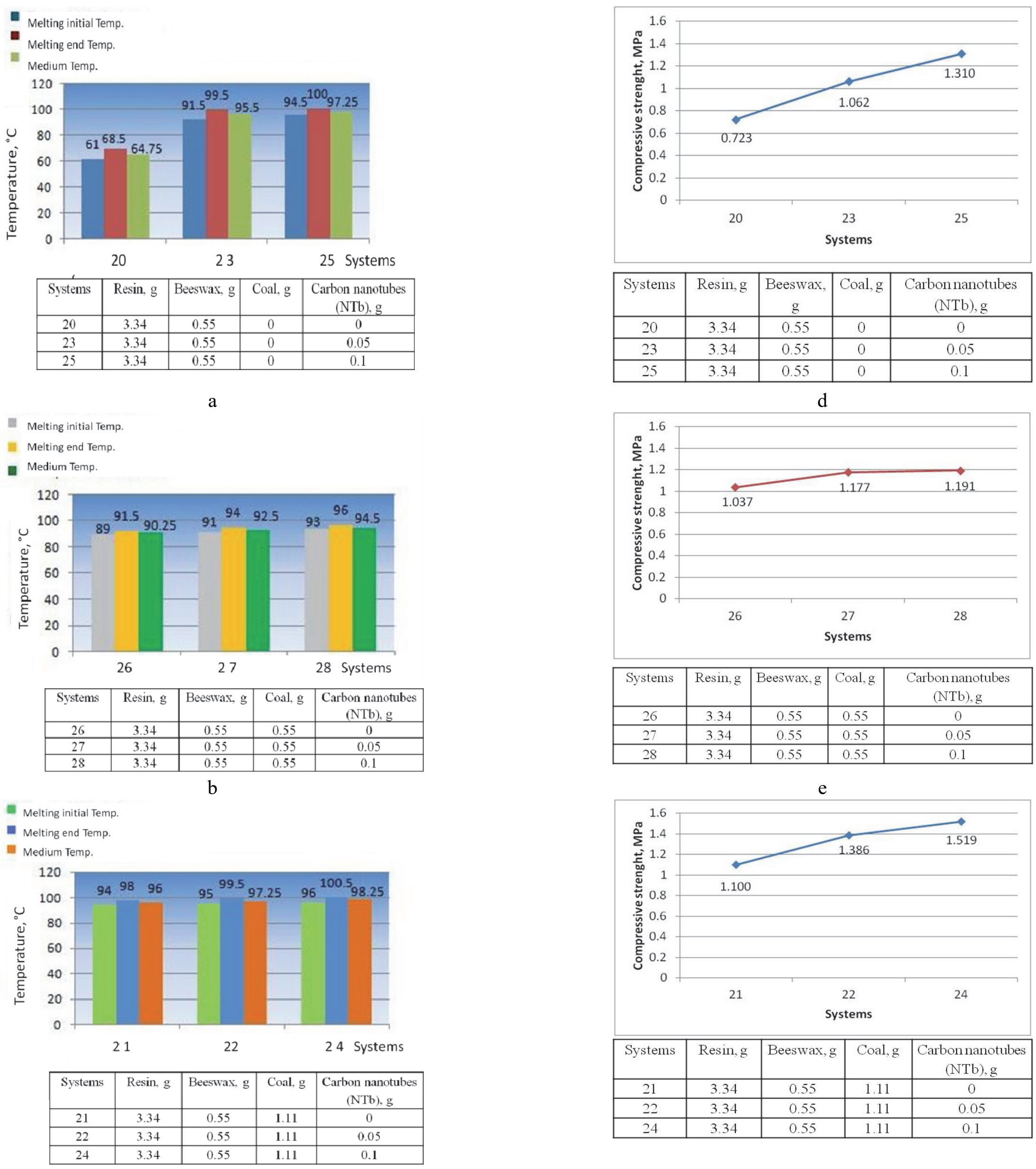
Fig. 6. (a) Glued support on a wooden base with the prepared mixture and support together with the milled surface at 45°, (b) Specimens with glued steel cylinders to connect them to the tear-off-adhesion tester. Adhesive strength: (c) Increasing amounts of coal using support with flat surface, (d) Increasing amounts of beeswax using support with flat surface, (e) Increasing amounts of coal using support with milled (45°) surface (f) Increasing amounts of beeswax using support with milled surface (45°)

The adhesion tests were performed on specimens containing carbon nanotubes and prepared with similar procedures as described in section 3.3. The following Figures show data obtained on specimens with flat surface (Figs. 8 a-b-c) and with the milled surface at 45 ° (Figs. 8 d-e-f).

The graphs reported in Fig. 7a show that carbon nanotubes can substitute coal, playing a similar role on the melting temperature of the systems.

Table 2. Weight percentages of the components used for preparing the glues with carbon nanotubes

System	*Pine resin*		*Beeswax*		*Coal*		*Carbon nanotubes*	
	wt%	*g*	*wt%*	*g*	*wt%*	*g*	*wt%*	*g*
20	85.86	3.34	14.14	0.55	0.00	0.00	0.00	0.00
21	66.8	3.34	11.00	0.55	22.20	1.11	0.00	0.00
22	66.14	3.34	10.89	0.55	21.98	1.11	0.99	0.05
23	84.77	3.34	13.96	0.55	0.00	0.00	1.27	0.05
24	65.50	3.34	10.78	0.55	21.76	1.11	1.96	0.10
25	83.71	3.34	13.78	0.55	0.00	0.00	2.51	0.10
26	75.22	3.34	12.39	0.55	12.39	0.55	0.00	0.00
27	74.39	3.34	12.25	0.55	12.25	0.55	1.11	0.05
28	73.57	3.34	12.11	0.55	12.11	0.55	2.21	0.10



a

Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
20	3.34	0.55	0	0
23	3.34	0.55	0	0.05
25	3.34	0.55	0	0.1

b

Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
26	3.34	0.55	0.55	0
27	3.34	0.55	0.55	0.05
28	3.34	0.55	0.55	0.1

c

Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
21	3.34	0.55	1.11	0
22	3.34	0.55	1.11	0.05
24	3.34	0.55	1.11	0.1

d

Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
20	3.34	0.55	0	0
23	3.34	0.55	0	0.05
25	3.34	0.55	0	0.1

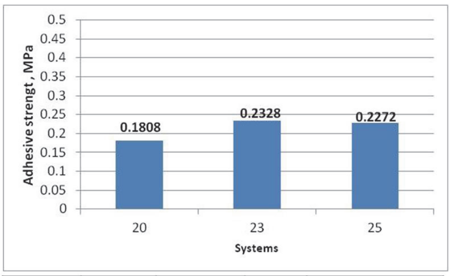
e

Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
26	3.34	0.55	0.55	0
27	3.34	0.55	0.55	0.05
28	3.34	0.55	0.55	0.1

f

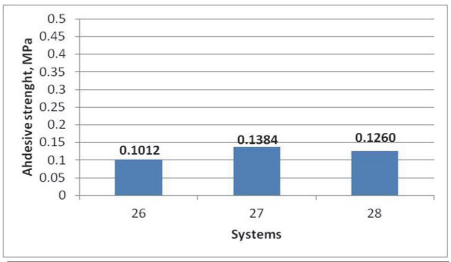
Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
21	3.34	0.55	1.11	0
22	3.34	0.55	1.11	0.05
24	3.34	0.55	1.11	0.1

Fig. 7. Melting temperatures of different systems obtained as a function of coal and carbon nanotubes amount (a, b, c); Compressive strength of different obtained systems as a function of coal and carbon amount (c, d, e)



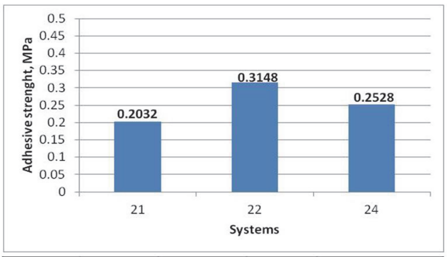
Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
20	3.34	0.55	0	0
23	3.34	0.55	0	0.05
25	3.34	0.55	0	0.1

a



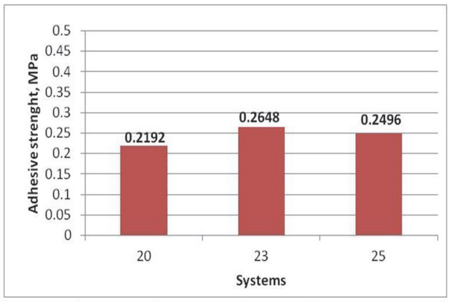
Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
26	3.34	0.55	0.55	0
27	3.34	0.55	0.55	0.05
28	3.34	0.55	0.55	0.1

b



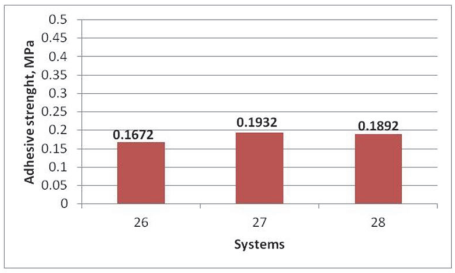
Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
21	3.34	0.55	1.11	0
22	3.34	0.55	1.11	0.05
24	3.34	0.55	1.11	0.1

c



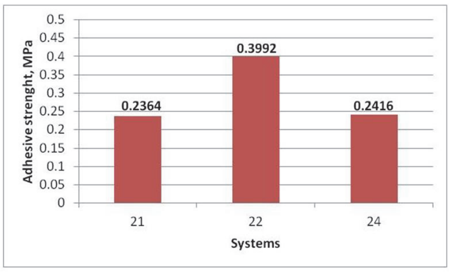
Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
20	3.34	0.55	0	0
23	3.34	0.55	0	0.05
25	3.34	0.55	0	0.1

d



Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
26	3.34	0.55	0.55	0
27	3.34	0.55	0.55	0.05
28	3.34	0.55	0.55	0.1

e



Systems	Resin, g	Beeswax, g	Coal, g	Carbon nanotubes (NTb), g
21	3.34	0.55	1.11	0
22	3.34	0.55	1.11	0.05
24	3.34	0.55	1.11	0.1

f

Fig. 8. Adhesive strength of different obtained systems as a function of coal and carbon nanotubes amount: (a, b, c) using support with flat surface; (d, e, f) using support with milled at 45°surface

The data obtained have shown that the carbon nanotubes tend to increase the adhesion resistance, and a fundamental role is played by the quantity of carbon nanotubes. In fact, there is a reversal of the trend, after a limited amount of nanotubes of 0.05 g, mechanical strength decreases. This can be justified by the fact that by increasing a particular value in the amount of carbon nanotubes, their dispersion in the system becomes difficult, therefore, compaction is less effective.

4. Conclusion

The aim of this experimental research was to use natural, local resources of the National Park of Sila in Calabria - Southern Italy, in order to prepare natural glue. Furthermore, the use of carbon nanotubes has been valuated in order to improve adhesion strength.

The data obtained allow us to draw the following conclusions:

- Natural raw materials such as: pine resin, beeswax, coal, inert mineral can be usedto prepare glues, with appropriate performance, for use in the field of green building.

The Larico pine resin from Sila National Park, of which we have no knowledge of literature on its characterization by NMR has been the key component for the preparation of natural glues. Three fundamental characteristics were evaluated, on various formulated systems, such as melting temperature, compressive and adhesion strength, since they are linked to the applicability and implementation of the glue, in relation to the nature and quantities of the components. Each component played an important role:

• The pine resin, if used alone as a “glue”, presents a high acidity and the lack of elasticity. However, by adding wax to the hot resin, it generally, has a double combined effect. On one hand, it increases the malleability and, on the other, with the combination of the acid compounds it forms new products that soften at a lower temperature.

• The beeswax lowers the melting temperature interval, mechanical strength and adhesion resistance by increasing amount in the system.

• Coal raises the melting temperature range that increases with its quantity in the system. The mechanical resistance tests carried out on the pellets obtained from the mixtures have confirmed an increase in resistance. Even for the tear-off-adhesion tests, higher values with increasing of its quantity were obtained.

• The mineral inert showed the same characteristics of the coal on the compressive strength tests, interval of fusion and adhesion tests, although with slightly lower values.

• Carbon nano-tubes improve, in a modest way, the resistance to compression and elevate the melting range, while they show an improvement on the adhesion strength. Carbon nano-tubes increase the resistance up until a certain value (0.05 grams), a decrease in resistance occurs from this value onwards.

Among the systems, without nanotubes, the system 12, containing:

Resin, wt%: 66.67; Beeswax, wt%: 11.10; Coal, wt%: 22.23, has reported the highest adhesion strength of 0.2844MPa, for support with flat surface.

Among the systems containing carbon nanotubes, the system 22, containing:

Resin, wt%: 66.14; Beeswax, wt%: 10.89; Coal, wt% 21.9; Carbon nanotubes, wt%: 0.99%, has reported the highest adhesion strength of 0.3148MPa for support with flat surface.

The latter systems, among those studied, represent the optimum quantitative ratio of components, each of which, as seen, has particular functions, to have a higher adhesion strength.

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SMART GROUND PROJECT: A NEW APPROACH TO DATA ACCESSIBILITY AND COLLECTION FOR RAW MATERIALS AND SECONDARY RAW MATERIALS IN EUROPE

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Abstract

Steady Raw Materials (RM) supply is essential for the EU economy and increasingly under pressure to sustain the businesses and industries demand. The supply of RM is not only a matter of availability of primary but also of secondary raw materials (SRM). In fact a great amount of waste can be regained as practical and valuable SRM by enhancing the recovery processes from industrial, mining and municipal landfill sites, especially if we consider that Europe is highly dependent on the imports of several RM. Nevertheless, there is to date no inventory of SRM at EU level. Smart Ground project aims to facilitate the availability and accessibility of data and information on SRM in the EU, as well as creating synergy and collaboration between the different stakeholders involved in the SRM value chain. In order to do so, the Smart Ground consortium is carrying out a set of activities to integrate in a single EU database all the data from existing sources and new information retrieving pilot landfills as progress is made. Such database will enable the exchange of contacts and information among the relevant stakeholders, interested in providing or obtaining SRM. Finally, Smart Ground project will also spin out the SRM economy and employment thanks to targeted training activities, organized during congresses and dedicated meeting with stakeholders and end users interested in calculating the potentiality for SRM recovery from selected landfills, contemporary constituting a dedicated network of stakeholders committed to cost-effective research, technology transfer and training.

Key words: circular economy, extractive waste, landfill mining, municipal solid waste, secondary raw materials

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1. Introduction

1.1. Short overview

Raw materials (RM) are essential for the EU economy and sustainable development. Concern about their availability recently led to the definition of critical raw materials (CRM), as materials of high economic importance to the EU combined with a high supply risk (EU Commission, 2017). In 2011, a first list of CRMs was established by the European Commission (EC). In May 2014, the EC published a

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revised and extended CRM list including 13 of the 14 materials from the previous list, with only tantalum moving out due to a lower supply risk. Six new materials appeared: borates, chromium, coking coal, magnesite, phosphate rock and Si metal, bringing the number up to 20 CRM. The other 14 RM are: Sb, Be, Co, fluorspar, Ga, Ge, In, Mg, natural graphite, Nb, platinum group metals, heavy REE, light REE and W.

Considering the increasing scarcity and raising prices of RM, their recycling and recovery from anthropogenic waste stream deposits is of high relevance. The *European Innovation Partnership* (EIP) on Raw Materials has been established as a stakeholder platform, with the aim to promote innovation on the RMs sector on both technology for waste recovery and development of more efficient recycling processes. CRM and secondary raw materials (SRM) can be recovered from municipal solid waste (MSW), including commercial and industrial waste, as well as from waste from extraction and processing of mineral resources, known as extractive waste (EW). It has been estimated that the number of landfills in Europe is between 150.000 and 350.000 covering more than 300.000 hectares of land (Hogland et al., 2011; Vossen, 2005). Furthermore, the European Enhanced landfill mining consortium reported that the total amount of landfills in Europe is estimated to be >500.000 (EURELCO, 2017). Historical background makes the numerous old waste dumps a possible source of CRM and SRM. However, data available on CRM and SRM present in landfills is scarce and there is yet not guidance available on best management practices to recover SRM from landfill sites.

Considering the complexity of the RM value chain, it is fundamental to boost coordination and networking activities; sharing best practices and promoting innovative solutions, with the involvement of stakeholders, citizens and public authorities; thus a more efficient use of RM and waste reduction will be assured.

The opportunity to recover CRM and SRM from urban landfill sites and EW facilities will require substantial investment, which will be initiated and funded by either public or private funding that will boost EU economic growth as well as enhancing the environment and societal quality of life (Dino et al., 2016; Jones et al., 2013; Marella and Raga, 2014). Effective stakeholder involvement is crucial for such opportunity to happen as it is characterized by being dimensionally huge, extremely complex, human-oriented and characterized by considerable impacts to the society, economy and natural environment (Careddu et al., 2013; Suthar et al., 2016).

In this context, Smart Ground project, funded by the EU's Horizon 2020 program (GA 641988), aims to facilitate the availability and accessibility of data and information on SRMs in the EU, as well as creating synergies and collaboration between the different stakeholders involved in the value chain (Dino et al., 2016).

1.2. Smart Ground objectives and activities

The main objectives and actions of the project can be summarized as follows:

a. To obtain quantitative and structural data from both existing and not known SRM resources of the most needed RM and SRM in EU that could be utilized profitably as a RM and/or energy

b. To review existing standards for RM and waste inventory and implement new methodology validated through selected pilot sites, as currently at EU level there is little shared information available for conducting harmonized waste inventory; in particular, there is no EU inventory for EW facilities.

c. To identify the most promising markets for recovered SRMs from the pilot scenarios. As quality and quantity of exploitable SRM/CRM is crucial, characterisation activities and impact analysis must be carried out.

d. To integrate and harmonize data and information collected by gathering them in a single EU database (SG platform), facilitating the access to information on available SRM for end-users. All datasets from the pilot studies and information collected from previous published studies by the partners, as well as from other sources, allowed the Smart Ground consortium to determine the most important characteristics of SRM for waste management decision making at EU level. This platform will be publicly accessible through a web portal that will facilitate the search of SRM-related information. Furthermore, the use of the platform will facilitate the registration and collection of new information from other landfills and EW facilities, thus creating a virtuous cycle "from waste to resource".

e. To raise awareness among policy makers and public opinion to support the social recognisability of the positive impact of landfill exploitation to obtain SRM. Implementing new approaches to decision-making within an established market is extremely challenging. Transferring knowledge into a sector such as the waste sector, which is conservative in approach and where profit margins are not high, requires dedicated resources: Smart Ground project tries to face this challenge.

2. Data collection plan and validation at pilot sites level

The main waste streams considered in the Smart Ground project are EW and MSW including commercial and industrial waste, and construction and demolition waste (C&DW), which represent 28.1%, 8.3% and 34.5%, respectively of the total EU waste production (Eurostat, 2017). The knowledge of the quality and quantity of such wastes is fundamental to evaluate the potential SRM exploitable from landfills at large and from the different waste streams. While there is a great deal of information available on MSW and C&DW. To date, there is little detailed data on EW. In order to collect useful information for waste characteristics and volumes of SRM within anthropogenic deposits, a total of 10 sites (4 MSW, industrial landfill sites and 6 EW facilities) have been investigated as pilot sites (Table 1); other six pilot sites, based on previous published data were also selected for Spain and UK (not included in the present paper).

2.1. Data Collection plan for the characterization of different types of waste deposits

As for MSW landfills the Data Collection plan included the following activities:

1. Collection of preliminary information such as operation history, depth of the landfill cell, degradation stage (for occupational safety), presence of hazardous waste (occupational safety), and geophysical characterization
2. Sampling activity: different sampling techniques were used including drilling, excavating and cactus grab crane for MSW sampling. Sample sorting was done either manually or mechanically to separate the different waste fractions. The physico-chemical characterization of the fractions was then carried (Fig. 1)
3. Sampling preparation to obtain representative samples for analysis (Fig. 1).

Table 1. Pilot sites for Data Collection plan validation

Waste stream types	***Name and location***	***Pilot description***	***Status***
Waste from extraction and processing of mineral resources	Montorfano mining area, NW Italy	Feldspar production from granite waste facilities exploitation	Active site
	Gorno mining area, northern Italy	EW facility characterized by a high content in metals as Zn, Pb and possible CRM as Ge, Te, In, Cd etc.	Closed site
	Campello Monti mining area, NW Italy	EW facility characterized by a high content in Ni, Cu, Co and possible CRM as PGE	Closed site
	Aijala mining area, Finland	EW facilities in Southwest Finland. Tailings from mining containing Cu, Zn, S, Ag, Au	Closed site
	Rudabánya, Hungary	EW facilities containing tailings from sulphides exploitation	Closed site
	Pátka, Hungary	EW facilities containing tailings of fluorite dressing plant	Closed site
Municipal Solid waste (MSW) including commercial & industrial Waste (C&I)	Metsäsairila landfill, Finland	MSW landfill	Both active and closed parts
	Kuusakoski Oy landfill, Finland	Private industry landfill; waste from vehicle and aluminum industry	Active site
	Debrecen, Hungary	MSW landfill	Active site
	CAVIT, La Loggia (Torino, Italy)	C&D waste treatment plant for the production of recycled aggregate	Active site

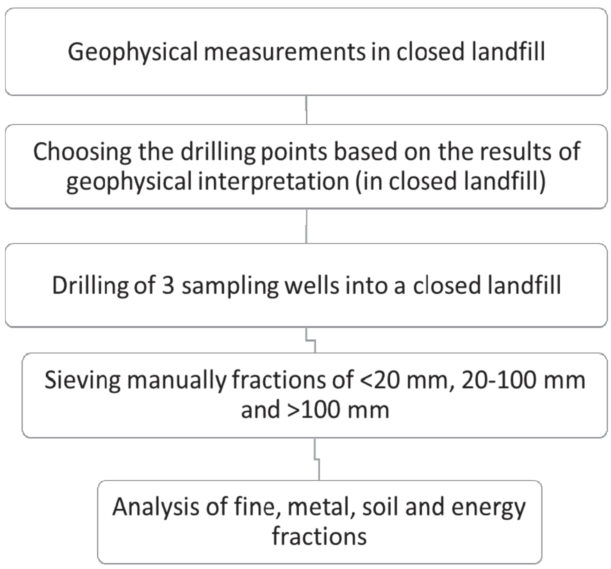


Fig. 1. Flow chart of suggested investigation process in Metsäsairila MSW landfill

As for EW facilities the Data Collection Plan comprises preliminary data collection, field activities and characterization (Fig. 2). In particular:

1. Preliminary data collection about localization, morphology, geology, info about ore bodies, mining and dressing activities etc.
2. Field activities, which have to be organized into two stages:
   a. Preliminary field activity in order to map the old mine tunnels, access roads, pedestrian paths and waste facilities. This early survey involves the recognition of the main characters of each dump, possibly including some geochemical features with the help of a portable XRF.
   b. Representative sampling of the different types of deposits (waste rock, operating residues and tailings). The sampling of the different types of deposit must be planned on the basis of the info collected during preliminary field activity, together with historical info about mining and dressing activities, info about geology, restrictions present in the area, etc... Representative sampling can generally be performed by applying a net scheme or a random sampling procedure; the samples can be collected using different tools, depending on the characteristics of the area and of the materials, such as: core drilling, excavating, sampling using hand shovel etc.
3. Characterization, organized in two main stages:
   a. Treatment to obtain representative samples for analysis
   b. Analysis for physical, chemical, mineralogical, petrographic characterization

Two pilot sites characterization studies are briefly presented below, as examples: one for MSW and another for EW.

2.2. MSW pilot site characterization: Metsäsairila landfill

Metsäsairila landfill is located in the City of Mikkeli around 200 km from Helsinki, in South-Eastern part of Finland. It has been operating since the beginning of 1970s, but the old part of the landfill was closed in 2007 and the new part opened in the same year. The surface area of the old landfill is around 8 ha and the currently active area around 3 ha. Waste in old and new areas consists mainly of MSW but also some industrial, C&DW and hospital waste have been deposited in the landfill area.

Sample collection wells were drilled by hydraulic piling rig from 5m until 17m depth, depending on sampling well, after removal of top layers of the landfill including cover materials. Aggregate waste samples from each well were taken to a sorting point, where they were manually sorted to different particle size categories (>100 mm, 20–100 mm and <20mm) and waste fractions by sieves. Waste fraction separation was carried out to fraction sizes of 20-100 mm and >100 mm and transferred to separate big plastic bags. Material size of <20 mm was packed in buckets. After the weighing procedure, all aggregate samples were transferred to laboratory for detailed analysis. Analysis of samples for elements, total organic carbon (TOC), dissolved organic carbon (DOC), chloride, and fluoride was implemented in an external laboratory (ALS Finland Oy). X-ray fluorescence (XRF) analysis for metals and calorimetric values for energy fraction were measured at Mikkeli University of Applied Sciences (Mamk).

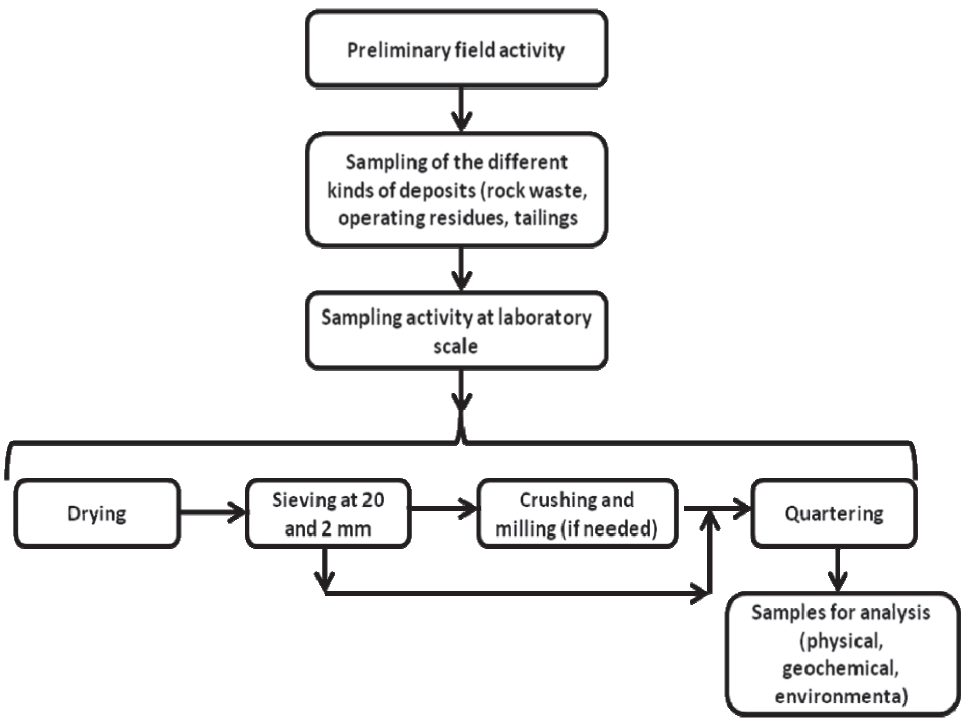
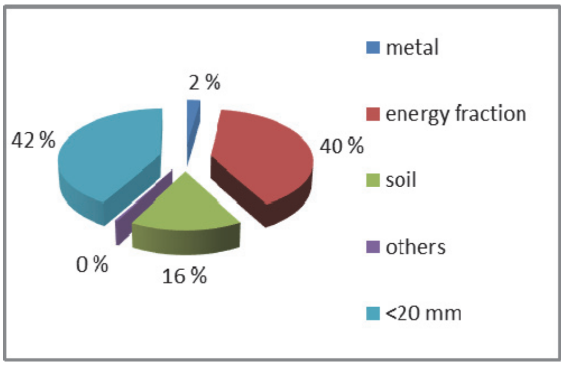


Fig. 2. Flow chart for field activity and characterization phases: EW facilities

Percentage distribution of different waste fractions is shown in Fig. 3.a and 3.b. Waste fraction distribution is quite similar in closed and currently active area; however, active area has more energy and fine material (<20 mm) fractions. Detailed results on the characterization of Metsäsairila MSW landfill are presented in annual research publication by Mamk (Soininen et al., 2016).



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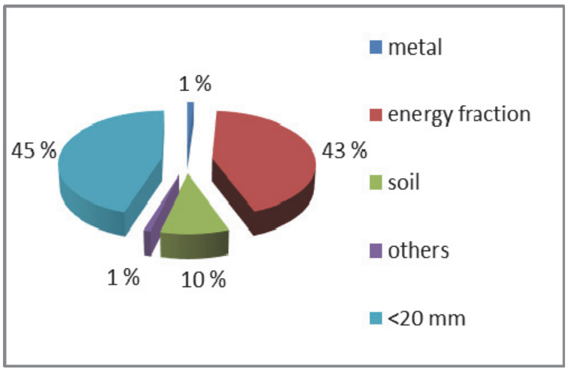

b

Fig. 3. a. Percentage distribution of sorted waste fractions from sampling well drilled in closed landfill area; b**.** in currently active landfill area

2.3. EW pilot site characterization: Campello Monti mining area

Campello Monti is located in Strona Valley (NW Italian Alps), at 1305m a.s.l. in the Verbano Cusio Ossola District (Piedmont Region). From the geological point of view the area is within the Ivrea Verbano Zone, a lower crust continental unit made of a voluminous body of mafic magmatic rocks intruded in a metasedimentary sequence. The mafic formation consists of cumulate peridotite, pyroxenite, gabbro and anorthosite grading to gabbro-norite, gabbro-diorite and diorite.

The mineralization occurs mainly within the pyroxenites and the ore assemblage is given by pyrrhotite, pentlandite and chalcopyrite, with locally PGE (platinum-group elements) enrichments (Rossetti et al., 2017).

The first historical information about the nickel mines of Campello Monti dates back to 1865 and the mining activity continued until the 2nd World War. The orebodies occurred as subvertical lenses broadly striking N-S to NNE-SSW, with an average grade of ca. 1-2 Ni wt. % (0.5 wt. % in the last years of activity). Nickel was extracted from pentlandite, as both relatively coarse-grained intergrowths and very fine-grained exsolutions in pyrrhotite.

Extractive waste facilities in Campello Monti are represented by:

- Waste rock: the most important waste materials in the area. The waste occurs in dumps, mainly located on the left side of the valley (WNW of the Campello Monti village).
- Operating residues: materials related to a first phase of dressing activity, cropping out in two sites: a first one on the lower-left side of the valley, close to the dressing plant, and a second one 200 m far away, on the opposite side of the valley. While the first one is a concentration of the material after milling, the second one is material deposited before transportation to the dressing plant.

Field activities have been organized into two stages: the preliminary field activity and the sampling of the different types of deposits (waste rock and operating residues). Each sample has been collected in an area of 1.5 square meters, which had been cleaned from the organic residues. After cleaning, the samples have been collected using hand shove, and, where necessary, hammer to reduce the grain size of the rock (Rossetti et al., 2017).

A total of 41 samples of rock waste and 12 of operating residues were collected.

All the samples have been taken to the Mineral Dressing and Sampling Laboratory (University of Torino) to be treated (dried, sieved at 20 and 2 mm, quartered and, when needed, crushed and milled) in order to obtain samples to be analyzed (physical, geochemical and environmental analysis).

The samples for geochemical analysis (important for SRM evaluation) were sent to an external laboratory (ACTLABS, Canada) and investigated for multi-elements geochemistry by ICP-MS and ICP-OES methods. Preliminary analyses have been performed on samples of three size classes (>20 mm, 20-2 mm, <2 mm) in order to verify the existence of significant compositional differences. As differences were not significant, the subsequent analyses were performed on the whole sample. Based on the preliminary results, part of the samples was selected for PGE analyses.

The geochemical data point out important differences among the waste deposits, in agreement with the field observations. In particular, four composition groups are recognized (Fig. 4): 1) operating residues extremely enriched in Ni (> 10.000 ppm), Cu (≥ 5 .000 ppm) and Co (> 600 ppm); 2) operating residues and waste rocks strongly enriched in the same metals; 3) waste rocks only moderately enriched in Ni, Cu and Co; 4) waste rocks characterized by a metals content relatively low, quite similar to ultramafic rocks not mineralized. The mineralogical and petrographic study, performed under optical and electron microscopy, shows that Ni, Cu and Co occur within minerals (metal sulphides) suitable for metals recovery.

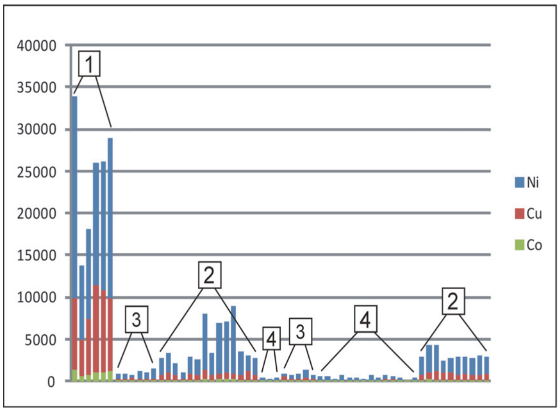

Fig. 4. Ni, Cu and Co content of samples from the Campello Monti area (values in ppm). The numbers refer to the four composition groups described in text

Preliminary data show that the PGE content is highly variable, the highest enrichments occurring in samples of the first composition group described above; PGE are mainly represented by Pd and Pt (Pd+Pd: up to ~0.8 ppm).

3. Materials flow, socio-economic and environmental impacts

Although landfill mining (LFM) could be a good solution for recovering SRM, LFM operations could have significant social, economic and environmental impacts (Garamvölgyi, 2016). These factors have been taken into account during the project activities, and qualtitative and or quantititaive information when available has been implemented the SG platform to assist user under the potential pros and cons of landfill mining. Environmental, social and economic impacts have been evaluated for different scenarios for the selected pilot sites in order to test the proposed methodologies.

3.1. Reasons for and against landfill mining

Reasons for LFM operations are either based on economic or environmental reasons. According to studies (Fisher, 2013; Warren and Read, 2014), main reasons for extraction can be:

- recycling potential – focusing on materials with the highest value and lowest degradation rate like metals,
- extraction for energy recovery – focusing on un-degraded biomass as a short term solution (mainly connected to MSW), or
- land reclamation, where the landfill site is a physical barrier to a development.

Besides the main reasons mentioned above, studies show that LFM could result in extension of the lifespan of landfill, by recovering the void space for reuse for different kinds of waste more suitable for long-term disposal. Also, if landfill is contaminating the groundwater and surrounding area, the source could be removed and further contamination could be prevented.

Despite benefits, LFM operations could have significant reasons against. Environmental risks of excavation of a landfill site include: nuisance caused during the LFM operation, potential presence of hazardous materials (such as asbestos), and escape of leachate or landfill gas (LFG) during the LFM operations and residual contamination of land or groundwater, which should be removed. Many of these risks are related to traditional mining operations, but are increased by the heterogeneous nature of waste in landfill (Fisher, 2013).

Uncertainty of LFM output is a clear economic risk for investors. There is a big concern whether the excavated materials will be marketable or not. Primary RM are qualitatively superior compared to recovered landfilled ones which are likely contaminated and not totally recyclable (Fisher, 2013; Warren and Read, 2014).

3.2. Identifying environmental impacts

There are numerous negative effects which landfill mining may cause. In general, it may lead to release of dust, liquids and leachate, landfill gases (LFG) and odours (expecially for MSW), with a risk to human health.

Hazardous waste is often uncovered, especially in older landfills where waste disposal practices and acceptance criteria were not very strict. Excavation of a landfill area could undermine the integrity of adjoining cells, which could lead to subsidence or collapse of landfill but also may attract various vermins. Landfill mining would certainly create noise and lead to additional traffic flow on the local road network (Ford et al., 2013).

Life Cycle Assessment (LCA) is suitable for identifying environmental impacts of different LFM or EW exploitation scenarios. Documented research investigated the difference in impacts between leaving the landfill to naturally degrade against the impact of a possible LFM project; the use of recovered materials as substitute; and RDF extracted from landfill compared to the use of traditional fossil fuels (Fisher, 2013).

3.3. Economic impacts - Investment decision making

According to a study from Scotland (Warren and Read, 2014) LFM is rarely self-sufficient. Economically viable cases usually include LFM operations involving onsite energy recovery at non-hazardous landfills; excavation, shredding, screening and removal of ferrous metal, with sale of metals; recovery of soil for use as daily cover. Besides, compaction of waste may be economically viable based on the recovery of void space.

LFM with resource and off-site energy recovery might be feasible where wastes are excavated anyway, assuming that the alternative is to pay for landfill elsewhere. In cases where industrial wastes are also landfilled more valuable materials can be recovered, thus resulting in economically feasible solutions (Ford et al., 2013). Some examples of profitable RM and SRM recovery from EW facilities still exits, mainly as for waste coming from recovery of dimension stone waste (Bozzola et al., 2010).

Consequently, waste composition, historic operating conditions, extent of waste degradation and market prices for recovered materials have also to be considered for LFM feasibility decisions.

3.4. Social impacts

LFM operations have significant social impact on local residents. LFM could lead to road congestion based on the intensive process activities near the landfill. At the same time there could be considerable concern over health, comfort and nuisance impact due to LFM process. Besides, decrease in value of properties which are close to landfill during the period of LFM can also occur (Ford et al., 2013).

However, after the removal of landfilled wastes, the value of those properties can increase. Excavation of landfill, as a process that reduces or eliminates on-going risks and impacts on health and the environment, would also imply new workplaces not just for experts but for low-skilled workers as well. Therefore, communication towards the local residents is always crucial in LFM strategies (Ford et al., 2013; Garamvölgyi, 2016).

3.5. Smart Ground approach for data collection

LFM calls for an appropriate technology to result in marketable SRM to fully achieve economic and environmental goals. To model such approaches, scenario models are being assembled in the framework of the Smart Ground project.

These scenario models cover not only pilot landfills, but a feasible technology line modelled by inputs, outputs and impacts (Fig. 5) to produce SRM from the excavated input originated from the landfill site. Besides, marketability will also be investigated in the scenario model in detail to identify industrial needs for the corresponding SRM.

First results available indicated that despite the highest environmental impact due to the recovery processes, savings gained from SRM as substitute material are often higher. Savings highly depend on recovered SRM types. As impacts of processes involved are often dominated by their energy need, overall environmental savings of the LFM or EW exploitation processes are highly determined by local energy mixes. Nevertheless economic burdens can hinder LFM and EW exploitation activities under the current economic circumstances.

4. Smart Ground databank platform

The Smart Ground IT infrastructure relies on an open source, modular architecture, which provides a reliable, scalable and responsive application, and enables spatial visualisation, search and analysis of the waste sites. The following diagram shows the platform's high level components (Fig. 6).

4.1. Data storage

The Smart Ground internal database will store heterogeneous information regarding the characterisation of waste sites, availability of RM, technologies involved, thematic maps, and the ontology or meta knowledge which formalises the personal knowledge provided by each user. The technology chosen for the database is PostgreSQL (PostgreSQL, 2017) with PostGIS (PostGIS, 2017) extension, which is a leader in open source geospatial databases. PostGIS is fast, has a lot of GIS features and can be used from GeoServer.

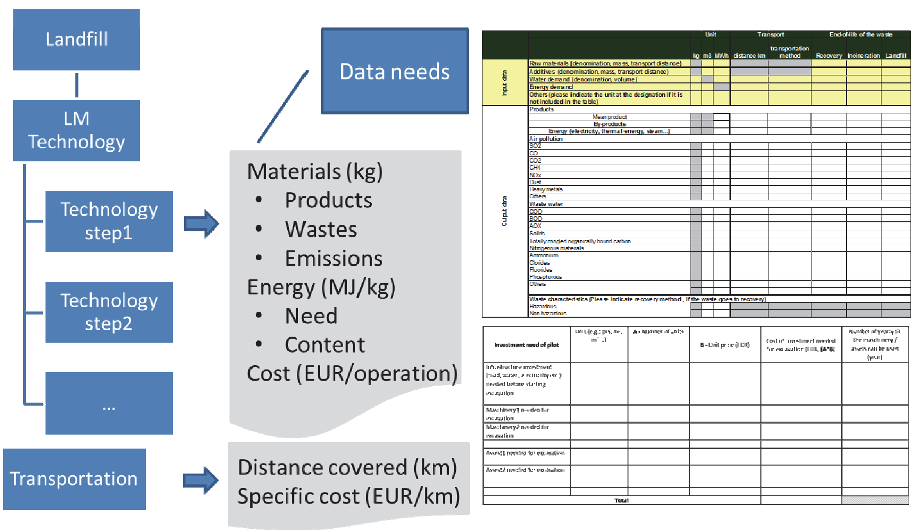

Fig. 5. Data collection for scenario models in the Smart Ground framework

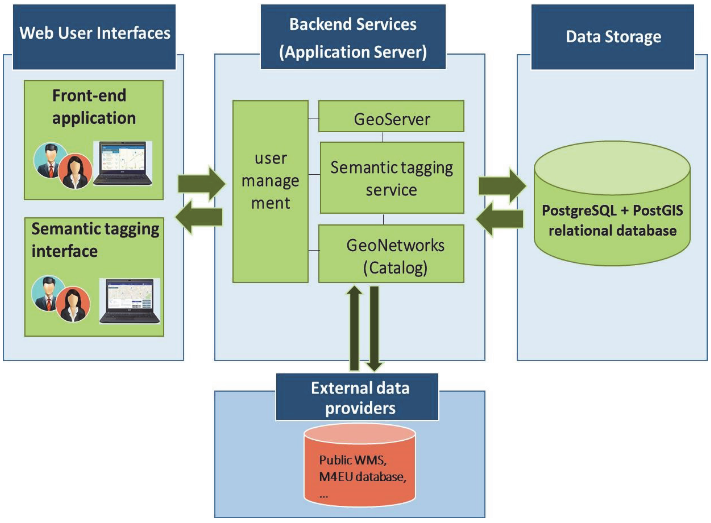

Fig. 6. High level components of Smart Ground Platform

A data model is currently being developed based on an iterative approach, supporting the storage of the above mentioned information and allowing the queries of the target users.

For the development of the Smart Ground data model several activities and projects were evaluated, primarily the INSPIRE Data Specification on Mineral Resources (INSPIRE, 2013) and the project Minerals4EU (Minerals4EU, 2017). Best practices such as table structure, naming conventions and the greater possible number of tables and code lists (dictionaries with predefined values) were reused to facilitate interoperability and mapping between data of the related platforms.

4.2. Backend Services

This category includes the components that serve the front-end services, having the capability to communicate with the required resources (internal database or third party services).

- **GeoServer** has been chosen as geospatial data server which is used for vector data rendering, publishing OGC services (WMS, WFS), serving plenty of different raster and vector data formats, or creating our own base map.
- **Semantic Tagging Service:** this service semantically enriches the data collected and aggregated in Smart Ground databank repositories, creating a layer of semantic annotations on top of them, and publishes these annotations as open linked data. The resulting ontology is expressed by means of the Resource Description Framework (RDF) formalism, which provides the tools to organize the information in form of a semantic graph where each node represents a concept, and each edge represents a predicate, i.e. a property, holding between two concepts. In particular, an RDF statement is an expression that asserts that a given relationship (called a predicate) holds between two concepts, a subject and an object, and represents the building block of the ontology. The ultimate purpose is to expand the scope of the classic database interrogation tools, namely SQL queries, thus combining the factual data with the meta-knowledge represented in the ontology, allowing each user the possibility to filter/extend the information extracted from the database according to their personal knowledge.
- **GeoNetwork:** Smart Ground information will be described and published in the catalog so that third parties can explore our database. It will also facilitate Smart Ground users to search data across multiple catalogs, e.g. ProSUM or MINERALS4EU.
- **User Management Service**: This component enables the security features such as authentication, authorization and user management across the services and components of Smart Ground.

4.3. Web User Interfaces

Two user interfaces are planned, one supports the decision making of different stakeholders regarding SRM available in waste sites, while the other aims at developing a RM thematic ontology (meta-knowledge).

- **Front-End Application:** this is the website that the end-user sees and acts on to display and collect all the information for the main functionality of the platform. It will be composed of a map viewer, a layer manager and a window to display most of the dynamic information. Planned functionalities include: management of operators' waste sites, and search and exploration of waste sites and RM of interest, calculation of predictions for specific waste sites.

The user interface is optimised for a desktop browser, appropriate for use inside a customer's organisation, as it will be the case for Smart Ground.

- **Semantic tagging interface:** It offers the Smart Ground users a way to make available their own knowledge, while also providing the tools to extend the traditional database query process to take into account both the existing factual data, as stored in the database, and the personal knowledge laid down by each user.

There are four ways for the users to enrich the system with their personal knowledge:

- By adding a statement to the ontology: the user can select a subject and an object from the existing concepts and connect the two by means of a predefined property.
- By defining a new concept, which can be interpreted as a subject or an object in a new set of statements.
- By defining a new property, providing a new way to connect existing concepts in the ontology.
- By including other users' personal knowledge, whether concepts, properties or entire statements.

Technical details about the semantic tagging interface are described in Di Mauro et al. (2016).

5. Implementing new approaches to decision-making within an established market, knowledge transfer

CRM and SRM recovery projects involve a wide range of stakeholders who come from diverse backgrounds and raise various issues that are at stake in the project (Lapko et al., 2016). These concerns might be favourably or unfavourably affected owing to the achievement of project objectives (Careddu et al., 2013; Frändegård et al., 2015). Although they are often conflicting and relate to diverse topics, stakeholder concerns springing from a CRM and SRM recovery projects are bonded with strong and dynamic interdependencies. As such, to maximize impact and implement new approaches in this sector, the Smart Ground project is developing a comprehensive stakeholder's analysis and training plan.

5.1. Stakeholder analysis methodology and results

The stakeholder analysis is designed as a four-step process and includes the following steps: (i) identifying stakeholders across European countries (ii) categorizing and mapping stakeholders (iii) identifying stakeholder allegiance and (iv) investigating stakeholders' knowledge, interests, positions, alliances, and importance related to the policy. To ensure low carbon footprint and minimize burden on stakeholders, a three stage online questionnaire using Qualtrics® software was used. The stage 1 survey, covering questions regarding the 'State of landfill mining and CRM recovery in the EU' was circulated to first interviewees' list of stakeholders (40 people) created following suggestions given by the Smart Ground experts in the field of MSW and EW management. In the stage 2 the survey was refined following feedbacks received and then sent to 750 stakeholders across 14 EU countries. Due to the low response rate, a stage 3 survey was sent to the updated database of 900 stakeholders. For this stage, the survey followed the same structure as the stage 2 survey but some aspects of the survey were shortened and simplified with the aim of reducing the number of stakeholders leaving the survey. Stakeholders have been classified into five categories according to their social roles, named administration, state-owned enterprise, private enterprise, research institute, social organizations and other types. The survey was available in 8 languages including English, Finnish, French, Hungarian, Italian, German, Portuguese and Spanish. The survey is available at Secondary Raw Materials recovery opportunities in EU.

From the 900 participants invited to complete the survey, 191 stakeholders opened it (21%). Completion rate of the survey was 53% (101 responses recorded in full for the survey) and 47% (90 partial responses recorded or participants left the survey within a minute). Survey respondents needed an average time of 20 minutes to answer the survey).

63% of survey respondents were classified as "Key Players". Stakeholders within this category are the key stakeholders with high influence/power and high interest and therefore, the group The Smart Ground consortium should dedicate more efforts and tailor training activities and project outputs. Besides, identifying their profile, sector, needs, perceived opportunities and perceived barriers has served as a basis for developing the stakeholder engagement strategies, training, networking and implementation strategies.

The sectors most represented by "Key Players" are the Recycling and waste management sector (27%), the Extractive industries (mines) (12%), Renewable energy (8%), Construction (7%) and Energy (7%). 21% stated "Other" as their industry sector (Fig. 7).

Further to the power *vs* interest grid, a stakeholders' influence analysis was carried out. Regulators and Governmental agencies are the most influential stakeholders, followed by Site owners, Site operators and Academics/researchers (Fig. 8). Therefore, the consortium should target networking and training activities towards these stakeholders as this will have a cascading effect down the network to all stakeholders. Therefore, Smart Ground materials will look to incorporate, where possible, the views and needs of all these groups.

This stakeholder analysis has provided the Smart Ground project with complex and in-depth information regarding the different stakeholders involved, their importance and interactions and their views and concerns regarding LFM. Fig. 9 summarises the opportunities and factors promoting LFM and the barriers, limitations and bottleneck as perceived by the stakeholders. Important to note is that economic factors were most important across all stakeholder groups for both positive and negative stances. Therefore, Smart Ground will aim to focus on economic factors in their output material and to facilitate discussion and knowledge-sharing in order to engage stakeholders in these topics to facilitate solutions and promote opportunities.

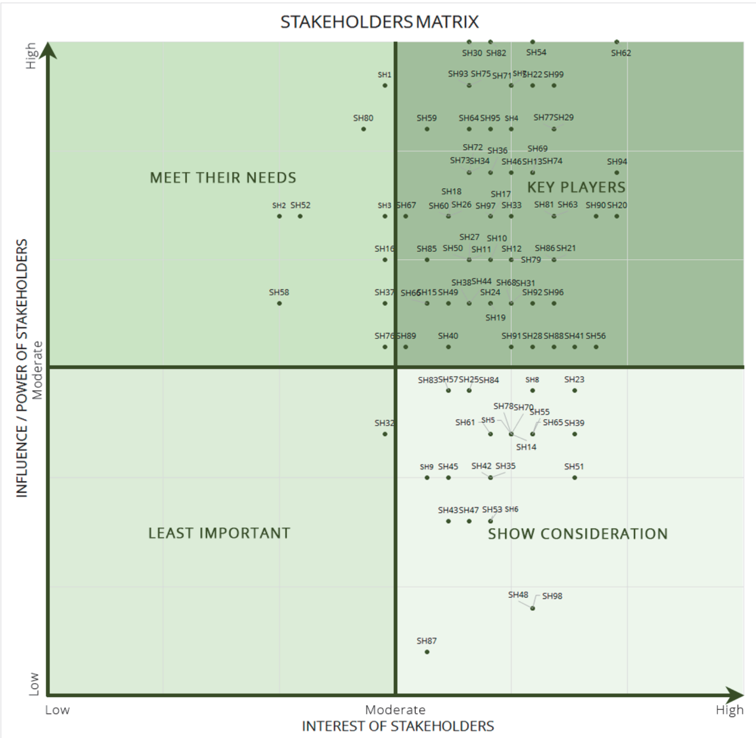

Fig. 7. Power vs interest grid for Smart Ground stakeholders

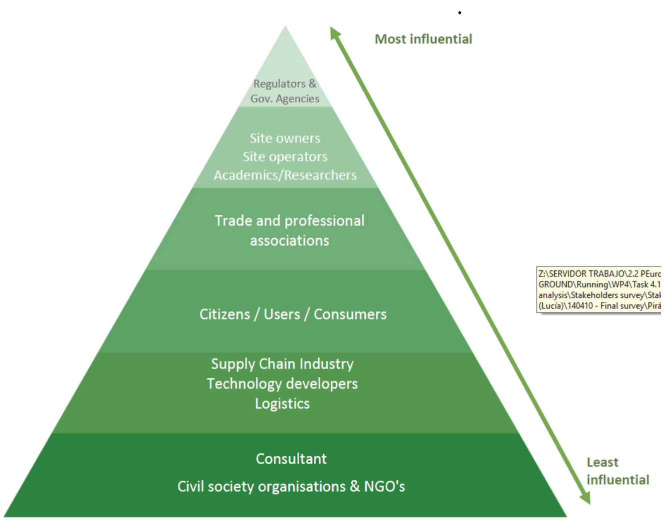

Fig. 8. Influence pyramid

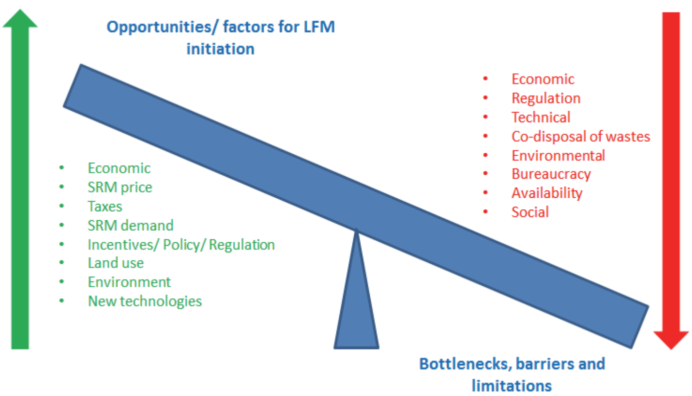

Fig. 9. Opportunities and barriers identified by the stakeholder analysis

Stakeholders also indicated a general willingness to share experiences, provide technical support and advice as well as case studies on best practices and successful LFM projects.

5.2. Smart Ground training materials

The training materials developed consist of (1) a landfill mining toolkit, (2) a range of decision support tools (DST) enabled through the Smart Ground database and (3) an E-book.

The landfill mining toolkit has been designed to give stakeholders information about what is needed to initiate CRM/SRM recovery from landfill sites or EW facilities, and scope out the potential viability of reuse of CRM/SRM in their specific circumstances. The toolkit cannot however been used to provide a full engineering study of your project or a complete and detailed business case. Rather it will give the users the understanding and basic data to allow users to progress into more detailed analysis with potential suppliers and technical advisors to build a technical and business case for your project.

The second material developed is the Smart Ground database and associated decision support tools. The database provides guidance on the validity of a potential landfill mining project. It will serve as an indication that should be followed by specific site analysis. The associated DST will be based on the waste age in a landfill, site life and other economic factors such as revenue of the additional space, value of the recovered soil and the avoided costs. Finally, the last material is the E- Book. The E- Book is an interactive pdf that will be available on Smart Ground website. It will be a stand-alone knowledge transfer output including online tools, decision support tool and toolkit.

6. Results and discussion

One of the results of the project is a shared a Data Collection Plan for the characterization of different types of waste deposits. Such Data Collection Plan includes field sampling, samples preparation and analyses protocols. The methodologies and protocols for field survey, sampling and characterization phases have been developed and validated through in-depth characterization studies of ten selected pilot landfills with strongly different characters: two samples are reported in the present paper. The validation phase suggest that such a methodology can be adopted for the estimation of the SRMs potential in landfill and facilities.

Furthermore, the data gathering about the specific waste streams, the technologies to recover SRMs/CRMs and the potential impacts (environmental, economic, social) associated to different scenarios, is fundamental to evaluate CBA and LCA on specific case studies. Modelling and decision support tools are in progress. They will predict the distribution of SRM available across EU landfills to allow targeted SRM recovery market.

The main achievement of the SG platform is the design of a data model to store the relevant information of waste sites which allows to register, search and access relevant information (materials, processing activities, samples, etc.) for the waste materials community (waste operators, public administrations, voluntary activists) at European scale. This complex data can be screened out by the platform using a range of search filters that will suit needs of different stakeholders. When ready (at the end of the project, March 2018), the SG platform will allow end-users to identify and match the supply and demand for SRM by interrogating the data and identifying suitable urban waste landfill sites and/or EW facilities for SRM recovery and other valuable materials. The platform is intended to provide a reliable and transparent source of harmonised and validated information on SRM estimates from anthropogenic deposits available across Europe.

The collection of the information is key for the adoption of the platform. It is not possible to implement a data harvesting system that automatically collects information from other public national platforms given the heterogeneous models, concepts, and languages of each database. In order to integrate information from external database the consortium has to deal on a case by case basis. Instead, the collection of data relies mainly in the engagement of different actors that will upload the information into the platform. When the platform moves in the future to operational phase the authenticity of data will have to be reviewed.

The development of added-value information and services on top of the baseline information will be important to support the adoption of the platform and establish a viable business model. In this regard the project is developing estimation of amounts based on the samples registered for each site. In the future the integration of real-time information from external sources will be considered e.g. market prices, environmental or social indicators.

The integration of the main platform with the semantic tagging module in the form of semantic queries is not without challenges. The users will define personal ontologies with new relationships for which the ecstatic search engine of the platform is not designed. In particular, users will be able to express factual knowledge not planned for at the data schema definition time (such as properties or attributes which might become relevant in the future, within the context of new laws and norms to be enforced), as well as personal, either persistent or temporary knowledge that they would like to use in the context of their access to the platform, to simulate some form of hypothetical queries (What-if queries, with the condition expressed in the form of temporary, personal knowledge).

7. Conclusions

The development of proper guidelines and best practices to recover waste from landfill and to recycle it into new products is useful to boost the systematic recovery of SRMs and CRMs from landfills and facilities. A continuous cooperation with past and ongoing EU projects and networks (ProSUM, SCREEN, Minerals4EU, EURELCO) has been assured, together with a close cooperation with EC initiatives as the Raw Materials Information System (RMIS).

Smart Ground findings and best practices will be transferred to different stakeholders to maximize its impact and to establish new approaches in the waste sector.

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A special thank to the entire consortium for their effort in Smart Ground activities.

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LIFE-CYCLE CARBON FOOTPRINT ANALYSIS OF THE PARMA HAM P.D.O. (PROTECTED DESIGNATION OF ORIGIN) ON-THE-BONE

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Abstract

The Rural Development Plan (RDP) represent the most important source of contributions and support for the agro-food sector companies in Italy. The European Community planning tool based on a European Structural and Investment Fund (SIE) allows the agricultural and forestry entrepreneurs to undertake projects and investments for the improvement of their companies. During the 2014-2020 RDP program, the Emilia-Romagna region (Italy), promoted a rewarding mechanism to support those companies carrying out Carbon Footprint (CF) study of their product supply chain.
For this reason Fontane del Duca Ltd decided to implement the CF of its Parma ham P.D.O. (Protect Designation of Origin) on-the-bone. The Functional Unit (UF) chosen for this study is 1 kg of Parma ham P.D.O. on-the-bone, net of the non-edible part. The Product Category Rules (PCR) considered in the analysis refers to the PCR "Preserves and Preparation of Meat", UN CPC 2117. Primary data was used for all the life cycle phases (slaughterhouse/sectioning, meat processing and distribution), except for the pig farming phase and the packaging end-of-life scenarios. Moreover, for the breeding stage modelling, processes from the Agri-footprint 2.0 database are used, adapting it to the Italian heavy pigs breeding method.
The goals of this study are two: first of all to evaluate the overall impact of the Parma ham P.D.O. on-the-bone and, on the other hand, to analyze how the real accuracy of the data influenced the results. The overall impact is 23.11 $kgCO_2eq$, with the most significant contribution due to the upstream module, in particular for the farming stage (68.4%), in line with other benchmark. Then a sensitivity analysis was performed to assess the effects on the total impact of the economic allocation data in the slaughterhouse stage.

Key words: carbon footprint, greenhouse gas emissions, ham, life cycle assessment, meat sustainability

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1. Introduction

The Rural Development Plan (RDP) is the European Community planning tool based on a European Structural and Investment Fund (SIE) and is now the most important source of financial contributions and support for companies in the agro-food sector. The RDP allows agricultural and forestry entrepreneurs to undertake projects and investments for the improvement of their companies. During the 2014-2020 program, the Emilia-Romagna region (Italy), promoted a rewarding mechanism to support those companies carrying out the Carbon Footprint (CF) studies for their product supply chains. By doing so, companies could evaluate their sustainability performances and identify potential environmental improvements. In particular, among all the applicants, there was a significant interest from the companies producing ham.

Meat is the food product with the highest environmental impact (Steinfield et al., 2006; Weidema et al., 2008). The process of converting animal feed into meat is highly inefficient, 75-90% of the energy consumed goes to body maintenance or lost through manure and by-products such as skin and bones (Röös et al., 2013). Then the opportunity

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to carry out studies with the availability of primary data relating to the meat industry sector is a precious importance, as well as to develop the necessary supporting databases to achieve significant advances in the use of LCA concepts and life cycle-based tools (Notarnicola et al., 2012). Furthermore, a numer of papers analyzed through a LCA approach the environmental impact of the production of pigs slaughtered at a standard liveweight of 90-120 kg (Aramayan et al., 2011; Basset-Mens and Van der Werf, 2005; Dalgaard, 2007; Dourmand et al., 2014; Mackanzie et al., 2015; Pelletier et al., 2010; Vergè et al., 2009) but studies focusing on the impact evaluation of heavy pig production are presently lacking (Bava et al., 2015).

Here the CF of Parma ham P.D.O. (Protect Designation of Origin) on-the-bone, is presented through an assessment of its complete life cycle, from the pigs farming phase up to end-of-life of the product packaging materials and the ham non-edible parts, which are discarded during the consumption phase.

The present paper gives a description of the goal and scope, inventory data and the results of the impact assessment. Moreover, given that the environmental impact of ham is mainly due to the breeding stage, according to other similar studies (Simonetto et al., 2016) and there is a strong dependence on the quantity of the pig live weight needed to the ham production, a sensitivity analysis is performed. In the last part of the study, the CF assessments with two different allocation values are compared in order to evaluate the variance of the results.

2. Materials and methods

Life Cycle Assessment (LCA) is an objective evaluation procedure to examine the energetic and environmental impact related to a product, process or activity. This procedure is carried out by identification and quantification of energy and materials used and by the amount of waste released into the environment.

The evaluation covers the whole life cycle of the product, process or activity and includes the extraction and treatment of raw materials, manufacturing, transport, re-use, recycling, and waste treatment. The four LCA phases are: goal definition and scope; Life Cycle Inventory analysis (LCI); Life Cycle Impact Assessment (LCIA) and interpretation (ISO, 2006a, 2006b).

2.1. Objective of the study

This study assessed the CF of the "Parma ham P.D.O. on-the-bone" produced by Fontane del Duca Ltd. according to the ISO/TS 14067:2013 international standard on "Greenhouse gases – Carbon Footprint of products – Requirements and guidelines for quantification and communication". The Life Cycle Analysis is applied referring to the "Preserves and Preparation of Meat" Product Category Rules (PCR), UN CPC 2117 of the International EPD System, containing the guidelines for "21171 – Pig meat, cuts, salted, dried or smoked (bacon and ham)", among many others.

2.2. Functional unit

The Functional Unit (FU) is 1 kg of Parma ham P.D.O. on-the-bone, net of non-edible part. The product non-edible part consists in the bone and in the scraps produced during the slicing (fat and rind). Each entire product (overall mean weight of 14 kg) contains 71% of edible part, as described in Table 1.

Table 1. Edible part of Parma ham P.D.O. on-the-bone

EDIBLE PART OF HAM net of bone, fat and rind	
Bone	1.15 kg
Scraps From Slicing	2.90 kg
Ham	14.0 kg
% Edible	**71.07%**

2.3. System description and boundaries

This study considered the complete life cycle assessment, from the pig farming phase to the end-of-life of the product packaging materials and the ham non-edibile parts, which are discarded during the consumption phase, including the pig slaughtering phase, the sectioning of fresh meat, the processing required for the ham production, the product distribution (up to the logistical platform) and all the required transports for each phase of the considered life cycle (Fig. 1). The following phases are excluded from the system boundaries:

- Ham storage after the distribution, because is indicated "cellar temperature" as preservation;
- Consumption, because the product does not need to be baked.

According to the PCR, the life cycle is divided into three main phases: upstream module, core module and downstream module.

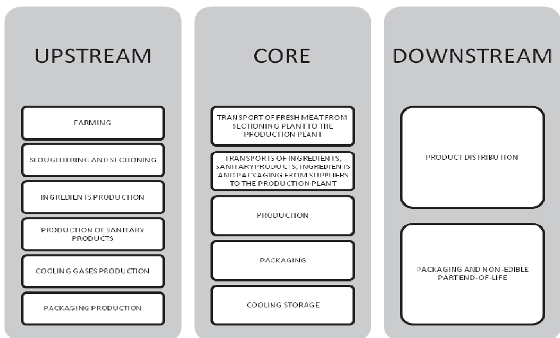

Fig. 1. System boundaries for the CF of the Parma ham P.D.O. on-the-bone

The Parma ham P.D.O. must be produced with fresh meat that exclusively come from some regions of Italy. In this case, all the pigs are slaughtered by Sassi slaughterhouse, which provides the fresh hams to the Fontane del Duca plant for the processing. How it is shown in Fig. 2, the Parma ham P.D.O. production starts with the reception of the fresh hams, to which is affixed the seal and sent to the salting phase. After about 20-25 days, the hams are desalinated and placed in the resting room for a period variable from 60 to 90 days. After the washing and drying phase the hams are aged for at least 12 months (Italian Ministry of Agriculture, 2010).

From the system boundaries the following items are excluded:

- the employees business travels;
- the transports of employees from their houses to the production plant;
- the research and development activities.

The applied cut-off rules are about <1% of the mass in accordance with the considered PCR.

2.4. Data quality

Primary data are used for all the life cycle phases except for the farming stage (upstream module) and the packaging end-of-life scenarios (downstream module). In these stages secondary data were used with an appropriate temporal, technological and geographic representativeness.

The Agri-footprint 2.0 (Blonk Agri Footprint, 2015), for the pig farms modelling, and ecoinvent 3.2 (Weidema et al., 2013) database are used in this study.

2.5. LCIA method

The LCIA phase of the CF study considered the potential climate change impact of each Greenhouse gases (GHG) emitted and removed by the product system. For this reason, it is calculated multiplying the mass of the released or removed GHG by the 100-year Global Warming Potential (GWP) given by the International Panel on Climate Change (IPCC) (IPCC, 2007; ISO, 2013). The unique impact category is then the Global Worming, expressed by the kgCO_2eq unit of measurement, as indicator. Finally, the LCIA is performed by means of the LCA software SimaPro 8.2 and using the IPCC 2007 method (IPCC, 2007).

2.6. Life Cycle Inventory (LCI)

2.6.1. Upstream module

The upstream module the whole processes involved in fresh meat production (farming of pigs and slaughtering), which is the principal input data, as well as the production of ingredients used for ham manufacturing, packaging materials, sanitary products and cooling gases (Fig. 2). Table 2 reports all the ingredients and their packaging used during the ham manufacturing. The data for the breeding phase refer to the pig life cycle, from the sow fecundation to the pig slaughtering. Lacking primary data, we refer to the Agri-footprint database process "Pig to slaughter, pig fattening, at farm/NL Economic" (Blonk Agri Footprint, 2015), adapting it to the Italian heavy pigs farming. As a result, the pig weight, the input quantity of feed, the emissions generate by the enteric fermentation or the manure management are modified as shown in Table 3.

Indeed, Agri-footprint database takes into account to light pig farming (118 kg), typical in the European scenario, while Parma ham P.D.O. is made with pigs that rise the final weight of 160 kg (Italian Ministry of Agriculture, 2010). The ration increases for heavy pigs are calculated by the Feed Conversion Ratio, calculated as feed quantity divided by the increase of live weight (Salvadori and Ventura, 2009).

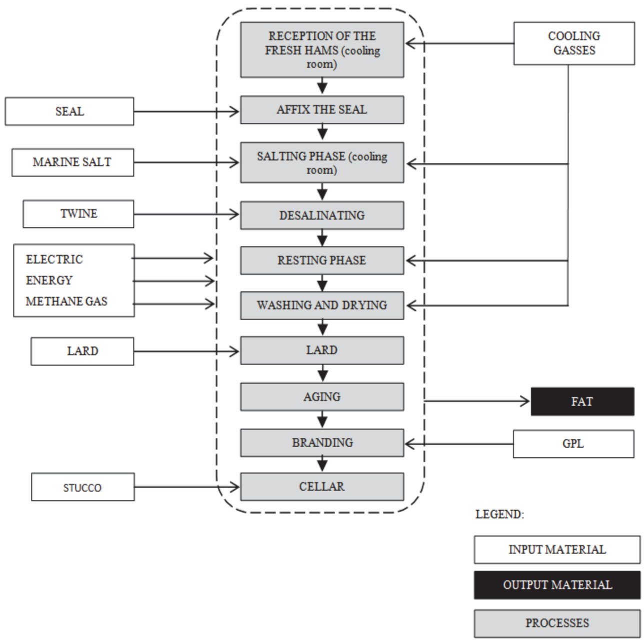

Fig. 2. Flow diagram of the Parma ham P.D.O. on-the-bone production phase (core module)

The Parma ham P.D.O. on-the-bone is sold without packaging, but the product is provide fitted only with a twine and an aluminium seal.

Table 2. Ingredients and associated packaging materials for the Parma ham P.D.O. manufacturing

Ingredients	***Amount (kg/kg of product)***	***Packaging***	***Packaging weight (kg/kg of product)***
Salt	0.0932	-	-
Lard	0.0073	Cardboard	1.65E-04
		HDPE bag	2.64E-05
Stucco	0.0004	Cardboard	1.03E-05
		HDPE bag	1.65E-06

Table 3. Modified heavy pig breeding process

	Agri-footprint original process	***Modified process – heavy pig***
Pig final weight	118 kg	160 kg
Conversion ratio	2.6 kg of feed/kg live weight	3.6 kg of feed/kg live weight
Air emissions		
Biogenic Methane (CH_4) – enteric fermentation	5.37 kg	7.27 kg
Biogenic Methane (CH_4) - manure management	1.5 kg	2.03 kg
Nitrous oxyde (N_2O) – direct	0.0982 kg	0.133 kg
Nitrous oxyde (N_2O) – direct	0.0635 kg	0.0859 kg
Ammonia (NH3)	4.9 kg	6.63 kg
Dusts	56.06 kg	75.9 kg

2.6.2. Core module

The core module are considered the whole production processes (energy consumption, emissions and waste) and the transportation of fresh meat, ingredients and other materials. The Parma ham P.D.O. on-the-bone production involves electric energy consumption, methane and water for the different phases (Table 4).

Table 4. Consumption of energy, methane, water and LPG

	Amount	***Unit measure***
Electric Energy	1.70	**kWh/kg of product**
Methane	0.05	**m^3/kg of product**
Water	5.5E-4	**m^3/kg of product**
Lpg	1.96E-4	**kg/kg of product**

2.6.3. Downstream module

The Fontane del Duca Ltd. Parma ham P.D.O. on-the-bone is provided in Italy for an average distance of 143 km from the production plant. The product end-of-life stage considered the disposal of twine, aluminium seal and the ham non-edible part (bone, rind and fat), which account for the 28.93% of the product (Table 1).

2.6.4. Allocation rules

Where, in the production process, co-products are present, as in the sloughterhouse, the multi-functionality is managed following the economic allocation criteria, as indicated in the considered PCR (International EPD System, 2016). The economic partitioning factors, shown in Table 5, were calculated as the share of the proceeds of one product in the total outcome of the proceeds of all the products (Ardente and Cellura, 2012) (Eq. 1):

$$P_i = (n_i * x_i)/[\sum (n_i * x_i)] \quad (1)$$

where P_i is the partitioning factor of the ith coproduct (i.e. ham), n_i is the quantity of the *i*th product, and x_i is the price of the *i*th coproduct.

The hams processing by-products were defined as alimentar scraps and were not allocated any impact because are tranferred for free. The allocation values are highly sensitive data for the impacts assessment, as is clearly explained in details in section 3.2. For the calculation of all the other input and output data, mass allocations were used.

Table 5. Allocation of by-products

Phase	***Products***	***Economic allocation %***
Fontane Del Duca Production	Ham	100
	By-products (scraps)	0
Sloughterhouse	Ham	34.15
	Loin	22.14
	Half-carcass	2.68
	Shoulder	11.10
	Coppa	6.27
	Bacon	7.12
	Ground meat	5.63
	Head	1.40
	Foot/bones	0.79
	Throat	1.86
	Lard	2.05
	Rind/fat	0.42
	Offal	1.12
	Ciccioli	2.51
	Blood	0.57
	Portioned	0.20

3. Results and discussion

3.1. Carbon footprint results of the Parma ham P.D.O. on-the-bone

The impacts calculated using the IPCC 2007 method referred to 1 kg of Parma ham P.D.O. on-the-bone FU. Table 6 shows the specific GHG contributions from fossil and biogenic sources, direct land use change (dLUC) and CO_2 removal. According to the results of the impact assessment, upstream module generates significantly more impacts than the two other life cycle stages (core and downstream modules), increasing the total GHG emissions to 89.7% (Fig. 3).

Table 6. Carbon Footprint of Parma ham P.D.O. on-the-bone (UF = 1 kg of product, net of non-edible part)

Carbon footprint contributions		*Unit of measure*	*Total*	*Upstream module*	*Core module*	*Downstream module*
Fossil GHG		**kg Co_{2eq}**	**13.817**	**11.600**	**2.048**	**0.168**
	CO_2, Fossil	kg Co_{2eq}	9.310	7.258	1.916	0.136
	N_2O	kg Co_{2eq}	3.901	3.867	0.014	0.020
	CH_4, Fossil	kg Co_{2eq}	0.566	0.448	0.115	0.004
	Others GHG	kg Co_{2eq}	0.039	0.027	0.003	0.009
Biogenic GHG		**kg Co_{2eq}**	**2.777**	**2.567**	**0.043**	**0.167**
	CO_2, Biogenic	kg Co_{2eq}	0.184	0.025	0.041	0.118
	CH_4, Biogenic	kg Co_{2eq}	2.593	2.541	0.002	0.049
GHG From Dluc		**kg Co_{2eq}**	**6.619**	**6.619**	**2.14e-04**	**5.03e-05**
CO_2 Removal		**kg Co_{2eq}**	**-0.099**	**-0.063**	**-0.034**	**-0.002**
Total		**kg Co_{2eq}**	**23.114**	**20.723**	**2.057**	**0.334**

This is mainly due to the pigs farming phase, contributing for 68.4% of the overall emissions, where production of animals feed and manure management are largely responsible. Moreover, fossil source generates most of the GHG emissions accounting for 59.7% and production of animals feed contributes for the 28.6% of the overall impact, highlighting the large consequences originated from the land use change.

The production phase (core module) is where the company can directly manage the consumptions and the emissions. In particular it generates only the 8.9% of the total impact on climate change, mainly caused by the energy consumption.

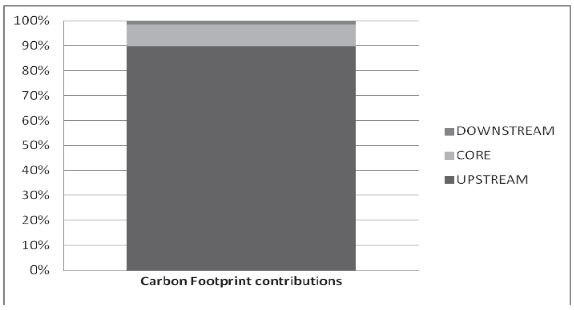

Fig. 3. Carbon Footprint contributions of the different life cycle phases of Parma ham P.D.O. on-the-bone

3.2. Sensitivity analysis

The Carbon Footprint impact depends mainly on the farming activities contained upstream of the pigs slaughtering process and refers to a specific quantity of pig live weight. On the basis of the primary data provided by the slaughterhouse, in order to obtain 1 kg of meat ready for the food industry, 1.56 kg of alive pig are needed in input. However, using the Agri-footprint process database, to obtain 1 kg of meat ready for food industry you need 2.05 kg of live pig. This difference between the two weights is due to a greater amount of by-products, for pet food, generated by the slaughter which the Agri-footprint database refers to. Moreover, the difference between the two processes, the primary one (Sassi slaughterhouse) and the database one, is in the percentage value of the products economic allocation: Agri-footprint assigns a value of 98.9% at the fresh meat in output, without distinction between the various anatomical parts, while Sassi provides a detailed list of costs for each anatomical part hence it is possible to calculate an allocation value of 34.15% for the hams (Table 5). Simulating the ham production entering the Agri-footprint database process, instead of the slaughter process with primary data, the Carbon Footprint results 79,11 kgCO_2eq, as shown in Table 7, much higher than the previous result of 23,114 kgCO_2eq (Table 6), calculating using primary data from Sassi slaughterhouse.

The results variability (Fig. 4) highlights that the values of economic allocation for fresh meat substantially affect on the impacts.

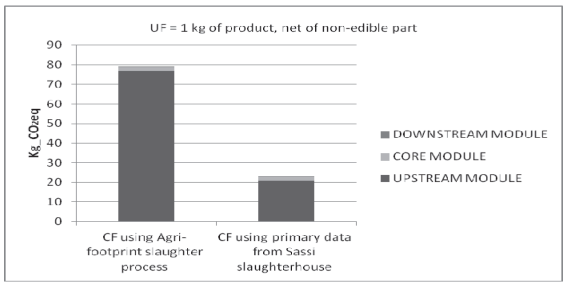

Fig. 4. Comparison of results: CF using the process of Agri-footprint slaughter vs. CF using primary data provided by Sassi slaughterhouse (UF = 1 kg of Parma ham P.D.O. on-the-bone, net of non-edible part)

4. Conclusions

The RDP funding program has been an effective instrument for the diffusion of environmental sustainability tools, like the Life Cycle Assessment and the Carbon Footprint. The sensitivity of the regional Public Administration has allowed, for the first time, the companies of the agro-food sector of Emilia-Romagna region to approach with calculation and reporting tools of their environmental impacts. The Carbon Footprint of 1 kg of Parma ham P.D.O. on-the bone, net of non-edible part, results 23,114 kgCO_2eq, with the main contribution of the pigs farming phase (68.4%) principally caused by the production of animals feed and the manure management.

Table 7. Carbon Footprint of Parma ham P.D.O. on-the-bone using Agri-footprint slaughter process (UF = 1 kg of product, net of non-edible part)

Carbon footprint contributions (using agri-footprint slaughter process)	*Unit of measure*	*Total*	*Upstream module*	*Core module*	*Downstream module*
FOSSIL GHG	kg CO_{2eq}	71.45	69.23	2.05	0.17
BIOGENIC GHG	kg CO_{2eq}	1.91	1.7	0.04	0.17
GHG from dLUC	kg CO_{2eq}	5.84	5.84	0.00	0.00
CO_2 REMOVAL	kg CO_{2eq}	-0.09	-0.05	-0.03	0.00
TOTAL	**kg CO_{2eq}**	**79.11**	**76.72**	**2.06**	**0.33**

The sensitivity analysis revealed also a great variability of the results, strongly influenced by the allocation values. The results showed the importance of primary data access, in order to improve the inventory processes not only for the breeding phase, but also for the evaluation of the allocation factors.

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VALORIZATION OF AGRO-INDUSTRIAL WASTES IN LIGHTWEIGHT AGGREGATES FOR AGRONOMIC USE: PRELIMINARY STUDY

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Abstract

This research was focused on the valorization of agro industrial waste/by products available in the local industry with the kilometer zero (km 0) concept, as a replacement of virgin raw materials (clay) to elaborate lightweight aggregates (LWA_S). The alternative raw materials were employed as pore forming agent, in order to reduce sintering temperature and energy consumption of the furnace. The three technical nutrients studied were provided for local food industries: sludge from wastewater treatment plant from brewery industry (SB), meat-bone meal (MBM) and corn cob (CC). These materials were characterized in terms of chemical (XRF and elemental analysis - CHNS) and mineralogical (XRD) composition, as well as their thermal behavior (TGA/DTA/DSC) and LOI.

For the production of LWA_S different percentage of waste/by product (0, 5, 10 and 15%) were mixed with three types of clays (white, black and red) in two different clay-based mixtures. With the addition of water were produced approximately spherical pellets and thermal treated at two different temperatures (900 and 1000°C) for 1 hour. Technological parameters such as bulk and absolute density, total porosity, water absorption capacity, pH, electrical conductivity and organic matter content were measured, to determine their potential use in agriculture. XRD and scanning electron microscope (SEM) were performed for the characterization of different samples.

The results indicate the potential for manufacturing high quality lightweight aggregates for agronomic purposes, using relatively simple processing and low sintering temperature that contribute to the reduction of greenhouse gases to the atmosphere.

Key words: agro-industrial wastes, circular economy, growing substrate, lightweight aggregates, waste valorization

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1. Introduction

It is estimated, that more efficient use of resources along the entire value chain could reduce the need for input of virgin materials in 17-25% by 2030 (Meyer, 2011), with a corresponding economical savings for European industry in the order of € 630 million a year (Innova Europe, 2012) and potentially raise the EU GDP (Gross Domestic Product) up to 11%. This fact reduces costs by inverting the economic chain, allowing to suppress landfills cost through the valorization, from waste to by product. The agro-industrial waste and by-products used in this research have a common thread, although they are composed mostly of organic matter, are produced in very large amounts and represent a significant environmental problem.

The progressive implementation of wastewater treatment plants leads to an increase of sludge requiring disposal. In the food industry, the sector of brewing in Europe had produced 395 million hectoliters in 2015 (Brewers of Europe,

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2016). The sludge is the final waste from the water purification process in a waste water treatment plant. It is decomposed and stabilized to reduce the odor, and subjected to treatment for its disposal and destruction (solidification/stabilization) (Cadet et al., 2015; Huang et al., 2007). Beer is the fifth most consumed drink in the world, surpassed only by tea, carbonated drinks, milk, and coffee. For this reason the behavior of wastewater treatment plant sludge within the ceramic matrix as pore forming agent, for structural ceramics was studied by many authors (Barbieri et al., 2013; Eliche-Quesada et al., 2011; Martínez-García et al., 2012; Szőke et al., 2014) and also for LWA_S (Cheeseman and Virdi, 2005; Farias et al., 2017; García et al., 2014).

Regulation (EC) Nº 178/2002 constitutes the new European legislation on food safety (EC Regulation 178, 2002). Animal by-products are defined as the entire bodies or parts of bodies of animals or products of animal origin not intended for human consumption. They represent more than 15 million tonnes of meat, dairy products and other products, including manure. Animal by-product, including meat-bone meals are classified in three categories where category 1 and 2 represent materials highly risk, while category 3 low risk. Category 1: all body parts, of animals suspected of being infected by a transmissible spongiform encephalopathy (TSE); products derived from animals that have absorbed prohibited substances or substances containing products dangerous for the environment. Category 2: manure and digestive tract content; products of animal origin containing residues of veterinary drugs and contaminants in concentrations exceeding the Community limits; products of animal origin, other than category 1 material, that are imported from third countries and fail to comply with the Community veterinary requirements; animals other than category 1 that have not been slaughtered for human consumption. Category 3: parts of slaughtered animals which are fit for human consumption but are not intended for human consumption for commercial reasons; parts of slaughtered animals which are rejected as unfit for human consumption but are not affected by any sign of a communicable disease; blood obtained from animals declared fit for human consumption. Animal by-products derived from the production of products intended for human consumption, including degreased bones and greaves. Materials belonging to category 3 can directly disposed of as waste by incineration in an approved incineration plant, used as raw material in a pet food plant; processed by a specific method in an approved processing, technical, biogas or composting plant. For materials belonging to categories 1 and 2 the safest alternative is the thermal treatment that ensures to destroy potential BSE pathogens in high-temperature processes.

The ashes from animal floor were studied by several authors as fertilizing agent for cultivated soils (Jeng et al., 2006; Masu et al., 2016; Mondini et al., 2008; Ylivainio et al., 2008) and for active glass production (Barbieri et al., 2014). In order to investigate new options for exploitation of meat-bone meal (MBM) easily feasible and industrially scaled up, we used the **category 3 - animal by product**, in this research.

Corn is one of the most consumed cereals in the world. In the EU, 60,279,000.00 MT were produced in 2016, in fourth place after the United States, China and Brazil (IndexMundi, 2016). The corn cob has many applications for its high calorific value, high liquid absorption capacity, wear resistance, discrete abrasiveness and high elasticity. Corn cob has been studied as a building material for its insulating properties (Pinto et al., 2011), as well as porosity forming agent to develope sustainable bricks (Njeumen Nkayem et al., 2016). The study and recovery of these wastes is a challenge and an alternative that represents a future course of action. Therefore, it is considered that the ceramic industry has a structure to absorb this waste, without most changing its industrial process, without causing additional costs.

The manufacture of LWA_S from waste/by products can become increasingly viable. Landfill disposal costs continue to increase, also the costs of extracting natural raw materials provided from increasingly distant sites. Artificial LWA_S have a unit weight ranging between 0.67 and 2.1 g/cm^3, showing properties of high porosity, low bulk density, high water absorption, low compressive strength, and low elastic modulus (Huang et al., 2007). These characteristics are promoted by high-temperature heating treatment (1200-1400ºC), where ceramic material receives a thermal shock which causes the formation of a hard vitrified layer on the surface, preventing the gases from certain elements present in the clay run out, forcing the material to swell, generating the characteristic porous structure.

The use of organic waste/by products promotes energy saving in the sintering process, by the exothermic reaction that released energy during the combustion of organic matter in the matrix of the ceramic structure. The three technical nutrients used come from the food industry: sludge from wastewater treatment plant in brewery industry (SB), meat-bone meal, by-product from meat industry (MBM) and corn cob, by product produced in corn crop (CC).

Producing LWA_S with less sintering temperatures (900-100ºC) (Arioz et al., 2008; Cultrone et al., 2004), means the possibility of producing materials with less environmental impact, reducing the emission of greenhouse gases to the atmosphere, boosting the local economy by offering innovative and eco-label materials.

There are different types of LWA_S suitable for construction purposes. Also, there are used as hydroponic growth media (Molineux et al., 2009) or mixed with other growth media such as soil and peat to improve drainage systems. Hydroponic crops are another possible use, since it is a crop that completely excludes land use and allows the growth of plants through the use of water and nutrients. A crop of this type requires approximately 70% less water than a traditional cultivation, with a faster rate of growth (about 50%), through the reduced use of fertilizers (Ecopneus, 2015).

The mixture in the soil prevents compaction and a lightening of the substrate (up to 10%) providing a higher oxygen level to promote plant growth. In turn it is used on the surface of the substrate to prevent the growth of weeds, retain moisture in the soil, protect the soil from erosion, as well isolation roots. The LWA suitable for culture medium has an apparent density of <1200.00 kg/m^3, a pH value in the range of 6.5-7.5 and electrical conductivity of <2.00 mS/cm (Martínez and Roca, 2011; Nye and Greenland, 1960).

The goal of this preliminary study is to determine the effects of recycled resources, for the production of LWA$_S$ as growing media, with different types of clays and sintering at lower heating temperature and the evaluation of physical and microstructural properties.

2. Material and methods

2.1. Raw materials characterization and optimization

Through collaboration between two research groups, different types of clays from two geographic locations were investigated. White and black clays were provided from a clay-pit in Bailen, Jaen Province, Spain, and red clay came from a clay-pit from Roncobotto, Modena province, Italy. The sludge from wastewater treatment plant (SB) was supplied for brewery industry, Jaen province, Spain, identified as non-hazardous waste, EWC 02-07-05, corresponding to the European waste code (Wastes from the production of alcoholic and non-alcoholic beverages, except coffee, tea and cocoa. Sludge from on-site effluent treatment). The meat-bone meal (MBM) and corn cob (CC) were provided from local industries from Modena province, Italy. MBM is a by-product derivated from the meat products industry.

The raw materials were tested to determine their physical and chemical characteristics, as follows: total content of C, H, N and S was determined by combustion of the samples in an O_2 atmosphere using the CHNS-O Thermo Finnigan Elementary Analyzer Flash EA 1112. Chemical composition was determined by X- ray fluorescence (XRF) using ARL-ADVANT`XP+ (THERMO equipment), software Uniquant. X-ray diffractometry (XRD), was carried out using an automatic diffractometer Bruker D8 Avance, with Cu and Ni filter anode, with Kα radiation operating at 40 kV and 30 mA, EVA software as interpretation tool. Thermal behavior was determined by thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimeter (DSC) by using a Mettler Toledo TGA/DSC 1 HT1600 model. Loss of ignition (LOI) was determined by weighing 1g sample, pre-dried at 105°C for 1 hour, and calcined for 2 hours at 1050°C.

The characterization and optimization of the different materials were carried out following two different steps. In the first step, WBC clay-based mixture (30% white and 70% black clay) was used with 0, 5, 10, 15% of SB, MBM and CC, sintered at 900 and 1000°C for 1 hour. In the second step, a different type of clay, red clay-based mixture (RC) was used with 0, 15% of SB, sintered at 1000ºC for 1 hour.

2.2. Preparation of samples

The waste/by-products/raw materials provided from local industries, were dried in an oven at 105ºC for 24 hours and subjected to grinding process. Clay materials were sieved to obtain 100 µm grain sizes; SB, MBM and CC 1000 µm grain size (Arioz et al., 2008; Kadir and Ariffin, 2013; Zhang, 2013). A relatively large particle value was used, taking into account the energy consumption for materials preparation. For this reason, it was intended to modify the reception conditions as little as possible (grain size and moisture).

Three different types of clay in two different clay-based mixtures were used, to determine the effect of the organic matter on the clay-matrix: WBC (30% white and 70% black clay) and RC (100% red clay), as clay-based mixtures; waste by-product were SB, MBM and CC. The mixing of the different materials in the different stages as it follows: First stage, WBC with 0, 5, 10, 15% of SB, MBM and CC, sintered at 900 and 1000°C, for one hour. The second stage, RC with 15% of SB, sintered at 1000ºC, for one hour. The appropriate quantities were weighed, mixed and manually shaped into approximately spherical pellets by the addition of water to obtain the adequate plasticity. Samples were dried at 105 ºC for 24 hours to reduce their moisture content. The dried samples were subjected to a firing process in laboratory electrical kiln (Lenton AWF13/12) that caused sintering of the grains and changes in their density and porosity (Farias et al., 2017).

In order to imitate the thermal shock produced in the rotary furnace, the samples were introduced and kept in the–furnace at the temperature required for 1 hour (900 and 1000ºC) (Farias et al., 2017). The samples were allowed to cool through natural convection. Weight loss percentages were obtained by difference between the weight after drying stage (105 ºC for 24 hours) and firing stage (900 or 1000 ºC for one hour). The diameters of the samples were in the range of 12.86 - 23.74 mm.

2.3. LWA$_S$ characterization

The sintered clay materials, LWA$_S$, were subjected to different physical-chemical tests in order to determine their possible use in agriculture, as follows: water absorption capacity by immersion of samples in boiling water (100ºC) for 6 hours, according to UNE-EN 772-7; bulk density (BD), by

Envelope density analyzer Micromeritics Geo Pyc 1360 equipment; absolute density (RD), by pycnometer Accupyc TM II 1340 (Micromeritics), Gas (He); total porosity percentage (TP%), by means of the following formula: TP%=[(RD-BD)/RD].100; pH value, according to UNI-EN 13037: 2011 standard, using Oakton CON6; electrical conductivity (EC), according to UNI-EN 13038:2011 Standard, using an Oakton conductimeter CON6/TDS6.

Ceramic samples were submitted to XRD analysis carried out using an automatic diffractometer Bruker D8 Avance. For the analysis of LWA_S surface microstructure scanning electron microscope SEM Quanta-200 was used, Oxford Instruments. For SEM analysis, samples were pasted with epoxy resin on an individual aluminum sample-holder and covered by sputter coating with a gold source (K550 Emitech).

3. Results and discussion

3.1. Raw materials

From CNH-S analysis reported in Table 1, it is evidenced that the high carbon and hydrogen content of the three waste/by-products provide a high calorific value, comparable to other alternative fuels.

Table 1. CNH-S analysis of waste/by products

Waste/by products	*% N*	*% C*	*% H*	*% S*
Sludge (SB)	3.024	23.452	3.324	≅ 0
Meat-bone meal (MBM)	8.340	31.720	4.320	2.160
Corn cob (CC)	2.723	39.104	5.001	≅ 0

The chemical analysis (XRF) of the three clays shows some differences in the chemical compositions. Red clay contains higher siliceous quantities, typical for this material, as well as alumina (Al_2O_3), corresponding to higher refractoriness, and iron oxide (Fe_2O_3 = 7.89%) (Table 2) corresponding to red colour. High amount of calcium oxide (CaO) attributable to the presence of carbonates was observed in white clay (20%).

The waste/by-products used show high amounts of calcium oxide, MBM: 21.75% and SB: 18.52%, CC: 1.25% and silica, CC: 31.64% and SB: 11.86%. CC contains high amounts of potassium oxide (K_2O), 31.70% and MBM 8.02% of phosphorus oxide (P_2O_5). The results of the XRF analysis show absence of toxic substances for a possible agricultural use.

White clay presents as predominant crystalline phases composition calcite, quartz and vermiculite, with presence of dolomite and biotite; for black clay, quartz and hematite, with presence of anorthite; red clay, quartz and dolomite, with presence of hematite.

Fig. 1 presents the XRD analysis from the pore forming agents. SB, the main phase was identified as calcite (C) and carbon content (CARB) (Fig. 1.a). For MBM, hydroxyapatite (H) and carbon content (CARB) (Fig. 1.b). CC by product presented a non-crystalline structural substances like cellulose, hemicellulose and lignin (Fig. 1.c) (Tortosa Masiá et al., 2007; Vassilev et al., 2010). The results obtained in the XRD agree with the chemical analysis results.

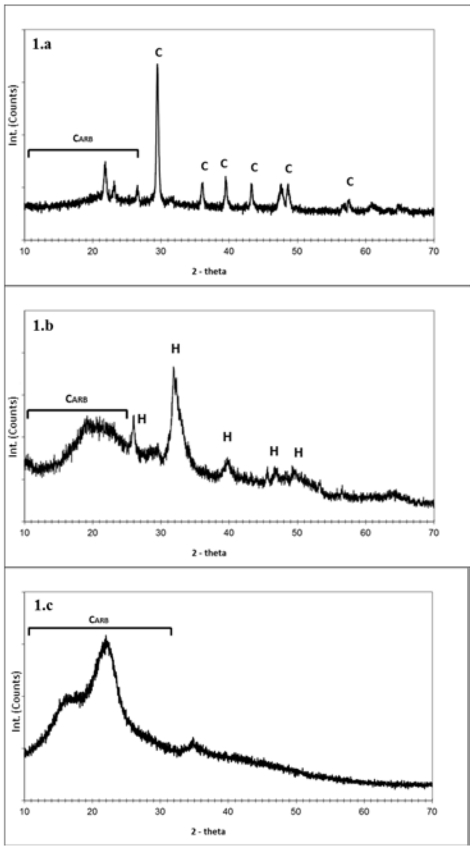


Fig. 1. XRD analysis from pore-forming agents. 1.a: SB, 1.b: MBM and 1.c: CC

Fig. 2.a shows WBC clay mixture thermogravimetric analysis (TG/DTG): loss of free water (around 100ºC), endothermic event; combustion of organic matter at 250-500ºC, exothermic event; loss of interlayer water in form of hydroxyl groups, dehydroxylation of clay (500-700ºC), endothermic event; decomposition of carbonates around 750ºC; over 800ºC the TG curve is fundamentally flat, demonstrating the absence of additional weight loss, endothermic event; melting (around 1200ºC), endothermic event. The loss in weight was in particular due to the loss of humidity (around 2%), deoxydration (around 4%) and carbonate decomposition (around 12%).

In Fig. 2.b, it is shown that RC clay mixture precents loss of free water (around 100ºC) is an endothermic event; combustion of organic matter at 250ºC – an exothermic event; loss of interlayer water in form of hydroxyl groups, dehydroxylation of clay (around 600ºC) - an endothermic event; decomposition of carbonates around 800ºC - an endothermic event; melting (around 1200ºC) - an endothermic event.

Table 2. Chemical composition (XRF) and loss of ignition value (LOI), white, black and red clay, brewery sludge (SB), meat-bone meal (MBM) and corn cob (CC)

Oxides (%)	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*MnO*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*TiO_2*	*P_2O_5*	*LOI*
W. Clay	43.90	8.50	3.30	0.10	2.10	20.00	0.20	16.00	0.40	0.10	19.90
B. Clay	41.89	11.74	4.06	0.04	1.94	15.64	0.27	2.33	0.69	0.15	13.23
R. Clay	52.77	17.95	7.89	0.19	3.88	2.57	0.66	2.85	0.78	-	9.90
SB	11.86	1.10	7.40	0.06	1.17	18.52	1.82	0.26	0.18	2.18	53.75
MBM	0.30	0.06	0.24	-	0.23	21.75	0.54	1.44	0.02	8.02	63.39
CC*	31.64	1.76	1.12	0.55	2.62	1.25	0.24	31.70	0.20	5.41	22.71

** After calcination*

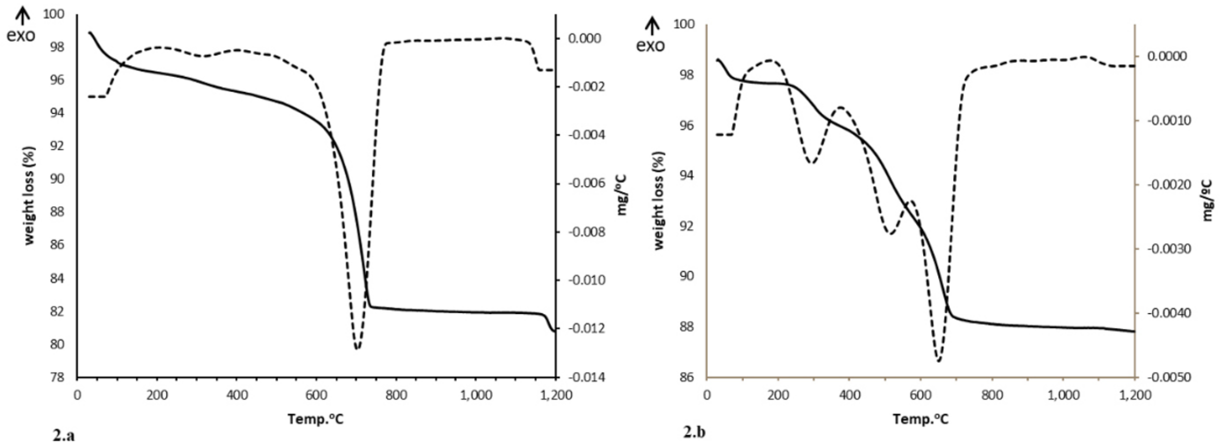


Fig. 2. TG-DTG analysis Clay materials: WBC (2.a) and RC (2.b)

The loss in weight, were in particular due to the loss of humidity (around 1.80%), deoxydration (around 4.40%) and carbonate decomposition (around 5%).

TG/DTG measurements related to SB, shows at 200ºC a decrease in weight by endothermic process due to the loss of moisture inherent in the material. In 250ºC-600ºC range were observed different exothermic events, with a particular relevance around 300ºC, attributable to the combustion of organic matter with significant weight loss (about 50%); another endothermic event was evident (400-500ºC), due to the decarbonisation, seen previously in clays; above 700ºC no variations were observed (Fig. 3).

TG/DTA for MBM and CC, Fig. 4 (a and b), highlighted: an endothermic peak around 100ºC relative to moisture loss, exothermic peaks in both cases (300ºC for MBM, 400ºC for CC) due to the combustion of organic matter, accompanied by a significant loss of mass (about 25% for MBM and 60% for CC). Once exceeded 800ºC/900ºC, no significant variations were observed probably due to the complete loss of organic matter, remaining carbonates compound.

3.2. Sintered materials. Chemical and physical properties

The results from the LWA_S tested in the first stage (WBC with 0, 5, 10, 15% of SB, MBM and CC, sintered at 900 and 1000°C, for one hour) can be seen in Table 3: the aggregates sintered at 900ºC, have shown satisfactory results, as in the case of samples $WBCC_{15}$ with water absorption capacity (WA) of 81.18%, bulk density (BD) of 820.00 kg/m^3 and total porosity (TP) of 69.06%. In the case of pH and electrical conductivity (EC) values were high, 11.8 and 3.87 mS/cm respectively, measured after pre-washing. For that reason, the samples sintered at 900ºC were considered unable for agriculture applications. On the other hand LWA_S sintered at 1000ºC shown a decrease in pH value being inversely proportional to the percentage of waste/by product added. Therefore, and based on the results of the first step, it was considered working in the second step with local Italian clay, red clay (RC), with different properties and less calcium carbonate content, to reduce pH value.

In Table 4, the results from first-second stage LWA_S physicochemical properties were listed and compared, aggregates with potential applications in agriculture ($WBSB_{15}$ and RSB_{15}) and aggregates without the addition of 15% SB (WBC and RC).

$WBSB_{15}$ and RSB_{15} present physicochemical parameters that were in range for their use as growth media. Also from a circular economy point of view was considered that these mixtures use a significant amount of waste generating important saving in the consumption of virgin raw materials and energy in the firing process. RSB_{15} mixture has low water absorption capacity of 28%. However, the values of BD and TP are on range.

This difference was due to ceramization temperatures, for red clay these are between 800-1000ºC, while white and black clays were sintered at temperatures between 1000-1100ºC. This difference can also be related to the type of thermal treatment carried out in this research by placing the ceramic material directly at the sintering temperature (1000ºC) for one hour, to promote the bloasting of the ceramic material.

In Fig. 5, XRD analysis shows mixtures without waste (WBC and RC), 100% clay material, compared with those containing SB (RSB_{15} and $WBSB_{15}$) for the recognition of the crystalline phases. In the image 5.a, corresponding to WBC samples, the main peaks were related to quartz (Q), corresponding to the high content of silica, and silico-aluminates of potassium orthoclase (O). The presence of carbonates (C) shows that a small carbon amount was trapped within the structure of the material, without reacting to the heat treatment. In the image 5.b corresponding to the RC mixture, it was observed that the main peaks were related to quartz (Q), with presence of hematite (H) and anorthite (A). For RSB_{15} sample, it can be observed the same crystalline phases, reducing its peak intensity of the hematite (H) and with an increase in the anorthite (A) peak due to higher amount of calcium carbonate by the replacement with 15% of SB. It was concluded that in both cases, the certain phases observed correspond to the structure of the ceramic clay-based material used, due to the low percentage replacement of clay and to the physicochemical characteristics of the SB, since it was a residue that can be considered organic and inorganic at the same time.

In order, to analyze the open porosity, the SEM micrographs (Fig. 6) and the physical-chemical tests data listed in Table 4, were compared. Corresponding to the microstructural analysis of the porous material, a diverse surface microstructure can be seen. In the Fig. 6b, corresponding to the mixture $WBSB_{15}$, was observed uniform and interconnected pores, with spherical and regular holes.

In contrast, Fig. 6a, corresponding to the WBC mixture, where a smaller porosity was observed, due to the absence of the pore forming agent. In the Fig. 6c, for RC samples can be noted that the ceramic surface matrix was almost completely sintered, presenting a smaller and dispersed pores. For sample RSB_{15} (Fig. 6d), the porosity was slightly higher, due to the addition of 15% SB. This difference could be related to the higher water absorption capacity of RSB_{15} sample reported in Table 4. The results demonstrated that the WA% of sintered samples increases with the addition of 15% SB, depending on the clay mix used, 20.9% for WBC-$WBSB_{15}$ and 15.97% for RC-RSB_{15}.

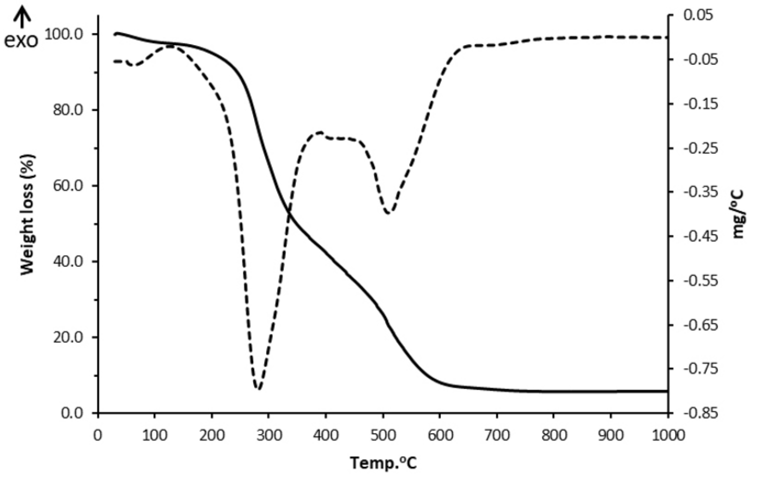


Fig. 3. TG-DTG analysis SB

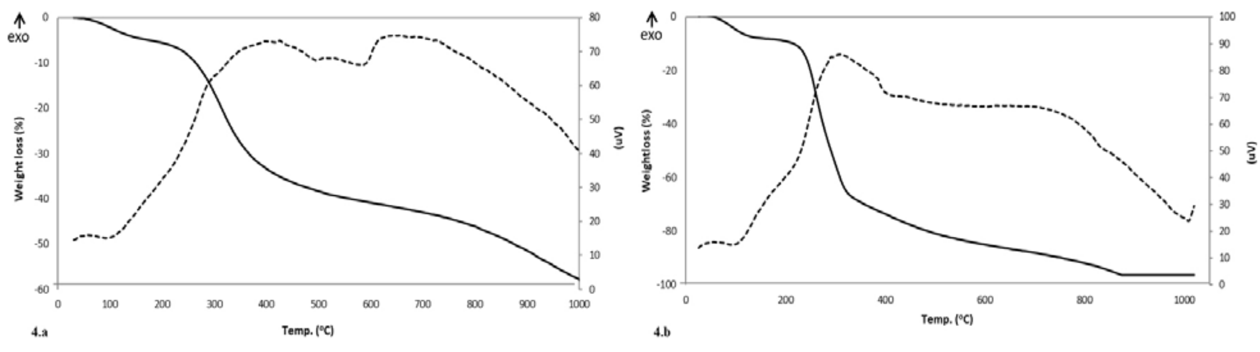


Fig. 4. TG-DTA analysis MBM (4.a) and CC (4.b)

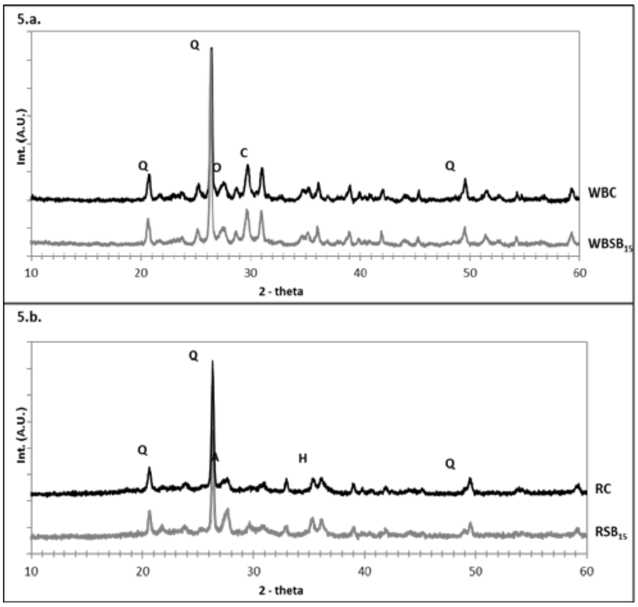


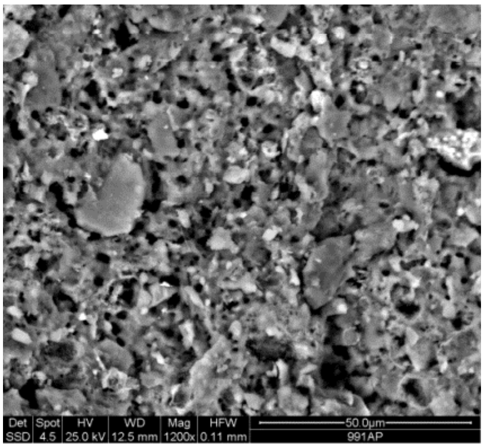
Fig. 5. LWA_S XRD results comparison. a:WBC/ $WBSB_{15}$ and .b: RC/ RSB_{15}, sintered at 1000°C

Table 3. First stage LWA_S. Physicochemical properties: water absorption (WA), bulk density (BD), total porosity (TP), pH and electrical conductivity (EC)

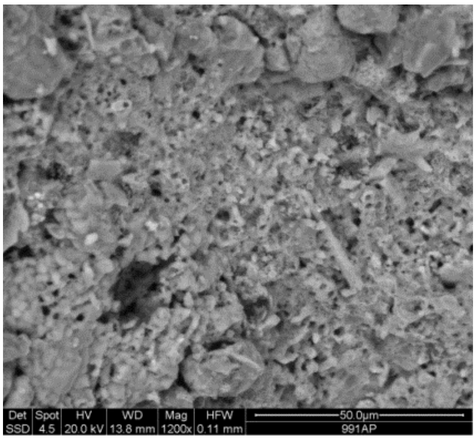
LWA_S	*WA (%)*		*BD (Kg/m³)*		*TP (%)*		*pH*		*EC (mS/cm)*	
	900°C	*1000°C*	*900°C*	*1000°C*	*900°C*	*1000°C*	*900°C*	*1000°C*	*900°C*	*1000°C*
WBC	30.78	30.12	1470.00	1490.00	20.40	20.13	12.34	11.30	7.32	3.42
$WBSB_5$	37.36	38.29	1340.00	1310.00	41.20	52.90	11.64	9.65	3.83	0.94
$WBSB_{10}$	41.33	43.73	1260.00	1240.00	49.81	55.85	11.44	7.26	3.40	1.26
$WBSB_{15}$	49.44	51.02	1180.00	1120.00	55.73	60.15	10.56	7.50	3.92	1.48
$WBMBM_5$	40.00	36.55	1060.00	1020.00	42.64	56.35	10.94	11.90	2.39	2.55
$WBMBM_{10}$	51.42	51.39	1050.00	920.00	53.92	59.89	11.96	11.29	6.37	3.39
$WBMBM_{15}$	37.18	66.64	1000.00	960.00	62.79	64.73	10.91	10.22	4.04	1.98
$WBCC_5$	53.56	44.51	1120.00	1120.00	49.08	58.13	11.81	11.28	5.23	3.35
$WBCC_{10}$	59.61	65.66	950.00	1020.00	57.22	61.29	11.25	11.00	3.89	1.74
$WBCC_{15}$	81.18	76.08	820.00	830.00	69.06	69.84	11.08	9.50	3.87	2.29

Table 4. Second stage LWA_S Physicochemical properties LWA_S sintered at 1000°C

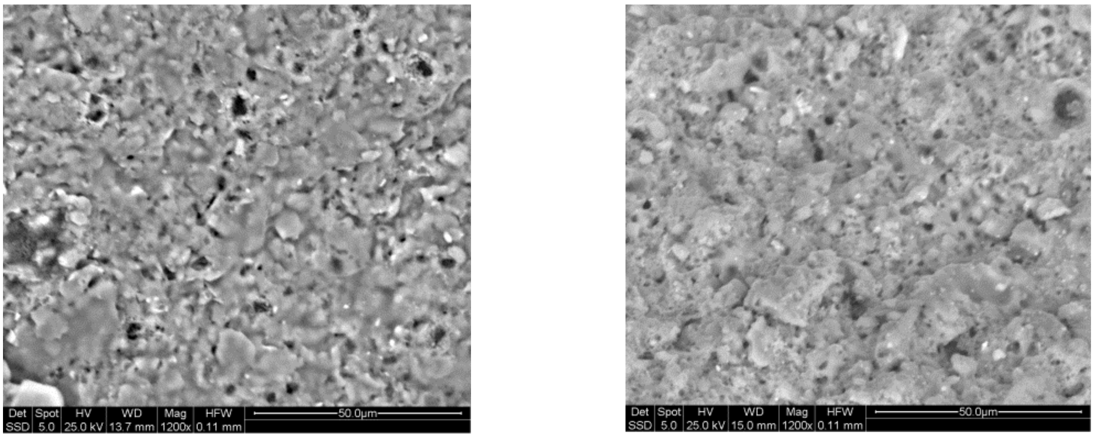
LWAS	*WA (%)*	*BD (kg/m³)*	*TP (%)*	*pH*	*EC (mS/cm)*
WBC	30.12	1190.00	20.13	11.30	4.39
WBSB15	51.02	1120.00	60.15	7.50	1.48
RC	12.35	524.00	80.54	7.04	0.15
RSB15	28.32	1157.30	49.61	7.59	1.11



a. WBC



b. $WBSB_{15}$



c. RC   d. RSB_{15}

Fig. 6. SEM micrographs of surface samples a: WBC, b: $WBSB_{15;}$ c:RC and d: RSB_{15} (1200x), sintered at 1000°C

4. Conclusion

From the results obtained in this preliminary study, it was determined that the LWA_S produced with this type of waste/by product are suitable as substrate/soil for agricultural application. The mixtures $WBSB_{15}$ and $RCSB_{15}$ present physicochemical parameters suitable for their use in agricultural use purposes.

The results indicate the potential for manufacturing high quality lightweight aggregates, using relatively simple processing. The energy saving, due to the combustion of organic matter inside the furnace and low temperature sintering (200-400°C lower), reduces the environmental impact produced by the greenhouse gases released into the atmosphere, resulting in the production of sustainable materials.

The LWA_S XRD analysis, confirmed that the percentages of SB added to different clay mixtures are vaporized by the heat treatment at 1000°C, ensuring its correct treatment/disposal, without forming new crystalline phases in the material.

The results shown that the three technological nutrients can be effectively used as porosity forming agents for the elaboration of lightweight aggregates, representing a saving in the consumption of virgin raw materials and an alternative of the disposal in landfills.

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CRITICAL ISSUES CONCERNING DRINKING WATER AND SANITATION MANAGEMENT IN VILANCULOS (MOZAMBIQUE)

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Abstract

The research work aimed at analysing the drinking water quality in Vilanculos (Mozambique) and at investigating the influence of poor sanitation management on drinking water quality. The purpose was to understand the reasons of water source contamination and re-contamination in the water supply chain, in order to define strategies to control source contamination and to suggest practical ways for reducing the risk of recontamination.
A first phase of microbiological drinking water quality monitoring allowed identifying the most critical areas to be valued in a next sanitation assessment activity, carried out by means of interviews to stakeholders and by direct observation.
The microbiological analysis carried out at the source showed that only in few cases there is compliance of water samples with the standard limit for all microbiological parameters. It was also found that the cases of compliance with the regulatory limit decrease moving from the source to the consumer, meaning improper hygiene habits in the supply chain. Microbiological contamination shows a potential danger for the health of consumers.
As regards excreta and wastewater management, a prevalence of unimproved sanitation facilities with direct infiltration into the ground and a bad management of septic tanks were identified.
In order to improve population's health conditions, a preventive approach should be implemented, including both the improvement of the structural characteristics of latrines and their management and the improvement of water supply infrastructures. Moreover, good practices at the household level resulted to be an important strategy to preserve water microbiological quality.

Key words: drinking water, microbiological analysis, Mozambique, water chain, water source contamination

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1. Introduction

In 2010, with resolution 64/292, the General Assembly of the United Nations stated access to water, in its qualitative and quantitative terms, as a universal and fundamental human right (UN Human Rights, 2010). Difficulty in access to drinking water sources is a problem that, in many parts of the world, still causes high infant mortality rates, proliferation of water-related diseases and general poverty. Globally, an impulse towards improvement has been given by the eight Millennium Development Goals, signed in 2000 by all 191 UN member states, and in particular by Target 7C concerning access to safe drinking water. The target requires, in fact, halving, by 2015, the proportion of people without sustainable access to safe drinking water and basic sanitation, compared to the situation of 1990 (UN General Assembly, 2000). Through the efforts and the objectives set by the international community, it was estimated that, between 1990 and 2015, 2.6 billion people gained access to an improved drinking water source, bringing the proportion of people without safe water access from 24% to 9% (UNICEF and WHO, 2015). Some studies show that the improved water sources (defined as such exclusively according to the adequacy of the infrastructure that supplies water), which do not meet the quality standards,

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represent a significant share of the total (Bain et al., 2012). Furthermore, even if water quality at source meets standard limits, this is not assured at the point of consumption. Water, in fact, along the route from catchment to consumption (water supply chain) is exposed to high risks of contamination due to improper hygienic habits and to variable external factors (Clasen and Bastable, 2003; Khadse et al., 2012; Leiter et al., 2013; Rufener et al., 2010; Wright et al., 2004). Ensuring access to safe drinking water thus remains a key objective in order to assure better living conditions and higher life expectancy for people. The 2030 Agenda for Sustainable development (UN General Assembly, 2015), adopted in September 2015 at the 70th Session of the UN General Assembly and in particular the SDG (Sustainable Development Goal) target for drinking water (6.1) take into account in some way this concept. In fact, it introduces a new higher threshold of service for drinking water termed "safely managed", defined as the use of an improved drinking water source which is located on premises, available when needed and free of faecal and priority chemical contamination. It differs from the "basic service level", defined as the use of an improved drinking water source where the collection time is no more than 30 minutes for a roundtrip including queuing (JMP, 2015; UNICEF and WHO, 2017).

In 2017 UNICEF and WHO published the first update of the SDG period: this report states that 71 per cent of the global population (5.2 billion people) used a safely managed drinking water service in 2015, but 844 million people still lacked even a basic drinking water service (UNICEF and WHO, 2017).

Access to drinking water in Vilanculos (Inhambane Region, Mozambique) is represented by three types of sources: water network (47%), protected wells (31%) and unprotected wells/surface water (22%). Water supplied by water network is partially treated before distribution, but its quality was neither regularly monitored at source, nor at (private or public) tap. Water from wells and surface water were not even monitored by local authority. For these reasons, water quality needed to be checked to verify the current contamination and risks associated with it.

The research work aimed at analysing chemical and microbiological drinking water quality in Vilanculos and at verifying compliance with international standards (WHO, 2011) and local legislation (MISAU DM, 2004) through monitoring all types of water sources used for human consumption. The purpose was to try to understand the reasons of water source contamination and re-contamination along the water supply chain (from source to mouth), in order to define strategies to control source contamination and to suggest practical ways for reducing the risk of recontamination.

This activity is part of a project funded by the European Union and coordinated by the water and sanitation utility Acque del Chiampo (Vicenza) and its main objective is to improve sanitary conditions of the population of Vilanculos, through a better governance of water services in the city. In addition to the University of Brescia, the project involved two local partners: the Conselho Municipal de Vilanculos, representative institution of local government and Empresa Moçambicana de Aguas (EMA), private operator of the water network in the town of Vilanculos.

2. Materials and methods

2.1. Water quality monitoring

Between 2012 and 2015, several monitoring campaigns were carried on about 355 water sources (209 in the dry season and 146 in the rainy season). Table 1 shows the detail of the number of samples per each type of source analysed. The samples were chosen randomly within the class of each kind of water sources in the city in three different campaigns (two in the dry season and one in the wet season). Thirty-two water samples were replicated in the dry and in the wet season.

Table 1. Number of samples per each water source analysed in the dry and in the wet season

Water source	*Number of samples - dry season*	*Number of samples - wet season*
Open wells	53	39
Protected wells with manual pumps	25	36
Protected wells with electric pumps	36	12
Public fountains	21	8
Taps	66	51
Deep wells	3	-
Tanks	5	-

About 130 families were involved for water quality monitoring in different points along the supply chain. The nine districts of Vilanculos are not uniformly covered by all kinds of source, which differs according to the distance from the main water supply pipelines and to the economic possibilities of the families. Fig. 1 shows the different types of source analyzed by district. In particular, the monitoring activities consisted in the following steps:

- meetings with households to record various information about the health habits through questionnaires and direct observation;
- water samples collection for the microbiological characterization of the various points in the supply chain (source, transport, storage, consumption);
- microbiological laboratory analysis;
- chemical analysis (in field and in laboratory).

The first activity was mainly based on inspections and interviews in local families, in order to gather all the necessary information to understand the sanitary-level education related to domestic water management, to assess the structural characteristics of water sources and to identify the water supply chain.

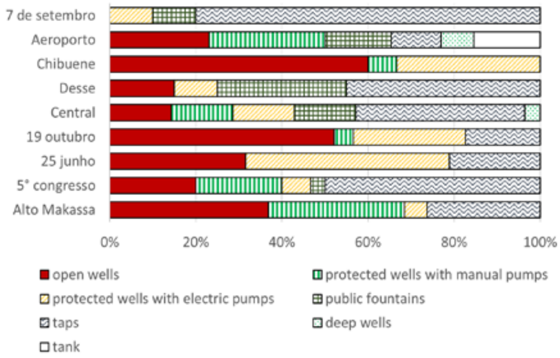

Fig. 1. Water sources analysed in the different districts of Vilanculos

As regards structural characterization of water sources, Sanitary Surveys were conducted according to the model proposed by WHO (WHO, 1997), while for characterization of the entire water supply chain (source-transport-storage-consumption) a questionnaire specifically developed was adopted.

Microbiological sampling was made using plastic sterile containers with a capacity of 500 mL. Samples were then stored in cool bags in order to preserve their quality, protecting them by light (ultraviolet and visible) and by high temperatures. Microbiological analyses were carried out within 24 hours after sampling and they included determination of parameters indicators of faecal contamination (faecal coliforms, *Escherichia coli* and *Enterococci*) and total coliforms.

The membrane filtration (MF) method, based on Nutrient Pad Sterile (NPS) Membrane and dry nourishing (in sterile Petri dishes), was applied for microbiological analyses, as outlined by WHO guidelines. During the various missions, random measurements of the total residual chlorine and free chlorine (via portable colorimeter) were furthermore carried out at various points in the water network to verify compliance with the recommended values of 0.2-0.5 mg/L for free chlorine (WHO, 2011).

As regards physical quality control, measurement of pH, conductivity and turbidity were carried out in the field thanks to portable instruments. Moreover it was possible to conduct analysis for 24 chemical parameters (Chlorides, Sulphates, Nitrates, Sodium, Calcium, Magnesium, Potassium, Total Iron, Aluminium, Arsenic, Antimony, Selenium, Boron, Cadmium, Mercury, Manganese, Nickel, Lead, Copper, Zinc, Barium, Total Fluorides, Molybdenum, Dry residue at 180°) by means of fixed laboratory equipment.

Thanks to the use of GPS, it was possible to record the coordinates of each point monitored in order to visualize on the city map the results of analyses carried out and to identify the most critical areas. For this activity, an open source GIS software called Quantum GIS (QGIS) was used.

2.2. Sanitation assessment

An assessment of the sanitation system in the town was performed in the most critical areas identified in the water quality monitoring activity described above. For this purpose, interviews to different stakeholders (93 households, 12 tourist facilities, 6 schools and 2 health centres) and direct inspections were carried out. In particular, following a protocol specifically developed, information regarding the types and the features of sanitation facilities used and the method for managing them were recorded.

3. Results and discussion

3.1. Microbiological water quality at source and along the supply chain

The microbiological analysis carried out at the source showed that only in few cases there is compliance of water samples with the standard limit (0 CFU / 100 mL) for all microbiological parameters. Fig.2 shows the data elaboration for Enterococchi, chosen because responses for this indicator were more evident, as the colonies could be identified and counted more clearly and there were fewer doubts in the interpretation.

In particular, it emerged that open wells are the less safe drinking water source, prone to the higher risks of faecal contamination. The situation related to improved water sources, as protected wells, is better, but still not good. However, we can observe that wells equipped with manual pump have on average a higher microbiological quality than the other types of source. This is because they are the only sources (apart from deep wells, which supply the water network) that draw water at great depths (about 50 m below the ground), where it is assumed that there is a more protected aquifer. The protected wells fitted with electric pump are mostly private and, for cost reasons, they are not very deep (they reach about 20 m depth) and they draw from the superficial aquifer.

Water supplied by the distribution network is not safe, despite supply deep wells provide water free from bacteria. The contamination of water, therefore, takes place along the network and this is due to the lack of an adequate disinfection system, to breakages along the existing network itself and to discontinuity of water supply. When pipes are not under pressure, pollutants in the soil, highly contaminated due to the presence of many traditional latrines (see section 3.4 for more details), can easily enter in the network. Moreover, household taps are placed at a short height from the ground and they are not protected, remaining thus exposed to the proximity of people, animals and other possible sources of contamination.

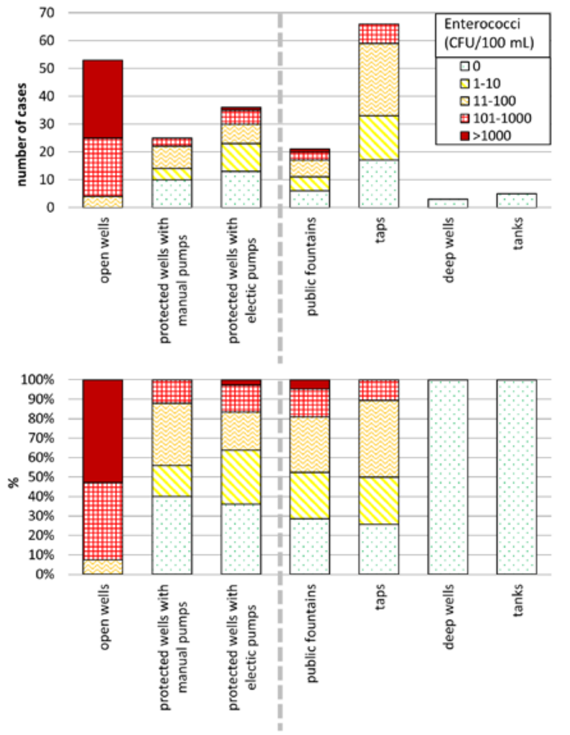

Fig. 2. Contamination by Enterococci for each water source in the dry season - Number of cases and percentages

Microbiological contamination shows a potential danger for the health of consumers (diseases such as typhoid, paratyphoid, dysentery and cholera are associated with this type of pollution).

The results of the Sanitary Surveys, conducted according to the model proposed by WHO (WHO, 1997), were compared with the water quality of the same water points to assess the health risk: it can be stated that the highest levels of contamination correspond to the worst structural conditions (example for open wells in Fig. 3).

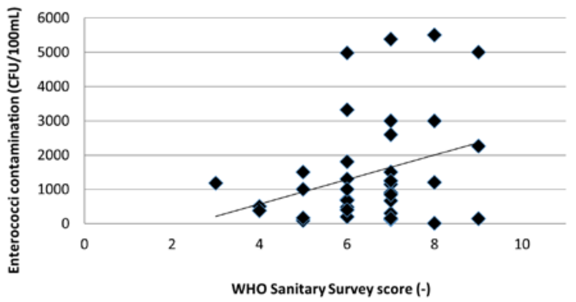

Fig. 3. Enterococci contamination and WHO scores (in a scale from 0 to 11, 0 means perfect structural conditions, 11 means very bad structural conditions of the source) – the case of open wells (43 samples)

It was also found that the cases of compliance with the regulatory limit decrease moving from the source to the consumer (example in Fig. 4), meaning improper hygiene habits in the various stages of the supply chain (behaviour also highlighted in the case studies analyzed by Wright et al. (2004)).

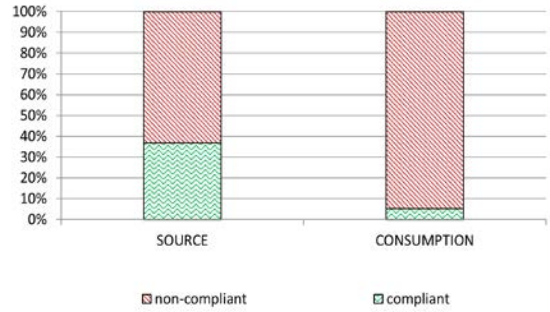

Fig. 4. Percentage of compliance with the regulatory limit (concerning Enterococci) during water distribution from source to consumption – the case of protected wells (19 samples at source and 19 samples at consumption)

In particular, the analysis of the results showed that the phases of transport and storage turn out to be the most critical of the chain. It was observed that the methodologies used in these two phases are deficient from the hygienic point of view. In particular, it was observed that during the transport phase the type of container used has a big relevance (Fig. 5): buckets and basins, which have a large opening, cause a greater contamination than jerrycans, which have a narrow opening.

What emerged is that during the storage phase the major causes of contamination are:

- the position of the container, inside or outside the house;
- the fact that the container is covered;
- the presence of animals.

Moreover, when people do not use the same container for transport and for storage, water recontamination is significantly increased.

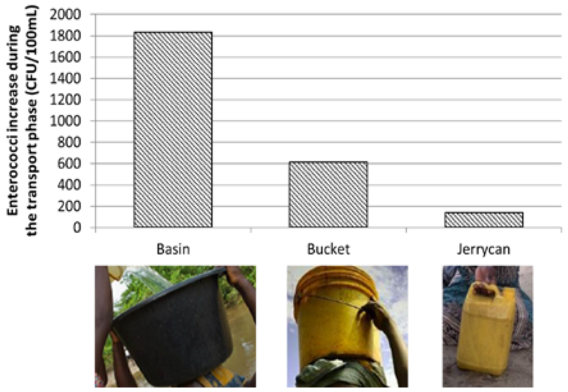

Fig. 5. Types of containers used for water transport, from left to right: basin, bucket and jerrycan

3.2. Microbiological water monitoring in dry and wet season - a comparison

Thirty-two water sources have been monitored twice during the project, once during the dry season (from May to November 2014) and once during the wet season (from December to April 2015), with the aim to compare and analyse the related differences.

In Fig. 6, the results related to the protected wells with electric pumps are shown.

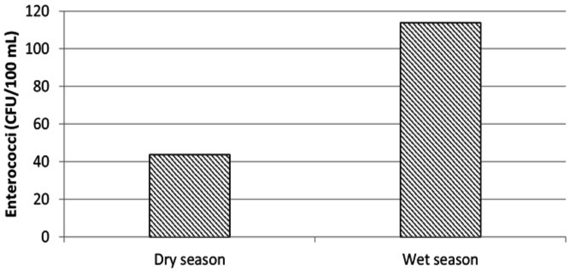

Fig. 6. Comparison between average microbiological contamination of protected wells with electric pumps during the dry season and the wet season (8 samples)

It is possible to observe that the average contamination increases from the dry to the wet season. The result is in line with most of studies in this field (Kostyla et al., 2015; Nienie et al., 2017) and this is because precipitations can facilitate infiltration and introduction of bacteria in the aquifer and in the distribution system. Moreover, precipitations can flush the dissolved nutrients present in the ground and increase the level of organic carbon.

It was also analysed the link between the single rain event and the variation of microbiological contamination at the water point. What emerged is that there is often a strong relation between the daily rainfall and the Enterococci contamination in different types of source.

3.3. Water chemical and physical quality

Chemical analyses showed that one of the main water problem is the high concentration of iron: values between 512 and 666 μg/L were registered in the deep wells supplying the water network. Such concentrations are above the limit for the local legislation of 300 μg/L (MISAU DM, 2004). No health-based guideline value is proposed for iron by WHO, but it is stated that at levels above 300 μg/L, iron stains laundry and plumbing fixtures, whereas below 300 μg/L there is usually no noticeable taste at iron concentrations, although turbidity and colour may develop (WHO, 2011). Manganese is often present in concentrations close to the legal limit, 100 μg/L for the local legislation (MISAU DM, 2004), which in some cases is also exceeded. WHO does not establish a formal guideline value for manganese, but it reports a health-based value of 400 μg/L and an acceptability threshold of 100 μg/L. The presence of manganese in drinking-water, like that of iron, may lead to the accumulation of deposits in the distribution system (WHO, 2011). In some cases, in particular in two public schools supplied with two protected wells with manual pumps, there is a concentration of nitrates close to the legal limit which is 50 mg/L NO_3 according to both local regulation and WHO guideline value (MISAU DM, 2004; WHO, 2011). This can be due to the presence of unimproved latrines that are not well managed, close to the water points.

Random measurements of the total residual chlorine and free chlorine (via portable colorimeter), carried out at various points in the water network, showed values lower than those recommended (0.2-0.5 mg/ L for free chlorine, (WHO, 2011)). A poor continuity and a lack of attention on the chlorine dosage, necessary to guarantee a proper microbiological quality of water in the distribution system, is emerged in correspondence to water network supply tanks.

Physical quality control did not show values beyond the regulatory limits regarding conductivity and turbidity, which are respectively 50-2000 μS/hmo and 5 NTU (MISAU DM, 2004). On the contrary, on 184 pH analysis performed, 110 cases resulted below 6.5 and 5 cases above 8.5. The range 6.5-8.5 is given by local regulation (MISAU DM, 2004) and it is suggested by WHO as the usual optimum pH range (WHO, 2011). Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters. For effective disinfection with chlorine, the pH should preferably be less than 8 however, lower-pH water (approximately pH 7 or less) is more likely to be corrosive (WHO, 2011). In Vilanculos, the pipes of the water network are mainly in PVC, which is resistant to acidic substances.

3.4. Sanitation

The sanitation assessment activity shows that most of the households (64% of surveyed population) has an unimproved sanitation facility that is a traditional dry latrine with direct infiltration into the ground. It is a pit without any type of lining, 2-4 meters deep, with a slab made by wood or cement. A superstructure, usually made of local material (reeds, palm trees, sheet, etc.), is installed on the pit to ensure privacy. This solution has several disadvantages because it generates odors and proliferation of flies. It can also collapse and it can lead to groundwater contamination for the lack of adequate systems of insulation of the pit from the ground (Martínez-Santos et al., 2017). These latrines in most cases are not handled properly and they can lead to the spread of some diseases. First cleaning is poor; moreover, the use of a cover for the closure of the latrine when this is not in use is rare. The latrine is considered full when the level of accumulated material in the pit reaches the ground level, failing to observe the recommended level of 0.5 m, not guaranteeing the separation between man and his faces. When the latrine is full, it is closed and another one is built (in 97% of surveyed population), not facing the management of such material.

In addition, a poor capacity of sanitary facilities management in general (improved and unimproved) and a lack of awareness of the risks associated emerged. The lack of a safe emptying service of septic tanks (used in Vilanculos in particular by public buildings, tourist facilities and by some families) leads Vilanculos population to proceed with a manual emptying (not safe), followed by an uncontrolled disposal (another possible cause of contamination of the ground).

3.5. Recommendations

Practical recommendations, based on the analysis of the results of the monitoring activity and of the survey carried out, were elaborated.

Drinking water management and use recommendations

Some specific recommendations were addressed to the manager of the water supply system. In particular, the key role of drinking water control with the main objective to ensure microbiological safety was highlighted. The systematic use of chlorine in the distribution network and a detailed routine maintenance program of the whole infrastructure were recommended.

Other suggestion, concerning specific hygiene practices and operations for water use, were addressed to the community. As regards water transport from the catchment point to home, it is important to optimize the type of container used: water microbiological recontamination is high in case of basin, while jerrycan represents the best solution to ensure good water quality. Concerning water storage at home, it is recommended to use for this purpose the same container used for water transport. In addition, it is desirable to keep closed the top of the container for water storage and to keep the container inside the building and far from domestic animals. It is also recommended to keep the glass for water final consumption in a protected place: far from the ground, far from the animals and upside down when not utilized and to stand water for at least 3 hours in order to reduce water microbiological contamination (especially during extreme weather conditions). It is finally advisable to have a household water treatment before consumption to guarantee further reduction of microbial contamination, derived from sources or from transport practices. In particular, it is recommended to boil water to eliminate any bacteria or to use "certeza", a disinfectant product that is known and used in the Mozambican market, approved by Ministério Mocambicano da Saúde (MISAU). Especially for water from an unimproved source (open well, surface water as river/Lake), it is suggested to leave the water in the storage jerrycan for at least 30 minutes -1 hour before performing one of the operations described above, to make possible the settling of suspended particles.

Finally, as it was found that a strong water contamination occurs when structural conditions of the source are inadequate, specific recommendations were elaborated in order to improve the structural characteristics of the public and private wells (not linked to the water network). Such suggestions were addressed to local constructors and authorities. As regards open wells, it is advisable to increase the level of the source protection, for example by equipping them with coatings to the hole walls and with surface covering through parapets and canopies. The upgrading of an unprotected well to a protected one is completed when the hole is isolated from surface infiltration, reducing the ways of contamination of the aquifer (WHO, 1997).

Sanitation management recommendations

As regards sanitation, it would be desirable, in the short term, to act on the management of existing sanitation facilities in order to ensure better protection of human health and environment. Concerning un-improved latrines, some practices suggested were: adding ash or lime in the pit after defecation, using a lid to close the latrine defecation hole, avoiding water into the pit, not throwing napkins or other non-biodegradable material into the pit, closing the pit (covering the site with soil) before the material reaches the ground level. Regarding the septic tank management, it would be desirable to create an emptying service and a centralized management of the extracted material, financially supported by tourist facilities.

In addition, it would be desirable in the future to realize improved latrines: the specific technology of a urine diverting dry toilet was suggested, based on the site-specific conditions and on the preferences of the population, acquired through questionnaires.

4. Conclusions

The monitoring of all the types of sources used for human consumption in Vilanculos showed a water quality often non-compliant with the national legislation and with the WHO guidelines for drinking water quality. In particular, from the microbiological point of view, it emerged that not only un-improved sources, as might be expected, were contaminated by faecal matter, but improved sources resulted to be often contaminated as well. Between the improved sources, those that draw water from the more superficial aquifers resulted to be more often microbiologically contaminated. Moreover, water distributed by the distribution network is not always safe at the tap, despite supply deep wells provide water free from bacteria. The causes of water source microbiological contamination resulted to be the presence of pollutants in the more superficial soil, mainly due to the spread use of traditional latrines, together with the structural deficiencies of the sources and of the distribution system.

In addition, the microbiological monitoring of the quality of water along the supply chain showed a decrease of the cases of compliance with the regulatory limit from the catchment to the consumption, especially during the phases of water transport and storage. This is due to the improper hygiene habits adopted in such phases: in particular, the type of containers used for the purpose resulted to be relevant in the microbiological recontamination.

The random check of physical and chemical water quality for all the type of sources showed some non-compliances to the regulatory limits for iron, manganese and pH and values lower than that recommended for total residual chlorine and free chlorine as regards the water network.

The analysis carried out, together with collection and processing of data from the field, led to the formulation of practical recommendations for the population and for the water service manager. Such recommendations were delivered in a written form (in Portuguese language) to the local partners in July 2015. In parallel with this, an awareness campaign on these issues was carried out in the community.

Good practices suggested to people at the household level (such as, for example, boiling water to eliminate all bacteria that may be present or using a disinfectant product, optimize the type and the position of the container for water transport and storage etc.) resulted to be an important strategy for reducing microbiological re-contamination of water from catchment to consumer. Moreover, specific recommendations were suggested in order to improve the management of the existing sanitation facilities, as a strategy to ensure better protection of human health and the environment compared to the current situation.

From the water manager point of view, the monitoring of drinking water quality and the control of the whole infrastructure (in particular of the disinfection phase) are crucial.

The European project, in which this research is included, led to the setting up of a laboratory for microbiological and chemical monitoring of drinking water in the city. Now this structure is in the hands of a local person properly trained, who can carry on an activity of constant monitoring and who can daily interface with the water service company and with the municipality, in order to implement possible corrective measures or to undertake actions to increase public awareness to good sanitation practices. In fact, at the time of project submission, there was neither a laboratory in the city, nor at a reasonable distance. Drinking water was then distributed and consumed without any regular monitoring of its chemical and especially microbiological quality, with related risks for the consumers health.

In order to enhance population's health conditions, in the long term, the improvement of the structural characteristics of latrines and of their management and the improvement of water supply infrastructures are recommended. Appropriate solutions have been suggested to the municipality and to the local population.

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ASSESSMENT OF PERFORMANCE AND ADVANTAGES RELATED TO THE USE OF A NATURAL COAGULANT IN THE INDUSTRIAL WASTEWATER TREATMENT

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Abstract

The paper deals with the demonstration of the technical and environmental advantages related to the use of a tannin based coagulant in textile wastewater treatments. The natural coagulant was tested to evaluate its performance in the coagulation/flocculation process, the level of biodegradability in both aerobic and anaerobic conditions and the eco-toxicological risks for aquatic systems. Results were compared with a common inorganic metal based coagulant. The findings at lab scale showed that the natural coagulant is more efficient than the inorganic allowing to achieve same performance with a dosage 36% lower. Moreover, the natural coagulant gave the formed flocs a high degree of dewaterability implying less excess sludge volume to be disposed after treatment. Additionally, the natural coagulant showed no toxic effects for the aquatic environment and the sludge biomass activity as well as high degree of biodegradability in both aerobic and anaerobic conditions. The efficiency of the natural coagulant on textile wastewater was further validated at pilot scale where, in optimized conditions, economic savings were achieved, reaching a specific treatment cost of 0.18€/m^3 of raw wastewater.

Key words: coagulation, flocculation, natural polyelectrolytes, textile wastewater

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1. Introduction

Textile industry consumes a huge amount of water and chemicals during the various processing stages. The resulting wastewater generally is characterized by poor biodegradability due to the high concentration of inorganic contaminants, dyes and other recalcitrant compounds which can be toxic for aquatic organisms and may pose serious health threat to human beings (Gao et al., 2008; Savin and Butnaru, 2009). Therefore, textile wastewaters require proper treatments before the final discharge into sewage networks or directly to the environment (Asghar et al., 2015; Aouni et al., 2009; Çabuk et al., 2015; Dulov et al., 2011; Kulik et al., 2007; Verma et al., 2012).

At industrial level, one of the most common strategy to reduce the pollution loads of the effluents from textile sector is the chemical coagulation-flocculation process commonly carried out in wastewater treatment plant (WWTP) as primary and/or tertiary treatment. Usually it implies the addition of inorganic polyelectrolytes such as metal based salts (i.e. alum, ferric salts, magnesium chloride etc.). Depending on both the nature of the coagulant agents and the characteristic of wastewater, the flocculation takes place directly or is aided by the addition of specific flocculating agents (Beltràn-Heredia et al., 2011; Wang et al., 2016). Cationic coagulants enhances strongly the physical separation of contaminants from the wastewater by adsorption and charge neutralization of the particles and

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dissolved substances, typically negatively charged, causing the rapid settling of the formed flocs (Van Nieuwenhuijzen, 2002). However, the use of metal salts heavily affects the overall environmental impacts and the cost of treatment system. Despite the low capital cost for the realization of the chemical coagulation-flocculation process, the application of metal salts implies many drawbacks such as high salinity of the final effluent and the production of great amount of chemical sludge with an economical increase for the sludge treatment steps and the final disposal. Moreover, the effectiveness in removal some contaminants (i.e. dyes) depends strongly upon the pH conditions. Therefore, the application of metal salts requires often the addition of chemical neutralizing agents (i.e. lime, NaOH, HCl etc.) which may increase the salinity of the effluent and produce extra chemical sludge (El-Gohary and Tawfik, 2009; Guendy, 2010; Moghaddam et al., 2010).

In recent years there has been an increasing interest in the development of bio-based coagulant extracted from natural matrices. In comparison with metal based ones, natural coagulants have shown to be safer for human health and environmental ecosystems (Šciban et al., 2009). Among the results highlighted by several studies the use of natural coagulants implies advantages in the reduction of both coagulant dosage and sludge production, elimination of other chemicals such as neutralizing agents and substitution of hazard chemicals. Moreover, other advantages are to be related to the improvement of biological treatment processes, sludge settling characteristics and conditioning (Bolto and Gregory, 2007; Renault et al., 2009). Actually, few reports have focussed on the estimation of the costs of raw materials for the natural coagulant productions and, in addition, the drawn conclusions are almost dissimilar: a direct comparison in terms of coagulant types, processing stages and prices in different geographical regions is made complicated by different exchange rates, inflation factor and varying accuracies of the costing values (Vijayaraghavan et al., 2011). Verma et al., 2012 carried out a deep analysis of coagulating and flocculating agents for colour removal in the treatment of industrial wastewaters. Among the others, they concluded that the applicability of the natural coagulants is very limited since the high cost. The authors highlighted the need for more research studies to properly evaluate the performance of natural coagulants in the removal of contaminants particularly in the textile sector.

A prominent example of natural coagulants are tannins extracted from vegetal tissues such as the bark and wood of *Acacia mearnsii* de wild*, Castanea sativa* and *Schinopsis balansae.* Tannins are mostly vegetal polyphenolic compounds which can be chemically modified through different reactions in order to improve their coagulating-flocculating activity in wastewater treatment (Beltràn-Heredia et al., 2011). The effectiveness of tannins as natural coagulants for wastewater treatments is influenced by their original chemical structure and by the degree of tannin modification.

In the present study some preliminary results concerning the use of a commercial tannin based coagulant are reported. The commercial product is covered by an intellectual patent but the cationization procedure of tannins is referred to as Mannich-based reaction where a quaternary nitrogen is introduced into the structure of the condensed polymers as shown in Fig. 1.

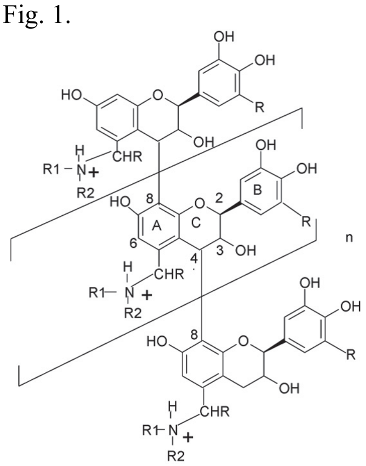

Fig. 1. Chemical structure of the modified tannin based coagulant (Graham et al., 2008)

The resulting polyelectrolyte acquires an amphoteric character thanks to the presence of both anionic polyphenols and cationic amines. Several earlier studies have been focused on the use of tannin derived coagulants for surface water and wastewater treatment showing the feasibility of the implementation at industrial scale of these natural product (Beltràn Heredia and Sánchez-Martín, 2009; Sánchez-Martín et al., 2011).

The actual study was directed to assess the biological implications connected to the use of a new cationic tannin based coagulant and, more generally, the potential environmental impacts and the eco-toxicological risks associated with its use. The coagulant aquatic toxicity, the potential effects on the activated sludge biomass as well as its biodegradability, in aerobic and anaerobic conditions, were evaluated combining biological essay both in batch and continuous trials. Furthermore, a pilot coagulation-flocculation unit was implemented in a textile industry in order to optimize the coagulant dosage for the treatment of a real textile wastewater.

2. Material and methods

2.1. Chemicals

The tannin-based product, named Adnatur, was supplied by Servyeco company (Alcora, Spain). The commercial product is an aqueous dark brown solution containing quaternary ammonium tannate produced via a Mannich type reaction involving ammonium chloride, formaldehyde and acid catalysis with hydrochloric acid. The product shows a pH value in the range of 1.9 – 2.5 in aqueous solution (10%), a bulk density of 1.1-1.2 g/cm^3 at 23 ºC, a viscosity of 50 mPa s and a solid content in the range 25-35%.

The supplied natural flocculating agent (i.e. Ecopol AS 575) from Servyeco was negatively charged with a medium charge density, presented in aqueous solution (0.5 %), a pH value in the range of 6-9, a bulk density of 0.93-0.97 g/cm^3, a viscosity of 550 mPas and a solid content greater than 87%.

For the purpose of comparing the coagulation flocculation performance with inorganic coagulant, ferric chloride ($FeCl_3$) and polyaluminium chloride (PAC) were employed in lab test and pilot trials respectively. Concentration of the stock solution (Kemira) were 40% (w/v) and 18 % (w/v) for $FeCl_3$ and PAC, respectively.

2.2. Experimental design

The experimental plan was established as follows:

- preliminary assessment of the coagulant performance in the removal of the main contaminants in the treatment of a real textile wastewater (Jar test);
- evaluation of the product biodegradability and its potential inhibition effects on both aquatic systems and biological compartments of a conventional activated sludge (CAS) system (*Vibrio fischeri* bioassay, respirometric analysis and biochemical methane potential test);
- optimization of Adnatur coagulant dosage by implementing a pilot coagulation-flocculation unit in a real textile wastewater treatment plant;

2.3. Jar test

A standard Jar test procedure was carried out on a real wastewater coming from the tanning cycle of a textile industry (Textile Mora – Spain) under ambient conditions (room temperature 21±1°C). During the coagulation phase, the raw wastewater was stirred at 100 rpm and, after the addition of the coagulants, the agitation was maintained for 3 minutes. During the flocculation phase the stirring rate was reduced to 60 rpm and kept for another 10 minutes, in order to achieve the floc aggregation, and then stopped to let each sample settle. After 30 minutes of sedimentation the clarified water was sampled and characterized in terms of pH, conductivity, chlorides, turbidity, chemical oxygen demand (COD), Suspended Solids (SS) and total nitrogen (TN). The chemical and physical parameters used to characterize both the inlet wastewater and the clarified samples were determined in accordance with the Standard Methods (APHA, 1998). Turbidity values were measured by means a turbidimeter (Hach Ratio XR) and reported in nephelometric turbidity units (NTU). The pH was continuously measured and, if necessary, corrected through the addition of neutralizing agent ($Ca(OH)_2$) up to the optimum coagulant working conditions achievement. According to authors practical experiences, for the treatment of textile wastewaters with ferric chloride the optimum coagulation activity is reached at a pH value of 8. Each experiment was carried out in triplicate and the average results are presented herein. Once defined the best dosage for both coagulants in terms of contaminant removal, several coagulation/flocculation tests were carried out by dosing the identified optimal concentrations to recovery as much settled sludge amount as possible for the following biochemical methane potential test (BMP test). The sludge obtained after the sedimentation step was characterized in terms of total suspended solids (TSS), volatile fraction (VSS), floc diameter, sedimentation time as well as floc resistance. The latter was determined by subjecting the floc to a mechanical stress. Specifically the sludge was exposed to a single level of increased shear within a containing vessel and the ratio of the floc size before and after breakage was measured. The strength factor was calculated as $R= D_f / D_i \cdot 100$ where D_i is the average floc size before breakage and D_f is the floc size after the floc breakage period (François, 1987).

2.4. Ecotoxicological test

Vibrio fischeri bioluminescence inhibition assay was employed to evaluate the toxicity of the natural and metal based coagulants on the aquatic environment. The test was carried out by using the system Lumistox™ 300 following the ISO 11348-3 (2007) standard procedure for the acute toxicity evaluation. The methodology was slightly modified by correcting the pH up to 5.5 (for both the sample and the control) avoiding the precipitation of coagulant solutions. The bacterial bioluminescence was read at 30 minutes and the data were elaborated to calculate the inhibition percentage (H%) and successively the EC_{50} values.

2.5. Respirometric assay and biochemical potential (BMP) test

In order to evaluate any potential inhibitor effects due to the dosage of the natural coagulant on the biological compartments in a municipal WWTP, two trials were carried out as follows:

- *the activated sludge inhibition* was evaluated by means respirometric techniques based on the rate of O_2 consumption measured as OUR (Oxygen Uptake Rate) (OECD, 1993; Polo et al., 2011). The sludge biomass for the batch tests was taken from the aerated basin at a municipal WWTP treating, for the most, urban sewage and a small amount of industrial agro-industrial effluent. The equipment employed was an automatic respirometer (MARTINA™, SPES) classified as a flowing gas-static liquid (LFS) (Spanjers et al., 1998). The respiration rate of the activated sludge samples (500 mL; SSV= 3 g/L) was evaluated first by spiking an easily biodegradable substrate alone as a reference substance (i.e. sodium acetate trihydrate, NaOAc) followed by the injection of the same amount of NaOAc together with increasing coagulant concentrations. The data were elaborated to calculate the inhibition percentage (H%) and the EC_{50}. The respirometer was employed to quantify also the biodegradable COD (BCOD) of the natural coagulant, expressed as a percentage of the total COD content, according to Roeleveld and van Loosdrecht (2002).

• *biochemical methane potential test* (BMP test) was employed in order to evaluate any potential inhibition effects of the coagulants on common anaerobic biomass. The tests were carried out using the sludge settled in Jar tests on textile wastewater: the coagulant dosage was chosen on the basis of the optimum concentration verified during the first Jar tests. The estimated biogas production rates were compared with the results of BMP tests performed on sludge settled without any coagulant dosages. The sludge used for these batch tests were all previously centrifuged. BMP tests were performed in triplicate under mesophilic conditions (38±1°C) by using a commercial laboratory instrument (AMPTS II– Automatic Methane Potential Test System), in accordance with the procedure given by the supplier (Bioprocess Control - Sweden). The apparatus follows the same measuring principles of the conventional methane potential tests (Raposo et al., 2011) and the data obtained were processed to evaluate the ultimate specific methane production (SMP: $Nm^3CH_4/kgVS$) as well as to achieve kinetic information on the hydrolysis phase (K_h: 1/d) by linearization of the first part of the experimental curve obtained. The gas-tight glass bottles were inoculated with the digested sludge taken from a full scale anaerobic digestion plants treating excesses sludge of a urban WWTP (Bologna-Italy). Each closed vessels were maintained in mesophilic conditions for at least 30 days applying an inoculum/substrate ratio around 0.5 (on VS base).

2.6. Pilot plant

A pilot-scale clariflocculation unit was designed and implemented as a tertiary treatment for a real industrial WWTP treating 30,000 m^3/year of wastewater coming from a textile SME that produces acrylic blankets (Textile Mora – Spain). The full scale WWTP is composed of an aerated equalization/homogenization tank followed by an activated sludge reactor. The effluent from the biological reactor is sent to a decantation unit and before the final discharge into the sewage network, the clarified water is sent to the tertiary treatment consisting of a flotation tank. The pilot plant (Fig. 2) consists of one coagulation (0.15 m^3) and one flocculation (0.3 m^3) compartment followed by a final lamellar settler (2 m^3) where the flocs are given the right time to settle. Table 1 lists the design parameters of the installation. A multiple digital controller system has permitted to monitor each single prototype section by measuring on time pH, oxidation reduction potential (ORP), turbidity, temperature and conductivity. A chemical dosing system, placed in the coagulation tank, automatically controlled the coagulant addition according to the turbidity values avoiding coagulant overdosage and permitting to maximize the process efficiency.

Fig. 2. Coagulation/flocculation pilot unit

Table 1. Design parameters of the pilot plant

Parameter	*Units*	*Value*
Flow rate	m^3/h	1
Coagulation tank capacity	m^3	0.15
Coagulation stirrer rate	rpm	150
Coagulant flow rate	L/h	0.2
Flocculation tank capacity	m^3	0.3
Flocculation stirrer rate	rpm	100
Flocculant flow rate	L/h	0.15
Decanter capacity	m^3	2
Decantation surface	m^2	1.2
Sludge outflow	L/h	75

The pilot plant decantation unit was equipped with a pump system for the final sludge extraction to be sent to the final dewatering system. During the experimental period, the pilot plant was fed with the supernatant taken from the secondary sedimentation tank of the full scale WWTP. Optimizing actions were carried out for 4 months and permitted to define the optimum coagulant dosage and validate the automatic control system. At the same time, the extracted sludge was evaluated in terms of dewaterability by using a portable Capillary Suction Timer (Type 304M CST, Triton Electronics Ltd) and the results were compared with the sludge settled in the flotation unit of the full scale installation where PAC was employed as coagulating agent. The measure is based on the estimation of the time the filtrate requires to travel a fixed distance in a filter paper. A larger CST usually implies a poor sludge dewaterability (Scholz, 2005).

3. Results and discussion

3.1. Preliminary evaluation of the product performance on raw textile wastewater

A first set of trials was performed dosing Adnatur coagulant in the range 0-500 mg/L. Once defined the best concentration in terms of turbidity removal and settling velocity of the formed flocs with Adnatur coagulant, a new series of Jar tests were carried out dosing $FeCl_3$ in order to establish a concentration able to get a comparable performance in terms of effluent quality. Table 2 summarizes the results obtained dosing 450 mg/L of Adnatur coagulant and 700 mg/L of ferric chloride: these concentrations were evaluated to be the most efficient in terms of turbidity and SS removal reaching an equal removal percentage around 98% for both the parameters. For such dosage the removal efficiency of COD resulted 76% for both the coagulants whereas Adnatur showed a higher abatement of TN (32%) compared to $FeCl_3$ (19%).

For further increases of Adnatur coagulant dosage greater than 450 mg/L, the removal efficiency was constant for turbidity and SS, whereas a slight increase of COD and TN content was observed in the clarified wastewater (data not shown). Such results could be connected to the presence of residual amounts of the coagulant dissolved in the clarified water and its organic nature and nitrogen content..

Table 2. Jar test results achieved on textile wastewater dosing Adnatur (450 mg/L) and $FeCl_3$ (700 mg/L)

Parameter	*Units*	*Inlet wastewater*	*$FeCl_3$*	*Adnatur*
pH	-	7.3	8.0	7.3
Conductivity 20°C	S/cm	5080	5400	5085
COD	mgO_2/L	3145	760	745
Chlorides	mg/L	532	815	656
Total nitrogen	mg/L	150	122	102
Suspended solids	mg/L	1008	16	13
Turbidity	NTU	2515	33	28

At the beginning of the executed Jar tests the initial pH value was 7.3. During the coagulation-flocculation test with $FeCl_3$, for each dosage a rapid decrease of pH was observed and $Ca(OH)_2$ was needed to regulate the pH to achieve the optimal coagulant working conditions (i.e. pH=8). With a ferric chloride dosage of 700 mg/L the required $Ca(OH)_2$ addition was 240 mg/L. When the natural coagulant was used, no neutralizing agents were required since the pH of the clarified water remained constant. This behavior may be due to the ampholytic character of the natural coagulant related to the presence of both positive and negative charges on its surface (Beltràn Heredia et al., 2011).

At the optimal conditions the anionic flocculant (i.e. Ecopol AS 575) dosage was 4 and 3.5 mg/l for $FeCl_3$ and the natural product, respectively.

Table 2 showed that the use of the natural coagulant implied a greater TN removal respect to the ferric chloride. This outcome resulted to be in line with many authors (Lee and Westerhoff, 2006; Pietsch et al., 2001; Vilge-Ritter et al., 1999) who, during some experimental tests, observed that Al and Fe salts were not efficiently able to coagulate organic nitrogen compounds. Lee and Westerhoff (2006) reported as cationic polymers help neutralize the negative charge on more polar organic matter, which is generally nitrogen enriched, leading to easy precipitation (Lee and Westerhoff, 2005).

Finally, the natural coagulant did not lead to a significant increase of electrical conductivity in the clarified effluent whereas ferric chloride implied a conductivity increase of 6.3% compared to the value detected in the inlet wastewater. Therefore, it can be remarked that by dosing the natural coagulant, the corrosive tendency of the treated wastewater on electro-mechanical equipment can be reduced and their lifetime extended.

3.2. Aquatic toxicity and product biodegradability

Table 3 reports the results achieved during the tests performed to evaluate the potential inhibition of the tested coagulants on both aquatic systems (i.e. *Vibrio fisheri* bioassay) and the biological sludge. Moreover Adnatur biodegradability is reported as BCOD.

Table 3. Results of ecotoxicological tests and coagulant aerobic biodegradability (n.d= not detectable)

	Adnatur	*$FeCl_3$*
Bioluminescence essay	EC_{50} (mg/L) (95% Conf. Interval)	
	5326.1 (2870.8-9881.3)	339.9 (263.9-435.5)
Sludge inhibition activity	EC_{50} (mg/L) (95% Conf. Interval)	
	n.d	313.4 (136.5-719.7)
Aerobic Biodegradability	COD (180 gO_2/L)	n.d
	BCOD 10% of COD	

Vibrio fisheri essay showed for the natural coagulant EC_{50} value at concentration of 5,326 mg/L which, however, came out of an extrapolation since the maximum achieved biolumiscence inhibition was around 48%. The essay revealed for the natural coagulant a very elevated EC_{50} value which results to be too high respect to the typical coagulant dosages in primary WWTP (i.e. 50-200 mg/L for $FeCl_3$). At the same time, the tests carried out on activated sludge samples for the evaluation of respiration rate inhibition due to Adnatur coagulant reported no effective toxic effects. Conversely, both tests performed with $FeCl_3$ reported EC_{50} value around 300 mg/L. Fig. 3 shows two respirograms obtained for the same dosage of Adnatur coagulant and $FeCl_3$. The former OUR peak is related to NaOAc addition (20 mg/L) whereas the latter is due to NaOAc and coagulant dosage spike (20 mg/L of NaOAc and 120 mg/L of coagulants).

Clearly, whereas the natural coagulant implied an increase in the respiration rate, the same $FeCl_3$ concentration caused a sludge inhibition effect. As confirmed from the product biodegradability evaluation, the biodegradable organic fraction (BCOD) is about 10% of the total COD amount (180 mg/L). This could easily explain the increase of activated sludge activity which appeared even stimulated by adding the natural coagulant at lower dosage.

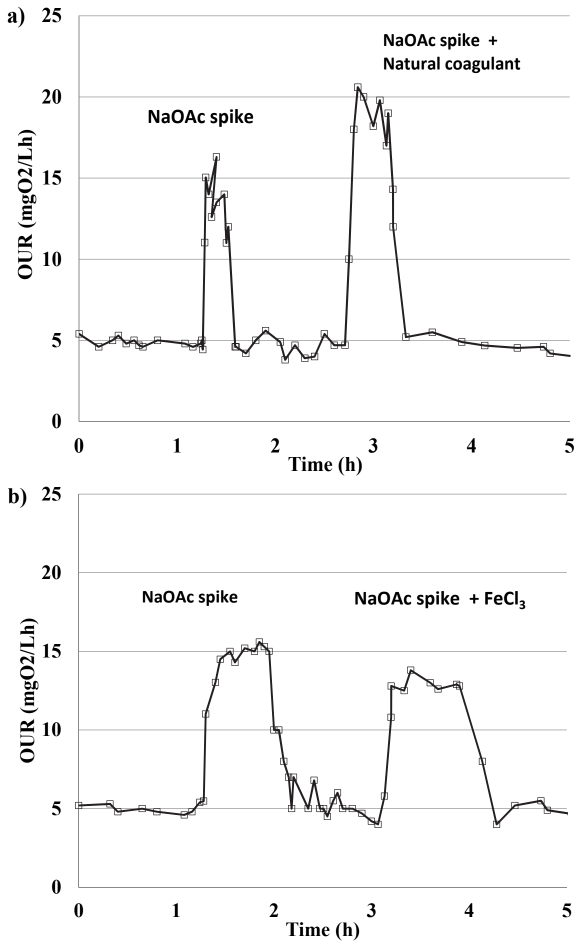

Fig. 3. Respirograms obtained dosing 120 mg/L of a) Natural Coagulant and b) $FeCl_3$ both togheter with 20 mg/L of NaOAc. The first peak (left) of both images was obtained dosing 20 mg/L of NaOAc

The EC_{50} values calculated for $FeCl_3$ resulted to be close to the common ferric chloride dosage range applied in the primary treatment of sewage water. Comparable results were achieved from ecotoxigological tests. In fact, both the *Vibrio fischeri* bioluminescence essay and the activated sludge inhibition activity estimation reported EC_{50} values around 300 mg/L. However it should be considered that downstream of the process of clariflocculation, the coagulant concentrations in the supernatant, herafter directed to the oxidation basin, result to be lower than the applied dosages. Moreover, the efficiency and the reactivity of a specific coagulant depends on several parameters such as the pH and the presence of carbonates in the wastewater to be treated. On the basis of these considerations, ecotoxicological effects on the active biomass of a WWTP are excludable also for ferric chloride. Table 4 reports some characteristics of the sludge recovered at the end of Jar test dosing 450 and 700 mg/L of the natural product and $FeCl_3$. The flocs formed after the dosage of the two coagulants exhibited great differences in their behaviour in terms of decantation time as well as resistance to mechanical stress, even though no significant differences in size and sludge volume were noticeable. The flocs growth by applying Adnatur coagulant was more rapid than $FeCl_3$ with a higher sedimentation velocity.

This result is certainly due to the coagulation-flocculation mechanisms involved and the strong cationic character of the product.

Table 4. Sludge characteristics and anaerobic biodegradability

	Units	*Adnatur*	*FeCl₃*
Coagulant dosage	mg/L	450	700
Floc Sedimentation Time	sec	4	10
Floc diameter	mm	4.5	4
Floc resistance	%	85	70
TSS	mg/L	6090	7690
VSS	% TS	88.2	79.9
SMP	Nm^3CH_4/VS	148.4	129.8
K_h	1/d	0.20	0.19

The primary sludge produced by applying the natural coagulant showed a TSS content equal to 6,090 mg/L with a high volatile fraction (88.2% on TS), whereas the sludge settled with $FeCl_3$ reported a concentration of 7,790 mg/L with a lower volatile fraction (79.9% on TS). This preliminary evidence suggested a difference in terms of potential energy recovery in anaerobic conditions between the two substrates. In fact, at the end of BMP trials, the sludge linked to the use of Adnatur coagulant showed a specific methane production (148.4 Nm^3/VS) greater than the sludge produced by $FeCl_3$ (129.8 Nm^3/VS). However the ultimate methane production obtained with Adnatur coagulant was 8% lower than one obtained without any dosage (155.4 Nm^3/VS). This aspect may be linked to the presence of polyphenols in the chemical structure of the tannins which inhibit the methanogens microorganism (Wikandari et al., 2015). Fig. 4 reported the time profile of the specific methane production (average values) obtained from batch trials (Fig. 4a) and the linearization of the first part of the experimental curve built for the determination of the ultimate methane production (Fig. 4b).

Although, the hydrolysis of complex organic material has been considered the rate-limiting step of the anaerobic digestion process, Fig. 4 shows that for both the samples, the most of the energy recovered from the substrates was reached within the first 10 days, when the methane production resulted more than 90% of the ultimate methane achieved for all samples. This aspect could be explained by the high inoculum to substrate ratio adopted in the experimental trials (Fernandez et al., 2001). The greater anaerobic biodegradability of the settled sludge was confirmed by the value of the first order hydrolysis constant (K_h) as reported in Table 4.

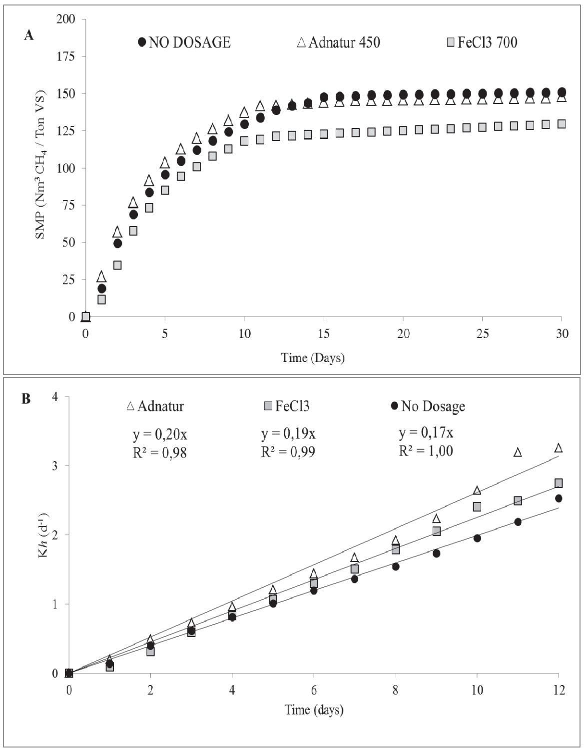

Fig. 4. Time profile of: a) specific methane production of the settled sludge and b) the determination of K_h

K_h values were calculated on the first part of the experimental curve according to Angelidaki et al. (2009). Indeed, the primary sludge produced by dosing Adnatur coagulant and $FeCl_3$ showed respectively a reaction rate of the hydrolysis step about 17% and 11% greater than the sludge settled without any coagulant (0.17 1/d).

The results of BMP trials showed that the natural coagulant produced a primary sludge with a higher anaerobic biodegradability respect to $FeCl_3$ (up to 5%). Likely, since the different origin and chemical characteristics of the two coagulants, the mechanisms they promote during coagulation/flocculation processes are different. As showed, the sludge settled by using the natural coagulant reported a greater SV to TS ratio in comparison with the sludge achieved by applying the inorganic coagulant.

3.3. Pilot scale trials

The pilot plant unit was monitored for 120 days and fed with 0.8 m^3/h of clarified water coming from the secondary sedimentation tank of the industrial textile WWTP. The inlet flow was characterized by an average value of TSS (172 ± 54 mg/L) and conductivity (1718 ± 178 mS/cm) already below the discharge limit. With specific reference to the COD content, the clarified water coming from the secondary sedimentation tank showed values around 1,222 ± 273 mgO_2/L. In the first experimental period, preliminary actions were carried out in order to verify and calibrate the automatic dosage systems. The applied Adnatur coagulant dosage was initially set on the basis of the Jar Test outcomes. Fig. 5 shows the time profile of the COD, TSS and conductivity for both the inlet and the effluent flows of the pilot unit.

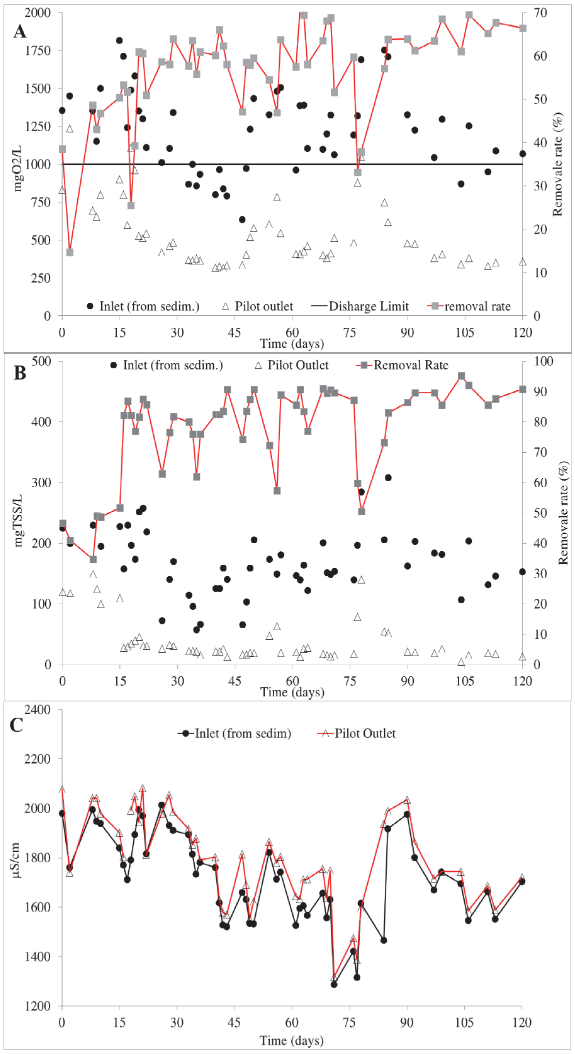

Fig. 5. Time profile and removal rate of A) COD, B) TSS and C) conductivity during the pilot trials

It was observed that, during the first 2 weeks, the removal rate of COD and TSS achieved in the pilot plant was less than 50% for both the parameters showing a poor process performance respect to the Jar test results. It is to consider that the results achieved in laboratory tests are not directly transferable to the real pilot plant conditions since the different conditions such as fluid dynamic and the coagulant dosage systems. In the light of this observation, the experimented natural coagulant dosage was gradually regulated in the range 200-450 mg/L. During the experimental period (days 18-75) a general improvement of the coagulation/flocculation process was observed in terms of contaminants removal for an averaged coagulant dosage of 350 mg/L. In the last 30 days, when the coagulant dosage was optimized, the removal percentages achieved were 69-77% for COD (Fig. 5A) and 85-95% for TSS (Fig. 5B) and a really low medium conductivity change (increase up to 5%) was observed (Fig. 5C)".

At the end of the experimental action, the achieved results highlighted as there was a 36% of reduction in the coagulant dosage (350 mg/L of Adnatur coagulant in front of 550 mg/L Aluminium polyclhoride) further increased to 63% (200 mg/L of Adnatur coagulant in front of 550 mg/L of PAC) after the optimization action.

Considering 30,000 m^3 per year of water treated and the costs of the coagulant product (0.90 €/kg), the optimization action on the pilot plant permitted to reach a specific treatment costs of 0.18 euro m^3 of water treated. This value is similar to the one paid by the industrial plant operator which in one year consumes 4000 kg of PAC, 2000 kg of flocculant and 4000 kg of NaOH (25%). In reason of such results, the industrial operator decided to adopt the natural coagulants in its WWTP flotation unit, obtaining a COD and TSS removal rate in the range of 75-91% and 87-99% respectively. At the same no significant variation (0-2%) of the medium conductivity was observed with a coagulant dosage range from 200 to 400 mg/L". Moreover, further cost savings are achievable due to the regional tax rate system.

The industrial operator is charged on the effluent final discharge, sent to a centralized municipal WWTP on the basis of a fare made up of fixed and variable charge which strictly depends on the pollutant loads. From this point of view, by dosing the natural coagulants a considerable tax reduction is achievable since the tested pollution loads removals is higher than the one reached in the pilot optimization action. Further it is to be considered that the sludge settled with the natural coagulant resulted to be more dewaterable since the CST measured was lower (14 sec) than the sludge settled by applying PAC (21 sec) in the real facilities.

The connected advantages are easily conceivable considering the WWPT sludge line and the sludge treatments phases such as the thickening and the conditioning before the final sludge disposal. It is to be born in mind that the costs for the final sludge disposal constitute approximately 50% of the total operating expenses of a WWTP. A less sludge volume which furthermore results easier to be treated would imply effective economic advantages. In addition, a single stage coagulation-flocculation could be investigated in the future to reduce the capital cost (Liang et al., 2014; Zahrim et al., 2015).

4. Conclusions

The use of the commercial tannin based coagulant for the treatment of a textile wastewater was previously investigated by means laboratory tests and, successively, during a pilot scale experimentation. The Jar tests showed a good efficiency of the product in promoting coagulation/flocculation processes and the settled sludge flocs had a high degree of dewaterability and resistance. During the tests neutralizing agents were not required and no change in the conductivity medium was detected. Bioluminescence essays and sludge inhibition activity tests showed as the natural coagulants do not really imply any toxic effects for both the aquatic life and the sludge biomass activity. Moreover the natural product resulted to have a good level of biodegradability in both aerobic and anaerobic conditions.

The laboratory results were further validated by means the implementation of an automatic dosage system in a pilot coagulation-flocculation unit which was employed to treat a real textile wastewater. The optimization action, performed dosing the natural coagulant in the pilot plant, permitted to reach a specific treatment costs of 0.18 euro m^3 with a dosage up to 63% lower than a commercial inorganic coagulant. Further advantages associated to the use of the natural coagulant were emphasised considering the WWPT sludge line and the sludge treatments phases. The natural product would not require during the wastewater treatment the use of chemical additional products such as neutralizing agents: in this view the worker would not handle such products and the WWTP electro-chemical equipment would have a longer lifespan since the wastewater corrosive tendency and/or fouling potential would be lowered. Moreover the excess sludge amount would be reduced and its good level of dewaterability would facilitate the sludge treatment and final disposal steps.

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EFFECT OF pH IN THE SYNTHESIS OF ORGANO-CLAYS FOR RARE EARTHS REMOVAL

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Abstract

Two montmorillonitic clays were modified with N-(methoxy-polyethylene glycol) ethylene diamine and tested as sorbents for removal of Rare Earths (REs) from aqueous solutions. Lanthanum was chosen as representing element of REs family and adsorption tests were performed with the aim of selecting a system with good uptake efficiency for the pollutant abatement in wastewaters. The effects of pH were studied and the properties of the obtained final materials were evaluated with simple model systems of the final application. The modified clays were characterized before and after the intercalation, combining the results of X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR), whereas the solutions were analysed by means of Chemical Oxygen Demand to quantify the amount of intercalated polymer and by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) to quantify the metal ions concentration. The results showed that the organo-clays have been efficiently prepared while the characterization techniques showed that the intercalation mechanism was strongly dependent on the pH of the preparation procedure, affecting the protonation of the amino groups.

Key words: environmental remediation, FT-IR spectroscopy, organo-clays, rare earths removal

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1. Introduction

Adsorption has become one of the main treatments for heavy metals removal, due to its versatility, wide applicability, and economic feasibility (Ajmal et al., 2015, Ganjali et al., 2004, Jamali et al., 2007; Tsekova et al., 2015). Indeed, technical applicability and cost-effectiveness are the key factors in the selection of the treatment technology. One of the open points regarding adsorption technology is related to the kind of solid matrix used. In this respect, the use of natural materials as sorbents gained a significant interest in the last years, mainly thanks to the high selectivity demonstrated for certain heavy metal ions, the low cost and the characteristic of being environmentally friendly themselves (Janos et al., 2016; Sheikhi et al., 2015). In the above scenario, clays have been suggested as a green alternative (Dikmen et al., 2015; Sen Gupta and Bhattacharyya, 2014) being characterized by low cost, high mechanical intensity, good tolerance towards harsh chemical environment, convenient solid-liquid separation and excellent reusability. Furthermore, clay minerals show a well-known adsorption behaviour towards metals (Moldoveanu and Papangelakis, 2012).

Although the primary purpose of the adsorption technologies is the reintegration in the environment of water with pollutant concentration compatible with ecosystem receptors, more and more attention is paid to the prospect of using the same processes also for resources exploitation. In this perspective, the study of adsorption mechanisms related to heavy metals with valuable interest and

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reutilization possibility could be worthwhile. REs correspond to these qualities: their limitation in wastewater is unregulated (Westerhoff et al., 2015) but only because insufficient data about their toxicity to human health are available (Fuad et al., 2013). Furthermore, REs are also added value elements since their demand is constantly increasing in the global market, due to the new technological applications that exploit these materials for their unique properties (Iannicelli-Zubiani et al., 2013).

The use of natural clays in treating aqueous wastes containing heavy metals and organic matter has been previously reported in other works (Sen Gupta and Bhattacharyya, 2014) and has been deeply investigated by the authors for REs recovery from aqueous wastes (Iannicelli-Zubiani et al., 2015). The obtained experimental results (Iannicelli-Zubiani et al., 2015) showed that two pristine clays, belonging to montmorillonite group, were able to capture and release La and Nd ions, by means of an ion exchange mechanism; in view of these results the use of suitably modified clays was proposed in order to enhance the recovery of REs. Smectitic clays, indeed, such as hectorite and montmorillonite are layered aluminosilicates that can be modified by intercalating agents in the interlayer through a combination of ionic and weaker forces (Malakul et al., 1998). As modifying agent, N-(methoxy-polyethylene glycol) ethylene diamine was selected, being characterized by a polyethylene-glycol chain able to intercalate in the clay interlayer (Zampori et al., 2010) and by two amino groups, already reported in the literature for the removal capability towards heavy metals (Gao et al., 2015). For all these reasons, the present work focuses on the adsorption of lanthanum, chosen as representing element of REs family, from aqueous solutions, performing adsorption tests using two suitably modified mineral clays with the aim of selecting a system with good uptake efficiency for the pollutant abatement in wastewaters.

Although the preparation procedure here proposed is quite easy, at least from the experimental point of view, of course the knowledge of the effect of any operative parameters, such as pH, is fundamental to handle the properties of the final material, thus its performance. Therefore, the effects of pH were studied and the properties of the final materials thus obtained were evaluated with simple model systems of the final application. The modified clays were characterized before and after the intercalation, combining the results of X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR), whereas the solutions were analysed by means of Chemical Oxygen Demand to quantify the amount of intercalated polymer and by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) to quantify the metal ions concentration.

2. Experimental

2.1. Materials

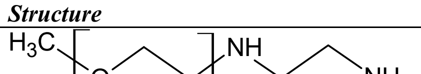
Two natural smectite samples were used, namely a Ca-montmorillonite (STx-1b which stands for "State of Texas", STx in the following) and a Na-rich montmorillonite (SWy-2, which stands for "State of Wyoming", SWy in the following) which were provided by the Clay Minerals Society. The average grain size of STx and SWy was 20 ± 10 µm and 30 ± 15 µm, respectively, and was measured by a laser particle size analyser (Cilas 1180). The Cation Exchange Capacity (CEC) of the clays was determined according to the ammonium saturation procedure proposed by Chapman at pH 7, resulting 120 meq/100 g for STx clay and 240 meq/100g for SWy (Kühnel, 1990). The main differences between the two used clays are the CEC values and the interlayer cations: STx is a calcium montmorillonite while SWy is a sodium montmorillonite. In this way it should be possible to observe potential different behaviours having interlayer cations with different: oxidation states, charges, dimensions.

A N-(methoxy-polyethylene glycol) ethylene diamine (AM in the following, supplied by Bozzetto Group) was used as modifying agent, whose formula and properties are reported in Table 1. AM is a yellow viscous liquid material at room temperature, soluble in water. Together with clays and polymer, the reactants used in this study were lanthanum nitrate ($La(NO_3)\cdot5H_2O$ 99.99%, Sigma Aldrich), HNO_3 (ACS, Sigma Aldrich), and deionized water.

2.2. Hybrid-clay materials preparation

Organo-clays (Finocchio et al., 2011, Zampori et al., 2012) were obtained according to literature(Iannicelli-Zubiani et al., 2017), via an intercalation reaction. In a typical experiment, 2.5 g of clay were mixed, in a jacketed reactor under vigorous stirring, with 50 mL of aqueous polymer solution for a fixed time of 90 min (Zampori et al., 2010). The initial polymer concentration was fixed at 30 mM (initial polymer/clay ratio = 0.7 g/g), considered enough to potentially remove all the lanthanum ions put in solution, being the amino group number three times higher than the contacted lanthanum. All the experiments were carried out at the controlled temperature of 30°C.

Table 1. Main properties of polymer AM

Label	*Formula*	*Structure*	*MW*	*pH*
AM	$H_3C(OCH_2CH_2)_nNH(CH_2)_2NH_2$ n = 25		1174	11

The pH of the solution was measured before and after the reaction using a Mettler Toledo FE20/EL20 digital pH-meter. The initial pH of the polymer solution was about 11. In order to evaluate the effect of the contacting pH on the intercalation reaction, this parameter was varied from 11 to 1 by stepwise addition of nitric acid to the initial polymer solution, and it was monitored throughout the preparation. At the end of the reaction, the solid phase was separated by the aqueous one using a centrifuge (HETTICH 32 RotoFix, 3500 rpm for 15 min). The amount of the reacted polymer was found as the difference of the polymer concentration, determined by COD (Chemical Oxygen Demand) analysis, in the aqueous solution before and after the intercalation experiment. The solid, upon drying (one day at room temperature), was ground in a mortar and fully characterized as reported in the following.

2.3. Adsorption tests on model solution: lanthanum ions uptake

2 g of the synthesized organo-clays (in the following STx-AM, SWy-AM) were contacted with 50 mL of an aqueous solution of $La(NO_3)_3$ at known concentration, vigorously stirred at room temperature and separated from the aqueous using a centrifuge.

2.4. Characterizations

The Chemical Oxygen Demand (COD) analyses were carried out using a Spectrodirect Lovibond instrument. In a standard instrumental procedure the unknown sample was oxidized by heating for 120 min at 150 °C (ASTM, 2006).

All the metal ions concentrations in solutions were measured by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analyses using a Perkin Elmer Optima 2000DV spectrometer. The measurement error is estimated to be 1%.

X-ray powder diffraction (XRPD) patterns of clays were recorded after each step of the recovery process with a Bruker D8 Advance diffractometer using graphite monochromated Cu K_α radiation; the scan step was 0.02° 2θ and the measurement time was 1 s per step. The XRPD line profile analysis was performed with TOPAS P 2.1 software (Bruker AXS, Karlsruhe, Germany) using a Pearson VII profile function, after background subtraction. The calculated profiles were used for the determination of basal spacing (d_{001}) of the clays. FT-IR analyses (mid-IR region) were performed on the powders with a FT-IR Thermo Nicolet 380 Avatar using the KBr pressed disk technique.

3. Results and discussion

3.1. Organo-clays preparation

Different organo-clay samples were prepared contacting the clay with a polymer solution at constant initial polymer concentration (30 mM, corresponding to a polymer amount of 0.6 mmol/g) but different pH, namely 1, 5, 8, and 11. In the following these samples will be identified by a label indicating the type of clay and the initial pH of the polymer solution: e.g. STx-AM1 is the organo-clay synthesized using STx and a polymer aqueous solution at pH 1.

The amount of the reacted polymer as a function of initial pH is reported in Fig. 1. During the contacting reaction, the presence of the clay did not influence the pH value of the mixture: the actual pH of the suspensions rapidly reached the pH value of the polymer solutions and kept constant throughout the experiments. However, the reaction pH influenced the total amount of the intercalated polymer, and this effect was exerted in different extent depending on the clay nature: indeed, at acid pH, larger amount of polymer interacting with the clay was found (70% of the initial one in case of SWy, to be compared with 35% measured for STx). Anyway, when the reaction was performed at pH ≥ 8 for STx and at pH ≥ 5 for SWy a marked decrease in adsorption capacity of polymer was found. This difference could be related to the CEC of clays and to the superficial charge of particles. The difference between the two systems became smaller on increasing pH, until reaching very close contents of polymer (about 30 and 25% for SWy and STx, respectively) when the intercalation is performed at pH 11.

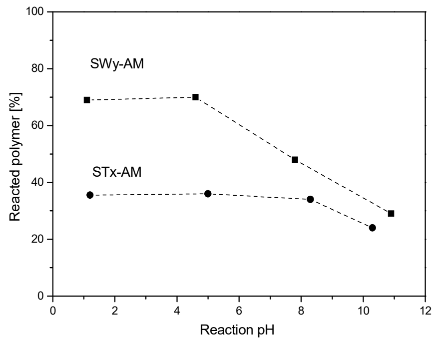


Fig. 1. Intercalated polymer as a function of the reaction pH

Accordingly, the same intercalation mechanism can be supposed for both the clays and the intercalation efficiency can be correlated specifically with pH, with a particular effect of the basic environment. Considering that the amino groups of the polymer are possibly more stable in the amine form at basic pH, the observed behaviour could be related preferentially to the nature of the polymer than to the nature of the clay. The effect of pH could be explained if the polymer speciation at the different pH is taken into account together with the polymer-clay interaction mechanism. It is well known that amino groups are largely influenced by pH: depending on their pK_a, they could be present in solution both as amine or protonated amino groups. The interaction of the polymer with the clay interlayer can occur via two possible mechanisms: i.e. intercalation by ionic exchange and intercalation by other bonds not involving cations exchange, such as, for instance, H-bonding with water in the hydration shells, ion-dipole interactions, coordination between the oxygen atoms of the PEG segments of the polymer and the interlayer exchangeable cations (Deng et al., 2006). The ionic exchange mechanism implies the presence of a charged organic molecule partially or totally replacing the interlayer cations via a charge compensation mechanism. Otherwise, the intercalation occurs via weaker interactions between some functional groups of the uncharged polymer and the interlayer environment (e.g. cations, water molecules). Hence, no permanent charges are involved (Chiu et al., 2013). Of course, both ion exchange intercalation and intercalation not involving ion exchange could be co-present in view of the nature of the intercalating molecule. Accordingly, the presence of protonated amino groups on the polymer should drive the reaction preferably towards the ion exchange mechanism, while the weaker interaction becomes active in the absence of charged species. Therefore, according to our results, at very low pH values, where the polymer amino groups are mainly present as ammonium ions, the ion exchange reaction will be preferred; while in basic environment, where only the neutral amine is available for the reaction, the intercalation based on weak bonds will be the main process. In between, where the polymer could be partially protonated, both the mechanisms could account for the intercalated polymer, thus mixed and quite complex interactions will result from the contacting reaction.

The extent of the intercalation reaction can be quantified on the bases of the reacted polymer via COD analysis, but this technique, accounting for all the polymer inside the clay, is unable to discriminate between the intercalation via exchange mechanism or not.

The exchange reaction, instead, can be directly evaluated analysing the ionic composition of the solutions after the contacting experiments. In presence of an ion exchange reaction, part or total of the interlayer cations should be found in the solution after the contacting reaction, having been replaced by the interacting molecules. Therefore, ICP-OES analyses were performed on the solutions after the contacting reaction at different pH, their results are summarized in Fig. 2.

First of all, ICP analyses were consistent with the interlayer composition of the pristine clays since, in the case of STx, calcium and magnesium were found, while for SWy large amounts of sodium were primarily present. Moreover, the pH of the reacting polymer solution had a marked effect on the release of the interlayer ions: not surprisingly, the lower the pH the larger the amount of the exchanged cations. Therefore, it can be assumed that the interlayer cations have been replaced by the charged polymer.

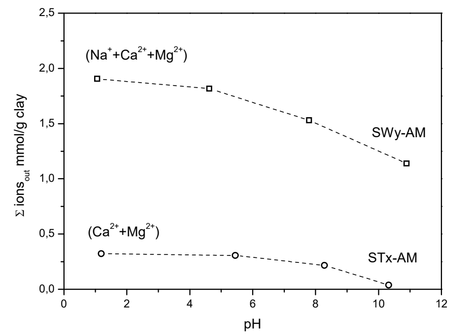


Fig. 2. ICP-OES analyses of the solutions after the intercalation reaction at different pH

Comparing Fig. 1 and 2 it is evident the strong correlation between the intercalated polymer and the replaced cations: in the case of SWy, the amount of intercalated polymer is higher compared to STx and this fact is confirmed to be linked to the higher amount of exchangeable ions in the interlayer (CEC of SWy 2.45 mmol/g of charge compared to 1.24 mmol/g of charge for STx). In both the clays, increasing the pH, the amount of cations in the solution after intercalation progressively decreased. In the case of STx, this amount goes down to near zero (at about pH 11), confirming that no exchange has occurred at alkaline pH (Fig. 2). The close similarity of the two clays at high pH (see Fig. 2) can be related once more to the nature of the amino groups. Indeed, at high pH, where the polymer is primarily intercalated without ion exchange, the similar amounts of polymer that were intercalated were just depending on the interlayer expansion capability of the clay.

For both the clays it can be concluded that at low pH the intercalation via ion exchange mechanism is predominant, while at high pH intercalation without exchange is the main reaction.

So, the following picture can be drawn. At alkaline pH, where the amine is not protonated, the intercalation based on weaker bonds is the prevailing mechanism, while on decreasing pH, the amino groups are progressively protonated and the exchange reaction becomes the most likely. At intermediate pH it is difficult to find out a priori the predominance of one on the other owing to the complexity of the system. In any case, the condition of ion exchange, even partial, is not good for the intended application. As already pointed out, the protonated amine is expected to be less effective for metal ions uptake purposes since the amino groups, i.e. the coordinating functions, are involved in bonds or interactions with the interlayer environment, thus the coordinating effect is lost.

Also the study of the solid phase is of considerable importance. The XRD results are shown in Figs. 3a and b. For both clays a shift towards lower angles (thus larger interlayer dimensions) of the basal reflection position (d_{001}) was evident. This effect was much more manifest in the case of STx, where the

position of the basal reflection can be clearly identified.
SWy is characterized by a very broad, low intensity basal reflection, not clearly detectable in Fig. 3. The sharpness and intensity of the basal spacing are related to the degree of order of the interlayers and the particle size, therefore the as-received SWy clay seems to have a particularly disordered state. Anyway, line profile analysis performed on the broad reflection allowed to roughly model it with two basal spacings at about 12 Å and 10 Å (Iannicelli-Zubiani et al., 2015). So, also in the case of SWy the same enlargement of interlayer dimension could be hypothesized if the poorly evident spectrum modulation centred around 7 (2θ) is considered as d_{001} in the pristine clay.

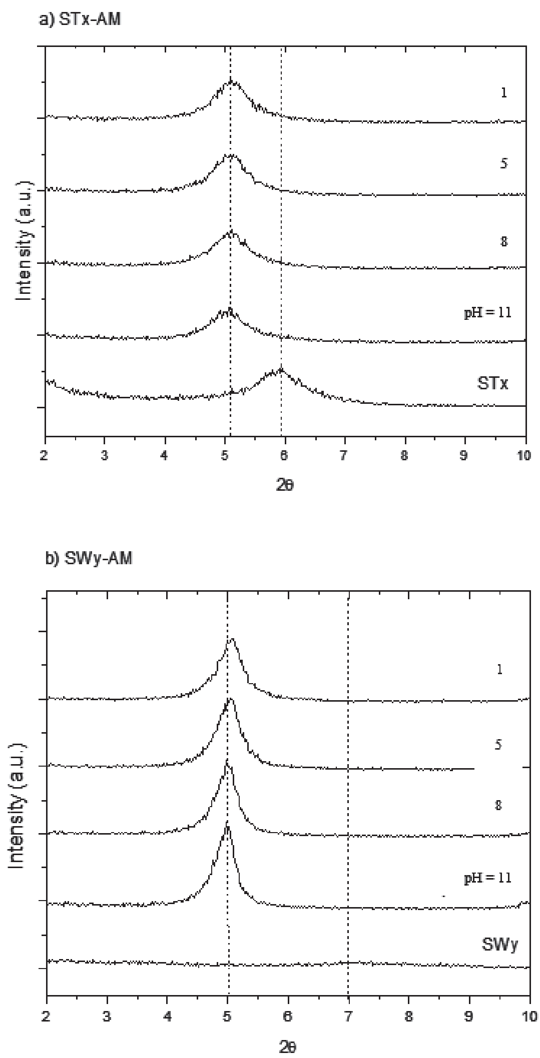


Fig. 3. XRD analyses of organo-clays obtained at different pH values: a) STx-AM and b) SWy-AM (pristine STx and SWy here reported for comparison).

In the STx-based system (Fig. 3a), in addition to the reported displacement of the d_{001} from 15.4 Å to 17.6 Å, no other remarkable effects were seen. The d_{001} enlargement arises just from the allocation of the polymer inside the interlayer (Finocchio et al., 2014, Zampori et al., 2010), but it does not depend on the pH environment as evidenced by the constancy of the d_{001}. Conventional XRD was not helpful for the evaluation of the polymer nature inside the clay possibly due to the fact that from the dimension point of view, no appreciable differences are present between an intercalated exchanged or not-exchanged polymer. Moreover, no particular ordering effects were observed in the STx-AM system: large and slightly asymmetric reflections were present at any pH values. It is reported in the literature (Brown and Brindley, 1980) that the sharpness and intensity of the basal spacing are related to the degree of order of the interlayers and the particle size. The absence of an ordering effect suggests that the polymer filled the interlayer in a quite random way without any preferential allocation site. The observed reflections asymmetry is also an indication of a random filling of the interlayers. Indeed, a random filling of the interlayers could result in a random d_{001} distribution, thus in the asymmetry of the corresponding XRD reflection.

A similar behaviour was found in the case of the SWy-based system, where no particular effect of the pH was present (Fig. 3 b), thus a constancy in d_{001} was detected also in these samples. On the contrary, the polymer amount allocated in SWy was strongly dependent on pH and higher than STx (up to 70% of the initial polymer contacted with the clay, as reported in Fig. 1). An ordering effect of pH is instead found in SWy-AM samples: upon the contacting reaction the XRD spectra showed the presence of sharp and quite symmetric d_{001} reflections at any pH value. The progressive ordering of the interlayers in presence of acid or basic environment was already observed and reported in the literature (Bieseki et al., 2013, Chalghaf et al., 2013) and by the authors (Iannicelli-Zubiani et al., 2015) for pristine SWy. Depending on the considered pH, the partial or total replacement of cations in the clay interlayer with protonated water molecules or basic species was considered responsible for the d_{001} sharpening (Iannicelli-Zubiani et al., 2015).

In further studies it could be useful to relate this sharpening of the d_{001} reflection to the amount of intercalated polymer and to the homogeneity of the polymer orientation in the clay gallery. Similar effects can be put forward to explain the observed behaviour in the presence of the polymer. This is not surprising in the case of STx, where almost a constant amount of polymer was allocated in the structure (Fig. 1). On the contrary, it is hardly understandable in the case of SWy, where the intercalated amount of polymer at low pH was found more than double with respect to high pH. The constancy of d_{001} values in SWy-based samples could be explained either with a planar configuration (Chiu et al., 2013, Deng et al., 2006) of the polymeric chains inside the interlayer or with the presence of some polymer interacting with the external surface of the clay.

Accordingly, the observed enlargement (about 17.5 Å) could account only for the maximum amount of polymer allocable inside the interlayer. A priori this hypothesis cannot be discarded either in case of the STx-based system.

An attempt to understand which polymer form, ammonium or amine, was interacting with the clay, FT-IR spectra were recorded on the solids. Results are reported in Fig. 4 for the STx-AM and SWy-AM samples prepared at pH 1 and pH 11. The overall IR spectra of both STx and SWy based materials show bands due to the clay matrix together with bands due to the organic component. In the high frequency region, the band at 3625 cm^{-1} detected in all the samples is assigned to stretching vibrational mode of inner OH groups, characterizing montmorillonite clay (Madejová, 2003). The spectra of organo-clays also show another weak shoulder at 3675 cm^{-1}, whose assignation is still doubtful, possibly due to hydroxyl groups of the clay matrix modified by the preparation procedure itself. In the samples prepared at pH 11 the NH stretching mode of the amine groups appears as a weak and broad band at 3260 cm^{-1}, overlapped with the band of H-bound hydroxyl groups. Moreover, in this spectral region, both STx and SWy based hybrid materials show bands typical of the polymer alkylic chain: a complex absorption centred at 2885 cm^{-1} with a shoulder at 2950 cm^{-1}, both components to be assigned to the CH stretching modes of the CH_2 units. In the low frequency region, beside the main and complex absorption below 1200 cm^{-1} due to Si-O and OH deformation/stretching modes of the clay matrix, several weak bands can be assigned to the AM chain. In particular, bands at 1470, 1455 (asymmetric CH_2 deformation modes), 1355 and 1250 cm^{-1} (CH_2 wagging and twisting modes), as well as bands at 950 and 845 cm^{-1} (CH_2 rocking modes) are due to the PEG-type chain (Finocchio et al., 2011). As for the amine group, at pH 11 the NH deformation mode can be detected at 1620 cm^{-1}, although strongly overlapped with the band due to the adsorbed molecular water. Bands at 896 and 823 cm^{-1} are also characterizing the amine moieties. Decreasing pH down to 1 results in the detection of a new weak IR band at 1530 cm^{-1}, which could be due to the protonated form of the amine (symmetric –NH_3^+ deformation mode), whose corresponding asymmetric deformation mode is expected at 1630 ca. (Fig. 5), thus masked by molecular water absorption.

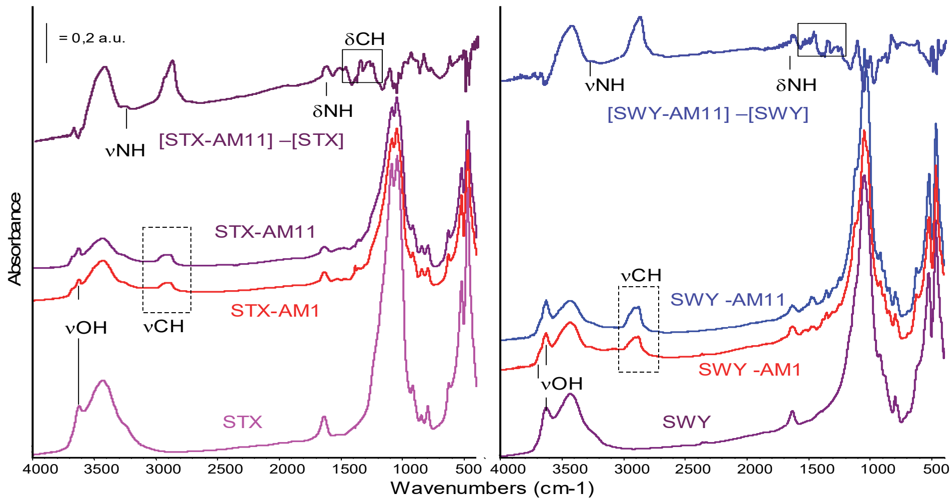


Fig. 4. FT-IR skeletal spectra of the STx and SWy series samples. Insets: subtraction spectra

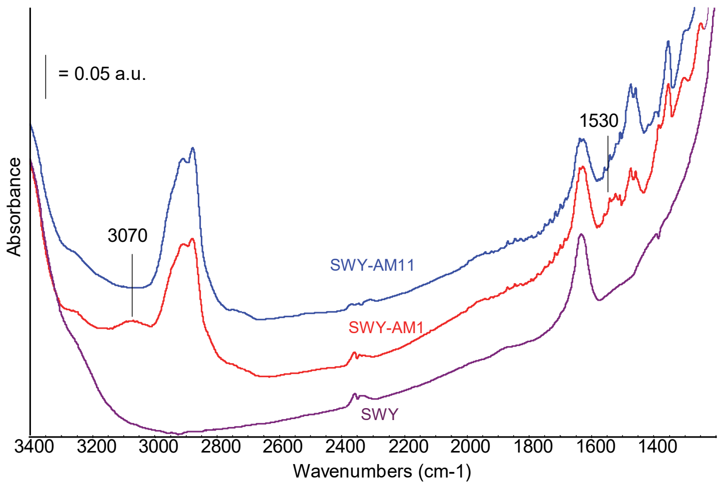


Fig. 5. FT-IR skeletal spectra of the SWy series samples. Insets: subtraction spectra

Correspondingly, another component is appearing at 3070 cm^{-1}, which can be assigned to the $–NH_3^+$ stretching mode (Colthup, 2012). On the other side, even at such a low pH, we have still some evidence of free NH/NH_2 groups (for instance, the broad absorption at 3250 cm^{-1} and the band at 1620 cm^{-1}). These data should confirm the protonation of at least a fraction of AM polymer, in agreement with the proposed interaction mechanism. Moreover, it is worth noticing that the spectra features assigned to the protonated AM are slightly more evident in the spectrum of SWy-AM1 sample, than in the spectrum of STx-AM1 sample.

3.2. Uptake capability towards a La ions model solution

In order to evaluate the effectiveness of the prepared organo-clays towards REs recovery, the new materials were tested by contacting with a La-based model solution and their capability of uptake towards these ions was evaluated. Starting from 19 mM La model solutions (corresponding to 0.48 mmol/g_{clay}), the amounts of adsorbed lanthanum ions are reported in Table 2. It is evident that all the organo-clays are effective in La^{3+} uptake, but with different uptake efficiencies. Such efficiencies are much more related to the nature of the intercalated amine than to its total amount. It is indeed evident in Fig. 6, that STx-AM1 and SWy-AM1, i.e. prepared at pH 1, presented quite a low uptake (both about 0.15 mmol/g), despite the large polymer content (0.43 and 0.78 mmol/g for STx-AM1 and SWy-AM1, respectively). This behaviour is even more stressed when considering the SWy-based system, where twice the polymer content did not correspond to a double La uptake.

These results have to be compared with those obtained for the organo-clays prepared in basic environment (STx-AM11 and SWy-AM11) where, although they contain at least the half of the polymer of the samples prepared in acid conditions, could account for, more or less, twice the lanthanum ions uptake.

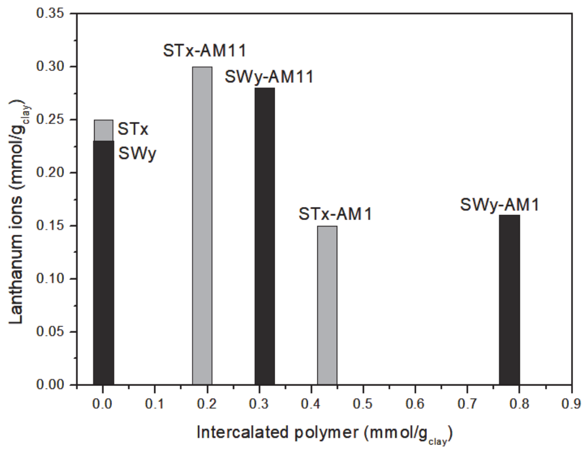


Fig. 6. Lanthanum uptake as a function of polymer content and pH

Table 2. Lanthanum uptake efficiencies

Sample	*pH*	*Uptake (mmol/g)*	*Uptake (%)*
STx-AM1	1	0.15	31
STx-AM5	5	0.15	31
STx-AM8	8	0.17	35
STx-AM11	11	0.30	62
SWy-AM1	1	0.16	33
SWy-AM5	5	0.17	35
SWy-AM8	8	0.19	39
SWy-AM11	11	0.28	58

Table 3. Lanthanum uptake efficiencies

Sorbent	*Measured adsorption capacity (mmol/g)*	*References*
Organo-clay STx-AM11	0.30	This study
Montmorillonite STx	0.25	(Iannicelli-Zubiani et al., 2015)
Montmorillonite SWy	0.23	(Iannicelli-Zubiani et al., 2015)
Bentonite	0.26	(Chegrouche et al., 1997)
Na-bentonite named GMZ bentonite	0.19	(Chen et al., 2012)
Sargassum biomass	0.52	(Palmieri et al., 2002)
Sargassum polycystum Ca-loaded biomass	0.90	(Diniz and Volesky, 2005)
Leaves powder of Platanus orientalis	0.19	(Sert et al., 2008)
Iron oxide loaded calcium alginate beads	0.89	(Wu et al., 2010)
2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester-grafted magnetic silica nanocomposites	0.40	(Wu et al., 2013)
Micro algal cells	0.72	(Birungi and Chirwa, 2014)
Granular hydrogel composite	2.40	(Zhu et al., 2014)
Lewatit TP 214 Resin	0.28	(Ferrah et al., 2014)
Polydopamine (PDA) membrane	0.43	(Hong et al., 2014)

These results can be explained on the basis of the polymer nature inside the organo-clays. In the materials prepared at low pH the amino groups are highly protonated, as demonstrated in the characterization section. Accordingly, the amino groups, that are supposed to exert the coordinating function towards the REs ions, are partially or at least totally deactivated by protons.Thus they are not available for the capture of positive charged ions as lanthanum ones. In conclusion, the nature of the intercalating polymer plays a major role than its amount and it is the parameter of interest to boost the process.

In Table 3 the obtained results were compared to the ones reported in literature for lanthanum adsorption, resulting interesting if compared with other clays or with other sorbent materials: only high specific and ad hoc synthesized composites as granular hydrogels are characterized by a strongly higher adsorption capacity but they are not natural materials and are characterized by high costs and syntheses issues.

4. Conclusions

Two families of organo-clay materials have been efficiently prepared, based on montmorillonite structure intercalated with N-(methoxy-polyethylene glycol) ethylene diamine.

The experimental procedure was proved to be appropriate to intercalate the polymer in the clay and the characterization techniques show that the intercalation mechanism is strongly dependent on the pH of the preparation procedure, affecting the protonation of the amino groups. Indeed, at alkaline pH the interaction is mainly based on weak bonds between the free amino groups of the organic moiety and the clay matrix and this is the required condition for the application of these materials in ions uptake. In this condition of pH 11 the obtained organo-clays were effective in lanthanum uptake (0.30 mmol/g and efficiency up to 60%), suggesting the possibility to use these innovative materials as finishing purifying materials for waste water treatment.

So, the studied clay-polymer system seems promising for the proposed application.

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BIOPHYSICAL FACTORS AFFECTING THE ANAEROBIC DIGESTION OF WASTE COOKING OIL IN MODEL SYSTEMS

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Abstract

The anaerobic digestion (AD) of fat-containing waste is often prolonged in time and problematic. Differences in AD performances could rely in a different probability for microorganisms to access the substrate. The aim of this study was to study the AD of waste cooking oil (WCO) with a biophysical approach. Two laboratory experiments were carried out using model systems consisting of WCO + hydration medium (HM) in 100 mL, static, in-batch reactors. In the first experiment, we assumed the WCO to HM (OtoW) ratio as an indicator of the accessibility of substrate to microorganisms: the higher the ratio, the greater the probability of feeding for the microbial cells. AD performances were evaluated in relation to 5 decreasing OtoW ratios. In the second experiment, we favored the formation of emulsions through alkalinisation, by adding to our model system 5 increasing amounts of KOH 1M (pH range from 6.7 to 10.1). High OtoW ratios (that is, relatively low volumes of aqueous phase) increased the CH_4 production rate while allowing CH_4 yields close to the theoretical. However, the highest OtoW ratio resulted in AD failure. A proper amount of alkali halved the time to join the maximum CH_4 production. Reasoning in terms of biophysical factors, more than in terms of oil concentration or inoculum-to-substrate ratio, could be helpful for the improvement of AD of fat-containing substrates.

Key words: alkalinisation, biogas, emulsions, interfaces, waste edible oils

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1. Introduction

Waste cooking oils (WCO), also called waste edible oils, are those remaining after cooking or frying of fat-containing foods. They can derive from catering, household or food-processing plants, and they may or may not have been used before disposal.

In Europe, restaurant and household sectors appear to be the main source of WCO (BioDieNet, 2009). The highest WCO production is in Spain, Germany and Portugal. Institutional systems for WCO collection are usually available in Western EU countries. Less information exists on ways of WCO disposal for the Eastern EU countries. In Italy, WCO are mainly of plant origin. The consumption of edible oils is around 1.4 million tonnes, divided equally between seed oil and olive oil, from which approximately 280,000 tons of waste vegetable oils are derived.

The production of vegetable oils in the vocational sectors (industry, catering) is about 100,000 tons, that is 36% of the total, while the remainder, 64% of the total amount, comes from domestic activities (CONOE, 2016). The WCO improper disposal has a highly negative environmental impact due either to the fat floating tendency, which gives rise to aquatic anoxic environments, or to clogging of the pipes in the wastewater treatment plants (El-Gawad, 2014). The WCO recovery and re-use permits exploiting it as a

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resource while contributing to the environmental quality control.

The currently most widespread way of WCO reusing is biodiesel production (Phan and Phan, 2008). In Italy, the main market outlet for the recovery of WCO is 85% its re-use as a raw material for the production of biodiesel, while 5% is utilized for the production of lubricants and the remaining 10% for other uses, such as energy production in direct combustion (CONOE, 2016).

Another use could be the WCO degradation in anaerobic digestion (AD). This process produces biogas, consisting of methane, carbon dioxide and traces of other contaminant gases. Lipids are an ideal substrate for methane production since, theoretically, their degradation can produce 0.99 L CH_4 g^{-1} of substrate (Alves et al., 2009). Methane yields up to 650-670 mL CH_4 g volatile solids (VS) were reported for WCO in AD (Labatut et al., 2011; Nazaitulshila et al., 2015). Moreover, biogas combustion is more environmentally sustainable than diesel combustion, because it produces lower amounts of CO_2, NO_x and particulate matter (Prasad and Dhanya, 2011).

During AD, lipase-producing microorganisms hydrolyze at first the triglyceride molecules to glycerol and long chain fatty acids (LCFA). Long chain fatty acids adsorb to cell surfaces and are transported into the cells of syntrophic acetogenic bacteria, where they are further degraded to acetic acid and hydrogen via intra-cellular β-oxidation (Weng and Jeris, 1976). Lastly, acetic acid and hydrogen are converted to methane by methanogenic Archaea. Even though *Syntrophomonadaceae* species are considered the most represented fatty acid-degrading group of microorganisms in anaerobic digesters, several other microbial groups have been identified as LCFA degraders (Hatamoto et al., 2007).

Despite the high biomethanation potential values, the AD of lipid-rich substrates is problematic. A main drawback in AD of lipid substrates is the time needed for AD completion. Neves at al. (2008), using restaurant food waste as substrate, demonstrated that the degradation of lipid-rich substrates in AD differed from that of the other substrates, because biogas production required a longer time to start, and part of the starting material remained undecomposed. Toxicity for microorganisms due to the LCFA accumulation (Cirne et al., 2007) and technological problems, such as foam formation (Kougias et al., 2014), are also reported.

An important factor affecting microbial degradation of organic substrates is the accessibility of substrate to microbial cells. When the substrate is perfectly soluble in water (i.e., glucose), the probability for the microbial cell to meet the substrate will depend on substrate concentration. In this case, that is, in an aqueous system, we call *chemical concentration* the ratio between substrate and solvent amounts. The higher the concentration, the higher the probability for a give number of microbial cells to have access to the food source. In case of oil-in-water mixtures, in a static system, the oil phase does not dissolve in the aqueous phase. Instead, it forms a laminar floating surface. In a biphasic static system, even though we increase the amount of oil per volume unit of water (*oil to water ratio*), the maximum area of the oil lens floating over the water surface at the interface oil/water will be the same, at a given temperature and for a container with given geometric characteristics. In a biphasic, stirred system, oil distributes in the water volume in form of droplets (or *micelles*), which coalesce and float again when the stirring stops. Emulsifiers reduce this trend. The micelle dimension will depend on stirring conditions and emulsifier concentration. Emulsions reduce the interfacial tension between the oil and the aqueous phase, and permit a reduction in the size of the oil droplets, with a corresponding increase of the total oil surface available to microorganisms for growth. Even in a stirred system, however, the access of microorganisms to the substrate will occur only at the micelle surface. The higher the number and the lower the volume (=higher surface/volume ratio) of the micelles, the higher the probability for microorganisms to feed on. For these reasons, oil layers or micelles represent surfaces where microorganisms may find food, and can be considered as interfaces for cell adhesion, in the same way as a solid substrate, and microbial activities can be studied with this approach (van Loosdrecht et al., 1990). Consequently, to improve AD performances, the probability for the cells to meet the substrate should be increased by increasing the ratio between the oil, lipid-containing phase and the aqueous, cell-containing, phase. In fact, theoretically, in a byphasic system only the microorganisms which are directly in contact with the substrate can have the opportunity to degrade it.

In the light of these differences between aqueous and biphasic systems, the *oil to water ratio*, although being dimensionally equal to *chemical concentration* (substrate amount / water amount), has a very different physical meaning: it is an indicator of the amount of oil available to cells and eventually of the probability for the microorganisms to access the substrate. For this reason, it seems a more suitable parameter to deal with when considering biphasic systems, rather than concentration.

In this work we tested, in in-batch laboratory experiments, the hypothesis of improving the AD performances of WCO by increasing the probability for microorganisms to access the substrate. We adopted the OtoW ratio as an indicator of this probability. To further increase the probability of contact between microorganisms and substrate, we also tried to favour oil in water emulsion by alkalinisation of the aqueous phase.

To test our hypotheses we used a simplified biphasic, static model system, including an oil phase, WCO, as C source, and a water phase, as hydration medium. A modified phosphate-based basal medium (HM) was used instead of water to ensure the availability of all those microelements and vitamins that are necessary for methanogens growth. A model system was chosen, instead of a complex one (for example, codigestion recipes) to simplify the interpretation of the results by reducing the number of involved variables. This model however included all the major protagonists of a complex system: oil, aqueous phase, and inoculum.

2. Materials and methods

2.1. Feedstock

The WCO used in the experiments was supplied by a private company collecting household and catering waste oil of plant origin in the regional area of the Lower Po Valley near our Research Unit. This waste oil originates mainly from palm oil and sunflower oil. The oil was centrifuged before use to remove water traces and suspended material. Selected analytical characteristics are: water content, < 0.05%, VS, 99.98%, total acidity (as oleic acid), 1.18 g L^{-1}, saponification value, 192.6 mg KOH.

The HM is a phosphate-based basal medium for methanogens containing 348 mg L^{-1} K_2HPO_4, 227 mg L^{-1} KH_2PO_4, 500 mg L^{-1} NH_4Cl, 200 mg L^{-1} $MgCl{\cdot}6H_2O$, 250 mg L^{-1} $CaCl_2{\cdot}2H_2O$, 2.25 g L^{-1} NaCl , 300 mg L^{-1} L-cysteine, 300 mg L^{-1} $Na_2S{\cdot}9H_20$, 0.1% resazurin. It contains also mineral salts and vitamins, and $NaHCO_3$ in the amounts reported in the modified ATCC medium #1043 recommended for the growth of *Methanosarcina* spp. (ATCC, 2017); final pH: = 6.8. Unlike ATCC medium #1043, however, no organic C was included in the HM, as C was supplied by WCO, which is the substrate to be tested. HM was used instead of pure water, in accordance with the established practice for biomethanation testing (Angelidaki et al., 2009), because it ensures the availability of all nutrition elements needed for methanogens growth.

2.2. Experimental setup

Experiment I: it was run with the aim of increasing the probability for microorganisms to meet the substrate. This goal was pursued by adding decreasing volumes of HM: 50, 30, 15, 5, or 0 mL to the same amount of WCO (500 mg per reactor). Five mL of inoculum were also added in each reactor, which summed up to the HM volume. Therefore, the OtoW ratios were: 100, 50, 25, 14, and 9 (Table 1). The WCO was forming a thin layer over the surface of the reaction mixture, without completely covering the entire surface.

In theory, due to microbial cell dimensions (microns) only the cells at the interface oil-water were able to degrade WCO (100% probability of degradation) whereas the probability of microbial degradation in the HM volume below the oil lens was expected to be 0. In practice, several elements can interfere with this assumption, during AD, in our model system:

i) *The inoculum behaviour and effect.* Once put into the reactor, the inoculum material (cell granules and amorphous debris) migrated in the aqueous phase, which became turbid, meaning either an incomplete deposit of the cells or the formation of emulsions. When only the inoculum was present (HM volume = 0 mL) the WCO floated over the inoculum material. In WCO+HM systems, after inoculum addition, as the incubation was in static condition, the inoculum material tended to deposit at the bottom of the reactor, for gravity reasons. The cell deposit was closer to the WCO layer in the reactors with higher OtoW ratios;

ii) *The occasional stirring of the reactors.* Even though the reactors were kept in static conditions, periodical stirring had to be applied when measurements of gas volume and composition were carried out. This stirring, common to all the reactors in each measurement occasion, involves a temporary mixing of substrate and cells, followed however by resettling of the inoculum material at the bottom of the reactors. Stirring involves some - though temporary - micelle formation: the lower the volume of the aqueous phase, the higher the number of micelles per volume unit of aqueous phase;

iii) *Gas formation.* The gas forming during the initial WCO degradation contributes to some - even limited - mixing effect within the reactor;

iv) *Cell motility.* Some lipid-degrading species are motile (Ruiz et al., 2005);

v) *Microbial metabolites* (for example, solvents) can modify substrate accessibility.

Following these considerations, we could not exclude the possibility for the cells to access the substrate even at a distance > 0 from the WCO layer. We assumed the OtoW ratio as an indicator of the probability for the microorganisms to access the substrate: the higher its value, the higher this probability. We recall here that the physical meaning we attribute to this parameter is very different from that of concentration, as already pointed out.

Besides the OtoW ratio, changing the HM volume modified also the inoculum dilution and the C to N ratio (Table 1). The inoculum dilution increased for increasing HM volumes. On the contrary, the inoculum to substrate ratio, expressed as g VS in the inoculum per gram of VS in the oil, remained constant, because the VS content of the inoculum in the reactors was always the same (0.48 g VS inoculum g^{-1} VS WCO). The C to N ratio in the reaction mixture was calculated to include the contributions of N and C from substrate (only C), HM (only N), and inoculum (C and N). The contribution of N by the inoculum (equal in all the reactors) largely exceeded that by HM. The mean C/N of the reaction mixture was 22.4. This value is included in the range of values explored as optima for fat AD in the literature (Tanimu et al., 2014; Wang et al., 2012) and its variability within the dataset was low (SD =2.4). For these reasons, we assumed that this variable did not interfere with the results.

Table 1. Experiment I details

Volume of the hydration medium, HM (mL)	*WCO to HM ratio[a] (w/v)*	*Inoculum dilution (mL HM mL^{-1} inoculum)*	*C/N*
0	100	0	24.9
5	50	1	24.2
15	25	3	22.8
30	14	6	21.1
50	9	10	19.1

[a)]Referred to the total aqueous phase volume (HM + inoculum). The weight of WCO and the inoculum volume were constant (500 mg and 5 mL, respectively)

Table 2. Initial and final pH values and residual WCO content depending on the amount of KOH added to the reactors in Experiment II. Standard deviation in parentheses

Treatment (mL KOH)	*Initial pH*	*Final pH*	*Residual WCO (% of the initial)*
0	6.74 (0.05)	8.49 (0.17)	0.30 (0.19)
0.15	8.60 (0.31)	8.54 (0.06)	0.25 (0.02)
0.30	9.22 (0.09)	8.24 (0.01)	0.18 (0.05)
0.45	9.42 (0.10)	8.45 (0.11)	0.29 (0.04)
0.60	9.76 (0.11)	8.47 (0.08)	0.32 (0.20)
0.75	10.10 (0.35)	8.40 (0.13)	1.69 (0.35)

Experiment II: it was carried out in static conditions with the purpose of further facilitating the contact between microorganisms and substrate, by favouring the emulsion formation**.** Manual stirring on measurement occasions was performed (Angelidaki et al., 2009). Potassium hydrate was used to alkalize the medium because fat alkalinisation facilitates soap formation, and soaps are typical emulsifying agents.

In this experiment, the oil content in the reactor was the same as in Exp. I, that is, 500 mg WCO in each reactor. The HM volume was kept constant at 14.25 mL, whereas increasing amounts of KOH 1M were added, specifically: 0, 0.15, 0.30, 0.45, 0.60 and 0.75 mL KOH 1M, plus distilled water amounts giving a total of 0.75 mL, when added to the KOH amount. The reaction mixture thus contained 500 mg WCO, 5 mL inoculum, 14.25 mL HM and 0.75 mL KOH and/or water. The total volume of the aqueous phase was 20 mL, with an OtoW ratio=25. This OtoW value was assumed as non-limiting for CH_4 production, on the basis of the results of Exp. I.

Potassium hydrate was chosen rather than NaOH because too high concentrations of sodium salts could be detrimental for methanogenic microorganisms (Rinzema et al., 1988). Some HM phosphate and chloride salts, in the HM medium, can combine with fatty acids to give esters which are included in the emulsifiers category (EFEMA, 2015). Since the amounts of HM were kept constant in all the reactors, any possible interfering effects of the mineral salts of the HM medium on emulsion formation should be considered constant for all the treatments. The KOH addition caused an increase of pH for the HM + oil system (Table 2). The amounts of alkali used in this experiment are lower than the amounts needed to completely saponify the oil (1.7 mL KOH 1M). These amounts would have produced pH values higher than 11, which we assumed to be inhibiting for microbial activities in the AD reactors, as they are very far from the optimal pH values for methanogenesis. Therefore, we chose to add KOH in amounts giving pH < 11, despite producing only a partial saponification of the oil.

In both experiments, three replicates were performed, for each treatment. Reactors with HM and inoculum, without C source, or containing 6.8 g L^{-1} Na acetate, were used as controls, in the incubation tests. The control without C source was needed to check any endogenous methanogenic activity of the inoculum, which should be substracted to CH_4 production by the samples. No CH_4 production was detected in our controls during the incubation period. The reactors with acetate were included to check the methanogenic performances of the inoculum, which were found regular, according to our laboratory routine tests. This means that the AD results were not negatively affected by poor inoculum performances.

2.3. Inoculum preparation

Pig slurry withdrawn from the farm storage tank collecting the liquid fraction of pig manure after solid separation was digested, and the digestate was used as the inoculum source. Digestate from animal effluents is often used as inoculum source in AD of agro-industrial waste (Gu et al., 2014). The inoculum was prepared following a laboratory-consolidated procedure (Vasmara et al., 2015). Inoculum composition was: total solids (TS), 7.83%, VS, 4.76%, organic C, 3%, total (Kjeldahl) N, 0.43%, pH, 7.76. All data refer to the fresh-matter volume unit. Five mL of inoculum were used in each reactor for AD.

2.4. Anaerobic digestion

Anaerobic digestion was carried out in 100 mL reactors (118.5 mL effective volume) according to Owen et al. (1979). The headspace of the reactors was gassed with 100% N_2 throughout all the preparation phases before inoculation. Reactors were plugged with butyl rubber stoppers and aluminum seals and they were incubated at 35°C for 105 days, at maximum. In both experiments, manual stirring was done at each measurement occasion (two days after inoculation and every week during the whole incubation period). At each measurement event, the reactors were randomly distributed on the incubator shelves. Biogas was collected by means of 100 mL glass syringes as previously detailed (Vasmara and Marchetti, 2016). Total gas volume was the sum of the gas collected by the syringe and that of the head space in the reactors. We ended the test when there was no more biogas production or, at the latest, 3.5 months after the start of incubation. No methane or hydrogen production were detected in the control reactors with inoculum without substrate.

2.5. Analytical methods

The WCO used in the experiments was analyzed according to the UE Regulation 1227 (2016). The oil acidity was determined by titration with KOH in a diethyl ether and ethanol solution with phenolphthalein as indicator. The saponification value was determined by titration of the excess KOH with phenolphthalein as indicator. Methane concentration in the biogas was determined by means of a MicroGC Agilent 3000 gaschromatograph (GC), equipped with 2 columns: Molsieve and Plot U; detector: TCD. Carrier gas: argon.

Residual oil content in the digestates was determined according to Brooksbank et al. (2007) after lipid extraction with solvent (ether was used instead of dichloromethane), drying with a rotary evaporator and weighting of the residual fat.

Total solids, VS, total N, organic C and pH were determined on the inoculum material according to APHA (1992). Total solids were determined gravimetrically by thermal treatment at 105°C at constant weight. Volatile solids were determined as the difference between TS and ashes. Ashes were determined by incineration in a muffle furnace at 550°C for 10 hrs. Total N was determined with the Kjeldahl apparatus after acid digestion with H_2SO_4 and copper as catalyzing agent. Organic C was determined by dichromate oxidation with external heating and reflux condenser. The pH of the digestates was measured potentiometrically, whereas the initial pH in Exp. II was determined using pH test papers (Macherey-Nagel) in the range 7.2-9.7 (with 0.3 intervals) or 9-13 (with 0.5 intervals), depending on the pH value to be determined.

2.6. Model fitting and statistical analyses

The parameters of the cumulative CH_4 production curves were evaluated by means of a modified 3-parameter Gompertz equation (Eq. 1):

$$M(t) = M_{\max} \exp\left\{-\exp\left[\left(\frac{eR_{\max}}{M_{\max}}\right)(\lambda - t) + 1\right]\right\} \tag{1}$$

where: M(*t*) (mL $CH_{4(STP)}$) is the total amount of CH_4 produced at the incubation time *t* (d), in standard conditions (STP) of temperature (273 °K) and pressure (101 kPa). *e* is the exp of 1; *Mmax* (mL CH_4) is the maximum cumulative CH_4 production; *R* (mL CH_4 d^{-1}) is the maximum daily rate of CH_4 accumulation; and λ is the lag time duration (d), that is the time of microbial adaptation before exponential CH_4 production. This function is helpful when interpolating growth curves, in general, and microbial growth curves, in particular (Zwietering et al., 1990).

All the statistical analyses were performed using the SAS package procedures (Littell et al., 1996). Fitting of the Gompertz model to measurements was performed using the PROC NLIN; the parameter values were estimated according to the Gauss-Newton method. The time (d) necessary to reach *Mmax* was estimated by calculating the *Mmax / R* ratio and adding to the quotient the lag time duration. For curve fitting purposes, a single curve was interpolated by merging the data of all the 3 replications (number of observations for each treatment, n = 36). This approach permits the obtaining of more robust parameter values.

Means of the measured values at each measurement occasion instead of individual measurement dots were used in the curve plots, for sake of clarity. In the OtoW ratio = 100 treatment, a lower number of measurements was carried out due to the low methane production (n=18). For analysis of variance purposes, parameter replicates were needed to estimate the significance of the differences between treatments. In this case the estimate of the parameter values was carried out using data of each replicate (n=12 or 6, for OtoW ratio = 100). The PROC MIXED was used to test the significance of the treatment effects on the AD parameters, λ, Rmax, Hmax, and Days to Mmax. Multiple comparisons of the means were carried out using the SAS LSMEANS statement. Factors and factor interaction effects were considered significant at P<0.05. The Tukey's Honestly Significant Difference (HSD) at P=0.05 was used to compare treatment mean values.

3. Results and discussion

3.1. Oil to aqueous phase ratio and methane production

In the reactors without HM (OtoW ratio=100), the CH_4 production stopped early (Fig. 1), 15 days after the start of the incubation. In the reactors where the OtoW ratio was intermediate (50 and 25), CH_4 production increased faster than in those where the OtoW ratio was lower (14 and 9). At the end of the experiment, all the curves had raised the plateau, except for the treatment with OtoW ratio=100. At the end of the incubation period, all the reactors with OtoW ratio<100 joined the same plateau value. The mean measured value of cumulated CH_4 production in the reactors with OtoW ratio from 50 to 9, (84 days after the start of the incubation), was 421 mL CH_4 $_{(STP)}$ (without significant differences between treatments), corresponding to 842 mL CH_4 g^{-1} WCO.

Even though the models were all highly significant (P < 0.0001), the model overestimated Mmax. In fact, the mean estimated Mmax for the same treatments (50, 25, 14 and 9) was 483 mL (Fig. 2a), 17% more than the mean measured CH_4 production at the end of the incubation period. The reason for this overestimation could be attributed to the nearly linear trend of CH_4 accumulation, observed for the OtoW ratios 14 and 9, in the first phase of AD, and a recovery in the CH_4 accumulation rate, starting at 50 days of incubation. This pattern of CH_4 accumulation gave rise to a curve more similar to a segmented-type (Buchanan et al., 1997) than to a Gompertz model.

The Gompertz parameters were used to study the relationship between OtoW ratio and AD performances (Fig. 2).

The treatment with OtoW ratio=100 (no HM in the mixture) differed from all the others. In this treatment, the lag phase duration and the time to join the plateau of CH_4 production were very short, but the maximum amount of CH_4 production was very low: only 45 mL of CH_4, on average. Mmax values were quite similar for the other treatments (Fig. 2a), despite the significance of the difference between the OtoW ratios 50 and 9, especially considering the overestimate of Mmax in comparison with the measured values, and the non-significance of the differences between treatments for the measured maximum amount of CH_4.

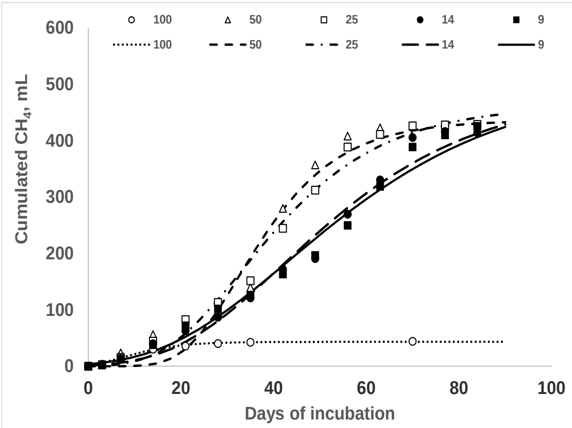

Fig. 1. Methane accumulation during the incubation period from waste cooking oil in the reactors with different values of OtoW ratio (100, 50, 25, 14 and 9). Dots are the mean measured values; lines are the values estimated using the Gompertz equation

The methane production rate (Fig. 2b) decreased from the OtoW ratio 50 to 9. At OtoW ratio=9 it was 55% of that at OtoW ratio=50. Also the lag phase duration was lower at OtoW ratio=9, even though the mean difference of λ between OtoW ratios 50 and 9 was 3.3 days, which is a short time in comparison with the overall duration of the incubation.

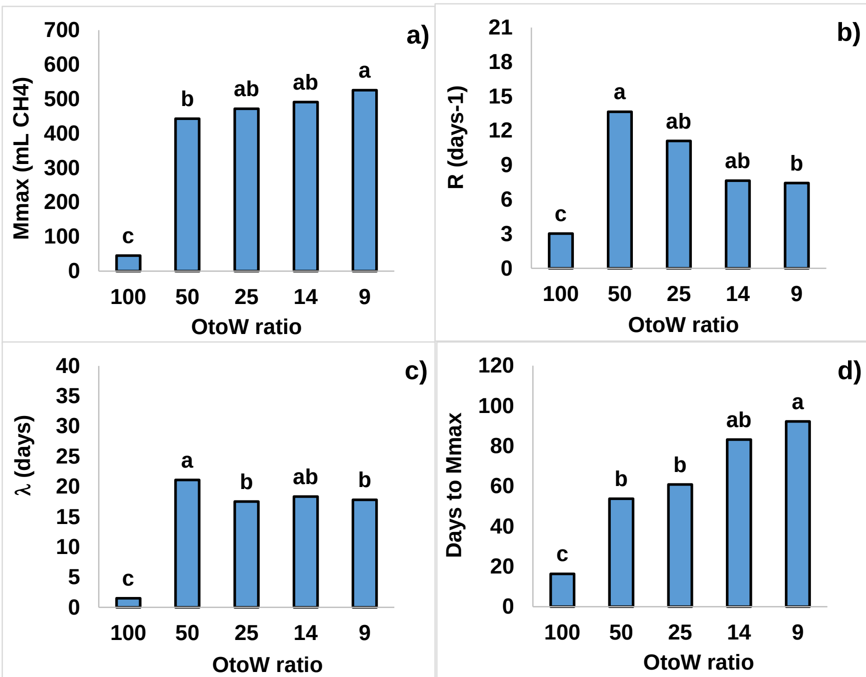

Fig. 2. Influence of the OtoW ratio on the Gompertz-derived parameter values describing CH_4 production from waste cooking oil: a) maximum CH_4 production, *Mmax* (HSD: 67.2 mL CH_4); b) maximum CH_4 production rate, *R* (HSD: 3.9 mL CH_4 $days^{-1}$); c) lag phase duration, *λ* (HSD: 2.9 days); d) time to join *Mmax* (HSD: 29.6 days). Treatments with the same letters are not significantly different at P=0.05

On the other hand, the time to join the plateau, summing up the effect of both lag phase duration and methane production rate, decreased by nearly 40 days, by increasing OtoW ratios from 9 to 50. In theory, at OtoW ratio=100 the maximum Mmax was expected, due to the highest probability for the inoculum to meet the substrate. Actually, the lowest CH_4 production occurred for this treatment. Several reasons are possible: the aqueous phase amount could have been insufficient to dilute the free fatty acids deriving from triglyceride hydrolysis, with a toxic effect on the AD microbial consortia. In fact, there is consolidate knowledge that LCFA exert a toxic effect on methanogenic consortia (Dasa et al., 2016; Kostner and Cramer, 1987; Sousa et al., 2013); lack of essential microelements and vitamins, due to the lack of HM in OtoW ratio=100; too low water availability for the hydrolytic enzymes activity. These results lead to the following considerations:

- Relatively low amounts of aqueous phase are sufficient to guarantee the same CH_4 yields that can be obtained with high aqueous volumes, for the same amount of oil. Excessive water phase volumes in relation to the amount of oil slow down the process, because the probability for the inoculum to access the substrate decreases. Consequently, the time needed to complete the digestion is longer.

- It is possible that the occasional stirring influenced differently R and Days to Mmax, depending on the OtoW ratio. In the reactors containing lower OtoW ratios (14 and 9), the amount of oil being the same, a relatively lower amount of micelles may have formed by stirring per volume unit, with a lower probability for the cells to meet the micelle surface, and longer times needed for AD completion. Moreover, the amount of inoculum being the same in all treatments, the inoculum density in the water phase was lower at higher HM volumes (Table 1): again, this led to a reduction in the probability for microorganisms to meet the substrate, even though the inoculum to substrate ratio was equal, in all treatments. However, since the initial amount of WCO (substrate) was the same in all the treatments, all the substrate was digested, in the end (except for OtoW ratio=100). At the end of the experiment, 175 mg (SD: 7.1 mg) of residual fat, that is, 35% of the initial WCO amount, were measured in the treatment without HM (OtoW ratio=100). In the other reactors, much lower amounts of residual fat were found (< 3% of the initial content).

The CH_4 yields obtained in non-limiting conditions (OtoW ratio<100) were overall very high and close to the theoretical values. Our results are in agreement with those of Pastor et al. (2013), who determined the biomethanation potential of used oils, urban landfill leachates and sewage sludge as possible co-substrates in AD. For the used oil they obtained a biogas production per kg of fresh matter over a period of 47 days (not completely degraded) of 970.6 NL kg^{-1}. Our results confirm WCO as an excellent feedstock for biogas production.

3.2. KOH addition and methane production

Methane accumulation started earlier at 0 and 0.15 mL KOH, but was faster in the reactors with KOH in comparison with the control (Fig. 3). In the control reactors, CH_4 production started earlier than in the reactors with the higher levels of KOH. However, 50 days after the start of the incubation, it continued at a slower rate than in the other treatments. The measured mean CH_4 production in the treatments with KOH at the end of the experiment was 443 mL $CH_{4(STP)}$, (SD: 33.8 mL) that is 886 mL CH_4 g^{-1} oil, a CH_4 yield very close to the theoretical one. The relationship between Gompertz parameter values and alkalinisation levels was examined (Fig. 4). A certain variability was observed between replicates, in the reactors with KOH, which increased the standard deviation of some means. However, the following trends could be recognized: the KOH addition did not significantly affect the estimated *Mmax* (Fig. 4a), which was on average 474 mL CH_4 (+31 mL, in comparison with the measured mean accumulated CH_4 amount). The *R* value (Fig. 4b) was much higher with KOH (15.4 mL $CH_4 d^{-1}$, on average) than without KOH addition (6.9 mL CH_4 d^{-1}). There was a trend to an increase of R for increasing levels of KOH, even though only R at KOH= 0.75 mL was significantly higher than R at KOH=0 and KOH=0.15 mL. The KOH addition more than doubled the lag phase duration (from 13 days, mean of the first 3 KOH levels, to 31 days, mean of the 0.6 and 0.75 mL treatments; Fig. 4c). Since the two parameters showed opposite trends, their effects were balanced in Days to Mmax (Fig. 4d), which is the sum of the lag time and of the time needed from the starting of methane production to join the plateau. As a result of this compensation, differences between treatments in Days to Mmax were not significant, except for the treatment with 0.3 mL of KOH.

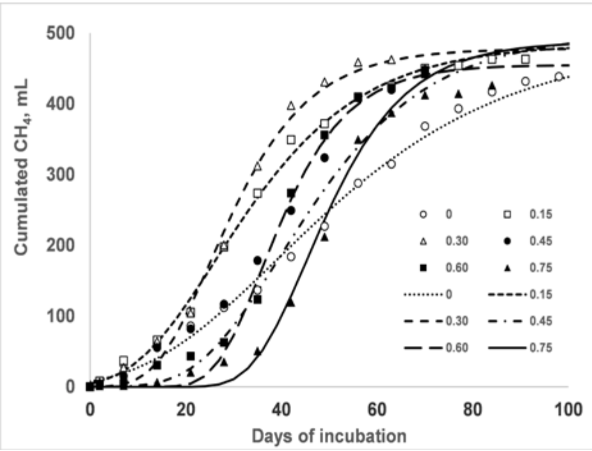

Fig. 3. Methane accumulation during the incubation period of waste cooking oil in reactors containing different amounts of KOH 1M (0, 0.15, 0.30, 0.45, 0.60, and 0.75 mL). Dots are the mean measured values; lines are the values estimated using the Gompertz equation

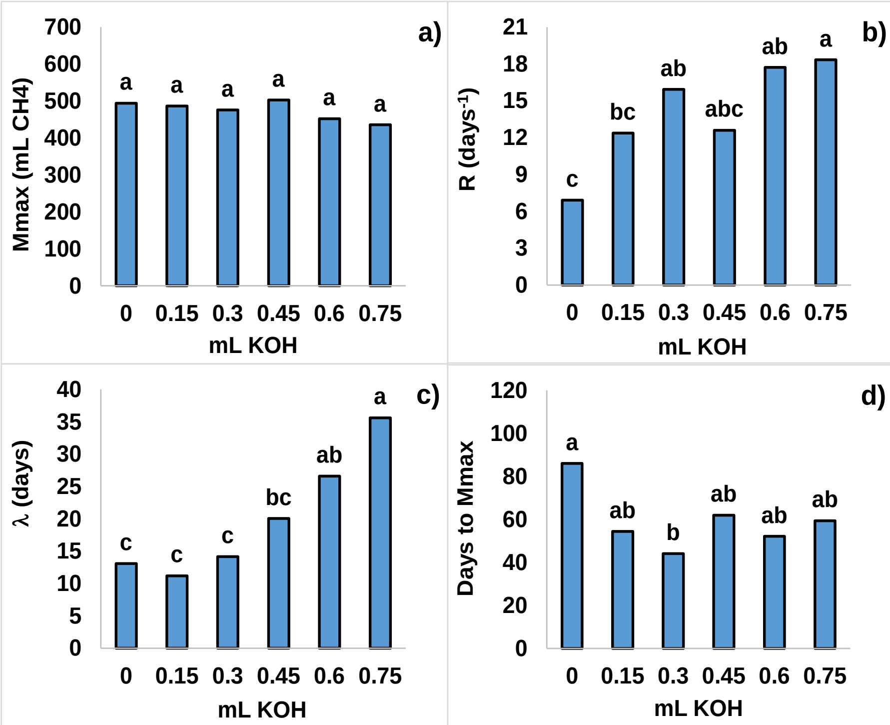

Fig. 4. Influence of the alkalinisation level (mL KOH 1M added to the reaction mixture) on the Gompertz-derived parameter values describing CH_4 production from waste cooking oil. a) maximum CH_4 production, Mmax (HSD: 109 mL CH_4); b) maximum CH_4 production rate, R (HSD: 5.9 mL CH_4 days^{-1}); c) lag phase duration, λ (HSD: 9.1 days); d) time to join Mmax (HSD: 35 days). Treatments with the same letters are not significantly different at P=0.05

In this case, there was a reduction by 51% in Day to Mmax, in comparison with the control (from 86 to 44 days). Therefore, we can consider that:

- it is useful to add KOH to accelerate the process, even though, in the end, CH_4 yields are not affected;
- to effectively shorten the digestion time the amount of KOH must be carefully calibrated;
- in our experiment, the optimal amount of KOH was the one corresponding to an initial pH=9.22.

At the end of the digestion, minimal amounts of residual WCO were detected in digestates, with slightly higher oil residues in the reactors containing 0.75 mL of KOH (Table 2).

Alkalinization has been proposed in AD as a pre-treatment of waste activated sludge and lignocellulosic materials to favour the degradation of recalcitrant molecules and cellulose (Li et al., 2008; Valo et al, 2004). When lipid-rich substrates are involved, since solid fat materials tend to clog the pipes, alkalinisation is proposed as a means to dissolve them and make them less harmful (Cammarota and Freire, 2006). Alkalinization reduces the amount of fats but has negative consequences on AD, because it favours the formation of floating matter. In our experiment, the oil dissolution by means of KOH (from triglycerides to glycerol + soaps) could have made the fatty acids more quickly available to the degrading microorganisms, in alternative to microbial lipolysis. In our experiment, the first purpose of alkalizing was to favour the formation of emulsifying soaps. Mouneimne et al. (2003) specifically studied the saponification effect on AD of lipid-rich substrates. Even though they did not directly measure CH_4 production, they found that free acidity and fat degradation were much higher at pH = 8.5 than at pH = 6.5.

Medium alkalinization brought about a raising of pH. Results can therefore be interpreted also in view of this evidence. The optimum pH for methanogens is neutral; however, several microbial groups are present in the AD reactors, which are responsible for the various intermediate transformations eventually leading to methanogenesis.

The prolongation of lag phase for increasing amounts of KOH could be caused by a growing difficulty of microbial consortia to adapt to the higher pH values. In fact pH = 10.1, corresponding to the maximum amount of added KOH (Table 2), was far away from the optimum for AD. A change in pH occurred during substrate degradation. In fact, the final pH of the digestates was on average 8.33 (SD: 0.13, n = 18), regardless of the pH value at the start of the experiment. This lowering of pH could explain the “recovery” in R and the fact that no significant differences were detected in Mmax, between treatments.

4. Conclusions

Optimum conditions for the anaerobic digestion of waste cooking oil appear to be a compromise between the increase of substrate accessibility to microorganisms, which can be pursued by an increase of the oil to water volume ratio, and the amount of aqueous phase capable of diluting and alleviating the toxic effect of the digestion metabolites.

The alkalinisation of the aqueous phase increased the CH_4 production rate, but at the cost of an increase in the time needed for microorganisms to adapt to the higher pH values. However, it was possible to identify KOH concentrations, which allowed us to shorten the duration of WCO digestion by more than 50%.

Our results highlight the opportunity of considering the biophysical factors controlling microorganism feeding, in the AD of an oil–in water biphasic system. Reducing the volume of the aqueous phase permits the increase of methane yields per reactor volume unit, as long as suitable solutions are adopted to avoid or remove the toxic effect of metabolites accumulating during anaerobic digestion. Increasing the knowledge of microbial behaviour in biphasic systems by means of a biophysical approach could be helpful for the improvement of AD of fat-containing substrates.

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WATER FOOTPRINT APPLIED TO CONSTRUCTION SECTOR

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Abstract

Water footprint is an indicator of freshwater use that looks not only at direct water use of a consumer or producer, but also at indirect water use; it can be regarded as a comprehensive indicator of freshwater resources appropriation, next to the traditional and restricted measure of water withdrawal. It could be counted in terms of the sum of direct and indirect water costs in all processes and input-output analysis to detailed water used in all plant.
In this paper, the application of the water footprint in a construction business located in Eastern Sicily is presented, its main activity is represented by the production of aggregates, bituminous and concrete mixes.
In order to identify the economic, social and environmental advantages, we quantify this multi-dimensional indicator and we analyse the water incorporation into products, evaporation, abstracted from ground-or surface water and returned to another catchments or sea, with unavailable degradation in quality. It consists of two main components: the operational (or direct) water footprint of a business is the volume of freshwater consumed or polluted due to the business's own operations. Thanks to the calculation of the Water Footprint the amount of water resources that a company of this size really requires was understood and greatly exploits the opportunity and the strategies to reduce its water consumption, such as installation of a system for collecting rainwater, continuous recycling system and new sleeve filters. The costs of these investments were calculated by choosing different alternatives to safe non-renewable water.

Key words: civil construction sector, freshwater treatment, ISO 14046:2014, non-renewable resources, water footprint

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1. Introduction

Before the twentieth century, the global demand for fresh water was very modest compared to the natural flows of systems. Population growth, industrialization and the expansion of irrigation in agriculture have caused the demand to increase dramatically, putting the ecosystems that sustain the water cycle at risk. So, while demand continues to grow, the supply capacity decreases (WWF Italia, 2014).

The amount of water present on the planet Earth is about 1390 million cubic kilometres, most of which is salt water, namely 97% and is present in the seas and oceans. The fresh water instead is enclosed for the most part in the ice of the polar caps, an amount of water that cannot be considered as it is ice. Only 93,000 cubic kilometres (0.3% of the total) is available, especially in the form of groundwater and lakes.

In addition, as is well known, the available water is distributed unevenly on the planet, some areas have more, others have a hard time getting drinking water; almost 20% of the world's population, that is about 1.3 billion people, in fact, have no access to hygienically safe water (Chambers et al., 2002; Tsertou et al., 2915). Areas with a greater availability of water are depicted in blue; as the water becomes less available, the colour intensity decreases (Fig.1). To this it must be added that in the twentieth century the worldwide consumption of water increased to 2,100 cubic kilometres compared to the 300 cubic kilometres. Of course, consumption changes if we move to different areas of the world (Table 1): in the United States of America: a US citizen annually consumes 1,280 cubic metres of

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water; in Europe: a European citizen consumes 700 m^3 annually; in Africa: African citizen consumes just 185 m^3.

Table 1. Worldwide consumption of water

WORLDWIDE CONSUMPTION OF WATER		
UNITED STATES	EUROPE	AFRICA
1,280 m^3	700 m^3	185 m^3

A new indicator could be considered through he dynamic global vegetation and water balance model LPJmL, Lund-Potsdam-Jena managed Land, (Bondeau et al., 2007); it is based on LPJ (Sitch et al., 2003), a dynamic global vegetation model that computes the establishment, growth and productivity of the world's major natural and agricultural plant types and the associated carbon and water fluxes as well as their spatiotemporal variations in response to climatic conditions and human interferences such as irrigation, typically on a 0.5° grid and at daily time steps.

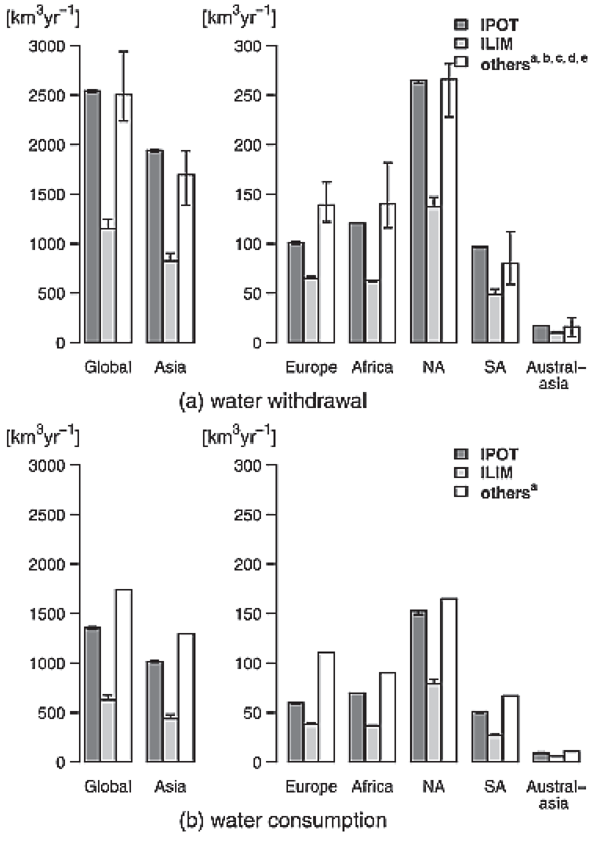

Fig. 1. Comparison of LPJmL-computed blue water withdrawal (a) and consumption (b) under potential (IPOT) and limited (ILIM) irrigation (km^3 $year^{-1}$, 1971–2000 averages) with other studies

The Water Footprint makes it clear how much an individual or a product causes an impact on the water environment in particular, what the main sources of the water are and is used and how much of it comes from abroad, as well as to what extent each person's consumption patterns can be improved.

Thus, hidden water consumption is brought to light by highlighting the dependence of some countries on other countries' water. In 2002 to this end the concept of the Water Footprint was developed, indicating the volume of freshwater used to produce a product, measured at the place where the product has been made (WWF Italia, 2014).

In this paper, the application of the water footprint in a construction business located in Eastern Sicily is presented, the main activity of this firm is represented by the production of aggregates, bituminous and concrete mixes. The company analysed products buildings structures and underground works, constructs structures foundations, thermal insulation of buildings and structures, construction of asphaltic jointing and flood-protections works. We quantified physical and monitoring water of soils, hydraulically bound mixes, wet and cured concrete, cement, bituminous binders, road and bridge pavements and materials for cohesive and non-cohesive soils. In particular, we quantify the extent of potential environmental impacts related to water in inert and cement productions because these are the most impactful phases in production cycles and moreover they represent the main source of revenue; identify the strategies for reducing the impacts just mentioned; promote water efficiency and the optimization of water resources management; provide information for the communication of the results of the water footprint studies.

According to identify the economic, social and environmental advantages, we quantify the consumption of fresh water that includes both the direct use and the indirect use by a consumer or a producer. It consists of two main components: the operational (or direct) water footprint of a business is the volume of freshwater consumed or polluted due to the business's own operations.

2. The Water Footprint

Climate change is affecting the planet Earth, the increase in world population and global economic development have focused on the theme of the use of water resources and especially on its management. The concept of the Water Footprint, whose logo is depicted in Fig. 2, was introduced in last years (Aldaya et al. 2010). It allows the water needed to produce goods or services for consumption in a given territory to be assessed (Manzardo et al., 2012).

It is a concept that has received international attention for its effectiveness in sustainably managing water consumption in a production process, in a body, in a region or an entire country (Amicarelli et al., 2009). The term WF has been used to describe the virtual water content of a product or commodity, summed over its life cycle (Hoekstra, 2008). The water footprint concept has been used by agricultural (Arabi Yazdi et al., 2011; Nana et al., 2014; Scott et al., 2015;), commercial (Lai et al., 2012; Steen-Olsen et al., 2012) and industrial

(Chilana et al., 2016; Kwok et al., 2011; Wang et al., 2013) water users to measure and report their water consumption, assess the magnitude of environmental impacts arising from this consumption, and to identify opportunities for risk mitigation strategies that promote sustainable water use.

Fig. 2. Logo Water Footprint

The objectives of this indicator are: synthesize information on water consumption; identify opportunities to integrate the water use into water utility planning efforts; understands how the water use offer a new approach within water utility sustainability initiatives; evaluate the available frameworks into water footprint organizations (Water Research Foundation, 2014).

The water footprint (WF) concept was proposed by Hoekstra (2003); The WF of a product can be defined as the amount of water used to produce, including all consumption throughout the supply chain (Hoekstra et al., 2011). By identifying the impacts of human production and consumption behavior on water consumption and pollution generation, WF can be used to measure the effect of humans on the available water resource and on the environment. WF provides a rational and holistic perspective on the relationship between consumers and producers and the water system that sustains them (Hoekstra et al., 2011). In recent years, three approaches have been applied assess the water consumption of a reservoir: in the gross water consumption method (Gleick, 1992; Mekonnen and Hoekstra, 2012), the gross water evaporation from different water sources is accounted for except for created wastewater (Zhao and Liu, 2013).

This index represents the volume of water consumed (evaporated) or polluted, also considering in this case, all the stages of the life cycle of a product and taking into account to what extent the catchment area from which the water is drawn has already undergone stress for withdrawals for other uses (Luciani et al., 2011). In particular, it is a multi-dimensional indicator of the consumption of fresh water that includes both the direct use and the indirect use by a consumer or a producer. So, the Water Footprint of an individual, a community or business is defined as the total volume of fresh water used to produce goods and services, measured in terms of the volumes of water consumed and polluted per unit of time giving much importance, as mentioned earlier, to the geographical location of the catchment of the resource (Jonsson, 2005). It includes water taken from rivers, lakes and aquifers (surface and underground), employed in the agricultural, industrial and domestic sectors and the water from rainfall used in agriculture. The Water Footprint, like the Ecological Footprint (EF), calculates the volume of water needed to produce the same goods and services while the EF calculates the productive area required to produce them; its purpose is exactly that of identifying waste and inefficiencies and promoting the activity of improvement in the management of this precious resource.

Through the official Water Footprint site, it is already possible to get an idea about the amount of water necessary to obtain some products (Scanferla, 2013):

- the production of one kilogram of beef requires 16,000 litres of water;
- the production of a kilo of cotton requires 10,000 litres of water;
- the production of one kilogram of cane sugar requires 1800 litres of water;
- these are just some of the available examples.

The Water Footprint concept is closely linked to that of "virtual water" a concept introduced by John Anthony Allan. It is an indicator that expresses the amount of water used for the entire chain, from production to direct consumption (Shen and Tam, 2002). The virtual water content of a product or a service is the volume of freshwater used for the production of the product in the place where it is produced (Amicarelli et al., 2009).

2.1. Water Assessment Manual

The manual, "The Water Footprint Assessment Manual" (Hoekstra et al., 2011) presents a scientifically rigorous method to help companies understand their impact on global water resources. It contains the global standard for the assessment of the water footprint and shows how the footprints of individual production processes and products, but also of nations and companies (Gleeson et al., 2012) are calculated.

- For a company, the calculation of the Water Footprint can be carried out in order to achieve different objectives (Amicarelli et al., 2009; Asdrubali, 2013; IFC, 2013).:
  - assess how water resources are allocated to various purposes;
  - locate where the purple water footprint the local requirements of the environmental quality of water;
  - reduce the water footprint;
  - define the environmental risk;
  - draft environmental documents;
  - achieve environmental certification;
  - enter the data in the labelling of products

Depending on the objectives that the company sets, the calculation of the WF directs the same company towards improvement strategies.

2.2. Composition of the WFP

The Water Footprint is made up of:

- *Green water*: volume of rain water evaporated during the manufacturing process. This first part is mainly calculated for agricultural products and refers to the total of rainwater evaporated during the growing season of crops (Gerbens-Leenes et al., 2009): Green = Green Water evaporated WF + built-green water [volume / time];

- *Blue water*: the removal of surface and underground fresh water used for domestic, agricultural or industrial purposes. It also includes the volume of surface water or groundwater evaporated due to the production of the product. In the case of agricultural production, the blue water is the sum of the irrigation water and the evaporation of water from the field. In the case of industrial production instead it is equal to the amount of water withdrawn from the soil or of surface water evaporated and therefore cannot return to the same place from which it is drawn: WF blue = Blue water evaporated + Blue Water incorporated +Blue water consumed [volume / time];

- *Grey water*: volume of water which is polluted during the production phase of a product. It can be quantified by calculating the volume of water required to dilute pollutants emitted during the production process and such that the quality of the water remains constant (Amicarelli et al., 2009): WF grey = L / (c max - c nat). It is then calculated by dividing the pollutant load (L = mass / time) for the difference between the maximum acceptable pollutant concentration (c max) and the concentration of the pollutant body in the natural receiving body (c nat). As far as the qualitative connotation of the water footprint is concerned, the first feature of the analysis is that of understanding the difference between these three major components. As can be seen from Fig. 3, the Water Footprint includes both the direct consumption of water but also the indirect one, and can be summarized in Eq. (1):

WF = Green WF + Blue WF + Grey WF
[volume / mass] (1)

2.3. Standardization of WFP

In the case of the Water Footprint, as in that of the Carbon Footprint, standards to measure the Water Footprint of products have also been implemented. The ISO 2014 issued the ISO 14046 Standard (2014), an international standard that specifies principles, requirements and guidelines for the assessment and reporting of water footprints. This standard is applicable to production processes, products and organizations and is based on the Life Cycle Assessment methodology.

The Water Footprint assessment can help to (Ridoutt et al., 2010):

- assess the extent of potential environmental impacts related to water;
- identify the strategies for reducing the impacts just mentioned;
- promote water efficiency and the optimization of water resources management;
- provide information for the communication of the results of the water footprint studies.

The market's attention to the issue of water is ever increasing. There are many companies, which by collaborating with the WWF, calculate the water footprint linked to all the production lines of their products. The water footprint assessment profile proposed by ISO includes a compilation of impact category indicators (scarcity, eutrophication, aquatic ecotoxicity, aquatic acidification), which address potential quantity and quality impacts and may provide for a more appropriate assessment of the water quality impacts on the water environment (Hoekstra and Hung, 2002; Warmark, 2015; Water Research Foundation, 2014).

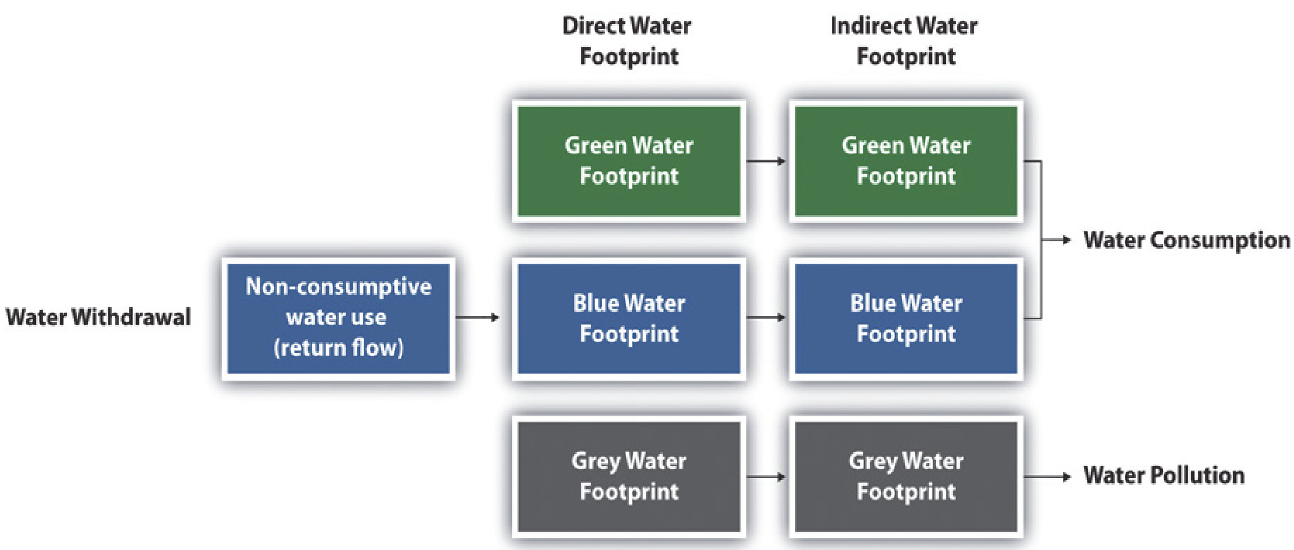

Fig. 3. Simplified Diagram of the Water Footprint

3. Experimental case: Application of water foot print in the construction sector

3.1. Construction: a high environmental impact sector

The "Roadmap to a Resource Efficient Europe", adopted in 2011 shows how power, transport and the construction industry are responsible for 70-80% of all environmental impacts in industrialized countries. For this reason, the European Commission has adopted new proposals to reduce the environmental impact of the construction industry, improving resource efficiency, but also increasing the available information about the performance of the construction works, especially about buildings.

These would result in numerous benefits for the construction industry (which it generates 10% of GDP) but also for the environment (Wei et al., 2010). It is in fact estimated that on a European level the construction sector is the sector with the highest environmental impact if it is considered that:

- it absorbs 45% of all the energy produced;
- produces 40% of air pollution;
- consumes 40% of non-renewable resources found in nature;
- 40% of waste is due to it (Pheng and Chuan, 2006).

It can be said, therefore, that the construction sector is the sector that contributes most to the environmental crisis, as seen above, it is the sector that reveals the major consumption of land, energy, and material resources, because of the extraction of manufacturing and processing of the materials necessary for the production and construction of public and private works. Remaining, however, on the theme of water resources, the human activities that consume and pollute water the most are: agricultural production, the domestic sector and, of course, the industrial sector.

The following section discusses the application of the Water footprint to a company operating in Syracuse, Italy in the industrial sector. The business that it carries out causes considerable environmental impacts, arising not only from the use of water resources, but also from electricity consumption, non-renewable resources, soil and finally by air pollution and CO_2 emissions. This company's main activity is represented by the production of aggregates, bituminous and concrete mixes.

In order to analyze the application of the Water Footprint to the case study, the water consumption for the year 2014 was considered. The data was collected through interviews with the manager, business database consultations, moreover through data collection sheet, histogram and Pareto diagram; moreover, with applied measuring and monitor water data direct from water resource in our firm.

The latter is divided into Green, Blue and Grey Water, and the Water footprint for each of them is calculated. Following this calculation, the three recorded indicators are added together to get the value of Global Water Footprint, which expresses the volume of direct and indirect freshwater consumed by the company. The assessment of the Water Footprint is therefore divided into three phases: the quantification of the Water Footprint, assessment of the environmental and economic sustainability of the same and identification of improvement strategies for the reduction of the footprint. It is noted that in recent years attention towards the issue of water resources has increased, and the water footprint, together with Life Cycle Assessment represent an assessment method even though neither models can be considered complete (Cucek et al., 2012; Fang and Fang et al., 2014; Feng et al., 2011; Galli et al., 2001; Heijungs, 2015; Jefferies et al., 2015; Muñoz et al., 2012). There are numerous case studies covering the subject in question, the scope is specially applied to the agricultural sector (Arabi et al., 2009; Kyounghoon et al., 2017; Rivas Ibáñeza et al., 2017 Xinchund et al., 2018), and just few applications were found on the industrial sector, (Ayres, 2014; Ene et al., 2013; Kucukvar and Tatari, 2013; Shao and Chen, 2013) and even service sector (Li and Chen, 2014).

The Water Footprint provides a perspective on what the relationship between the consumer or the producer is, and the use of water resources. It does not, however, measure the severity of the impacts of consumption and pollution, rather it should be considered as a volumetric measurement of consumption and water pollution.

3.2. Water consumption

The first stage of the calculation of the Water Footprint is the quantification of the Water consumption, which is the result of the aggregation of the various Water consumptions of all relevant processes in the company's production. For each phase of the life cycle of the various production processes, inherent to the year 2014, the consumption of water was studied, dividing this into different categories required by the Water Footprint: Blue, Green and Grey water. In the end, the latter are added up all together in order to calculate the total Water Footprint.

For the company, the subject of the study, an underground aquifer is the source of supply of water resources. Only drawings of the volumes of water taken from the company's well are considered, as these are the only source of water withdrawal, despite the existence of a meter, and therefore the possibility of using the local waterworks for the drinking water.

The aforesaid well has a depth of 90 m for drawing water, even if the suction tube is positioned at a lower height, 110 m, in such a way as to have a greater safety in the periods in which the water level is lower. The drawing capacity of the well is equal to 110,000 m³ per year and in 2014 17,870 m³ of water were withdrawn.

The activities involving the withdrawal of water may be summarized as follows:

- Crushing is the phase in which, the material taken from the quarry, is transported to the crusher by truck to be transformed into inert material and this activity, compared to the others, requires the greatest consumption of water;
- The production of cement or concrete mixes, this product represents one of the most widely used building materials in construction and is made from a mixture of cement, inert materials (sand and gravel) and water, in certain percentages, for each m³ of concrete Gravel 0.8 m³, or Sand: 0,4 m³, or Concrete: 350 kg; or water: 150 litres.
- The production of cement mixes is a phase that requires the use of water both in the relative production of the concrete, and for filling of the tank of the cement mixing truck;
- The production of bituminous mixes consists of a mixture of coarse aggregates, fine aggregates and mineral fillers (fine materials that are used as filling of the empty spaces left by the cement granules and which make much more compact conglomerate) which are mixed with bitumen. This production takes place in the specific asphalt making plant which does not involve use of water;
- The washing is the stage that determines the consumption of water both for the washing of motor vehicles and in relation to the amount of water contained in settling tanks, which collects the sludge in cases when the filter press is not in operation. Like the filter press, its purpose is to dehydrate the sludge obtained from the washing of the aggregates to reuse it later on.

3.3. Calculation of WF

It is observed that the direct components with respect to the production cycle are: water included as an ingredient during the production cycle (production of cement mixes) and the water consumed during the production process (washing of the aggregates). Instead, indirect components are: the water required for the washing phase of the vehicles and the water used for services, and that used for gardening. For these components, direct and indirect, the consumption of water is determined by adding the three results obtained by calculating the different categories of the WF or rather Green, Blue and Grey Water Footprints. So WF = Green WF + Blue WF + Grey WF [volume / mass].

Green water refers to the volume of rainwater evaporated during the production process, and the following formula permits an understanding of how the latter is calculated: WF Green = evaporated green water + incorporated green water [volume / time]. It is calculated mainly for agricultural products, and because there is no use of rainwater (green water) during production, it is not considered. Therefore, the Green Water Footprint will be null. The blue water, however, refers to the removal of surface and underground fresh water used for agricultural, domestic and industrial purposes. It also includes the volume of evaporated water due to production. In the case of industrial production, it is equal to the sum of water subtracted from the soil or to the sum of surface water evaporated, and thus it does not return to the place where it has been withdrawn.

The formula for determination is: WF blue = Blue water evaporated + Blue water incorporated + Blue water consumed [volume / time]. Finally, the grey water is defined as the volume of water required to dilute pollutants emitted during the production process and, such that, the quality of the water remains constant. It is calculated by dividing the pollutant load (L = mass / time) for the difference between the maximum acceptable pollutant concentration (C max) and the concentration of the pollutant in the natural water body (c nat). The formula that expresses this calculation is: WF grey = L / (c max - c nat). The water used by the company in the production process is always recycled, and since other pollutants are not emitted into the production system, the grey WF will be 0.

Therefore, only the consumption of water that is obtained from the calculation of the Blue WF is considered. Additionally, it is necessary to consider all the activities involving the use of water resources, the total amount of water taken from the well, during the period of reference. Then the direct activities related to the WF are analysed. They are crushing, an activity thanks to which the material is transformed into inert material, and the production of cement or concrete mixes.

The first activity requires the greater amount of water resource. The production of aggregates in 2013 was 29.8700 tons, corresponding to 229,769 m³, and it is estimated that the mill used, in the same year, 15,200 m³ / year of water for washing the aggregates. It suggests a consumption of 66 litres of water per m³ of inert material, which represents the amount of blue water required for washing one m³ of product. 10% of such consumption is not recovered as it remains embedded in the product, which then is allowed to dry and the water (about 7 litres per m³) evaporates. For the second activity, it has been estimated that, in the production of 1 m³ of concrete, 1.50 litres of water are present, corresponding to 0,150 m³ of water. Since the company produced 21,727 cubic meters of concrete in 2014, water consumption amounted to approximately 3200/m³. This value represents the total of incorporated blue water in the concrete produced in the year in reference. It is also necessary to consider the water that is inserted into the tank of the cement mixer. In 2014 this figure was calculated at 700 m³ / year. The abovementioned results are shown in Table 2. The washing of the vehicles and the consumption of water for rest rooms are the indirect components with respect to the production cycle, involving water consumption.

Table 2. The WF of direct production components

Direct activities	***Quantity produced (m³/Year)***	***Blue WF (m³/Year)***	***Water consumption (m³/Q)***
INERTS	229,769	15,200 cc.	0.066
CEMENT MIXES Production Cement mixing truck	21,727	3,260 700	0.15 700
TOTAL WF		**19,160**	

For the calculation of the WF no amount of rain water is used (green water). Moreover, such activities, not emitting into the environment highly polluting substances for the water, do not determine the volume of grey water. It can be assumed that the consumption of water used in the washing stage of the means of transport is 115 m³ / year of water. Thus, the company consumed 115,000 litres of water for washing vehicles. This water is considered to be blue, since it is water coming from the well and that does not return to the place it was removed from. With reference to water used for the restrooms, the company has no data so it is assumed that consumption is 25 litres of water per day per person. Therefore, in this case, the consumption varies in relation to the number of employees in the plant. On average there are 15 employees, so it is estimated a daily consumption of 375 litres / day of water, corresponding to 75,750 litres / year and considering 202 working days (Table 3). Instead, for the collection of waste water, the company uses the septic tank.

Table 3. Shows the WF of the indirect production components

Indirect components	***Blue WF (m³/year)***
WASHING VEHICLES	115
TOILETS/RESTROOMS	76
TOTAL WF	**191**

From the comparison of the tables shown above, it can be established that the activities requiring a greater amount of water are those of direct production. In particular, crushing is the one which produces the highest absorption of water resources, due to the washing of the inert products.

3.4. Assessment of the sustainability of the Water Footprint

In order to assess the sustainability of the Water Footprint, determined by calculating the Global Water Footprint, a comparison of the latter with the relevant Water Footprint of other companies operating in the Italian industrial sector was made.

The majority of studies carried out on the calculation of the Water Footprint, as previously stated, concern agriculture. Therefore, the information available belongs to the same company: Buzzi Unicem, an industrial group with a large number of employees (about 11,000), with an annual production capacity of 38 million tons of cement and about 15 million cubic meters of ready-mix concrete. The company, besides Italy, has plants in Germany, Luxembourg, Poland, the Czech Republic, Ukraine, Russia, the United States, Mexico and the Netherlands. In Italy, it boasts 13 production plants with a production capacity of about 10.4 million tons per year. In 2004, it made the first registration of an Environmental Product Declaration (EPD) in relation to the cement produced in Italy in the factory in Vernasca, becoming the first case in the world. Thus, the WF of the cement produced by Buzzi Unicem can be defined. Previously it was analyzed that the average cement produced at the plant in the province of Siracusa, consumed 1,454 litres of water per ton of finished product.

Buzzi Unicem, makes use of a company it owns for the production of concrete, the Unicalcestruzzi.

The latter as regards the direct production activity, as can be seen from Table 4, uses 175 litres of water in the production of 1 m³ of concrete compared to the 150 litres of water used by the Siracusan company for the production of the same amount of finished product. Although few data are available, a comparison can be made of the two companies and, as noted, the Siracusan company, uses a smaller quantity of water resources with reference to the production of concrete.

Table 4. Composition of the concrete company Unical

Components	***Unit of measurement***	***Average concrete***
Cement	kg/m³	263,6
Ashes	kg/m³	45,6
Additives	l/m³	1,5
Water	l/m³	175
Aggregates	kg/m³	1871,7

It is not possible, however, to make a comparison of the other direct activities of the Siracusan Company, or rather the crushing that is the activity which is responsible for the consumption of the greatest quantities of water, as there is no data from other companies to be able to compare with. Instead, it can be seen that for the indirect production activities like the washing phase of vehicles uses 115,000 litres / year of water, whereas for the washing of cars takes 800 litres of water, it can be inferred that 145 trucks a year could be washed. But since the water consumed will be higher for trucks and less for cars, it is argued that the company complies with the urban standards. Data from the second indirect production activities, however, have been hypothesized as the company had no information about these.

It can be concluded that the company fits positively within the territory in respect of water resource consumption, that it does not further deteriorate the environmental situation. Of course, it would have been more appropriate and effective for the purposes of discussion, to carry out an analysis of the assessment of environmental sustainability comparing all the various factors and the various activities that require a consumption of water but, this was not possible as the industrial sector is not a field of applicability of the Water Footprint.

3.5. Improvement strategies adopted by the company

In the past, the fumes from the burner passed though the columns for dust suppression, where there was a purpose-built column for this activity, which had nozzles on the inside through which water was sprayed, allowing the dust to be deposited at the bottom. Today, in order to avoid the consumption of water another type of that column is used inside the company having two elements which are the sleeve filter, whose upper part houses 513 sleeves in filtering fabric (Nomex) placed vertically, and the pneumatic valves for the supply of compressed air. Each module is fully inspected. The lower part, however, with the sleeve filter, acts as a collection hopper and is separated from the top in order to facilitate the transport. The operation of the sleeve filter can be described as follows: the particles of dust in suspension, passing through the filtering part, are retained, while the filtered air is sucked up by a fan. The cleaning of the sleeves is carried out, as mentioned earlier, by a compressed air system which, cyclically placed into the nozzles, mounted on the axis of each row of filter fabric, allows, through special diffusers, the expansion of the sleeves. This allows dust to fall to the bottom of the hopper. In this way, the filler will be recovered, and therefore the plant no longer uses the water resource for the production of bituminous mixes and there is no consumption of water.

This process has been considered an improvement strategy adopted by the company itself and, also, has a high purification efficiency, even with sub-micronic particles. For the company, the costs both of running and maintenance are very low. In addition, the company adopts a total water recycling system, which recycles virtually all the water used for washing of the aggregates in the production, an amount that is obtained through the use of the crusher. The only part of non-recovered water is that incorporated in the aggregates that once these dry, evaporates.

3.6. Proposed improvement strategies

The company's improvement strategies could be supplemented with further solutions capable of allowing the company to obtain a further reduction of the consumed water resource. It should be observed that the consumption and pollution of water resources, are closely linked to the operating mode of the same, and the overall structure of the economy. In fact, communities, production chains and companies greatly influence the consumption and pollution of water in quantitative terms.

The company draws all the water necessary for the performance of its activities, from a well, which is the only source of supply of water resources. An improvement strategy could be the use of alternative sources of water such as rainwater. The company also may not totally replace its only source of supply, but may try to identify additional sources in order to obtain a reduction, albeit minimal, of water withdrawn. Rainwater, preserved through an appropriate system of collection, recovery and re-use, could be used both for the direct production activities and for the indirect ones.

Such a solution would be possible by installing a collection system on the roof of the building. It would be made up of the following elements: a collection surface positioned on the roof; a conveyer system, consisting of gutters; a drain conduit that leads the water collected to a storage container; a filtration system that separates the water from suspended material (leaves, debris, etc); a storage container; a dispersion system to drain the water in the event of the maximum capacity is reached; a recycling system that carries water from the container to the point of use.

In order to assess the cost effectiveness of the system, it is first necessary to consider that such a system, according to a study conducted by the International Centre of Dutch Research, maximizes its effectiveness in the areas where the amount of rainfall is between 100 and 500 mm per year. In fact, if the rainfall exceeds 500 mm per year, the costs exceed the benefits, just as if the amount of rainfall does not reach the 100 mm per year, the benefits may not cover the costs in a reasonable time. From an analysis of the amount of rainfall in Sicily in the period from January to April in 2014, the year taken into consideration in the analysis of the water footprint, the area where the company is located lies in the band of rainfall ranging from 125 to 150 mm. Whereas the Data expressed are quarterly, annually this band presents a rainfall range of 375-450 mm. So, it can be concluded with the statement that a rainwater collection system installed in the company would produce positive effects both in terms of cost effectiveness, and in relation to the impact on the environment. The only negative factor could be represented by the fact that for the installation of a plant of this type the company would incur costs that maybe minor, but only if carried out on a new building. By contrast, if only cost effectiveness is considered, such an intervention would not be profitable on an already existing building. However, it can be assumed that such an intervention is a viable option, as it would result in multiple benefits such as:

- various possible uses: washing vehicles, watering lawns and green areas, toilet flushing;
- floor washing, replenishing stocks of fire prevention, industrial cooling;
- lower consumption of water resources;
- collection of about 767,000 litres of water per year with 1,500 m^2 of surface;
- water catchment from the well;

- savings achieved through lower water costs;
- sustaining the environment.

It may in fact, be assumed that from the economic point of view, a collection tank of 9,000 litres costs about 4,000 Euros. The costs of digging works must be added to this, as well as those relating to all other necessary accessories. Therefore, following the evaluation of all the highlighted factors, and considering the fact that such intervention is inherent in a company and not to a dwelling, it is believed that such a strategy is viable for the company under study.

4. Results and discussions

The application of the Water Footprint indicator to a company in the construction industry, takes into account the spirit of entrepreneurship of the control group, in respect of the regulations and requirements for the production of materials, but also in compliance with the mandatory environmental regulations. Moreover, due to the desire to constantly innovate, it is very important to take into account the important role played by all the companies in the sector in the environmental field which has led to positive results, both from the point of view of the enlargement of the scope of the same indicator, as well as from the environmental point of view. In fact, despite being an experimental study it has made it possible to understand the huge potential of the indicator and its adaptability to various sectors and products.

In order to achieve the intended purpose, it was not considered sufficient to directly apply the calculation of the Water Footprint, but it was felt to be necessary to understand the company's ideology and the way it operates in the market. This was done through the analysis of the same company as a whole, the innovations used in the construction field and the most important production stages. Finally, thanks to the calculation of the Water Footprint the amount of water resources that a company of this size really requires was understood.

A solution was also offered for improvement, consisting in the installation of a system for collecting rainwater, which could be used for irrigation, in the phase of washing the vehicles, but also in the direct production phases. Of course the system will have a cost, which compared to the high efficiency, is relatively low. The only limit could be represented by the capacity of the storage tank; the collection surface would not be, however, a limit since, as previously seen, it is very wide. Moreover, the collecting tank, could be placed externally and anchored to the building, if the company does not want to make an excavation for its placement, given the relative costs. Having considered the cost effectiveness of the system, the following conclusion was reached: the company greatly exploits the opportunity to reduce its water footprint, thanks to the continuous recycling system and new sleeve filters, but it could install the rainwater collection system, integrating a new source of supply of water resources compared to only the well and thus allowing a greater reduction of water consumption.

The illustrated indicator has made it possible to fully understand how a well-established company impacts on the water-resource level, and with a fairly complex reality. It has been highlighted how the company through the management's efforts and attention to environmental issues has managed to improve its environmental performance with obvious savings in economic and environmental terms, but also in competitive advantages in a few years, tank to the use of new technologies.

Moreover, thanks to the proposed strategy, with an investment the company could obtain numerous advantages both in economic terms but also in the field of the preservation of water resources, since as mentioned earlier, in the last few decades an increasing significant use thereof has intensified the attention of consumers and producers towards the sustainable use of water resources and, more generally, of all resources. By calculating the Water Footprint of the company, it can be understood, not only how the company itself impacts, the aim of this paper, but what each individual, personally, can do to try not to further jeopardize the environment. To this end, the voluntary labelling system was created that has made it clear how it is possible for a company to certify its own products or services. It has also been seen how, to date, certification exists for any product or service. Obviously, environmental brands belong to the category of environmental management tools, along with environmental management systems.

This paper was characterized not only by a great interest in the theme and the very purpose of the study, but also by many difficulties. Unfortunately, in fact, the method of application of the calculation of the Water Footprint is still in an experimental approach; This was an issue addressed in the paper, because the standardization of the indicator is still being developed, there are regulations that rigidly indicate which rules and criteria are to be followed to measure the Water Footprint, let alone the parameters already established to be taken as a reference in assessing the sustainability of a result.

Moreover, despite numerous studies on the Water Footprint, none of them refer to the industrial sector. So, it was not easy to find information about other companies in the sector that have calculated its Water Footprint. Nevertheless, it is believed that a set goal has been achieved: applying an important indicator, the Water Footprint to a business reality. It is also believed that positive results were achieved.

5. Conclusions

As it turns out, the Carbon Footprint and Water Footprint respond to this need well. Moreover, even if they are both close to the concept of

Ecological Footprint, they are more specific, especially the Water Footprint, because it refers to the territory where the removal of water resources actually takes place. Before the ISO 14046 Standard there were no international standards related to water consumption and the companies were applying different techniques to get the data for environmental reports. Thanks to the increasing interest also from Certification Bodies, any organization that wants to certify their commitment precisely to reducing the environmental impact of its production processes can do so.

This is a great achievement that has been reached: a step towards the preservation of a resource that represents a key asset to life, water.

It is considered essential to emphasize how important environmental labels have been in recent years of "environmental crisis", and how important the use of a brand for water would be, one which certifies the commitments of the producer, of the product, or the service provider. And, maybe in the near future, consumers will have the chance to choose the products to be purchased and the services to be enjoyed, also on the basis of their ability to consume a smaller amount of water throughout their life cycle.

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LOW ENVIRONMENTAL IMPACT OF ALTERNATIVELY SUPPLIED CARS. RESULTS OF AN INVESTIGATION CARRIED OUT IN THE NORTH-EAST OF ITALY

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Abstract

The transport of both goods and passengers notably influences air quality. If strong decisions by the governments will not be taken, oil consumption for transport will be nearly doubled in 2030 if compared with 2000, thus considerably increasing the atmospheric presence of greenhouse gases. To boost the purchase of alternatively supplied cars would avoid serious, if not catastrophic, climatic changes. Our investigation shows what the situation is concerning new cars sold by SINA, an official concessionary firm of ten brands in the province of Pordenone, in the North East of Italy, covering about 40% of the local market. The supply types and the brands of the new cars sold in the branch offices of the firm from 2011 to August 2015 have been taken into consideration. The most sold cars are still petrol and diesel supplied, whereas alternatively supplied cars (liquefied oil gases, methane and electric) represent nowadays only 7.51% of the total in this territory. Processing of the data that have been put at our disposal by the firm allowed to compare the situation of the province of Pordenone with the Italian one, and to put in light the critical aspects still hindering the purchase of alternatively supplied cars.

Key words: alternatively supplied cars, carbon dioxide emissions, North East of Italy

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1. Introduction

The quality of air is a prior factor for the environmental welfare. The environmental pollutants are due in particular to industrial activities, heating systems and vehicular traffic. Specifically, combustion processes which take place in all (terrestrial, marine and aerial) vehicles are one of the main causes of non-desired atmospheric emissions, which provoke harms to the environment and consequently possible negative effects to human health (Burgarella, 2014; Gasana et al., 2012; Stankovic et al., 2015). Atmospheric pollution is a global, not only local, problem; in fact, pollutants, because of the atmospheric agents, can easily move and provoke harmful effects also very far from where they are produced. In detail, the transport sector is a significant source of the both CO_2 (the main responsible for greenhouse effect) and particulate (PM_{10} and $PM_{2.5}$) air emissions (Ilyas et al., 2010; Kim et al., 2004; Stefan et al., 2015). This situation is particularly worrying in Italy, where the main part of commodity and person transport is carried out on rubber, in comparison with other Countries (in Europe and in the world), where railway transport is leasing with a consequent emission reduction. In 2014, road traffic was responsible for 25.5 % of total CO_2 emissions (Ispra, 2015). Furthermore, the amount of CO_2 emitted by private cars moving in Italy during 2013 was 166.0 g/km, referred to petrol cars, and 158.6 g/km for diesel cars (Ispra, 2015).

Current European rules concerning air quality control are specifically represented by the Directive 2008/50/EC (EC Directive, 2008). In Italy, this Directive was adopted by the Legislative Decree No 155/2010, which fixed the objectives for PM_{10} and

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$PM_{2.5}$ reduction. In particular, it defined the limit of PM_{10} concentration as 50 µg/m^3, relatively to the daily average, not to be exceeded for more than 35 times a year (Legislative Decree, 2010). The same Legislative Decree imposed limits gradually more restrictive for $PM_{2.5}$, by establishing that the year average, from January 1st 2015, cannot exceed 25 µg/m^3.

In 2009, the European Parliament ratified the so-called "20-20-20 package" (Directive 2009/28/EC), which fixed the following guidelines:

a) to reduce by 20% the emissions of greenhouse gases within 2020, compared with those of 1990;

b) to reach 20% of energy saving, in general heat recovery from combustion processes;

c) to increase to 20% consumption of energy from renewable sources (EC Directive, 2009).

European policies for reduction of greenhouse gases in the transport sector brought to voluntary agreements between the associations of car makers, European Car Manufacturers' Association (ACEA), Japanese Automobile Manufacturers' Association (JAMA) and Korean Automobile Manufacturers' Association (KAMA). The goal of these agreements was to fix the average CO_2 emissions for the new registered cars at 140 g/km in the European countries within 2008.

This target would be obtained by technological innovations upgraded on the cars. This commitment was not observed by the car makers, so in 2009 the Regulation 443/2009/EC fixed, from 2012, the average CO_2 emissions at 130 g/km and the goal of 95 g/km within 2020 (EC Regulation, 2009). This Regulation stated that the limit of 130 g/km would be obtained by technological motorcar innovations. The difference, 10 g/km, would be obtained by technical measures on pneumatics, fuels, air conditionings, etc. To reach this goal, the Regulation fixed the limit values for CO_2 emissions of the cars depending on their mass; so the limit to be respected increases with the increasing of vehicle mass.

Every year car producer companies have to demonstrate that the sold cars have average CO_2 emissions in line with the limits fixed by the above-mentioned Regulation. These limits are calculated by considering the number and the mass of the sold cars. Otherwise the car producer companies are subjected to sanctions by the European Commission. Actually an agreement was reached on the topic, in order to calculate the weighted average of 95% of the sold cars and excluding some sport cars characterized by high levels of CO_2 emissions.

In 2011, the Regulation No 725/2011/EU was issued, with the aim of further reducing CO_2 emissions, by providing incentives to the car companies able to develop new, innovative technologies in order to reduce environmental pollution (EU Regulation, 2011). In 2014, the Regulation No 333/2014/EC was promulgated, partially revising the Regulation No 443/2009/EC, keeping the goal of 95 g/km (as emission level) for the new cars from 2020. The main modifications of this Regulation are:

a) define the average CO_2 emission of every vehicular brand. The following percentages have to be considered: 65% in 2012, 75% in 2013, 80% in 2014, 90% from 2015 to 2019, 95% in 2020, 100% from 2021;

b) assign "super credits" for the achievement of the goal of 95 g/km: every new car with emission lower than 50 g/km will be counted as two cars in 2020, 1.67 in 2021, 1.33 in 2022 and 1 starting from 2023 (EC Regulation, 2014).

1.1. The environmental pollution due to vehicular traffic

The Legislative Decree No 155/2010 fixed the limits for the main air pollutants in Italy: PM_{10}= 50 µg/m^3; $PM_{2.5}$= 25 µg/m^3; NO_2= 40 µg/m^3 (maximum annual average) or 200 µg/m^3 (average value), not to be exceeded in 25 days a year. The increase of vehicular traffic is due to increased population and industrial activities. At a local level, emissions depend on the fuel supply, but also on the local environmental policy.

Vehicular traffic is one of the main causes of climate changes: in fact, it is responsible for 25.5% of the total CO_2 emissions, due to fossil fuel combustion (Ispra, 2015). Other pollutants, coming from fuel combustion, are: CO, NOx, SOx, VOC, secondary O_3 (Serafini, 2008). Volatile hydrocarbons from petrol vehicles have been studied because of the production of photochemical smog (Schauer et al., 2002). Vehicles are responsible for the major amount of fine particles in urban air (Sharma et al., 2010).

Many investigations were carried out on health environmental implications. Air pollution due to traffic generally has important effects on respiratory diseases, allergy and asthma (Ilyas et al., 2010; McConnell et al., 2010), in particular on respiratory children's health (Gasana et al., 2012; Kim et al., 2004). Polycyclic aromatic hydrocarbons (PAHs) are very dangerous for human health because of their cytotoxicity and mutagenicity (Slezakova et al., 2011), particulate matter, coming from vehicular heavy traffic of highways, is associated with cardiac and pulmonary mortality (Brugge et al., 2007). "Secondary" ozone, produced by the reaction of benzene, formaldehyde, small organic particles, NO_2 and other organic substances deriving from fossil fuels in the presence of sun light, is very dangerous for human breathing apparatus. Finally, PAHs and benzene can cause cancer pathologies (Burgarella, 2014).

1.2. The influence of fuels on air pollution

From January 1st 1993, to install a catalytic converter is mandatory in all the cars fed by petrol, in order to reduce pollutant emissions, in particular of carbon oxide (CO), unburned hydrocarbons (TOC) and nitrogen oxides (NOx).

Cars fed by liquefied oil gases (LOG) emit less CO_2 if compared with petrol and diesel cars and can be considered to emit zero particulate matter (Econometrica, 2009). Furthermore, they release lower amounts of PAHs, if compared with petrol, methane and diesel cars; the last ones are the most pollutants from this point of view. Sulphur (S) amount is very low, as well (Orsini et al., 2014).

Methane combustion produces 72% less NOx in respect of petrol; it produces 14% less CO_2 and 95% less NOx if compared with diesel combustion (Econometrica, 2009).

1.3. Less pollutting cars: hybrid cars

Hybrid vehicles are characterized by two propulsion systems: the thermic and the electric one. Three types of cars are distinguished, depending on hybrid system, power and electric energy installed in respect of total power supplied by the car: micro hybrid, mild hybrid, full hybrid. In particular, full hybrid are the only hybrid cars able to run by using also the electric propulsion; in fact, they can move by using the electric or the endothermic engine or by a combination of both. Usually the electric propulsion feeds the start phase of the vehicle or the way at low velocity, by ensuring zero both fuel consumption and CO_2 emissions. The endothermic engine ensures the supplementary power needed during the speeding up phase and when high velocity of the vehicle is required. The full hybrid system is able to choose the best suitable feed by storing, for example, the energy wasted during the baking to recharge the electric accumulators.

Among the hybrid vehicles, the solution "plug-in" (cable equipped) represents a further evolution, similar to the electric cars: these cars have a set of batteries that can be recharged by a cable, in specifically equipped service stations or otherwise by a domestic 220V socket, but in a longer time for the complete recharge. The car can move according to the vehicle set up modalities, either in electric or in hybrid way. Generally, when the car exceeds a certain speed (i.e., 50 km/h), or a greater power is required, for example during an overtaking, the endothermic engine starts up, anyway saving fuel and therefore with lower pollution.

During the last years, the marketing of this type of vehicles has increased significantly, representing a right compromise between the traditional and the electric cars. Hybrid vehicles are much more efficient in comparison with the traditional ones, not only for their lower environmental impact, but also for their advantage, due to their lower fuel consumption. In fact, average fuel consumption is about 20-30% lower than a traditional car fed by petrol along urban roads.

Unfortunately, up to now, the criticalities of these cars are the purchasing costs, still too high, also due to the electric equipment and their innovative technology. The use of these cars is more suitable in particular for the urban cycle, because their higher weight can reduce the saving advantages or fuel in comparison with traditional engines along the highways. The greatest part of hybrid cars is constituted by a petrol + electric engine; diesel + electric engine is not yet very present in the market, even if it could represent a good alternative for the lower consumptions and emissions with respect to a traditional diesel car, using the diesel characteristics for the extra-town and highway runs and the electric characteristics for the town runs (Melis, 2012).

1.4. Electric cars

At present, electric cars are equipped by a set of lithium rechargeable batteries, able to improve the vehicle autonomy with respect to the previous batteries, in particular the lead ones, and with an average performance three times higher in terms of operation time. Nevertheless, they are still more expensive and their high price is an important disincentive for the success of this type of cars. Another important criticality is the limited autonomy that does not allow long trips without battery recharge; for this reason they are normally used within urban tours, not for long times. These vehicles are equipped with electric engines; batteries are periodically recharged by the electric main supply. The recharge timing depends on both battery type and supply. Normally, if they are recharged by an electric 220V cable, a period from six to eight hours is necessary. The needed recharge time is shorter if dedicated electric power supply sockets are used. Electric cars represent the only cars with zero CO_2 emissions. Electric energy would be obtained by renewable sources, like the photovoltaic one, in order to be considered sustainable. According to a study of the Commissione Italiana Veicoli Elettrici Stradali (Cei-Cives) and the University of Pisa (Menga and Ceraolo, 2010), an electric car or a hybrid plug-in one in electric modality presents a total environmental impact three times lower than a petrol Euro 5 car, considering the reduction of greenhouse gases, the reduction both of oil consumption and of costs for human health and the eco-system due to the emissions.

In this segment of vehicles, technology has developed the electric cars with fuel cells, fed by hydrogen, even if this technology is still in progress. The combustion cell represents an electrochemical generator producing electric energy directly from hydrogen or other fuels, either liquid or gaseous, containing hydrogen. In this way, energy is produced by a chemical reaction between hydrogen, stocked on board, and oxygen contained in the air (Pizzolato, 2011; Sartori, 2011). Hydrogen fuel cell vehicles are able to improve air quality, health and climate (Jacobson et al., 2005).

In the last years, several papers have been published on the development of innovative technologies and the promotion of buying of cars with alternative supplying (Engerer and Horn, 2010; Hillman and Sanden, 2008; Hoyer, 2008; Kley et al., 2011; Orbach and Fruchter, 2011; Petschnig et al., 2014).

The aim of this paper is to put in light the diffusion of alternative cars in the Province of Pordenone, in the North East of Italy, by the analysis of the new cars sold by SINA, official car dealer of ten brands in the territory considered. Data related to the last years are examined to establish whether critical conditions are hindering the development of alternatively supplied cars.

2. Case study presentation

From about the last 50 years, SINA is a firm marketing and assisting cars and commercial new and used vehicles. At the beginning, it was the unique concessionary firm for the brand Fiat car; at present it markets Fiat, Fiat Professional, Alfa Romeo, Lancia Abarth, Jeep, Volvo, Nissan and Subaru.

The main branch is located in Pordenone, while the other offices are located in Spilimbergo, Sacile, Portogruaro and Venice. Pordenone, Spilimbergo and Sacile are located in the Friuli-Venezia Giulia region, while Portogruaro and Venice in the Veneto region, both in the North-East of Italy. With more than 300,000 cars sold during its whole activity, SINA represents one of the most important realities in Italy in the field of automotive. Furthermore, it sells about 35-40% of the total cars sold in the province of Pordenone (about 320,000 inhabitants).

Our attention has been focused on the selling of alternative cars in the North-East of Italy, in order to compare the behaviors of the citizens of this part of Italy with the rest of the country. For this aim, we have interviewed the society management about the new car selling in all the branches, classified for both brand and type of fuel supplied. Only private cars have been taken into consideration. Data were collected from the company offices located in the province of Pordenone: Pordenone, Spilimbergo, Sacile, Nuova di Corva. Data available refer to the years from 2011 to 2014 and to the first eight months of 2015.

3. Results and discussion

3.1. Italian situation

In 2013, the cars on road were more than 70% of the total road vehicles. In 1990, the cars were little more than 27 millions, while in 2013 they were almost 38 millions, with an increase of about 38% (Ispra, 2014). In 1990, this meant 0.484 cars per capita, while in 2013 it corresponded to 0.611 cars per capita.

As can be observed in Fig. 1, from 2007, with the record of cars sold close to 2 millions and 500 thousand units, the market suffered a huge recession until 2013, with 1304454 registered cars, which means a decrease of 48% with respect to 2007. The car market began to increase only in 2014, the last year for which national data are available, when the registered cars were 1360441. However, a more detailed analysis can be made by taking into consideration the registered cars in the last 10 years, divided by the various types of fuels (Table 1).

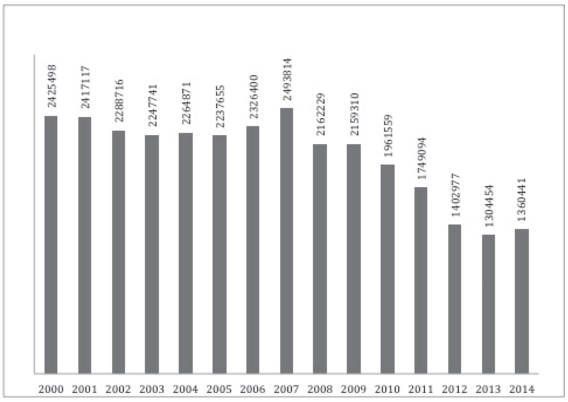

Fig. 1. Registered cars in Italy from 2000 to 2014 (Unrae, 2015)

We can observe an almost constant decrease of the selling of cars fed by petrol, which in 2014 represented 28.96%. Cars fed by diesel do not show a clear trend, even if they always presented the largest percentage in the global car market. During the last years, a significant interest in alternative cars has been observed (petrol-LOG, petrol-electric, petrol-methane, electric, methane); in 2013 they reached 15.34% and in 2014 16.13% of the market. In particular, in 2013 the share of cars fed by LOG was 8.89% and in 2014 9.15%.

Also the percentage or cars fed by methane increased slightly with respect to the previous year, reaching 5.32%, without financial incentives specifically dedicated. Hybrid cars switched from 15156 in 2013 to 21488 in 2014. Electric cars reached 864 units registered in 2013 and 1100 in the following year. In the last two years, registered electric cars, in particular hybrid cars, increased in a significant way, even if they still represent a very low percentage of the global car market. The consumers do not know if electricity is generated by renewable, not renewable or a mix of renewable-not renewable sources (Rezvani et al., 2015).

The share of cars fed by gases (methane and LOG) circulating in Italy is the biggest in Europe: in fact, Italian people choose alternative feeds that are able to provide the same performance and comfort, but with lower utilization costs, in comparison with traditional cars (Orsini et al., 2014). It is interesting to consider CO_2 average emissions of the cars registered in Italy in the last 10 years, which has progressively decreased up to a value lower than 120 g/km in 2014 (Fig. 2). In particular, according to an Anfia (Associazione Nazionale Filiera Industria Automobilistica) elaboration, the emissions in Italy of the new cars divided by supplied fuels in 2013 were: 122.3 g/km for cars fed by petrol, 123.8 g/km for those fed by diesel, 120.1 g/km for those fed by

LOG, 99.2 g/km for those fed by methane and 88.2 g/km for hybrid cars (Anfia, 2014).

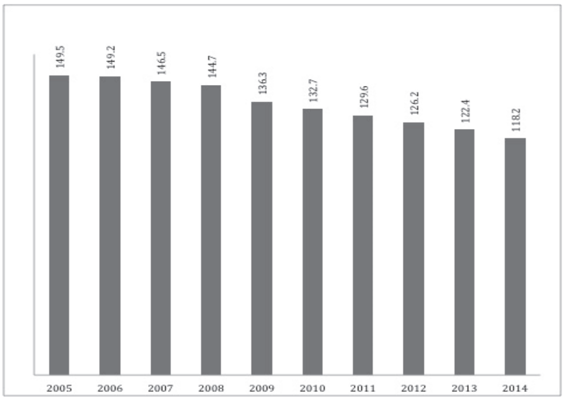

Fig. 2. CO_2 average emissions (g/km) of the cars registered in Italy from 2005 to 2014 (EEA, 2014)

The factors responsible for the efficiency of the car emissions are several, such as the feeding, the car weight and the power of the engine. Finally, at the individual level, users can reduce CO_2 emissions by 10-15% with good driving practices (safe driving style, respect of the rules of the road, etc.) (Unrae, 2015). To understand consumers' behavior is the starting point for any market decision. In the last years, consumers' behavior changed, since it was influenced mainly by the international economic crisis. In such a critical context, which is characterized by a both strong demand decrease and fierce competition, the definition of consumers' characteristics became more and more complex. Present situation relative to spread of the various types of car supplies and to emissions produced may be represented by a pyramid.

Table 1. Number and percentage of registered cars in Italy, divided by year and supplied fuel (Unrae, 2015)

Supplied fuel/year	***2005***	***2006***	***2007***	***2008***	***2009***	***2010***	***2011***	***2012***	***2013***	***2014***
Petrol	903628	941781	1011681	911780	780931	710785	683980	467625	401725	393972
%	40.38	40.48	40.57	42.17	36.17	36.24	39.10	33.33	30.80	28.96
Petrol + electric	1110	2179	3450	3337	7584	4843	5150	5638	14057	20831
%	0.05	0.09	0.14	0.15	0.35	0.25	0.29	0.40	1.08	1.53
Petrol + ethanol			7	96	125	77	59	52	5	1
%			0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Petrol + LOG	1822	3502	30004	74262	339596	279129	55792	128833	115938	124476
%	0.08	0.15	1.20	3.43	15.73	14.23	3.19	9.18	8.89	9.15
Petrol + methane	19296	24655	52203	71013	122189	62310	35614	48323	56076	60562
%	0.86	1.06	2.09	3.28	5.66	3.18	2.04	3.44	4.30	4.45
Diesel	1308379	1352271	1387985	1093445	903116	901127	965488	745411	702725	747018
%	58.47	58.13	55.66	50.57	41.82	45.94	55.20	53.13	53.87	54.91
Diesel + electric	2	13	2				12	1198	1099	657
%	0.00	0.00	0.00				0.00	0.09	0.08	0.05
Electric	30	28	25	132	63	117	307	524	864	1100
%	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.04	0.07	0.08
Methane	3338	1971	8457	8164	5706	3171	2692	5373	11965	11824
%	0.15	0.08	0.34	0.38	0.26	0.16	0.15	0.38	0.92	0.87
Total	2237655	2326400	2493814	2162229	2159310	1961559	1749094	1402977	1304454	1360441
%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The most required types of supplying, diesel and petrol, producing the greatest emissions, are located at the base of the pyramid. By going up along the pyramid, the alternatively supplied cars are found; both their request and the level of emissions decrease at the same rate. Electric cars are placed at the vertex; they represent the less required cars, but at the same time they are characterized by zero emissions. However, the patterns of car purchase are destined to change: the pyramid pattern may be substituted by a clepsydra pattern, where the both base and vertex are made up by important contributions, whereas the central area is represented by a lower number of consumers.

According to a future purchase estimate, in 2020 consumers will buy smaller, lighter, safer and more comfortable cars, characterized by lower both consumptions and emissions. Selling of plug-in and electric cars will considerably increase, thus contributing to the decrease of atmospheric pollutant emissions. Furthermore, a greater amount of synthetic fuels could be used, as e-Deasel, a new synthetic fuel which can be produced without employing fossil sources, as it is obtained by water, CO_2 and renewable energy (Candelo, 2009). A recent investigation put in light that Italian motorists think that three characteristics are essential when choosing a car: safety, reliability and fuel efficiency. The 39% of Italian consumers prefer full-optional cars and are willing to pay more in order to obtain surer cars (Mohanarangam, 2014).

The item relative to consumptions represents a determining element nowadays in the choice of a car. This essential factor led potential consumers to take into greater and greater consideration mainly hybrid cars and to a lesser extent electric cars, in particular by consumers living in the cities.

3.2. The situation in the Friuli-Venezia Giulia region

In the Friuli-Venezia Giulia region, 624.7 cars were circulating for one thousand inhabitants in 2013; this meant a car fleet of 767990 cars (ACI, 2015). The number of cars sold in the last ten years, divided by the four provinces, is shown in Table 2. A general and almost constant decrease may be observed starting from 2007, as the effect of the well known economic crisis.

The number of cars supplied by LOG is greater than that of methane cars in the Friuli-Venezia Giulia region, where an important distributive network is present: in fact, there are 81 filling stations, of which 29 in the province of Pordenone. Methane cars are penalized in respect of LOG cars, as a consequence of a poor distributive network. Only four methane filling stations are present in the Friuli-Venezia Giulia region; two are located in the province of Pordenone. Electric cars are even more penalized by the lack of stations of battery recharging, which are concentrated in the main cities. Only one recharging station, which is not yet active it is present in the province of Pordenone. Furthermore, reductions are not available for electric cars as far as parking is concerned.

In 2014, the alternatively supplied cars sold in the province of Pordenone reached the level of 8.8 per cent. This figure is in line with the Italian mean value.The CO_2 average emissions of the cars registered in the Friuli-Venezia Giulia region in the last years are shown in Fig. 3. The trend is similar to that relative to Italian situation, already presented in Fig. 2. However, the values of the Friuli-Venezia Giulia region have always been slightly higher than the Italian ones, and in 2014 the objective of 120 g/km was not reached.

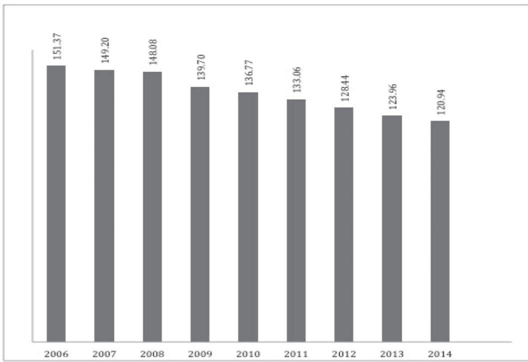

Fig. 3. CO_2 average emissions (g/km) of the cars registered in the Friuli-Venezia Giulia region from 2006 to 2014 (Unrae, 2015)

3.3. Case study

The results relative to the case study are shown in Table 3. In line with the situation of the Friuli-Venezia Giulia region and of the province of Pordenone, which has been already reported in Table 2, total car sell decreased progressively from 2011 to 2015. However, it is important to understand also the choices of the buyers with respect to the type of fuel. The cars supplied by conventional fuels largely represented the highest percentage of the selling for all the period considered, even if the trend showed some fluctuations. Furthermore, the percentage of diesel cars overcame that of petrol cars starting from 2012. However, some types of the most sold cars exceed (even if slightly) the limit of 120 g/km fixed by European rules for CO_2 emissions; almost all other types exactly respect the limit or are characterized by emissions only slightly lower.

One of the most sold cars in the last three years shows emissions of 99 g/km, but its price is about twice the other most sold cars. In 2012, the alternatively supplied cars quadrupled the selling percentage in respect of 2011, but a constant decrease was observed in the subsequent years. Electric cars began to be sold only in 2013, but in 2015 their number increased in a very significant way in respect of the two previous years, even if their share is quite insignificant in respect of the other types of cars. SINA began to sell hybrid cars only during 2016.

Table 2. Number of registered cars in the Friuli-Venezia Giulia region, divided by province (Unrae, 2015)

Province/ year	*2005*	*2006*	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*	*2013*	*2014*
Gorizia	5347	5513	6567	5430	6162	4271	3796	2377	2239	2618
Pordenone	11417	12085	12946	11518	11191	9915	9448	7084	6550	7335
Trieste	8009	8215	9182	7421	7770	6464	5676	4126	3956	4231
Udine	19792	19254	22059	18318	19106	16668	15539	11819	11024	11777

Table 3. Number and percentage of cars sold by SINA, divided by year and supplied fuel

Supplied fuel/year	*2011*	*2012*	*2013*	*2014*	*2015[a]*
Petrol	1745	1098	899	862	827
%	49.69	41.75	36.84	36.65	42.52
Diesel	1647	11 64	1225	1283	972
%	46.90	44.26	50.21	54.55	49.97
Traditional fuels	3392	2262	2124	2145	1799
%	96.59	86.01	87.05	91.20	92.49
Petrol + LOG	70	281	227	147	107
%	1.99	10.68	9.39	6.25	5.50
Methane	50	87	87	58	20
%	1.42	3.31	3.57	2.47	1.03
Electric	-	-	2	2	19
%			0.08	0.08	0.98
Alternative fuels	120	368	316	207	146
%	3.41	13.99	12.95	8.80	7.51
Total	3512	2630	2440	2352	1945
%	100.00	100.00	100.00	100.00	100.00

[a] *January-August*

People living in the province of Pordenone preferred to buy diesel supplied cars during the considered period of time, at least from 2012 afterwards. Methane fed cars were less required, even if methane is less pollutant than petrol and diesel. Electric cars seem to be the best solution to reduce the both use of fossil fuels and environmental pollution, as they do not emit CO_2, but their number is still very low.

4. Conclusions

Petrol and diesel cars are still the most bought ones both in Italy and in the province of Pordenone. Alternatively supplied cars are little bought; in particular, methane cars are penalized by an insufficient distributive network, but also by a limited range of car models. Hybrid cars, in particular plug-in cars, represent a compromise between conventional and electric cars. This type of cars represents the most ecological solution for the near future and from this point of view the data relative to domestic selling are comforting.

Electric cars would be the best solution, but their number is almost negligible, as the conditions which may warrant their commercialization are lacking.

Our analysis, carried out in the province of Pordenone, showed that the preferred supplying is diesel, followed by petrol. The obtained results underlined the weak interest towards alternative supplying, which is characterized by a clear predominance of LOG cars in respect of methane and electric ones.

The critical aspects of the distributive network represent a serious drawback for the growth of methane and electric cars. In fact, it was put in light that only two methane and one electric recharging (even if not yet active) stations are present in the province of Pordenone. Furthermore, reductions for the motorists who are owners of electric cars are not available in the municipality of Pordenone.

A further consideration relative to methane and electric cars is the poor supply in the market: car firms are not yet interested in boosting these types of supplying, even if the range of electric cars offered by the various firms is destined to increase in the future.

The objective to be reached would be a substantial reversal of present pyramid, to reduce the contribution of the most polluting types of supplying to a minimum.

Italian motorists are sensitive to environmental topics and therefore they are ready for innovative and ecological choices; however, these choices are hindered by distributive networks and incentives that are insufficient or even non-existent.

Also the incorrect behavior of some car firms has not to be underestimated: the official data relative to consumptions and emissions are sometimes different in respect of the real ones, thus leading consumers astray.

The definitive change in environmental protection will depend mainly on new European and domestic rules, which have to be more incisive and feasible. A deep improvement towards these themes will be necessary, with a series of practical interventions aiming at boosting production and purchase of ecological cars, by granting greater advantages to the owners of these cars and by providing the national territory with suitable services as a satisfactory distributive network.

Some solutions to reduce the environmental pollution in the central areas of the cities, due to vehicular traffic, could be: to limit the private vehicular traffic; to promote public local transport for both extra-urban and urban areas; to give tax concessions for season tickets for public transport, in particular for the shifts home-work-school; to improve electric car parking for the commodity logistic in the town centres; to promote pedestrian and bicycle mobility; to promote the use of fuels with a low environmental impact, in general by pushing the sustainable electric mobility (Arpat, 2016).

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PRELIMINARY ANALYSES ON AN ALGAE-BASED WATER SCRUBBER FOR SYNGAS CLEANSING

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Abstract

Common issues of the gasification systems relate to filtering apparatus. Dry filtering processes are simple and reliable. However, the filtering material defines the maximum and minimum temperature at which the filter can operate properly. In addition, dry filtration is not effective on light tar compounds (i.e. benzene and toluene) or ammonia compounds. On the other hand, despite being very efficient, wet filters drop the gas temperature below the line of condensation of tar, ammonia and steam. The resulting condensate is normally disposed at a high cost on account of the high amount of hydrocarbons it contains. This work investigates the effects of a specific micro-algae growth on the waste-water from a syngas water scrubber. The results demonstrated the capability of the algal growth in the tar-contaminated water in which a certain amount of contaminants have been dissolved. Quantitative analyses of the compounds outlined the effect of algal growth on the reduction of several chemical species derived from the syngas filtration.

Key words: gasification, microalgae, Neochloris oleoabundans, syngas purification, water scrubber

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1. Introduction

One of the major problems of recent decades is the growing energy consumption coupled with increasing fossil fuel sources and greenhouse gas emissions. Many studies have focused on renewable and sustainable energies, such as first or second generation biofuels, or on providing new biomass sources from the waste materials. Microalgae have a potential twofold advantage: providing biomass and purifying the waste material under aquatic conditions. Microalgae are a group of prokaryotic and eukaryotic photosynthetic microorganisms typically found in freshwater and marine systems (Altunoz et al., 2016; Li et al., 2008; Florenzano et al., 2016). Algae play a critical role in global carbon, nitrogen and sulphur cycling and approximately 45% of photosynthetic carbon assimilation is achieved by such organisms (Zhang, 2013). Therefore, they can be considered as a promising feedstock for biomass production. Many studies focus on coupling the ability of microalgae to remediate wastewater and the related potential for biofuel production (Acién et al., 2012; Altunoz et al., 2017; Dalrymple et al., 2013; Park et al., 2011; Pittman et al., 2011; Pedrazzi et al., 2015). Nutrients have an important activity on the efficiency of microalgal production according to life cycle analysis (Collet et al., 2011). The problems of the relation between water and nutrients also involve water scarcity and non-renewable nature of phosphorus sources (Cordell et al., 2009). These environmental and economical problems can be

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solved by use of wastewater as feedstock for microalgal biomass production. If the production cost and environmental impacts of wastewater bioremediation can be reduced, the necessity of freshwater and industrial nutrients can also be reduced considerably. Furthermore the studies on sustainable energy focused on CHP (combined heat and power) modules, power generations, anaerobic digestion or/and production of biogas as well (Allesina et al., 2014; Allesina et al., 2015; Bavutti et al., 2014; Pedrazzi et al., 2012).

Thermo-chemical processes play an important role in converting waste material created from agricultural, forest or other organic residues into products which contribute approximately 14 % of the Earth's energy supply. It is notable that this proportion can reach up to 40 % or 50 % in some developed countries (Caputo et al., 2005; Cui et al., 2004; Lin and Tanaka, 2006; Wang et al., 2008). However, there are still difficulties especially upon biological conversion of low-value lingo-cellulosic biomass, such as efficiency, cost etc.

Thermochemical conversion technologies consist of three methods: combustion, gasification and pyrolysis which are used to generate heat and power from biomass. Combustion of biomass is a well known method in terms of providing the most technically simple process; however, overall efficiency of energy generated in this process is low (especially for small and micro-scale systems) and the net electricity efficiency generated ranges from 10 % to 20 % (Caputo et al., 2005). Accordingly, the gasification processes can be performed by low-value feedstocks which provide both electricity and heat (Stiegel and Maxwell, 2001). Applications of pyrolysis technologies are known to have limitations in use, due to the difficulties in downstream processing of bio-oil (Wang et al., 2008). Gasification of biomass is a promising technology at the moment and will be in the future.

Through the gasification process, it is possible to convert biomass into a mixture of syngas composed by 10-20 % hydrogen, 15-30 % carbon monoxide, 2–4.5 % methane, 5–15 % carbon dioxide, 45–60 % nitrogen and 6–8 % water vapour. The producer gas, also called syngas, can be easily transported and utilized for several power generation technologies (Allesina et al., 2013; Devi et al., 2003; Kumar et al., 2009; Pedrazzi et al., 2016). The syngas can be used in internal combustion gas engines, gas turbines or as chemical reagents to produce liquid fuels and chemicals (Erich, 2007). The main by-product of the gasification process is a mix of inorganic carbon and ashes called biochar (Lehmann et al., 2006; Lehmann, 2007a, 2007b). Thermal processes have been characterized to enhance the production and quality of the biochar which are more similar to pyrolysis compared to gasification. Even if the gasification process produces lower amounts of biochar than pyrolysis, it is still an important process for biochar production and also utilizes syngas released for power production (Allesina et al., 2014a, 2014b). In addition, the biochar storing in the soil can provide long-term carbon sequestration (Aznar, Caballero, Gil, Martin and Corella, 1998). It has been observed that the soil treated with biochar shows higher characteristics considering the physical, chemical and biological aspects, leading to an increased crop productivity (Lehmann, 2007a, 2007b; Woolf et al., 2010). The biochar has carbon structures which have high chemical recalcitrance and resistance against biological decomposition compared to raw wood biomass. Furthermore, biochars capture the carbon from the atmosphere and transfer it to a slower life cycle (Lehmann et al., 2006). Physical and chemical properties and the amount of biochar depend on the thermochemical conversion parameters and the composition of biomass. The feedstock composition and temperature of the process are two main factors which affect the biochar structures (Enders et al., 2012; Zhao et al., 2013).

In this study, the microalgae *Neochloris oleoabundans* has been used in conjunction with gasification systems to enhance the ways of obtaining renewable and sustainable energy. *N. oleoabundans* is used for the purification of the syngas contaminated water (SCW) as well as providing new biomass yield from microalgae growth by using syngas contaminant together with standard BG_{11} microalgal growth medium (Rippka, 1988) as a feedstock. A 10 kW imbert type downdraft gasifier fueled with wood chips has been used to obtain the syngas for the purification process (Allesina et al., 2015a, 2015b).

A certain amount of the producer gas derived after the biofiltering process is sent to the Water Algae Photo-Bio-Scrubber System (WAPBS): a series of Drechsel trap bottles filled with water was used to clean the gas producing a contaminated liquid called Syngas cleansing water (SCW). At the end of the process char and tar content of the syngas contaminant were used by microalgae and the growth of *N.oleoabundans* have been monitored.

2. Material and methods

2.1. Gasifier process

In this study, an Imbert type downdraft gasifier fueled with wood chips has been used (Allesina et al., 2015b). The producer gas was roughly filtered in a drum filter where wood chips were used as filtering media (Fig. 1). Syngas produced by the gasification was bubbled in a series of 3 Drechsel trap bottles (two of them filled with water) where tar, particulate and condensing water are trapped inside and available as a growth medium for microalgal growth.

In line with the bottles, a G4 (house grade) standard gas meter was used in order to evaluate the volume of the bubbled producer gas. Downstream of the bottles, the syngas was drawn by an engine. Passing through the bottles, the syngas was cooled down, in such a way that tars, condensing water and particulates were trapped in the liquid. Syngas flow through the bottles was regulated to approximately 0.5 Nm^3/h using ball valves. Fig. 2 shows the experimental facility.

2.2. Growth of microalga N. oleoabundans

Three different syngas cleansing water samples (SCW_1, SCW_2, SCW_3**)** were obtained at different syngas bubbling volumes and diluted with BG_{11} microalgal growth medium in three different ratios: 30%, 50% and 70% (Table 1) for a total of 9 different samples (2 replicates), and the pH was adjusted to 7.4 ±0.1.

A 10 mL of concentrated solution of *N. oleoabundans* microalgal cells (1 x 10^6 cell/mL) was diluted with 90 mL of SCW+BG_{11} microalgal growth mediums into glass flasks and the microalgal growth was monitored within 10 days. For the period of 10 days, microalgal cell concentration, growth rate, optical density (OD), pigments content and biovolume of microalgal cells have been monitored. The flasks containing the microalgal cultures were exposed to a photon flux density of 150 µmol m^{-2} s^{-1}, at 26 °C with a dark/light photoperiod of 8/16 h in the incubator.

2.3. Microalgal cell concentration and growth rate

Cell counts of the microalgae strains were performed by using Neubauer haemocytometer (McAteer and Davis, 1994) under the light microscope (Nikon Corporation Instruments Company, Advanced Research Microscope Eclipse 80i, Japan). The microalgae cells have been counted between specific time periods during the experiment and their cell concentrations were calculated (Guillard, 1978). The growth rates of the microalgal strains µ [1/days] were derived from the cell concentration values on the basis of (Eq. 1) (Guillard, 1973):

$$\mu = (\ln W_f - \ln W_i) / \Delta t \qquad (1)$$

where: W_f [cell/mL] is the cell concentration at the end of the growing period; W_i [cell/mL] is the cell concentration at the beginning of the growing period; Δt [days] is the time interval.

2.4. Microalgal cell volume and optical density

The sizes of the microalgal cells of each strain have been measured by the calibrated software of digital imaging microscope systems.

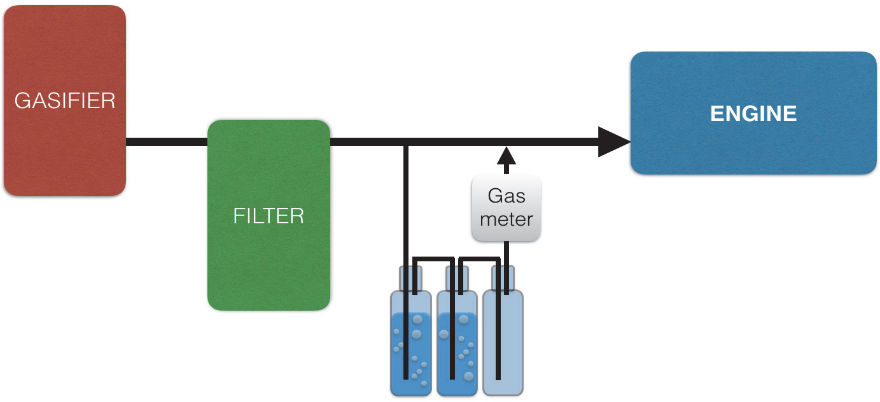


Fig. 1. Experiment layout

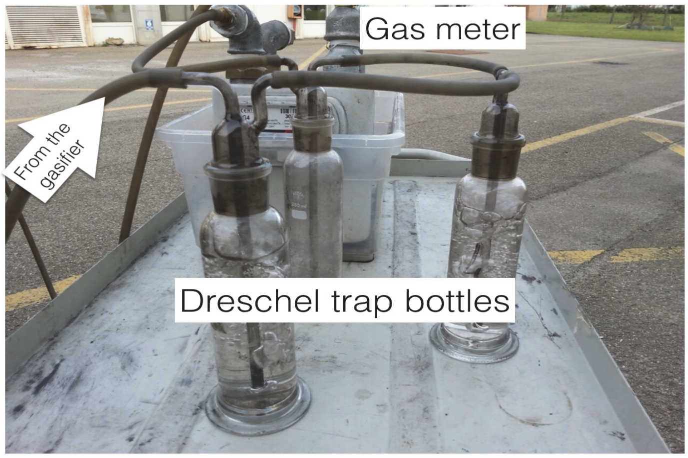


Fig. 2. Experimental facility

Table 1. SCW pollutants and BG_{11} microalgal growth medium proportions

Microalgal Algal Growth Medium	*Diluted Microalgal Growth Medium*	*Syngas Cleansing Water (SCW) (%)*	*BG_{11} (%)*
SCW_1 + BG_{11}	SCW_1-H	70	30
	SCW_1-E	50	50
	SCW_1-L	30	70
SCW_2 + BG_{11}	SCW_2-H	70	30
	SCW_2-E	50	50
	SCW_2-L	30	70
SCW_3 + BG_{11}	SCW_3-H	70	30
	SCW_3-E	50	50
	SCW_3-L	30	70
BG_{11} (Control)	BG_{11}	-	100

Spherical microalgae cells mostly have an approximately similar cell length and width. This fact provides an estimate of one of the unknown dimensions (3rd dimension) of the cell according to measurable two dimensions of the spherical microalgae cells (Sun and Liu, 2003; Verity et al., 1992). During volumetric determination of the spherical microalgal cells, 20 cells were measured from each strain.

The average microalgal cell sizes of the strains have been compared by using their mean values. Consequently, the cell volumes have been calculated by using cell dimensions. The optical density of *N. oleoabundans* supernatant was measured at 665 nm wavelength which is the maximum red light absorption peak in these experimental conditions.

2.5. Analytical determination of photosynthetic pigments content

A certain amount of microalgae cells have been filtered by means of glass microfiber filters (Whatman, GF/C). Photosynthetic pigments of the microalgal cells have been extracted by using 90 % methanol, and supernatants were measured between the absorbance spectrum of 350 – 800 nm via UV-Vis/NIR spectrophotometer (The JASCO V-500/V-600 Series Instruments, Japan).

The analytical determination of chlorophyll a, chlorophyll b and carotenoids (carotene and xanthopylls) was performed at 470 nm, 652.4 nm and 665.2 nm by using UV-Vis/NIR spectrophotometer. The light absorbance value at 750 nm has been subtracted from each of the wavelengths in question (Ritchie, 2006). The formula to determine the pigment content depends on the solvent used for the pigment extraction. In this study, the formula has been used according to methanol solvent (Lichtenthaler and Buschmann, 2001).

2.6. Tar and particle quantification in the syngas cleansing water samples

Solid particles content and tar content in the syngas cleansing water samples without microalgae has been evaluated through gravimetric analysis. First, for the particles evaluation, the samples have been filtered with a filter paper, 3 micron retention, which had been dried overnight at 110°C and weighed (accuracy of ± 0.01 mg). After filtering, the same weighing procedure has been followed to determine the dried particle content. The weight concentration of solid particles in syngas cleansing water has been calculated using Eq. (2):

$$C_p = W_{sp} / V_w \quad (2)$$

where: C_p [mg/mL] is the concentration of solid particles in syngas cleansing water; W_{sp} [mg] the experimental weight of solid particles; V_w [mL] is the volume of analysed water without algae.

Tar components have been then extracted with dichloromethane (purity ≥99%) solution by means of a liquid-liquid extraction using at least 10 aliquots of fresh solvent and a total amount of dichloromethane 2 times the volume of syngas cleansing water. Finally, the mass of tar has been determined with an accuracy of ± 0.1 mg by solvent evaporation at 30°C and 80 mbar. The concentration of tar in syngas cleansing water has been calculated using Eq. (3):

$$C_p = W_t / (V_s \times U_i) \quad (3)$$

where: C_p [mg/mL] is the concentration of solid particles in syngas cleansing water; W_t [mg] the experimental weight of tar; V_s [mL] is the volume of analysed solution; U_i is the volume fraction of SCW in the solution.

At the end of 10 days of microalgal growth, each of the experimental microalgal strains reported in Table 1 was filtered with a 3 micron retention filter paper in order to separate the microalgae from the liquid phase. Tar components have been subsequently extracted with dichloromethane (purity ≥99%) solution through a liquid-liquid extraction by using at least 10 aliquots of fresh solvent and a total amount of dichloromethane 2 times the volume of the water sample. Finally, the mass of tar has been determined with an accuracy of ± 0.1 mg by solvent evaporation at 30°C and 80 mbar. At the end of microalgal growth, the algae inoculum and BG_{11} dilution were taken into account to calculate the tar concentrations of the SCW samples by using Eq. (3).

3. Results and discussion

3.1. Tar and particle quantification

The pollutant content in syngas cleansing water has been analyzed. The syngas volume column reports the volumes of syngas purged into the bottle for every SCW sample. SCW_1 has the highest ratio in terms of pollutants concentration which presents a high amount of tar concentration (661 mg/l) (Table 2).

Table 2. SCW pollutant concentrations before microalgal growth

SCW sample	*Syngas vol.[l]*	*Water vol.[l]*	*Tar conc. [mg/l]*	*Particulate conc. [mg/l]*
SCW_1	750	0.4	611	262
SCW_2	500	0.4	436	175
SCW_3	263	0.3	306	123

Consequently, syngas cleansing water contents led to the optimization of microalgae growth medium for the experimental design.

3.2. Microalgal growth

In this study; the growth of microalga *Neochloris oleoabundans* exposed to syngas cleansing water contaminant and the amount of tar used by the microalgae have been monitored (Fig. 3). According to OD and cell concentration measurements, it is observed that $SCW_{1\text{-}L}$ strain has shown the highest value of OD and cell concentration. The relation between optical density and cell concentration of the strains provide information about the cell size or biovolume. Additionally; to verify the relation between cell concentration and OD, cell sizes have been measured and biovolumes of the strains have been calculated (Fig. 4). The largest biovolumes of the microalgal cells have been observed in the $SCW_{1\text{-}L}$ strain within 10 days' growth. According to this data; the greatest cell size of microalgae *N. oleoabundans* was observed in the SCW_1 algal growth medium.

Biochemical composition of the microalgal cells depends on the cultivation and geographical conditions, while species selection is playing a critical role (Marchetti et al., 2013). The microalgal cell growth, biomass yield, micro and macro metabolites of the microalgae are primarily affected by the growth conditions such as pH, light and temperature (Weiner et al., 2007).

The carbon metabolism of the microalgae is affected by the type of carbon source. The source of carbon can promote physiological changes in the cell of *Chlorella vulgaris* which belongs to Chlorophyta (Green algae) and one of the close species to *N. oleoabundans* in terms of their physiological features. The type of carbon source strongly affects the metabolic pathways of carbon assimilation, size of the cells, volume densities of storage materials, such as starch or lipid grains (Martinez, Ascaso and Orus, 1991) and photosynthetic pigments, proteins, RNA and vitamin contents (Endo et al., 1974).

3.2. Photosynthetic pigment content of *N. oleoabundans*

Photosynthetic pigment content; *Chl a, Chl b, Carotenoid* (carotene and xanthophyll) have been measured (Fig. 5). $SCW_{1\text{-}L}$ strain that contained a 30% concentration of SCW_1 has shown the highest pigment content during the experimental period followed by $SCW_{1\text{-}E}$ and $SCW_{1\text{-}H}$, respectively.

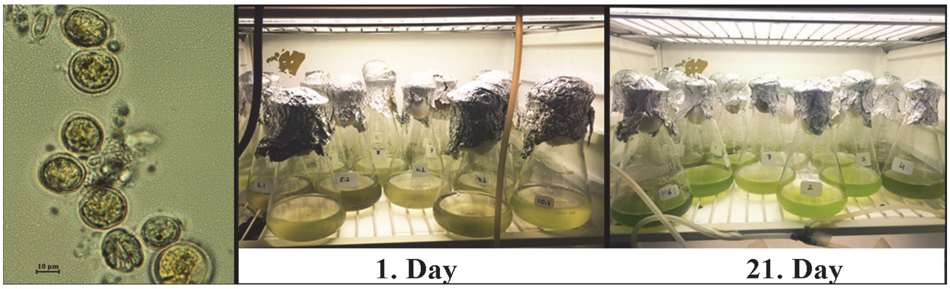


Fig. 3. Photoautotrophic growth of *Neochloris oleoabundans* within 21 days

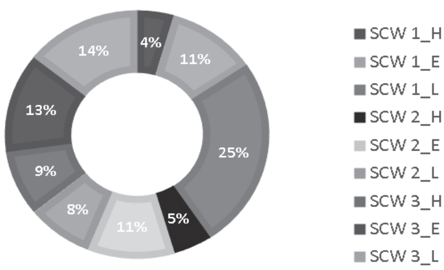


Fig. 4. Total biovolume of the microalgae growth in each sample within 10 days

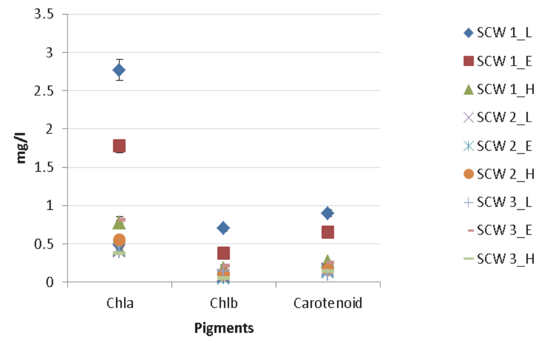
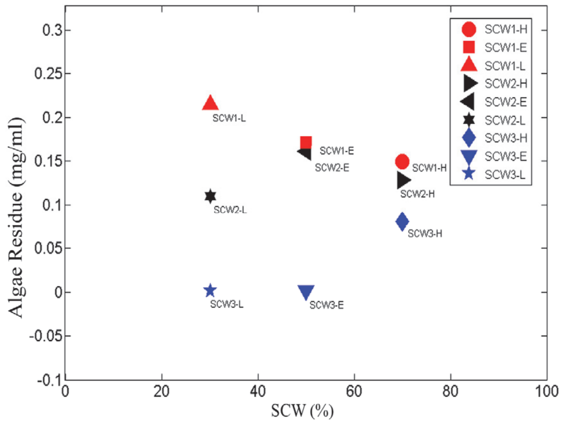


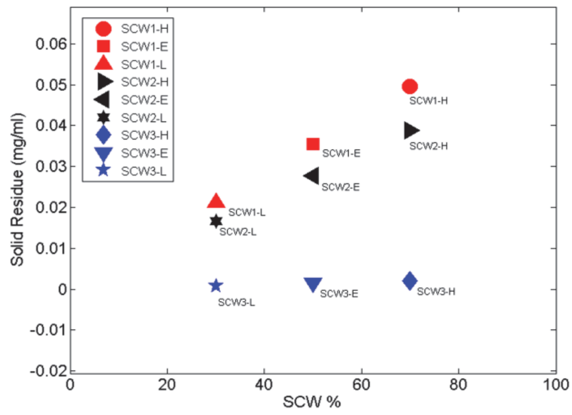
Fig. 5. Photosynthetic pigments content within 10 days

3.3. Tar reduction and algae residue

Fig. 6a depicts the algae solid residue after the growth period. SCW_{1-L} which has the lowest dilution of SCW_1 has shown the largest solid residue of microalgae *N. oleoabundans* (mg/mL) at the end of the bioremediation process.



(a)



(b)

Fig. 6. (a) Algae residue, (b) Tar abatement after bioremediation

Fig. 6b summarizes the tar abatement of each sample within 10 days of microalgal growth. In the SCW_1 samples, the largest amount of tar has been used by microalgae N. oleoabundans as shown in Fig. 6b.

4. Conclusions

The syngas cleansing water samples that contain highest volume of syngas (SCW_1) have been observed to be the most suitable syngas cleansing water for the two major aims of this study: microalgal growth of *N. oleoabundans* and amount of tar removal from the aquatic environment by microalgae bioremediation. The tar amounts of the water samples that contain the highest volume of syngas (SCW_1) are observed to be higher than the tar amounts of second (SCW_2) and third cleansing water samples (SCW_3) as well. This coincides with the volume of gas bubbled in the Drechsel bottles during the gasification process.

Future studies aim to be performed by adjusting the tar amount used by the Water Algae Photo-Bio-Scrubber system to enhance the microalgal biomass efficiency and purification of syngas contaminant. On the other hand, transcriptome analysis in response to the syngas contaminant water will be mandatory to deeply understand these results and to better employ the microalgae's cleansing/purification potential, providing new targets and strategies for bioremediation and/or biofuel production.

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ENVIRONMENTAL IMPACT OF SECOND-GENERATION SUGARS PRODUCTION FROM CARDOON RESIDUES

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Abstract

Biofuels and biochemicals are currently centre stage in the on-going scientific and political debate. The prevalent opinion is that their use can significantly reduce the greenhouse gases (GHGs) emissions and primary energy demand along their whole value chain. This study aims at evaluating the environmental impact in terms of GHGs related to carbon dioxide (CO_2) of second-generation sugars (2GSs) production from cardoon residual biomass. Cardoon is a favourable crop in Mediterranean areas for its adaptation to cold winters and hot summers as well as its abundant yields. 2GSs are essential in the production of bio-BDO, a high-quality intermediate widely used for producing bioplastics. The whole value chain is considered, from cardoon cultivation to 2GSs production. Transport of raw materials from field to biorefinery is also included. The approach followed for the systematic evaluation of the environmental impact is that of the Life Cycle Assessment (LCA). Since the use of sugars is not considered, a *cradle-to-gate* analysis is performed. Data on cardoon cultivation refer to a 3-years field experiment conducted at the ENEA Trisaia Research Centre and concern the use of seeding material, fertilizers, water and fuel. Residual biomass is not the only product derived from cardoon cultivation, hence an energy-based allocation procedure is adopted. Transport of raw materials occurs with a 40 t truck on a reference distance of 30 km. A biorefinery plant for 2GSs production is designed. It treats 60,000 t/y residual biomass and returns almost 20,000 t/y sugars. The sustainability of the value chain is measured in terms of $kgCO_{2eq}$ per kg of 2GSs produced. Primary energy demand is computed. Results show that GHGs emissions associated to 1 kg of produced sugars is equal to 5.33 $kgCO_{2eq}$. The overall installed power amounts to 1,370 kW. As regard electrical and thermal energy, the whole production process demands about 7,890 MWh/y and 191,802 MWh/y respectively. The work falls within the scope of the Rebiochem® Project funded by the Italian Ministry of Education and Research and coordinated by Novamont S.p.A.

Key words: cardoon, biorefinery, LCA

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1. Introduction

In recent time there has been an increasing interest in using renewable raw materials of natural origin in different industrial sectors. In particular, the use of residual biomass has attracted the attention of the emerging biorefinery sector for biofuels and biochemicals production. Biofuels and biochemicals are currently centre stage in the on-going scientific and political debate. They have the potential to replace or sometimes overtake their fossil-based alternatives, opening up new frontiers in the field of bioproducts and, consequently, bioeconomy. The prevalent opinion is that their use can significantly reduce the greenhouse gases (GHGs) emissions and primary energy demand along their whole value chain.

Among all the various available biomasses able to ensure abundant yields in terms of residues, cardoon is considered a favourable crop in Mediterranean areas because of its excellent adaptation to moist and cold winters as well as dry and hot summers (Fernandez et al., 2005; Fernandez et al., 2004). Its yield is also abundant even in water-

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constrained conditions and lands: the harvest is fine when precipitation reaches 450 mm annually. Cardoon requires deep soils with moderate lime content and light texture, better if loamy with a good capacity of retaining water along the soil profile. It grows well in basic soils so that only basic fertilization is needed. The presence of gravel or stones does not affect its growth, even no stony soils are preferable for agricultural operations. In Italy, cardoon has been selected by Novamont S.p.A., the European leader in the production of biodegradable bioplastics, to feed the biorefinery complex Matrìca®, located in Porto Torres (Sardinia, Italy).

This study aims at evaluating the environmental impact in terms of GHGs emissions related to carbon dioxide (CO_2) of second-generation sugars (2GSs) production from cardoon residual biomass. 2GSs are essential in the production of bio-BDO, a high-quality intermediate widely used for producing bioplastics. The whole value chain is considered, from cardoon cultivation to 2GSs production. Transport of raw materials from field to biorefinery is also included.

The approach followed for the systematic evaluation of the environmental impact is that of the Life Cycle Assessment (LCA). Since the use of sugars is not considered, a *cradle-to-gate* analysis is performed. The work falls within the scope of the Rebiochem® Project funded by the Italian Ministry of Education and Research and coordinated by Novamont S.p.A.

2. Materials and methods

A brief description of the LCA methodology and its application to the case study is given hereafter.

2.1. Life Cycle Assessment (LCA)

LCA is a tool for the systematic evaluation of all the environmental aspects that regard a product system through all stages of its life cycle.

The methodology was established in the early 1990s and soon after was adopted and standardised by the International Organisation for Standardisation (ISO). The standard ISO 14040/14044:2006 currently provide a reference with respect to principles, framework and terminology for conducting and reporting LCA studies and are internationally recognised and used.

A typical LCA consists of the four elements: i) Goal and Scope Definition, ii) Inventory Analysis, iii) Impact Assessment and iv) Interpretation.

Goal and Scope Definition describes why and how to use a LCA. During this initial stage decisions are made regarding the definition of the functional unit, system boundaries, allocation procedures, choice of impact categories to be studied and methodology of the impact assessment.

Inventory Analysis quantifies all inputs and outputs of a product system and thus involves data collection and calculation procedures.

Impact Assessment translates the inventory data into contribution to impact categories.

Interpretation is the final step of LCA. Conclusions are drawn from both the Inventory Analysis and Impact Assessment.

LCA is usually used to compare and improve both products and processes. In this study, due to the particular nature of 2GSs, no comparison is made with their fossil-based, non-renewable counterpart.

2.2. Application of the LCA to the case study

2.2.1. Goal and scope definition

The goal of this study is to assess the GHGs emissions associated to the production of 1 kg of 2GSs from cardoon residual biomass. All the steps in the whole value chain are considered. First, cardoon cultivation is analysed. Then, biomass transport from field to biorefinery is modelled.

Finally, processing operations are evaluated. Fig. 1 shows a picture of the system boundaries taken into account. This system boundaries consider any emissions associated with the cultivation, transport and biorefinery phases.

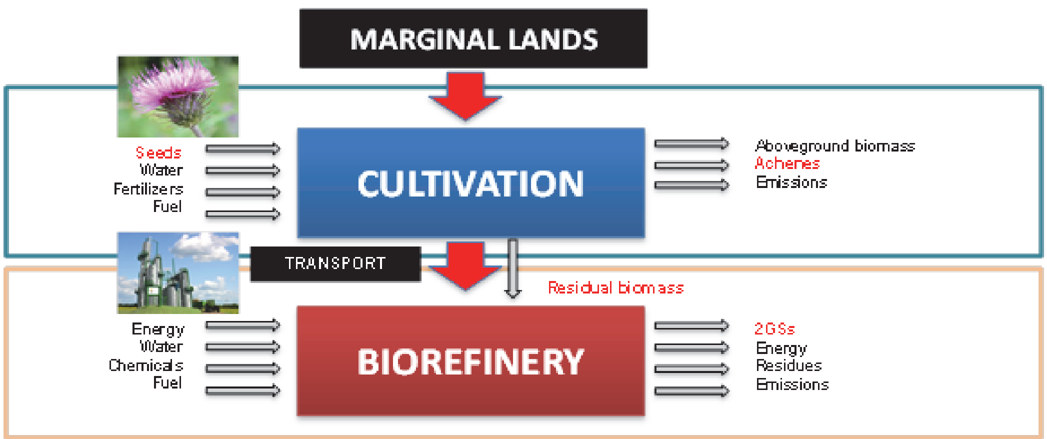

Fig. 1. System boundaries

LCA follows a *cradle-to-gate* approach (Cambria et al., 2016; Cherubini and Jungmeier, 2010; Ghinea et al., 2014). The GHGs emissions are calculated using the formula outlined in the Renewable Energy Directive (RED) (Alberici and Hamelinck, 2010; Buratti et al., 2010). Land-use change and N_2O field emissions are also included. Emissions from the manufacture of machinery and equipment are computed (Uihlein et al., 2009; Weiss et al., 2012; Wernet et al., 2009). The GHGs emissions calculation formula (Eq. 1) are detailed below:

$$E = e_c + e_t + e_p \tag{1}$$

where: E = total GHGs emissions
e_c = emissions from cultivation
e_t = emissions from transport
e_p = emissions from biorefinery

Since cardoon cultivation produces co-products (achenes from which it is possible to extract oil), GHGs emissions are allocated on an energy content basis.

2.2.2. Inventory analysis

Data on cardoon cultivation refer to a 3-years field experiment conducted at the ENEA Trisaia Research Centre and concern the use of seeding material, fertilizers, water and fuel. At the end of the third year, a yield of 12.9 t/ha aboveground biomass is obtained in standard non-irrigated conditions, corresponding to 9,675 t/ha residual biomass (moisture 17.3% and LHV 15.8 MJ/kg). The list of all cultivation parameter inputs is given in Table 1.

Table 1. Cultivation parameter inputs

Parameter	***Input***	***Units***
Seeding material		
Seeds	5	kg/ha
Agrochemicals		
N-fertilizer	200	kg/ha
P_2O_5-fertilizer	100	kg/ha
K_2O-fertilizer	200	kg/ha
Fuel		
Diesel	41.8	kg/ha
Field N_2O emissions		
N-fertiliser	200	kg/ha
Soil Organic Carbon (SOC)		
SOC change	3.4	tC/ha

For the purposes of this study, a land area of 1 ha at the ENEA Trisaia Research Centre is considered. Typical farming techniques of the Mediterranean regions are applied. First, ploughing and harrowing are practiced. Then, 5 kg of seeds are used for seeding. Fertilization (N: 200 kg/ha; P_2O_5: 100 kg/ha; K_2O: 200 kg/ha) and harvesting are done after planting.

Diesel consumption is directly measured. Primary data are available for all the inputs linked to the cardoon cultivation phase. Additional fertilization and harvesting are carried out for more two years. The third year is chosen as a reference. The IPCC methodology is employed for calculating N_2O direct and indirect emissions. Soil Organic Carbon (SOC) is also computed. Biomass residues are transported by road to biorefinery. Transport parameter inputs are given by the round-trip distance travelled and truck chosen (Table 2).

Table 2. Transport parameter inputs

Parameter	***Input***	***Units***
Distance (round-trip)	30	km
Truck	40	t

Biorefinery layout is designed. Considering the actual availability of cardoon biomass in Italy, a medium size of 60,000 t/y residual biomass is considered. This value corresponds to 20,000 t/y approximately. The process layout is given below (Fig. 2).

It includes, among others, the main technologies being researched at ENEA Trisaia Research Centre: pre-treatment via steam explosion and enzymatic hydrolysis, above all. Modules design and integration is developed thanks to the ENEA expertise (De Bari et al., 2008), references documents, bench-scale data and manufacturers information (CTI, 2007; Kadam et al., 1999; Pizzichini et al., 2009; Voitkevich et al., 2012). Energy recovery system is not considered. Biorefinery parameter inputs correspond to the main mass and energy streams.

2.2.3. Impact Assessment

The GHGs emissions related of second-generation sugars from cardoon are calculated by multiplying all the *inputs* by pre-determined *emission factors*, also known as standard values.

2.2.4. Interpretation

Interpretation of results is given on the basis of emissions savings and primary energy demand reduction. Amongst all the strategies, the adoption of improved agricultural practices, the reduction of the fuel use or the optimization of energy recovery systems and wastewater treatment units can be considered.

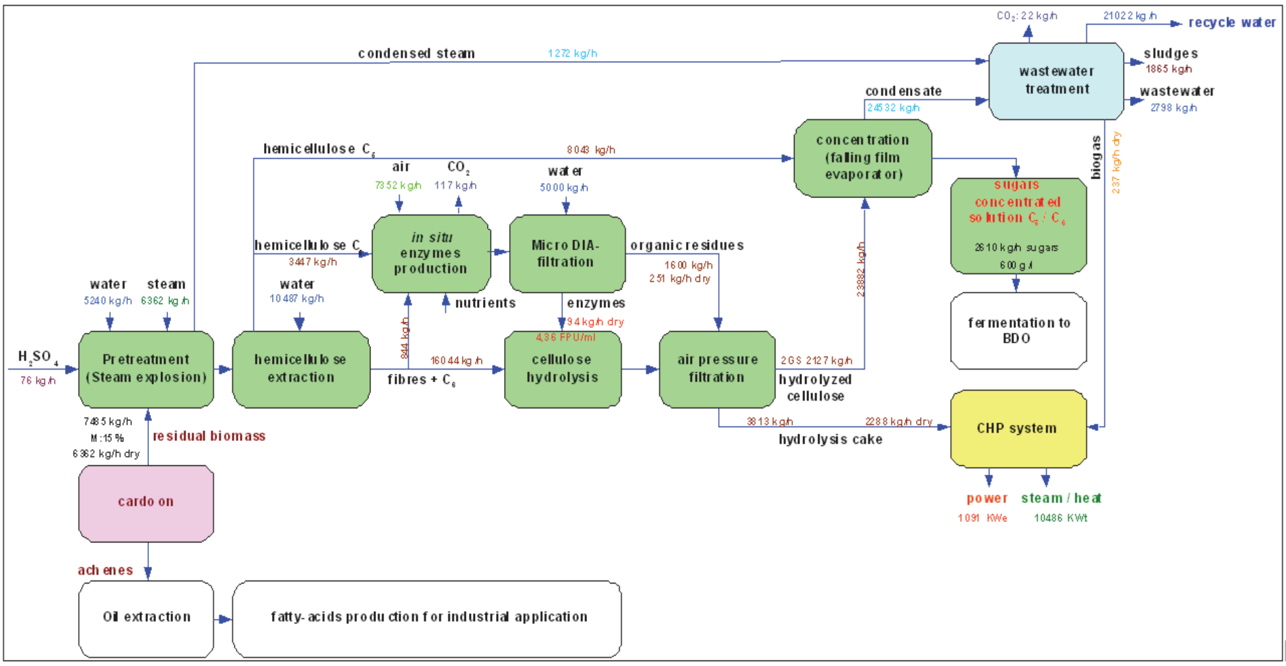

Fig. 2. Biorefinery plant

3. Results and discussions

3.1. Calculation of GHGs emissions per phase

The calculation of GHGs emissions per phase is reported in Table 3.

3.1.1. Cultivation

For that it concerns cultivation, the emissions related to 1 ha of cultivated land are equal to 2,795.47 $kgCO_{2eq}$. If considering a yield of 9,675 t/ha residual biomass, the emissions related to 1 kg residual biomass are 0.29 $kgCO_{2eq}/kg_{residual\ biomass}$, corresponding to 0.87 $kgCO_{2eq}$ per kg of produced sugars (kg_{2GSs}). The allocation parameter based on the energy content is equal to 0.83.

3.1.2. Transport

The emissions related to transport are computed on a reference distance of 30 km (round-trip) with a 40 t truck (27 t payload). Transport emission coefficient is given by multiplying transport efficiency (0.94 MJ/t, km) and fuel emission factor (0.087 $kgCO_{2eq}$/MJ). It returns a value of 2.47 $kgCO_{2eq}$ GHGs emissions for tonnes of transported residues, corresponding to 0.007 $kgCO_{2eq}/kg_{2GSs}$.

3.1.3. Biorefinery

Biorefinery phase contributes to GHGs emissions for 4.45 $kgCO_{2eq}/kg_{2GSs}$.

3.2. Electric and thermal energy demand

As aforementioned, biorefinery operations are designed for a reference plant size of 60,000 t/y residual biomass (corresponding to 20,000 t/y produced sugars with a concentration of 600 g/l). Process layout includes pre-treatment via *steam explosion*, hemicellulose extraction, enzymes production, micro/ultra-filtration, wastewater treatment, cellulose hydrolysis, filtration, energy recovery and concentration.

Table 3. Output values

Phase	*Output*	*Units*
Cultivation		
N-fertilizer	1,176.12	$kgCO_{2eq}$/ha
P2O5-fertilizer	101.07	$kgCO_{2eq}$/ha
K2O-fertilizer	115.22	$kgCO_{2eq}$/ha
Diesel	157.89	$kgCO_{2eq}$/ha
Direct N_2O emissions	930.28	$kgCO_{2eq}$/ha
Indirect N_2O emissions	302.34	$kgCO_{2eq}$/ha
SOC change	12.46	$kgCO_{2eq}$/ha
Total GHG emissions with allocation	**0.87**	$\mathbf{kgCO_{2eq}/kg_{2GSs}}$
Transport		
Total GHG emissions	**0.007**	$\mathbf{kgCO_{2eq}/kg_{2GSs}}$
Biorefinery		
Pre-treatment	952.25	$kgCO_{2eq}/t_{2GSs}$
Hemicellulose extraction	125.64	$kgCO_{2eq}/t_{2GSs}$
Enzymes production	49.70	$kgCO_{2eq}/t_{2GSs}$
Micro/Ultra-filtration	4.30	$kgCO_{2eq}/t_{2GSs}$
Wastewater treatment	16.60	$kgCO_{2eq}/t_{2GSs}$
Cellulose hydrolisis	20.21	$kgCO_{2eq}/t_{2GSs}$
Filtration (*Pneumapress*)	140.71	$kgCO_{2eq}/t_{2GSs}$
Concentration	3141.37	$kgCO_{2eq}/t_{2GSs}$
Total GHG emissions	**4.45**	$\mathbf{kgCO_{2eq}/kg_{2GSs}}$

The overall power demand for the whole sugars production process (energy recovery system excluded) results as 7,890 MWh/y, whose distribution among the different process steps is reported in Fig. 3. The overall installed power amounts to 1,370 kW. As regard thermal energy, the whole production process demands about 191,802

MWh/y, distributed as reported in the following chart (Fig. 4).

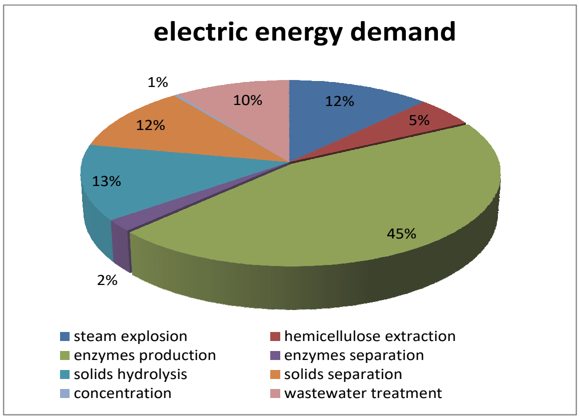

Fig. 3. Electric energy demand

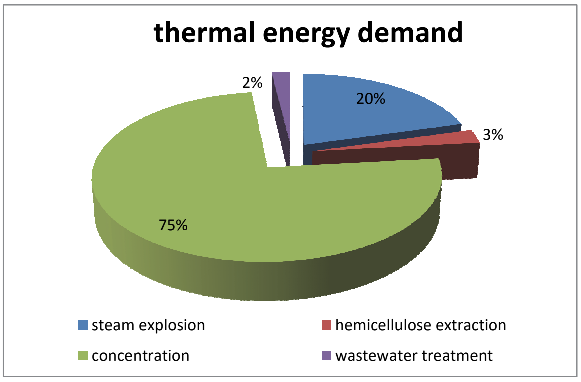

Fig. 4. Thermal energy demand

4. Conclusions

The environmental impact of second-generation sugars (2GSs) production from cardoon residual biomass is analysed. It is given in terms of GHGs emissions related to carbon dioxide (CO_2) whose effects on global warming are reported as the amount (kg) of CO_2 equivalent ($kgCO_{2eq}$) per kg of produced sugars ($kgCO_{2eq}/kg_{2GSs}$). The whole value chain is considered, from cardoon cultivation to 2GSs production.

Transport of raw materials from field to biorefinery is also included. The approach followed for the systematic evaluation of the environmental impact is that of the Life Cycle Assessment (LCA). Since the use of sugars is not considered, a *cradle-to-gate* analysis is performed. Data on cardoon cultivation refer to a 3-years field experiment conducted at the ENEA Trisaia Research Centre and concern the use seeding material, fertilizers, water and fuel.

An energy-based allocation procedure is adopted. Transport of raw materials occurs with a 40 t truck on a reference distance of 30 km. A biorefinery scheme for 2GSs production is designed. It elaborates 60,000 t/y of residues and gives back almost 20,000 t/y of sugars (with a concentration of 600 g/l). The sustainability of the whole value chain is measured. It is equal to 5.33 $kgCO_{2eq}/kg_{2GSs}$. Cultivation and biorefinery have the greatest environmental impact. The overall installed power amounts to 1,370 kW. As regard electrical and thermal energy, the whole production process demands about 7,890 MWh/y and 191,802 MWh/y respectively. The energy and environmental loads referred to the case study do not consider any optimization strategy, neither for cultivation nor for biorefinery (i.e. reuse of process water, energy recovery systems).

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CO-DESIGN FOR A CIRCULAR APPROACH IN GREEN TECHNOLOGIES: ADAPTATION OF REUSED BUILDING MATERIAL AS GROWING SUBSTRATE FOR SOILLESS CULTIVATION OF LETTUCE (*Lactuca sativa* var. *capitata*)

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Abstract

Improving the awareness of the responsibility of our actions is the basis of achieving the ambitious aim of waste management and prevention established by the European Waste Framework Directive 2008/98/CE and the most recent Circular Economy Package. Circular Economy is connected both to improve manufacturing technologies and also educate people towards responsible consumption and waste reduction. Due to its educational and institutional role, universities provide a context to rethink not only at our technological system through the adoption of eco-innovation, but also to reconsider the entire system of our values through the education of the society in many aspects of sustainability. Most sustainability education courses co-generate knowledge in an explorative way through inter- and trans-disciplinary methodologies. A Living-lab of sustainability called Terracini in Transizione is ongoing at the School of Engineering and Architecture of University of Bologna. This Living-lab offers new opportunities and useful feedback to research and teaching, as well as contributing to the engagement of engineering students. As a result of the Living-lab, various experimental green technologies for Urban Resilience have been co-designed by students, researchers and professors. In order to strengthen the sustainability of the proposed solutions, some of them are being constructed using recycled materials. The aim is to close the cycle of utilized materials, and the hereby presented experiment focuses on testing the water and rooting capacity of innovative recycled materials as substrates for edible plants cultivation in innovative green technologies (e.g. soilless cultivation). Tested substrates include a control (mix of perlite-vermiculite) and recycled substrates, either made of crushed plasterboard panels, synthetic wadding or panels of rockwool. The present study addresses the definition of the hydraulic properties of the substrates and their effect on the yield of hydroponically grown lettuce (*Lactuca sativa*).

Key words: circular approach, green technologies, lettuce, soilless growing, waste and water management

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1. Introduction

1.1. Circular economy and resources use: addressing green technologies and education at the Living-Lab of Terracini in Transizione

Waste management and prevention can be considered a key factor in sustainability: reducing the amount of waste and its hazardousness by both avoiding the presence of dangerous substances in products and improving the sustainable production

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and consumption. This will result in more virtuous environmental and economic behaviors (Mihajlov and Stevanović-Čarapina, 2015).

According to the European Union's approach on waste management (EC, 2008), a priority is given to the minimization of waste production, the reusal of goods at their end of life, as well as the recycling to other forms of recovery to reduce the final disposal. Recently, the European Commission adopted the ambitious Circular Economy Package "Closing the loop - EU action plan for the Circular Economy" (EC, 2015). "Closing the loop" consists of a real action plan with measures covering the whole product cycle: from production and consumption to waste management and the market for secondary raw materials. The aim is to stimulate the transition towards "continuous positive development cycles that preserve and enhance natural capital, optimize resource yields, and minimize system risks" (Ellen MacArthur Foundation, 2012). Three are the principles of circular economy:

- Preserve and enhance natural capital by controlling finite stock and balancing renewable resource flows.
- Optimize resource yields by circulating products, components, and materials at the highest utility at all times in both technical and biological cycles.
- Foster system effectiveness by revealing and designing out negative externalities.

The circular approach will contribute to "closing the loop" of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy. Circular economy approach is regenerative by design and aims to keep products, components and materials at their highest utility and value at all times, distinguishing between technical and biological cycles. With cost-efficient, better-quality collection and treatment systems, and effective segmentation of end-of-life products, the leakage of materials out of the system will decrease, supporting the economics of circular design. An example of nature-based solutions for urban planning and building design strategies are Green Technologies. They allow cities to increase their abilities to better respond and adapt to the economic, social, and physical stresses they will face as they confront the challenges of increasing energy scarcity, climate change, and population change. Green roofs, green streets, and vegetated walls help cities to adapt and mitigate the effects of climate change, achieve environmental benefits, enrich architecture and life quality, improving the microclimate, the valorization of natural capital, water cycle, water and resources saving, pollutants and air particulate capture (Bonoli et al., 2013a).

Another key principle of circular economy is education. Actually, the Ellen MacArthur Foundation report (2012) states: "Education can play an important role in preparing future professionals for a new economic paradigm, particularly to create the skill base to drive circular innovation. Governments should encourage the integration of circular economy into school and university curriculums".

Actually education can generate unique insights into creating innovative solutions that are driven by environmental sustainability (Martinez, 2014). According to UNEP (2014), enhancing the participation allows the achievement of more sustainable results and the user engagement can allow making a direct experience of green, resource-efficient and low carbon campuses. Also the International Sustainable Campus Network Guidelines comprise among their basic principles: "the alignment of the organization's core mission with sustainable development: facilities, research, and education should be linked to create a "living laboratory" for sustainability" (ISCN-GULF, 2010). A case of participatory process implemented into an educational context is Terracini in Transition. In particular, a "living laboratory of sustainability" has been created in Unibo Terracini Campus for the promotion and implementation of best management practices of natural resources as energy and water, waste reduction and recycling (Bonoli et al., 2013b; Cappellaro and Bonoli, 2014).

Adopting a "living-lab" approach, Terracini campus students were involved in some practical and educational laboratories aimed at the design of sustainable initiatives (Cappellaro, 2015). The scope was not only to improve the sustainability performances of the campus but also to foster the awareness of the university community (Rizzo et al., 2015). This paper proposes the experimentation conducted within one of the different innovative circular projects with the involvement of students, researchers and teachers of Univeristy of Bologna, Unibo. Accordingly, concrete actions were carried out, with the aim to apply circular approaches in green tecnology, expecially experimenting recycled materials for substrate and soil amendment, including the realization of a soilless growing infrastructure within the university premises. Green technologies and practices reproduce natural processes by the use of natural or engineered systems. The effect is to improve the whole environmental quality and simultaneously to offer utility services. Within a green infrastructure, main elements include the vegetation and the growing substrate, whose water relations are interconnected by way of infiltration, evapotranspiration and/or recycling of storm water runoff. Green infrastructures may be independent from natural soil, and this is the case of hydroponics or soilless growing, which is defined as a cultivation system which is implemented without the use of the soil and which provides for the use of water as a vehicle of nutrients (Pasotti et al., 2006). In such systems, appropriate nutrient and water management become crucial to ensure cultivation success.

1.2. Water management in green infrastructures

The volume of water and air within the substrates are two important parameters for a growing medium. The water needs to be available at the lowest energy state possible and adequate air percentage must be guaranteed to the roots. However, these two parameters are antagonistic in the rhizosphere: if all the pores are filled with water, there is a lack of air and vice versa (Hartmann and De Boodt., 1974). The Field Capacity (FC) is an important parameter in soilless growing. FC is the amount of water that is retained in a certain volume of a substrate at the end of the drainage. After drainage, the next more relevant loss of water from the plant-soil system is generally associated with evapotranspiration. Indeed, not all the water within the substrate is equally available to the plant: once drainage water is removed, the remaining water becomes gradually less absorbable by roots in function of the relative percentage and by the physical characteristics of the substrate (Da Silva et al., 1993; Hartmann and De Boodt, 1974).

1.3. Scope of the research

This paper explores the possibility of integration of a circular approach and innovative green technology solutions, through the adoption of recycled engineering materials (e.g. thermal or phono-absorbent materials) as growing substrates for the hydroponic cultivation of lettuce (*Lactuca sativa*). Within the research, both the hydrologic properties of the studied substrates and the agronomical performances of lettuce plants will be described.

2. Case studies

2.1. Implementation of soilless cultivation system using substrates deriving from industrial waste: agronomical and physiological implications

At the greenhouses of the Department of Agricultural Sciences were conducted a series of experiments aimed to analyze the possibility to use a variety of industrial wastes as substrates for plants growing in soilless systems.

An experimental station composed by a soilless growing system and close loop irrigation to monitor supply of water and fertilizers was used (Fig 1). Parameters of food production, water managements, aesthetic performances such as leaf area development and color were evaluated in two independent experiments.

2.2. Experiment 1: Hydrological properties of innovative substrates for plant cultivation

During the experiment 1, different materials were tested as growing medium:

- A mix of perlite-vermiculite in equal volume ratio was chosen as control due the common utilization in soilless growing, in measure of 150±5 grams of substrate (perlite-vermiculite 50:50) per pot.

- Plasterboard panel: a portion of 1.2 x 2 m with thickness 13 mm and density of 795 kg m^{-3} was shattered into pieces smaller than 10 mm in diameter. The pasteboard fragments were then screened using sieves of 20, 8, 4, 2 and 1 mm in order to separate these five classes. Each granulometric class was added in equal proportion to each pot to obtain a dry weight of 350±10 grams.

- Synthetic wadding with a density of 110g m^3. In each pot, 41 grams of synthetic wadding were placed.

- Panels of rockwool derived by used sound and thermic adsorbent panels were comminuted in portions to be placed within the pots. In each pot, 55 grams of rockwool were used as substrate.

Humidity and electric conductivity were measured with GS3 EC/humidity sensors and collected with Em50 datalogger (Decagon Device, WA, USA). GS3 were previously calibrated for each substrate correlating the weight of the pots with water at field capacity until complete drying with measures acquired at intervals of one hour. Calibration was repeated 3 times per 15 hours in each experimental replicate.

Fig. 1. Experimental soilless growing system used to test different substrates

2.3 Experiment 2: Lettuce performances on soilless cultures using innovative substrates

For the experiment 2, sixteen pots per each substrate were used (Fig. 1). Plants of lettuce *Lactuca sativa* var. *capitata*. were transplanted at the age of three leaves within the pots (15 days after germination). Pots had both height and diameter of 8 cm.

Fertigation was guaranteed through a close hydroponic system. Drippers were placed in all pots in order to supply the same amount of water and nutrients to all the plants. Each of the four blocks was composed by 16 pots and was fertigated with separated hydroponic systems in order to monitor water and nutrients use. Water was supplied with a hydraulic pump (Syncra Silent 1.5, Sicce, Pozzoleone, VI, Italy) immersed in 40-liters water tanks. A half-strength Hoagland solution was used for plant nutrition (Hoagland and Arnon, 1950).

The acquired data were used to set the irrigation, maintaining humidity between 100-65% of the field capacity to improve the physiological condition (Gallardo et al., 1996) and avoid the accumulation of salts (Savvas et al., 2007).

Values of pH were measured at harvesting time from the water tank of each close hydroponic system in order to analyze the effect of different substrate, taking in consideration that for soilless growing the optimum range for lettuce is between 6 and 7 pH (Brechner and Both, 2016).

Measured conducted on the plants included leaf area index (LAI), leaf color, leaf greenness and biomass production at harvest. Image analysis were conducted in homogeny condition of distance and light within a light-box lighted with cool-white LED lamps. The pictures were acquired with a digital camera Canon EOS 350D set at f/6.3 and exposition of 1/100s. Aesthetic parameters of LAI and color were then measured with the software APS ASSESS 2.0 (Analysis software for plant disease quantification, American Pathological Society). Leaf greenness was measured using a N-tester (Yara, Oslo, Norway)

3. Results

3.1. Hydrological properties of studied substrates

The substrate constituted by rockwool showed an abundant percentage of humidity retained in the medium and a constant drainage (20%) throughout the test period (Fig. 2).

PET showed similar water retention to rockwool and reached in a few hour the field capacity condition with a water loss among the 12 hour measurements of 10%. The plasterboard showed a low water retention and slow drain that reduced the water content of only 4% after field capacity. The control showed a similar FC to the plasterboard but higher humidity content among the analysis period.

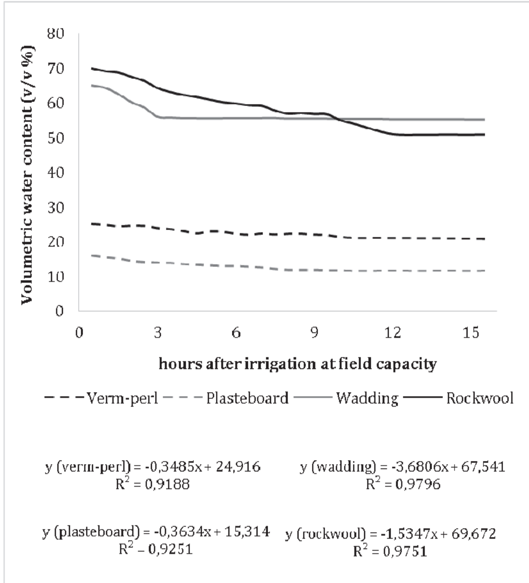

Fig. 2. Average water content in pots with the four substrates measured without the plants

Analysis of the pH revealed that control substrates maintained a properly range of value 6.81±0.13 (b), as well as plasterboard that given lightly alkaline values 6.26±0,10 (c), while synthetic wading and rockwool increased the acidity with values respectively of 7.40±0.06 (a) and 7.35±0.15(a) (data not shown). Considering that the optimum pH values for hydroponic growing are slightly alkaline (pH 6, Brecher and Both 2016), the mix of perlite-vermiculite was considered acceptable as control substrate for the next experiment.

The data at harvesting time showed significant differences for most of the measured data. As showed in Figs. 3 and 4, the biomass produced in substrate from plasterboard panel given similar yield from control vermicule-perlite, while wadding and rockwool produced progressively lower edible biomass of lettuce. Root: shoot ratios revealed higher values in control and synthetic wadding while in rockwool and plasteboard root had the same lower development.

5. Discussions

Based on the results acquired during the agronomical tests it is possible to state that the different industrial waste used as substrates have induced significant differences on most of the principal parameters taken in consideration. The vermiculte-perlite used as control confirmed its attitude to be used for soilless farming showing the major productive and aesthetic performances (Brecher and Both 2016; Znidarcic, 2016). Among the substrates tested as industrial waste, the plasteboard and rockwool had the most performing results.

In particular, plasterboard and rockwool reveal both a good possibility to promote leaf greenness (associated with chlorophyll biosynthesis and nitrogen assimilation) in lettuce altogether with a lower root: shoot ratio, which are both associated with the absence of stressful conditions (Fallovo et al., 2009).

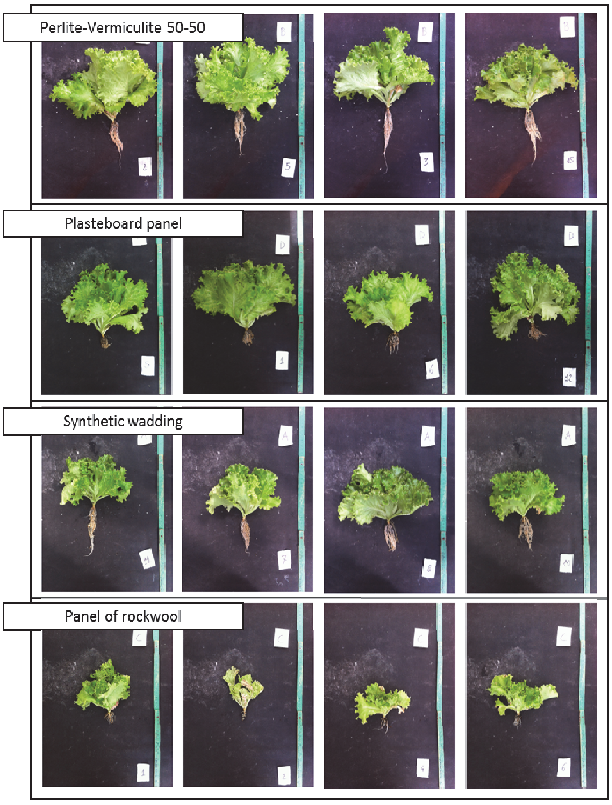

Fig. 3. Lettuce at harvesting time at 36 DAT. Pictures acquired within light-box at homogeneous lighting conditions. Different experimental substrates are divided per raws

Lettuces are often marketed by single head rather than solely by individual weight, therefore both parameters (fresh weight and leaf area), are determinant in affecting the potential rentability of the species (Cook, 2011). Accordingly, while rockwool (a substrate that already finds application in hydroponic cultivation, Benko et al., 2008) promoted edible biomass production similarly to the control, whereas highest leaf area was associated with plasteboard. On the other hand, wadding showed a net inadequacy to be used as cultivation substrate, as evidenced by the extremely limited yield and leaf area obtained.

6. Conclusions

Enhancing the participation allows the achievement of more sustainable results in the direction of waste management, environmental preservation and sustainability. The re-utilisation of building material as growing substrates for plant cultivation is hereby suggested as a strategy for limiting industrial waste production. According to the presented results, both insulating rockwool and plasterboard may be efficiently used for lettuce cultivation overall providing satisfactory results respectively in terms of yield or leaf area.

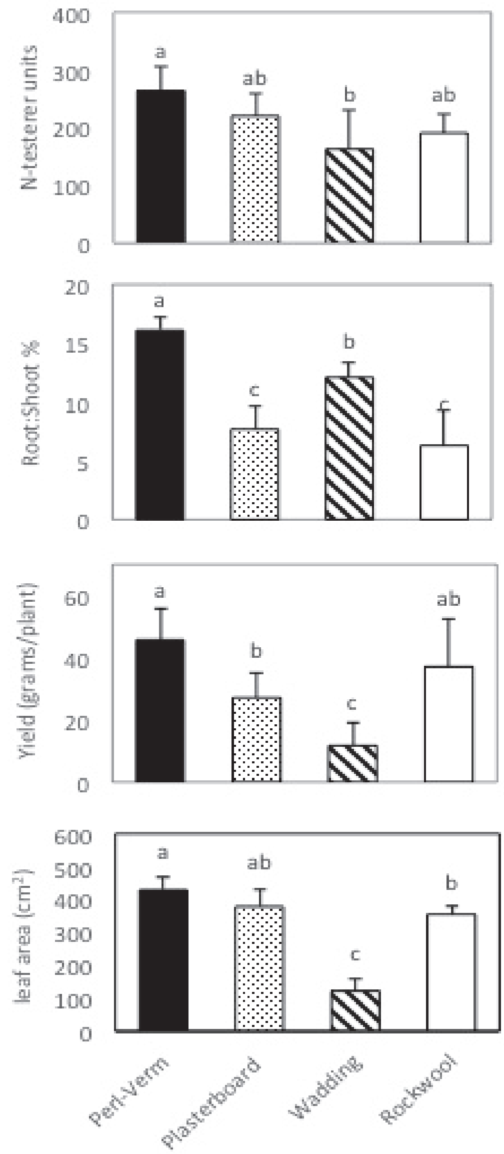

Fig. 4. (A)Leaf greenness (N-tester units, (B) Root: shoot ratio (as % of dry weight,), (C) Yield (g plant^{-1}), (D) leaf area (cm^2 plant^{-1},). Mean values (n=16) at harvesting time (36 days after transplanting). ±SE. Different letters indicate significant differences at P≤0.05

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CARBON FOOTPRINT OF MUNICIPAL SOLID WASTE COLLECTION IN THE TREVISO AREA (ITALY)

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Abstract

Carbon Footprint (CF) is an environmental indicator used in Life Cycle Assessment (LCA) that allows measuring the total amount of CO_2 emissions caused directly or indirectly by an activity or accumulated through the life cycle stages of a product (ISO 14064-14067).
In this article CF was used to analyse and assess the environmental impacts of the resources used for the collection of municipal solid waste by the company Contarina S.p.A. Contarina oversees waste management for part of the Treviso province (Italy), serving about 260,000 appliances in 50 municipalities distributed in the territory.
The presented case study assessed CF of year 2015 related the whole fleet involved in door-to-door collection of municipal solid waste without taking into account treatment processes. In addition, a future scenario, in which part of the current fleet is replaced by compressed natural gas engine (CNG) based vehicles, was assessed and compared to the current status. The CF was performed by adapting the SimaPro software from PRè, one of the most widely used LCA software since the nineties, by introducing fuel based analysis and creating CNG lorries. The analysis aimed at improving sustainability of Contarina's services while fostering an informed development and testing of new technologies aimed at reducing its overall greenhouse gas emissions.

Key words: carbon footprint, transport, waste management, sustainability

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1. Introduction

Solid waste management (SWM) is a complex process composed by various components among which waste collection is one of the main contributors as far as costs and environmental emissions (Chalkias and Lasaridi, 2009; Schiopu and Gavrilescu, 2010). According to Chalkias and Lasaridi (2009) waste collection contributes up to 40% of total costs of municipal SWM regardless variations due to location, labor costs, population and population density while, as far as emissions, those from waste collection vehicles are the most predominant in SWM systems due to their fuel-intensive nature. Focusing the analysis on the collection process is therefore necessary in order to develop sustainable waste management systems able to minimize environmental emissions in a cost-effective way (NREL, 1995).

Among the tools currently available to evaluate the environmental emissions' impact of waste collection, the Carbon Footprint (CF) is constantly gaining more and more attention (Bamonti et al., 2016; Pandey et al., 2011). Wiedmann and Minx (2008) defined CF as a measure of the exclusive total amount of carbon dioxide emissions that is directly and indirectly caused by an activity or is accumulated over the life stages of a product, conceptually being a global warming potential indicator. CF is one of the instruments which are

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currently used for sustainability assessment, it also corresponds to the "Global warming" impact category in Life Cycle Assessment (LCA) which aims at evaluating environmental impacts due to development, use and disposal of goods and services (Ghinea et al., 2014; ISO, 2006a).

All Greenhouse Gases (GHG) included in the Kyoto protocol (ISO, 2006b) are considered as part of CF: Carbon dioxide (CO_2), Methane (CH_4), Nitrous Oxide (N_2O), Hydrofluorocarbons group (HFC_s), Perfluorocarbons group (PFC_s) and Sulfur hexafluoride (SF_6). All those gasses are mainly generated by energy processes; among all CO_2 is the major contributor to the greenhouse effect because of the amount annually produced (WRI/WBCSD, 2004) and for this reason it was decided to adopt the kilogram of CO_2 equivalent ($kgCO_{2eq}$) as CF's unit of measure (Franchetti and Apul, 2013) as also one of the common practice with other carbon footprint measures and tools (Bacenetti and Fiala, 2016).

CO_{2eq} is obtained by multiplying emissions of the different GHG by their Global Warming Potential (GWP) (ISO, 2006b) which represents the ratio between warming produced by the gas in a specific time frame (usually 100 years) and warming produced in the same period by the same mass of CO_2 (ISO, 2006b). It represents the contributions caused by all gases to the overall greenhouse effect including both the radiation characteristics of the gaseous molecules (i.e. to the diverse ability to absorb different wavelengths of solar radiation and specifically, infrared radiation) and their time of persistence in the atmosphere (Franchetti and Apul, 2013). A generic model for assessing the waste collection process CF on the basis of distance or customer number demonstrated not to be feasible due to the limited amount of information regarding vehicles' fuel consumption and operating conditions as well as the infinitely many different working environments and conditions (Agar et al., 2007). While consistent efforts have been performed in characterizing waste collection processes as reported in (Farzaneh et al., 2009; Ivanič, 2007; Sandhu et al., 2014; Sandhu et al., 2016), the multifaced nature of the system consisting in different lorries fleets, route conditions, house density and dumping systems imposes case specific assessments and characterizations (Agar et al., 2007). Even though the Waste tool developed by the Universita Autonoma de Barcelona (Sevigné Itoiz et al., 2013) could have been a feasible solution, the authors decided to perform anyway a specific assessment by adopting one of the most widely used LCA software (i.e. SimaPro) to obtain more precise results.

The objective of this study was to establish the annual environmental impact, by means of CF, of the solid waste collection process of Contarina S.p.A. in the province of Treviso, Italy, and to investigate its possible reduction by simulating a hypothetical scenario where most of the door-to-door service vehicles is turned from Diesel to Compressed Natural Gas (CNG) powered engines.

2. Case studies

2.1. Description

Contarina S.p.A. is a municipally participated company (i.e. a company in which the municipality is a shareholder) in charge of waste collection, management and disposal for part of the Treviso province, including the Municipality of Treviso. The managed area is about 1300 square meters with a population of nearly 554000 inhabitants served by different vehicles' typologies according to the peculiarities of their residential areas. The door-to-door service spreads among 50 municipalities summing up to more than 260000 households.

Door-to-door waste collection follows a schedule which allows collecting all different waste typologies like non-recyclable, wet, glass/plastic/cans, vegetable, paper and cardboard (Artuso et al., 2015). Different color coded bins are exposed by inhabitants following the predefined daily schedule which are collected by means of specific vehicles selected on the basis of route characteristics (e.g. route width and population density). Routes are optimized in order to avoid the paradox where waste transportation for recycling impacts more than avoiding recycling at all (Salhofer et al., 2007). Although Treviso is one of the municipalities with higher pro-capita income in the Veneto region, its waste production is the lowest among those having similar pro-capita income in Italy. Municipality of Treviso has been subdivided into three zones: Zone 1: Old town (inside the historic walls), Zone 2: Treviso city center (outside the old city walls) and Zone 3: Suburban area outside Treviso, called urban belt. Zone 1 also embeds historical centers of other municipalities such as Castelfranco Veneto, Montebelluna ed Asolo where waste collection frequency is higher due to reduced bins' size (Cuccu et al., 2015).

In order to establish the GHG emissions impact of door-to-door solid waste collection in the area of Treviso, CF assessment was performed. To keep track of all GHG elements, CF was assessed by applying the SimaPro 8.2 LCA software from Prè with the Ecoinvent v.3.2 database. The selected impact assessment method was the "Greenhouse Gas Protocol method" which has been developed by the World Resources Institute (WRI) and the World Business Council on Sustainable Development (WBCSD) and aims to test the usability of the draft GHG Protocol CF standards (WRI/WBCSD, 2004).

GHG Protocol's characterization factors per substance are identical to the IPCC 2007 GWP (100a) method (Solomon, 2007) in SimaPro. The only difference is that carbon uptake and biogenic carbon emissions are included in this method and that a distinction is made between direct impacts: Fossil based carbon (carbon originating from fossil fuels and indirect impacts: i) Biogenic carbon (carbon originating from biogenic sources such as plants and trees); ii) Carbon from Land transformation; and iii)

Carbon uptake (CO_2 that is stored in plants and trees as they grow).

To evaluate the GHG emissions, the Ecoinvent processes developed for different transport lorries were used and adapted. For each lorry process, five different sources of GHG emissions are assessed: lorry construction & disposal, lorry maintenance, road construction & use, fuel extraction & transport and fuel combustion.

The default main unit of measure to estimate the emissions for lorry, used in Ecoinvent, is tons per kilometre, which is based on the average tons transported during operation multiplied by the mileage in the assessed period. The direct use of this default unit of measure was not suitable in our study because, even though information about total kilometres and total tonnage per year was available, the number of trips (or average kilometres per trip) was necessary to calculate average trip load from the total annual amount. Moreover, the variability in trips' distances is very large and would bring too uncertainty in the final estimation. To face this issue, the selected unit of measure was defined as the total amount of annual fuel consumption which was provided by Contarina for each lorry. GHG emissions are in fact directly related to fuel consumption allowing for a more precise estimation. The procedure used to perform the proposed fuel-based CF assessment is further explained in the next sections.

2.2. Data

The waste collection fleet of Contarina is wide and differentiated; vehicles utilized for door-to-door collection of solid waste are 290 subdivided into 6 typologies as reported in Table 1.

Table 1. Vehicles utilized for door-to-door collection of solid waste (CNG: Compressed Natural Gas; LPG: Liquid Propane Gas)

Type of vehicles	***Description***	***Type of fuel***	***Number of vehicles***
RU	Vehicle with a single tank	Diesel	250
ADV	Vehicle with double tank	CNG	8
ADV	Vehicle with double tank	Diesel	1
ACM	Mini rear compactor	Diesel	18
PM	Porter	LPG/Petrol	5
TR	Truck	Diesel	8
TOTAL			**290**

Each vehicle typology includes many categories of lorries characterized by fuel type (diesel, petrol, Liquid Propane Gas - LPG, Compressed Natural Gas - CNG), Euro emission class (spanning from Euro 2 to Euro 6) and mass category (metric tons' classes in: less than 3.5, 3.5 – 7.5, 7.5 – 16, 16 – 32, more than 32). These differentiating aspects are the same used by the Ecoinvent database under the transport category for lorries allowing to assign a specific Ecoinvent process to each assessed vehicle category.

Three waste collection management scenarios were assessed, characterized by the covered area and used vehicles: *Scenario 1* - Annual CF of the whole door-to-door collection service; *Scenario 2* - Annual CF of the door-to-door collection in historical centers only and; *Scenario 1bis* - Annual CF of the whole door-to-door collection service under ameliorative sustainability conditions.

Scenario 1 considers the whole Contarina fleet and door-to-door solid waste collection in the whole managed area for year 2015 by assessing emissions generated by all vehicle typologies and categories.

Scenario 2 considers only the small lorries used for the door-to-door solid waste collection in Zone 1 (i.e. the historical centers) for year 2015.

Scenario 1bis is a hypothetical scenario, based on Scenario 1, which considers the whole Contarina fleet and door-to-door solid waste collection in the whole managed area and where all diesel powered RU vehicles have been substitutes with CNG powered vehicles with the same load performance characteristics.

2.3. Converting unit of measure

As stated before, the selected unit of measure for the presented CF assessment is fuel consumption. Information about fuel consumption of the different vehicles was provided by Contarina in different units of measure according to fuel type: diesel, LPG and petrol were supplied in Liters, while CNG in kilograms. None of these units of measure has a correspondence in Ecoinvent which uses kilograms for diesel, LPG and petrol and cubic meters for CNG. Conversion of the different units of measure were performed by using conversion factors provided by the Department for Environment Food & Rural Affairs (DEFRA) U.K. (DEFRA, 2016; Ronco et al., 2014) as reported in Table 2.

Table 2. Units of measure conversion factors divided according to fuel typology

Fuel type	***Unit***	***To***	***Factor***
Diesel	lt	kg	0.851
CNG	kg	m^3	0.008
LPG	lt	kg	0.510
Petrol	lt	kg	0.749

2.4. Defining lorry categories

While most lorry categories used by Contarina for door-to-door solid waste collection were directly associated with the related Ecoinvent transport process by finding the correspondent lorry on the basis of the three aspects already mentioned in this section (i.e. fuel type, Euro emission class and mass category), this was not possible for some specific categories such as the Euro 2 emission class lorries and lorries with non-diesel powered engines. The Euro 2 issue was resolved by approximating the five Euro 2 vehicles present in Contarina's fleet with the corresponding Euro 3 processes in Ecoinvent. Non-diesel powered engines are not included in Ecoinvent transport processes while Ecoinvent's processes are available for passengers' cars large size powered by petrol, LPG and CNG. The latest were adapted to simulate equivalent lorry emissions. To this end, first a conversion factor *k* was calculated starting from a lorry diesel and a passenger car diesel by dividing car's fuel consumption by lorry fuel consumption. Because fuel consumption for all cars is based on one kilometre movements regardless of fuel type, this means that *k* can be used for all cars. Given the assumption that all sources of emissions being part of the lorry process (lorry construction & disposal, lorry maintenance and road construction & use) are linearly related to fuel consumption, *k* was then used to calculate the amount of the three processes to be set in the new equivalent lorry processes by multiplying original lorry diesel sources of emissions by *k*. Since fuels consumption was used as unit of measure, the frequent start and stop of vehicles has been implicitly taken into account.

2.5. Creation of hypothetical CNG powered lorries for scenario 1bis

Scenario 1bis is based on the hypothetical substitution of all diesel powered RU vehicles with CNG powered vehicles having the same load performance characteristics. Assuming that CNG powered lorries will be used as the current diesel powered lorries are, the information on annual total amount of mileage and collected tonnage of the current diesel powered lorries can be used to formulate a hypothesis on the amount of CNG which will be necessary to perform the same work. To this end a statistical model was developed to correlate mileage and tonnage to CNG consumption by generating a linear correlation model starting from the known CNG lorries already present in Contarina's fleet. Linear models were created for correlation between CNG consumption and mileage only, tonnage only and both, to find which of the three options better fits the data according to their coefficient of determination (i.e. R^2). The best fit resulted for the model where both predictors were used. The obtained linear predictor was applied against all diesel powered RU vehicles from Scenario 1 to finally obtain the hypothetical Scenario 1bis which simulates ameliorative sustainability conditions.

2.6. Calculating impacts in Simapro for the different lorry categories

Once all scenarios data were elaborated according to the previous sections, they were ready to be input for application in SimaPro. Total fuel consumption data for each lorry category in the correct unit of measure was input in the correspondent process in the software. As stated before, the unit of measure for lorry transport in SimaPro is tonnes per kilometre (tkm) while the selected unit of measure for our application was fuel consumption. In order to convert between the two, the fuel quantity per tkm reported in each transport process was used to calculate the tkm to be input in the process, according to Eq. (1):

$$y = \frac{x}{k} \tag{1}$$

where: *y* is the amount of tkm to input in SimaPro, *x* is the overall fuel consumption and *k* is the amount of fuel consumed for each tkm.

Processes related to all lorry categories were grouped into the three scenarios and each scenario was assessed with the GHG Protocol method in order to evaluate the overall emissions as well as the contributions of each of the four transport sub-processes and four method's results.

3. Results and discussion

The application of the previously described methodology led to the following results for the three considered scenarios. Total CF emissions were assessed by analysing direct and indirect emissions (i.e. emission related to direct and indirect impacts as mentioned in Section 2). As direct emissions represent the main contribution in the results their five constituting emission sources (i.e. lorry construction & disposal, lorry maintenance, road construction & use, fuel extraction & transport and fuel combustion) were also further analysed.

Results of Scenario 1 and Scenario 1bis were compared and CF results are reported in Table 3, where contributions of direct and indirect emissions are displayed alongside with contributions of the five direct emissions sources.

Table 3. CF for scenario 1 and 1bis divided by emission sources typology

Source of emissions	***Scenario 1 (kg CO_2eq)***	***Scenario 1bis (kg CO_2eq)***
Indirect emissions	**1.41E+05**	**2.62E+04**
Direct emissions	**7.73E+06**	**1.53E+06**
lorry construction & disposal	5.84E+05	7.74E+04
lorry maintenance	4.28E+05	5.69E+04
road construction & use	4.13E+05	1.13E+03
fuel extraction & transport	9.83E+05	1.99E+05
fuel combustion	5.32E+06	1.08E+06
Total	**7.87E+06**	**1.55E+06**

The comparison between the current scenario 1 and the ameliorative scenario 1bis (Fig. 1), clearly pointed out that CF would be remarkably reduced by converting part of the fleet to CNG (scenario 1bis). Specifically, CF due to direct and indirect emissions could be reduced by 80% and 81%, respectively, compared to 2015's situation. An additional comparison of 1 and 1bis scenarios' CF caused by direct emissions (Fig. 2) showed a clear decrease in the contribution of each of the five sources of emissions as the use of CNG increases. Specifically, emissions due to lorry construction & disposal, lorry maintenance, road construction & use, fuel extraction & transport and fuel combustion are reduced by 87%, 87%, 73%, 80% and 80%, respectively.

As far as Scenario 2 is concerned, CF results are reported in Fig. 3, in which contributions of direct and indirect emissions are also specified for each investigated historical centre. As reported in Fig. 3, the historical centre of Treviso has the lowest CF, although it has the most numerous fleet (9 vehicles) for the door-to-door collection service, serving the highest number of users (6.888). For Asolo, Montebelluna and Castelfranco, 1, 2 and 3 vehicles are employed respectively, serving 379, 2.198 and 2.547 users. This result can be explained considering that 8 out of 9 vehicles used in the historical centre of Treviso are CNG powered and only one is petrol / LPG powered, while the vehicles employed in the other historical centres are all diesel powered.

The same conclusions are further confirmed by the analysis of the CF due to direct emissions estimated for the four historical city centres (Fig. 4).

In fact, for the historical centre of Treviso not only the emissions related to fuel combustion and fuel extraction & transport decrease significantly compared to the other historical city centers, but also the emissions resulting from the other three sources of emissions (lorry construction & disposal, lorry maintenance and road construction & use). This is perfectly normal as CF (and LCA in general) directly relates emissions to the selected unit of measure, which is fuel consumption in the proposed methodology. This justifies the fact that all sources of emissions are always directly proportional to the amount of fuel used and to the different emissions generated by the combustion of different fuel types (CNG and petrol / LPG). Similar studies were conducted in other municipalities such as Rome, Bologna and other southern Italy cities (De Feo et al., 2016; Ripa et al., 2017; Tunesi et al., 2016; Vitale et al., 2017). In all cases similar results were obtained where fuel consumption accounts for the highest contribution in CO_2eq emissions.

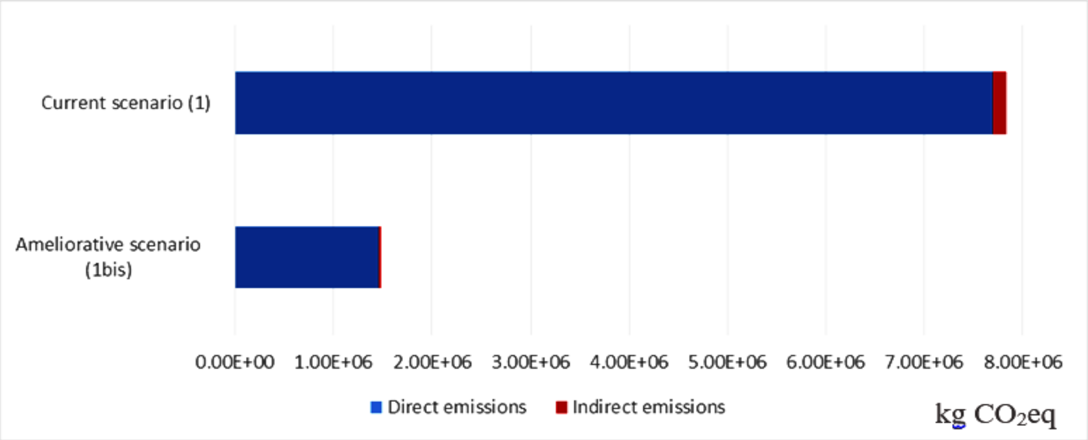

Fig. 1. Comparison of the CF for the current (1) and the ameliorative (1bis) scenarios

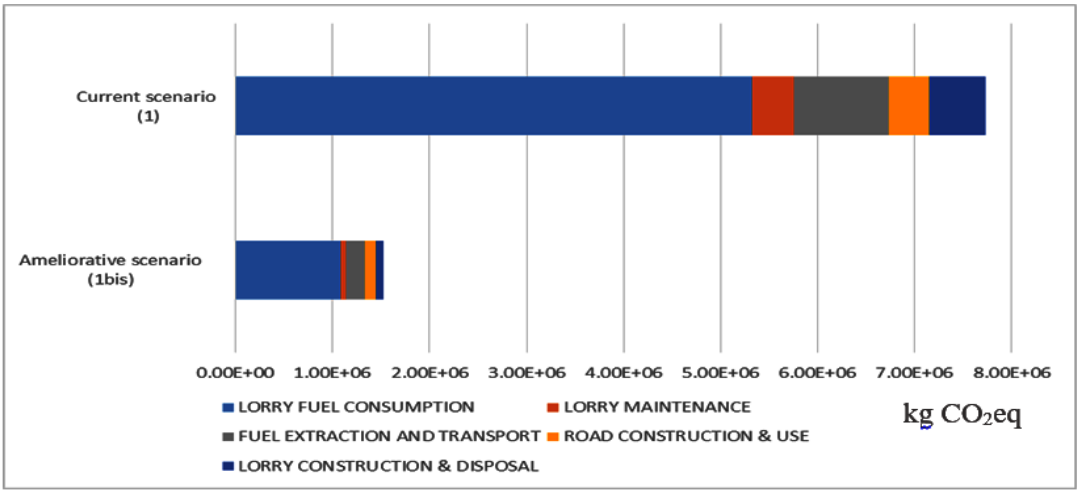

Fig. 2. Comparison of direct emission sources between current (1) and ameliorative scenarios (1bis)

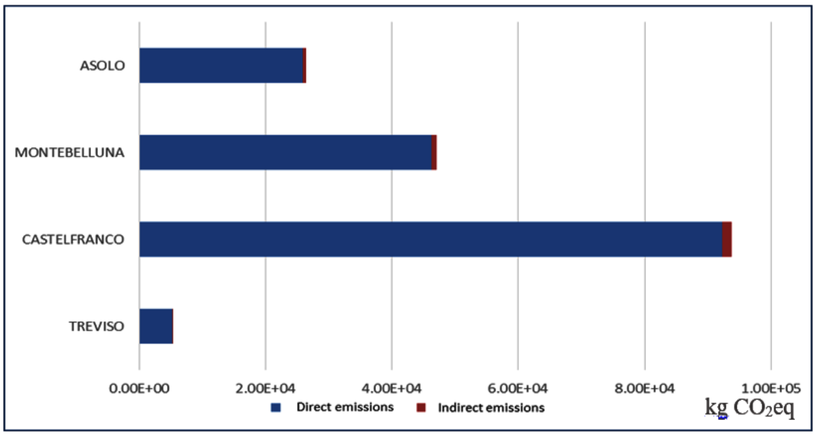

Fig. 3. Comparison between direct and indirect emissions in the four historical centres, Scenario 2

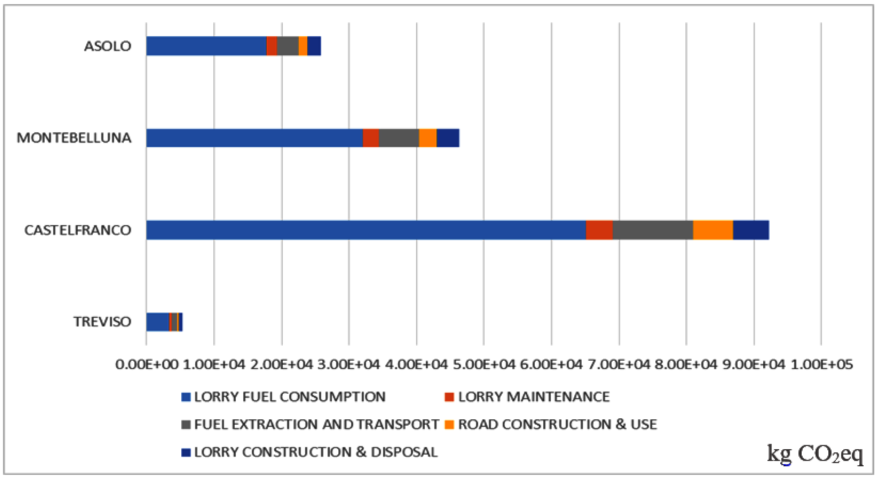

Fig. 4. Comparison of the four historical city centres for the direct emissions resulting from the five elements

4. Conclusions

This study applied the CF approach to evaluate the environmental impacts of the door-to-door waste collection service operated by the company Contarina S.p.A. (Italy).

The assessment was performed for both the currently employed fleet (with figures for 2015), with a specific focus on the service performance for the four historical city centres, and for a hypothetical fleet where all 250 diesel powered RU vehicles are replaced with CNG powered vehicles with the same load performance characteristics.

The results of this study clearly showed that the use of CNG, compared to the use of diesel, would be an environmentally sustainable alternative. In fact, by applying the ameliorative scenario Contarina could reduce the CF of its door-to-door collection service by 80%.

The choice to replace only the RU vehicles is dictated by the different power of CNG engines compared to diesel ones. Only the RU vehicles, in fact, can guarantee similar efficiency and safety of operation conditions, even if fully loaded, when CNG powered.

The conversion to CNG of vehicles with higher capacity such as ACM or road tractors (which handle up to 20 tons of waste), would not be as efficient. Finally, a simple economic analysis (results not shown) allowed to highlight that CNG is responsible for a lower amount of emissions of CO_{2eq}, at a lower cost.

However, this reduced cost would not be sufficient to amortize, by the life time of the new vehicles, the costs Contarina should initially invest for converting the 250 diesel trucks to CNG. The company is therefore investigating the possibility of producing in-house bio-methane by processing the wet waste collected in the area of Treviso province. This solution would allow to further reduce its overall CF and improve the outcome of the economic analysis.

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1788

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WASTE MANAGEMENT COMPANIES TOWARDS CIRCULAR ECONOMY: WHAT IMPACTS ON PRODUCTION COSTS?

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Abstract

Waste production and management is a strategic issue for all countries, because it relates to environmental, social, and economic conditions. The European Commission pushes EU member states to implement the "hierarchical principle", which aims to prevent negative environmental impacts caused by waste. Within this context, the article deals with Italian municipal companies operating in the field of waste management. The objective is to verify if and how separate waste collection rates impact production costs, accounting for size factors number of employees and-total quantity of waste collected), and contextual factors population and the land area covered by companies' services). Conforming to the latter, we verify if the impact of separate waste collection rate on production costs changes at varying population density levels, evaluating the interaction effect. For this purpose, an empirical analysis on 52 Italian municipal waste management companies has been conducted, using the analysis of covariance (ANCOVA) statistical method. Findings show that separate waste collection has a positive impact on the dependent variable (production costs), after the means of production costs have been adjusted to remove the influence of covariates (number of employees and total quantity of waste collected). Thus, the trend of companies' costs seems to be mainly influenced by size factors, assigning a primary role to efficiency issues. Even the population density factor shows a significant effect on the production costs. Whereas, the interaction between separate waste collection rate and population density is not statistically significant.

Key words: circular economy, Italian companies, production costs, separate waste collection, waste management

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1. Introduction

In the past few decades, waste management (WM) has become an increasingly more and more crucial issue for all countries because it has multiple impacts:

- environmental effects, as each disposal method may have consequences such as air pollution, groundwater contamination, and soil deterioration;
- social impacts, concerning public health and quality of life issues for people leaving in various territories;
- economic effects, due to diverse WM actions and options incurring different costs that have to be assessed and compared.

The "circular economy action plan" recently issued by the European Commission (2015) recalls and confirms the "hierarchical principle" that aims to prevent negative environmental impacts caused by waste, boosting reuse, recycling, recovery (for example for energy production) and, finally, disposal (Cutaia et al., 2016; Gharfalkar et al., 2015; Zaman, 2015). The plan provides measures that cover the whole waste cycle from production and consumption to waste management (WM), and supports the market for "secondary raw materials".

Moving from the fact that EU countries are affected by more or less important lack of natural resources, the circular economy approach's main idea consists of a more efficient use of waste that can be re-introduced into the economic system as

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"secondary raw materials" (Cossu and Williams, 2015; Pauliuk et al., 2012).

Although the circular economy is a wide concept concerned with reducing the need for raw materials by designing a zero waste product and process (Tukker, 2015; Vezzoli et al., 2015), implementing the circular economy worldwide still seems in the early stages, and is mainly focused on recycling rather than reuse. Nonetheless, the same circular economy EU package is strongly focused on increasing the recycling rates (Bartl, 2015). However, important results have been achieved in some activities of the WM sector where large waste recycling rates are sometimes fairly significant in developed countries (George et al., 2015; Ghisellini et al., 2016).

The literature concerning environmental economy often focuses on benefits in terms of physical impacts and neglects the economic effects of the WM processes; therefore, from this perspective, more knowledge is needed (Aminoff and Kettunen, 2016). In other words, environmental and economic sustainability should be combined because companies can operate and produce goods and services respecting the hierarchical principle only if this will be sustainable from an economic point of view and, therefore, profitable. This could facilitate an effective implementation of the circular economy principles in a context in which citizens and businesses – as waste producers – and governments at different levels – as policy makers – are also strongly involved.

In this context, the article is focused on companies working in the field of collection, treatment, and disposal of municipal solid waste (MSW) with the aim of understanding if and how practices complying with the circular economy approach, in terms of separate waste collection (SWC), influence the production costs that this kind of companies incur.

Despite the issue of WM being a strategic topic for all countries, and given the enormous rise in the quantity of waste produced, the empirical literature regarding the economic impacts of the circular economy on companies' costs and performance is rather limited. Thus, this article strives to contribute towards filling the literature gap.

The empirical analysis available in the literature often employs the volume of MSW collected in specific municipalities as a variable determining the total cost supported for waste collection and treatment.

Bel and Fageda (2010) analyze the factors determining the WM services costs and highlight that the quantity of waste can influence such costs. Specifically, in municipalities of fewer than 50,000 residents, the costs rise less than proportionally with increases in waste quantity, whereas, a high level of solid waste collection does not produce a significant growth of total costs, aside from the important improvements it brings in environmental terms.

Callan and Thomas (2001) identify the determinants of recycling and disposal costs as the main variables influencing the total annual cost of MSW services, verifying the existence of economies of scale and scope.

Carroll (1995) asserts that collection of recyclables appears to be subject to economies of density (costs of collection tend to be lower in municipalities with higher population density), but not to economies of scale. Dubin and Navarro (1988) are of the same view: they analyzed a population of 261 US municipalities, finding that the population density allows relevant cost savings in municipalities up to 20,000 inhabitants. Evidence of cost savings due to a higher level of waste quantity in smaller municipalities is also provided in relation to other countries, such as Sweden (Ohlsson, 2003) and Spain (Bel and Fageda, 2010).

Abrate et al. (2014) analyze the costs incurred by 529 Italian municipalities providing waste disposal and recycling services over the period 2004-2006 and find that strategies aimed at increasing recycling (first of all separate collection) would not imply a considerable growth in waste management total costs.

Greco et al. (2015) found that undifferentiated waste has the highest cost reduction when the collected quantity rises, so thate waste production growth could lead to boost collecting undifferentiated waste. It could cause a reduction of the separate collection that has higher costs and lower economies of scale.

In our study the main objective is to verify if and how the rate of SWC has an impact on the production costs incurred by WM companies. We also took into consideration both size factors, such as the total number of employees (EMPL) and the total quantity of waste collected (WQ), and contextual factors, such as the population and the land area covered by companies' WM services. According to the latter, we verified if the impact of SWC rate changes on varying of the population density level, to evaluate the interaction effect.

The choice to focus our attention on SWC is justified by the fact that it is a precondition for reuse, recycling, and recovery of waste. Therefore, we want to understand if the environmental sustainability of SWC may be realized without jeopardizing companies' profitability.

Table 1. Abbreviations and acronyms in alphabetic order

ANCOVA	analysis of covariance
ANOVA	analysis of variance
DENS	population density
EMPL	number of company's employees
IFRS	international financial reporting standards
MSW	municipal solid waste
SWC	separate waste collection
WM	waste management
WQ	total quantity of waste collected (undifferentiated and separated)

2. Material and methods

Consistent with the research goal mentioned above, an empirical study was carried out on a group of 52 Italian companies working in the field of collection, transport, and disposal of MSW for the year 2014. These companies have been selected in Italian capital city municipalities (*capoluoghi di provincia*) and municipalities with a population of more than 50,000 inhabitants. In these selected cities, the supplier of WM services has been identified, taking into account that sometimes these services are carried out in several municipalities, in geographical areas not always contiguous and with the same orographic characteristics. We selected the group of companies based on criteria identified below.

First we took into consideration limited companies and other companies preparing their financial statements according to the Italian accounting principles, to compare financial statements of the same type. For this reason, we excluded companies listed on the Italian stock exchange or belonging to listed groups, because these companies prepare their financial statements in accordance with IFRS (International Financial Reporting Standards); furthermore, a listed company' size often differs significantly from that of a non-listed company.

Moreover, multi-utility companies, the ones supplying services that go beyond the integrated cycle of collection and disposal of MSW (for example, energy production, parking services, and cemetery services) were also excluded, mainly due to the difficulty of separating costs related to WM activities from other costs. After applying all the criteria mentioned above, we identified 52 Italian companies, all owned or controlled by local government: in fact, in Italy, these represent the clear majority of companies operating in the sector of our interest. Circular economy principles should guide their management choices and programs, as they are responsible for providing and controlling MSW collection and disposal services, according to the Italian rules.

The analyzed companies deliver WM services to 880 Italian municipalities, which are about 11% of the total, regarding both the number of municipalities and the land area served. Here is the geographical distribution of the selected companies in Italy: 40% in the North, 20% in the Centre, and 40% in the South and islands. Total production costs incurred by the selected companies and the number of employees were obtained from a documental analysis conducted on financial statements related to 2014. As our focus is on companies, we chose to manually collect these data only from official documents (financial statements) to assure their reliability and avoid validity problems which often occur when using existing sector analysis data.

As regards the physical-technical parameters, the rate of SWC, the WQ (in tons), and the population were taken from the database of the Institute for Environmental Protection and Research (ISPRA) – Ministry of Environment; whereas, the land area values were retrieved from the ISTAT (Italian National Institute of Statistics).

Table 2. Descriptive statistics (thousands)

North	***Mean***	***Median***	***Std Dev***	***Min***	***Max***
PC	23,895.00	17,808.00	16,876.60	5,457.60	65,006.10
EMPL	0.16	0.13	0.14	0.01	0.60
WQ	93.78	84.05	45.05	31.62	168.64
SWC%	58.17	59.54	13.20	30.03	80.56
DENS	1.04	0.81	1.30	0.15	5.91
Center					
PC	38,973.90	32,488.10	36,974.80	7,653.80	134,241.80
EMPL	0.25	0.18	0.27	0.05	1.02
WQ	131.18	84.55	108.49	30.27	408.20
SWC%	40.49	43.79	18.21	11.32	69.08
DENS	1.04	0.27	2.28	0.07	8.22
South					
PC	24,991.60	12,107.40	36,539.60	3,102.40	160,169.00
EMPL	0.34	0.13	0.53	0.06	2.33
WQ	99.88	33.33	128.74	13.59	500.09
SWC%	30.77	21.36	21.20	7.59	67.61
DENS	1.20	0.66	1.66	0.12	6.42

Table 3. Variables' units of measurement

Variable	***Unit of measurement***
Production costs (PC)	thousands of €
Number of employees (EMPL)	thousands
Total quantity of waste collected (WQ)	thousands of tons
Separate waste collection rate (SWC%)	percentage of total collection
Population density (DENS)	thousands of inhabitants/km^2

Table 2 presents the most common statistical values of the variables used in the model, allowing us to make some considerations. The companies had similar features due to the above-mentioned selection criteria, however, they show different index values. This is particularly evident for the SWC% and the WQ, especially for the South.

High heterogeneity is proved by the relative standard deviation (standard deviation/mean ratio) and the gap between the minimum and the maximum values. Especially in the Center and South, there are some cases of companies that have SWC% very close to the minimum value (cases with a substantial absence of SWC), and others that represent a WM excellence. This means that the spread of WM good practices is still rather fragmented, especially in the regions of central and southern Italy.

Since the aim of the paper is to evaluate the "true" effect of the SWC rate on production costs, we used the analysis of covariance (ANCOVA). It is a type of general linear model that combines analysis of variance (ANOVA) with a regression analysis. It allows us to test if the independent variable (SWC rate) influences the dependent variable (production costs), after the effect of the "concomitant" independent variables (the covariates EMPL and WQ) has been removed. In fact, this statistical method allows to control potential bias due to heterogeneity factors, such as the EMPL and the WQ, making the companies as comparable as possible (Keppel and Wickens, 2004).

Finally, we applied factorial ANCOVA to analyze the interaction effect between SWC rate and population density. This is the proper data process in the case of more than one factor, as in our study.

In more detail, the method we used can be organized in the following steps:

- data pre-processing: the group of companies was divided into two groups, based on the SWC rate, using the median of the distribution (49.5%) as the discriminating value;
- preliminary analysis: the means of production costs for the two companies' groups were calculated, and an F-test was used to test the statistical significance of difference;
- running ANCOVA: we considered the two control variables mentioned above, and then we calculated the adjusted-means of production costs for the two groups;
- running factorial ANCOVA: we analyzed the interaction effect between SWC rate and population density, using a factorial ANCOVA. When an interaction effect is present, it means that interpretation of the single variables may be incomplete. The factorial ANCOVA was used to test if the impact of the SWC rate on production costs changes depending on the level of the population density.

3. Results and discussion

3.1. Results

3.1.1. Data pre-processing and preliminary analysis

To achieve the research objective, we first pre-processed the data via a "grouping" of the SWC rate variable; the resulting categorical variable is composed of two groups, with values below and above the median, respectively. In this way, we reduced the data by replacing low level concepts (numeric values for the variable SWC rate) with higher level concepts (low and high SWC rate).

Consequently, we compared the means of the production costs for the two companies' groups. According to Table 4, that shows the results obtained, the mean for the low SWC% group is higher than the mean for the high SWC% group, but the difference is small.

Table 4. Means of the dependent variable "Production costs" (thousands €)

Groups	***Mean***
SWC% low	28,352.05
SWC% high	27,283.12
Total	27,817.59

We used the F-statistic to test if this difference is statistically significant. As shown in Table 5, F test has a p-value of 0.90, therefore the null hypothesis of equality between the means cannot be rejected. This would indicate that the rate of SWC does not have a significant influence on the production costs it seems the available data does not support the existence of a relationship between the rate of SWC and production costs.

Looking at the first row of Table 5, we notice that the amount of unexplained variance is very large (Mean of Squares of Intercept), indicating the presence of other variables that might influence the results. In fact, as mentioned above, to properly evaluate the effect of the independent variable, it is necessary to consider any "concomitant" factors, which may influence the dependent variable and confuse the effects, leading to erroneous conclusions. In our case, production costs are influenced by size factors, both of a structural nature, such as the EMPL and relative to the WQ.

Table 5. Test of between-subjects effects. Dependent variable "Production costs" (thousands)

	Sum of Squares (SS)	***degree of freedom (df)***	***Mean of Squares (MS)***	***F test***	***p-value***
Intercept	40,238,546,066.08	1	40,238,546,066.08	41.22	0.000
SWC%	14,854,039.41	1	14,854,039.41	0.02	0.902
Error	48,806,778,649.02	50	976,135,572.98		

For the above reasons, the research objective should be better specified, moving to verify if the rate of SWC (independent variable or factor) has an impact on the production costs (dependent variable), after removing the effects of the heterogeneity resulting from EMPL and WQ (covariates), to adjust the means of the two groups. To test this hypothesis, we performed an ANCOVA.

3.1.2. Running ANCOVA

Before running the ANCOVA, several assumptions in addition to the standard linear regression should be met (Montgomery, 2008). ANCOVA assumes that (1) the covariates and the factor are independent, and (2) the regression slopes of covariates are equivalent (i.e., parallel) among groups (homogeneity of regression slopes). This assumption is very important and means that the relationship between the covariates and the dependent variable is about the same for all groups (i.e., the difference of regression coefficient estimates in each group should not be statistically significant). Furthermore, we performed a test for the multicollinearity of covariates (i.e., the covariates should be uncorrelated each other) and for the homogeneity of variance.–The Levene's test should not be significant, that is the groups should be homogeneous regarding variance.

Since these assumptions were satisfied (see Appendix 1), we run an ANCOVA with two covariates (EMPL and WQ) and one factor, the SWC rate. Table 6 shows the ANOVA results when the covariates are included. We note that the covariates have significant effects on production costs, and explain a large amount of variation in the dependent variable, as shown in the last column by the η^2 partial.

The most important result is that the effect of SWC rate becomes significant (the p-value is less than 0.05), after removing the influence of covariates. Without this adjustment, we would conclude that the SWC rate does not have a significant influence on production costs, but the ANCOVA results clearly show that this statement is wrong.

The adjusted means, so-called Least Squares (LS) means, are reported in Table 7. We notice that the small difference in the original values (see Table 4) has become considerably larger, and thus it is possible to more accurately assess the effect of the SWC rate on production costs. Consequently, the error variance has been greatly reduced (136.67). The adjustment produced by ANOVA is useful to obtain an unbiased estimate of the "true" influence of SWC rate on the dependent variable.

3.1.3. Running factorial ANCOVA

Considering our aim, we evaluated if the effect of SWC changes depending on the level of population density (e.g., for the presence of economies of density). Therefore, we investigated both the main effect of population density on production costs and its interaction effect with SWC rate.

For this purpose, we considered two levels of the population density: "high" if the municipalities served by the company have a density higher than 600 inhabitants per square kilometer (the median of the distribution as the discriminating value), and "low" if the density is below this value. Then, we performed a factorial ANCOVA, with the same covariates and two factors. The results of the ANCOVA model are reported in Table 8.

Table 6. Test of between-subjects effects. Dependent variable "Production costs" (thousands)

	Sum of Squares (SS)	*degree of freedom (df)*	*Mean of Squares (MS)*	*F test*	*p-value*	*η^2 partial*
Intercept	193,460,119.14	1	193,460,119.14	1.42	0.240	0.029
EMPL	7,254,041,913.70	1	7,254,041,913.70	53.07	0.000	0.525
WQ	2,456,000,467.88	1	2,456,000,467.88	17.97	0.000	0.272
SWC%	624,233,637.27	1	624,233,637.27	4.57	0.038	0.087
Error	6,560,479,522.08	48	136,676,656.71			

Table 7. Least squares means. Dependent variable "Production costs" (thousands €)

Groups	*Mean*	*Standard Error*	*Lower bound (95%)*	*Upper bound (95%)*
SWC% low	24,278.22	2,317.59	19,618.39	28,938.05
SWC% high	31,356.96	2,317.59	26,697.13	36,016.79

Table 8. Test of between-subjects effects. Dependent variable: "Production costs" (thousands)

	Sum of Squares (SS)	*degree of freedom (df)*	*Mean of Squares (MS)*	*F test*	*p-value*	*η^2 partial*
Intercept	41,442.42	1	41,442.42	0.00	0.986	0.000
EMPL	7,003,902,621.36	1	7,003,902,621.36	54.11	0.000	0.541
WQ	2,789,645,879.02	1	2,789,645,879.02	21.55	0.000	0.319
SWC%	602,975,799.51	1	602,975,799.51	4.66	0.036	0.092
DENS	547,544,254.30	1	547,544,254.30	4.23	0.045	0.084
SWC%*DENS	60,258,061.74	1	60,258,061.74	0.47	0.499	0.010
Error	5,954,688,031.10	46	129,449,739.81			

The format is the same as Table 6, adding two rows, one about the main effect of population density, the other one about the interaction effect with SWC rate; in fact, the evaluation of the former is a precondition for analyzing the latter.

We notice that all the main effects are significant (p-value <0.05): it means that the population density has an impact on production costs. If we look at the adjusted means, we can conclude that the population density has the effect of reducing the production costs, indicating the presence of economies of density. The graphs of means below (Fig. 1) summarize the effect of the two factors on the dependent variable, after the means of production costs have been adjusted to remove the influence of covariates.

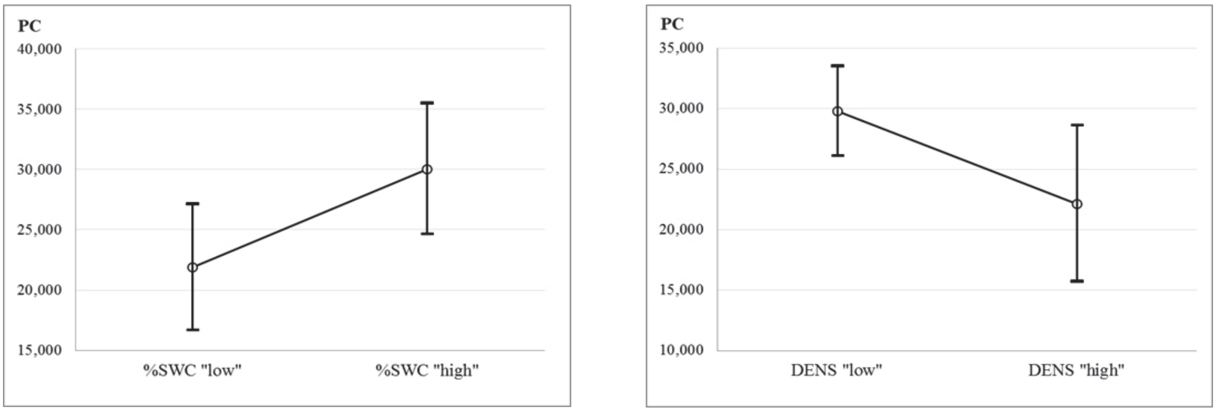
Whereas, the interaction effect between SWC rate and population density is not statistically significant (p-value=0.4985). This indicates that, according to the available data, the relationship between the SWC rate and production costs does not vary across different levels of population density.

3.2. Discussion

3.2.1. Comparative analysis of findings

In the following table, we show a comparison between some of the most relevant studies focused on costs related to the separated or recycled waste activities (dependent variables) which have similar factors as those that have been used in this article. Nevertheless, the studies included in Table 9 use various data sources and waste collecting methods: this may partially explain the not always converging results.

In some of the analyzed studies the parameter used to measure the separated/recycled waste is the absolute value of quantity, thus the results are rather expected and highlight an increase in the dependent variable caused by the augmentation of waste quantity. Instead, we focused on the SWC rate obtaining findings that seem to be particularly significant because the incidence of SWC on WQ allows us to assess the level of companies' environmental good practices.



(a) (b)

Fig. 1. LS means, with upper and lower bound (95%). Dependent variable "Production costs" (thousands €)

Table 9. Comparative findings table

Authors	*Dependent variable (DV)*	*Sources of DV*	*Measures of separated/recycled waste*	*Results*
Abrate et al. (2014)	total costs	provided by companies for statistical purposes	tons of waste recycled	positive impact
Bel and Fageda (2010)	total costs	provided by government institutions	percentage of the total waste volume designated for recycling	not significant
Callan and Thomas (2001)	total costs	provided by government institutions	total quantity of solid waste recycled	positive impact
Carroll (1995)	total costs	provided by government institutions	recycling tonnage per household	positive impact
Dijkgraaf and Gradus (2003)	total costs	calculated by ad hoc procedure on the base of data provided by government institutions	percentage of different material separately collected	negative impact (only for composted)
Dubin and Navarro (1988)	average cost per yard	gathered by survey (with local communities)	fraction of refuse collection trucks that do on-site compaction	negative impact
Greco et al. (2015)	full costs	gathered by survey (with companies)	percentage of separate collection on total collection	positive impact (for paper and organic waste)

Moreover, the other articles included in Table 9, even when using an independent variable in percent values, obtain results sometimes not statistically significant, or with an impact (positive or negative) only for specific types of waste.

3.2.2. Research implications and future developments

In this article, we focused our attention on companies operating within the WM sector and studied the production costs they incur. Within this "interdisciplinary" issue, we analyzed the SWC rate impacts on companies' costs, whose trend critically influences the overall companies' sustainability and, consequently, their ongoing viability.

The results of this study are useful for policy makers. It is well known that the EU targets related to SWC should be achieved within the next few years, however, in some areas of Italy there is still much to do because the SWC rate is far from the planned targets. It is important to define public policies that also consider economic aspects, so we can identify the best tools capable of supporting companies in implementing the EU requirements.

This article also provides some useful insights for WM companies and their managers, who must plan and control waste collection and disposal services while monitoring and controlling the related costs. This kind of information is important to support companies' decisions regarding the implementation of circular economy's principles.

In the future, it could be interesting to deepen this issue, widening the research object, including those activities following the SWC (i.e. the implementation of waste to energy technologies) useful in shifting the linear economies toward circular economies: this could be realized jointly considering production costs together with environmental and social costs (Nizami et al., 2017; Ouda et al., 2016).

4. Conclusions

Despite WM being a strategic issue for all countries due to its environmental, social, and economic implications, literature regarding the economic impacts of circular economy principles on companies' costs is rather limited.

This article attempts to help fill this gap, in order to understand if and how practices complying with the circular economy – in particular, the SWC – influence their production costs, taking into account both size factors (EMPL and WQ), and contextual factors (population density of the municipalities served by the companies). As regards the latter, we verified if the impact of SWC rate changes on varying of the population density level, evaluating the interaction effect.

The results show that the SWC has a positive impact on the dependent variable (production costs) after we removed the influence of covariates (EMPL and WQ) from production costs. Thus, they seem to mainly influence the trend of companies' costs, giving the size factors a primary role in efficiency issues. Even the population density factor shows a significant effect determining a reduction in production costs (removing the effects of the covariates), indicating the presence of economies of density.

We also verified that the interaction between SWC rate and population density is not statistically significant. This indicates that, based on available data, an increase in the population density does not change the effect of SWC rate on the production costs, once the heterogeneity factors have been eliminated.

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SHARING ECONOMY AND CIRCULAR ECONOMY. HOW TECHNOLOGY AND COLLABORATIVE CONSUMPTION INNOVATIONS BOOST CLOSING THE LOOP STRATEGIES

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Abstract

Sharing economy business experiences are rapidly rising worldwide and deeply changing structures and models of customers purchasing attitudes and needs. Inspired by principles of sustainable consumption, its starting point is the idea that every underutilized resource is a wasted resource. Beyond the digital services implemented by sharing platform, there are also social and physical places where communities are experimenting the potential of collaborative and innovative solutions: purchasing groups, time banking, social street, co-working spaces. Goods and services access promoted by sharing business models are emerging in the place of older model based on private propriety and a consumerist view of society. This is strongly connected with circular economy strategies, particularly referred to waste prevention, reduction and resources valorisation European goals. This paper gives an overview of sharing economy including drivers and barriers which can affect its effective expansion. Moreover, collaborative models in the most strategic and critical sectors (such as mobility, agro-food, buildings and goods production and consumption) by a resources perspective, will be analysed to show how sharing economy can contribute to circular economy. At this end, this paper explores the circularity approach and in particular it identifies the role of sharing economy in products and services from a life cycle thinking (LCT) approach. The focus will be the benefits of the sharing economy models considering mainly two aspects; a) the length of the product's use phase (lifetime) and b) the intensity of use. A review of available data considering the most strategic sectors in terms of environmental impacts, will also be presented from a sharing economy point of view.

Key words: circular economy, life cycle thinking, sharing economy, waste prevention

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1. Introduction

Circular economy is a term to define an economic system that foresees restorative and regenerative mechanisms (Ellen MacArthur Foundation, 2012). It is representative of a broad number of interpretations that have in common an increased efficiency of resources by minimizing waste and resource extraction (Chertow, 2000). Its main objective is to oppose linear economy by closing the loops in terms of resources and materials.

Recently the European Commission adopted an ambitious Circular Economy Package which consists of an EU Action Plan for the Circular Economy (EC, 2015) to help European businesses and consumers to make the transition to a stronger and more circular economy. This document underlines among others, the contribution of the sharing economy to the reaching of the circular economy objectives. Specifically "Innovative forms of consumption can also support the development of the circular economy, e.g. sharing products or infrastructure

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(collaborative economy), consuming services rather than products, or using IT or digital platforms" (EC, 2015).

Sharing economy represents a social and economic system that supports a sharing access to goods, services, information and competencies aiming at optimizing and redistributing the use of resources (WEF, 2013). There are many collaborative initiatives that offer new opportunities for a radical transformation of business models to a more efficient use of resources (PwC, 2015). Nevertheless, these new models show up in a number of types, specificities and terms as "sharing economy", "peer economy" or "collaborative consumption" are frequently used as synonyms. (Botsman and Rogers, 2010). In order to guarantee a common reference framework on collaborative economy and avoid different and divergent positions, the European Commission has presented the Communication "A European agenda for the collaborative economy" (EC, 2016a). The objective is to provide non-binding common guidelines aiming at "encouraging a regulation that allows new business models to develop while protecting consumers and guaranteeing equal conditions in fiscal and employment issues (EC, 2016a).

This paper aims at providing firstly an overview of concepts of sharing and collaboration. Thereon the document focuses on the linkage between sharing economy and circular economy approach. In particular, the paper identifies the role of sharing economy business models in life cycle thinking. Moreover, strategic sectors have been analysed and contribution of sharing economy to circular economy models and objectives has been underlined. Finally, benefits and weakness have been highlight in order to allow the identification of further improvements of sharing economy.

2. Sharing Economy: a short overview

The concepts and practices of "collaboration" and "sharing" trace back their roots in ancient times, but new ways of shared use regulated by the new market rules and technologies, are being spread. Especially, four drivers have been crucial for sharing economy growth: technology innovation, values shift, economic realities and environmental pressures. The basic principal underpinning the collaborative economy is that an underutilized product/service is a loss of the latter, underlining this way the importance of access to goods and services instead of ownership (the so-called "access economy"). This means that the role of consumers is crucial especially regarding the responsibility in eco-sustainability (Androniceanu and Drăgulănescu, 2016). Currently five pillars of collaborative economy have been identified: consumption, production, finance, learning and governance (Stokes, 2014).

The Sharing economy is strongly expanding and there are different new business models that are being developed (Codagnone et al., 2016):

- P2P (Peer-to-Peer), where the exchange happens among individuals intended as "private",
- B2P (Business-to-Peer) among companies and single consumers (from B2C to B2P, consumers become now individuals linked in virtual communities),
- P2B (Peer-to-Business) among single consumer to companies,
- B2B (Business-to-Business) among companies themselves.

Examples of initiatives among privates (P2P) are the networks of consumers that gather aiming at obtaining services similar to those delivered by companies. Examples of collaborative models among companies (B2B) are; the sharing of utility and infrastructure; the joint use and management of common resources as gas, electricity, water; joint service supply as cleaning service, canteen, transport, waste management; exchange of by-products such as the use of waste or other material generally discarded for substitution of commercial products or raw materials.

According to EC (2016a), there are three categories of collaborative actors: service suppliers that share goods, resources, time and/or competencies; the users of these services and the mediators that act through collaborative platforms. The role of the platforms is essential because they link suppliers with users and allow transactions among them. They have grown rapidly thanks to digital progress like internet, applications, social networks and geolocalization services. The sharing economy appears therefore strategic for the accomplishment of different objectives of sustainability.

Nevertheless, its effectiveness can be improved in relation to different economic sectors where the models are implemented. From an economic point of view, there has been a remarkable growth starting from 2013, and has further increased in 2015 thanks to important investments of bug platforms that have extended their activities in Europe. The total gross income in EU of the sharing economy has been estimated at around 28 billion euros for the year 2015. Compared to the previous year, the revenues of the five key sectors in the EU (short term renting, transport, services to families, technical and professional services and collaborative finance) have doubled and the trend is a stable increase. A study of Price Waterhouse Cooper (PwC, 2015) estimates that in future the collaborative economy may guarantee in EU a turnover from 160 to 572 billion of euros.

According to the EC reports, the current model of producing and using products and resources in the considered sectors, cost to EU around 7.2 billions of euro every year. On this total amount, the costs of real resources are 1.8 billions of euro, while other costs such as expenditure of families and public expenditure are equal to 3.4 billions of euro. Externalities, meaning expenditure related to environmental problems such as traffic congestion,

CO_2 emissions, pollution and rumours are equal to 2 billion of euros.

Concerning the waste production, according to the French agency ADEME (2014a, 2014b), around one third of domestic waste may turn into potential sharing goods and the 33% of the total environmental impacts can be avoided through collaborative economy models. A report of the study office of the European Parliament (EPRS, 2016) concludes that more than 46% of domestic consumption in Italy is recoverable/reusable through Sharing Economy models (ISTAT, 2015).

Data show that although sharing economy is rapidly growing, its potential is far from being explored and there is a great margin for its further development.

3. Circular approach of Sharing Economy

The development of Sharing Economy can bring new opportunities in economic terms, but the sharing models also are able to bring interesting environmental advantages in terms of resource savings and avoided wastes. For this reason, the collaborative economy can be considered strictly connected to circular economy issues. As the European communication "Towards a circular economy: A zero waste programme for Europe" (COM/2014/0398 final/2) states: "These are based on experience of successful initiatives that could be scaled up and applied more widely, and include among others, in the consumption phase, collaborative consumption models based on lending, swapping, bartering and renting products, and product service systems to get more value out of underutilised assets or resources (e.g. cars, tools, lodging)" (EC, 2015). In other words, the collaborative initiatives allow to overcome wastes and inefficiencies of linear economy and support the transition to circular economy.

Figure 1 explores the connections among Sharing economy business models and Circular economy. Collaborative economy P2P business model brings advantages through the reuse, the sharing use and other collaborative practices. On one hand, it reduces waste production (less products, more co-users), on the other, it extends the good's lifetime thanks to use optimization.

The B2P area integrates sharing approach into current "linear" market paradigma. This transition creates a new market place where customers are individuales that cooperate with companies to satisfy their needs. In this way the current "product system" switches into a more sustainable "product service system" where the purchase is the access to goods and consumables when needed. Consumers are evolving in this context into "prosumers" (producer + consumer), deeply changing the interactions between consumers and business world by spreading and developing the concept of "co-creation" and "co-design" of products.

Regarding collaborative models among companies (B2B) sharing models can bring benefits especially within industrial districts. Industrial Symbiosis approach is a very important example of resources sharing among companies. It is a strategy addressed at transforming the residues of one activity in an input resource for another activity within the industrial district. As shown in Fig. 2, the principle behind industrial symbiosis is that, instead of being thrown away or destroyed, surplus resources generated by an industrial process are captured and then redirected for use as a 'new' input into another process by one or more other companies, providing a mutual benefit or symbiosis (Cutaia et al., 2015, 2016). This approach is not only a factor of competitiveness for industrial activities, but also an asset in which all resources are exploited locally and not dissipated, delegated, or given away to third parties.

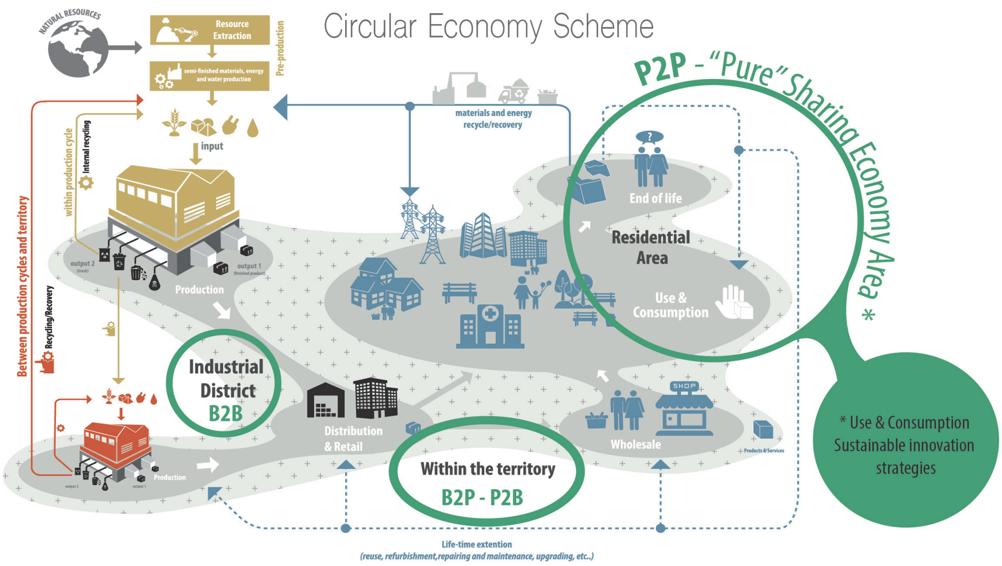

Fig. 1. Sharing economy new business models (P2P, B2P, B2B) within circular economy scheme (ENEA, 2014)

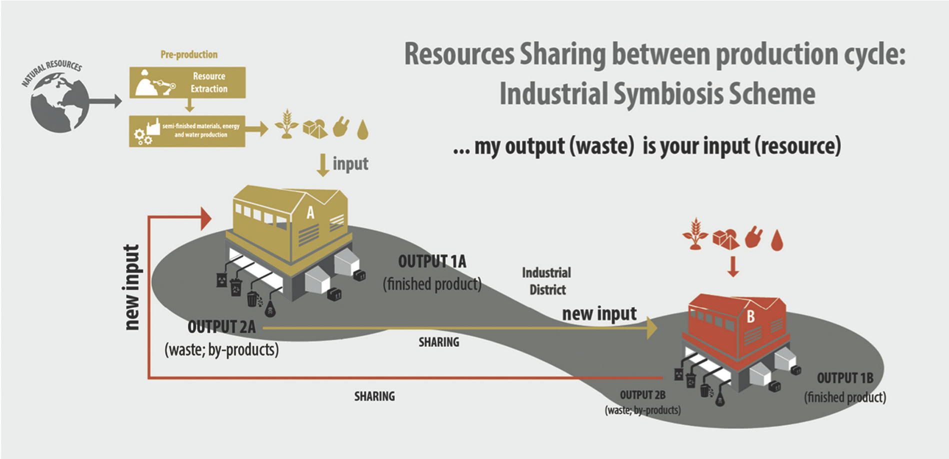

Fig. 2. Industrial symbiosis scheme

4. Limits of Circular Economy and Sharing Economy business models

The shift to circular economy is generally advocated for a number of reasons, such as economic growth, innovation, and what is more important, for environmental concerns. Nevertheless, although the environmental gain seems to be intuitive in the circular economy approach, and specifically in the sharing economy business models, recent scientific research has raised some issues concerning the rebound effect of these practices. According to Zink and Geyer (2017), circular economy may have adverse effects which can be primary and secondary, depending on its nature. Two different mechanisms have been detected that can lead to circular economy rebound: the substitutability of secondary goods and the effects of secondary goods on market practices. Shortly, if the secondary goods don't push consumers to displace or reduce the consumption of the good, circular economy may not reach any environmental benefit. Furthermore, circular economy practices need to effectively draw the consumers from the primary consumption in order to have a final desirable result.

Similarly to the Circular Economy, Sharing economy practices have also been discussed on rebound effects related to the overconsumption of the products, once they are shared and their related cost is lower. According to Demailly and Novel (2014) environmental benefits are not as obvious as they may seem because of two main reasons: a) different consumption does not necessarily mean consuming less, by contrary, it may produce the rebound effect and b) the spread of sharing models may produce ambivalent response on public policies, such as limiting investments in public transport.

5. Materials and methods

The paper wants to explore how and at which extent sharing economy contributes to the circular economy approach. Although this field of research is still lacking of systematic studies, data and standard terminology, the authors have put together two methods to explore this aspect;

- a theoretical approach, indicating the impacts of sharing economy in the different lifecycle stages, according to a life cycle thinking approach;
- an empirical approach, using available data of sharing economy in some sectors. The empirical research, far from being an exhaustive one due to evident lack of data and related consolidated indicators, doesn't consider adverse effects of the sharing economy on environment and economic equilibrium in general, which deserve a deep separate study. On the other hand, available data have been systemized to show where the environmental benefit of the sharing economy practices is.

6. Analysis and results

6.1. Life cycle thinking in Sharing Economy

In order to better explore the advantages of transition from linear to circular economy, this paper considers the sharing economy model according to the whole product/service life cycle system and adopting a Life Cycle Thinking (LCT) approach. In this study all life cycle stages of production and consumption have been considered. In the following Figures it is shown how sharing economy business models can impact and modify the traditional life cycle scheme by creating new phases never considered before. To do this, two sharing business models (P2P and B2B) have been analysed and integrated within the following product/service life cycle scheme.

In the pure sharing economy practice (P2P) the model is introduced in the use and consumption phase (Fig. 3) such as: re-use, co-use, bartering, swap, leasing etc. As a consequence, P2P extends the product lifetime by reducing the number of products needed and its related environmental impacts (use of resources, waste production, emission to soil, water and air). Considering the B2P practice, the new life cycle scheme not only ensures the same opportunity of P2P models, but it also offers new potentials for closing the loop (Fig. 4). B2P model produces a disruptive change that pushes the market into a transition from the traditional system of production and consumption to a new one: product service system. As a result companies are not just product/goods producers, but they become products suppliers. In other words, they don't offer anymore products to customers, but a full service for products to be used or upgraded, maintained or substituted along the whole lifetime. According to this approach, B2P has a higher potential in terms of circular economy approach (European Parliament, 2016).

The Life Cycle Thinking approach (LCT) integrated to sharing economy models allows to identify environmental benefits and criticalities so that to carefully assess the opportunity of the application of the models in different scenarios. This approach avoids the adverse effect in which the improvement in one single life cycle phase may create major negative impacts in other phases.

Benefits and critical issues can be outlined for each stage, as follows:

- **Pre-manufactory (1, 2) and manufactory stage (3):**

- *Direct benefits*: due to lower impacts related to avoided production of products (materials, energy, water, toxic and harmful substances etc.)

- *Potential benefits*: improved products and services design because if these have to be shared, they should be of a higher quality, meaning "more durable", innovative and more focused in eco-design (i.e. products that can be easily updated and disassembled, etc.) Other potential benefits may come because of reduced packaging.

- **Packaging and distribution stages (4)**

- *Critical issues*: potential negative impacts because of the redistribution of the product. Nevertheless, these impacts should be compared to the ones related to avoided purchase distribution ones. There can be greater impacts due to energy consumption because of the use of digital technologies such as logistic platforms.

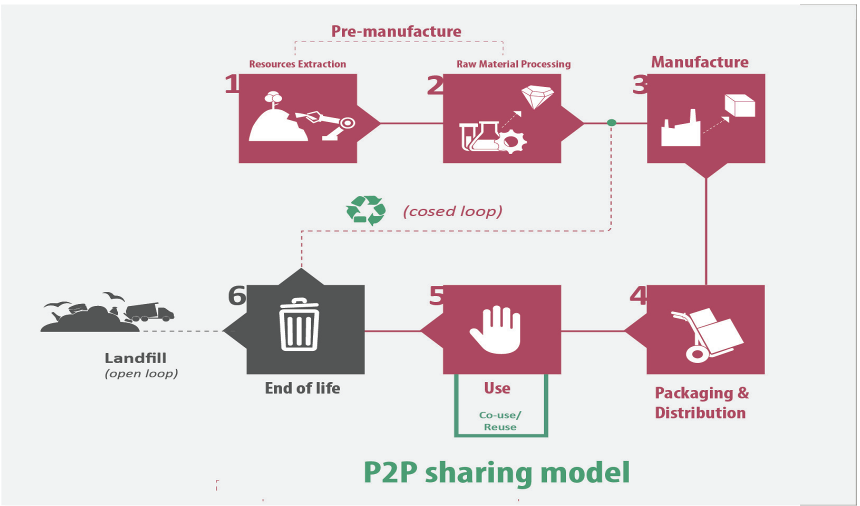

Fig. 3. Product Life cycle scheme with the integration of P2P sharing models (elaboration of the authors)

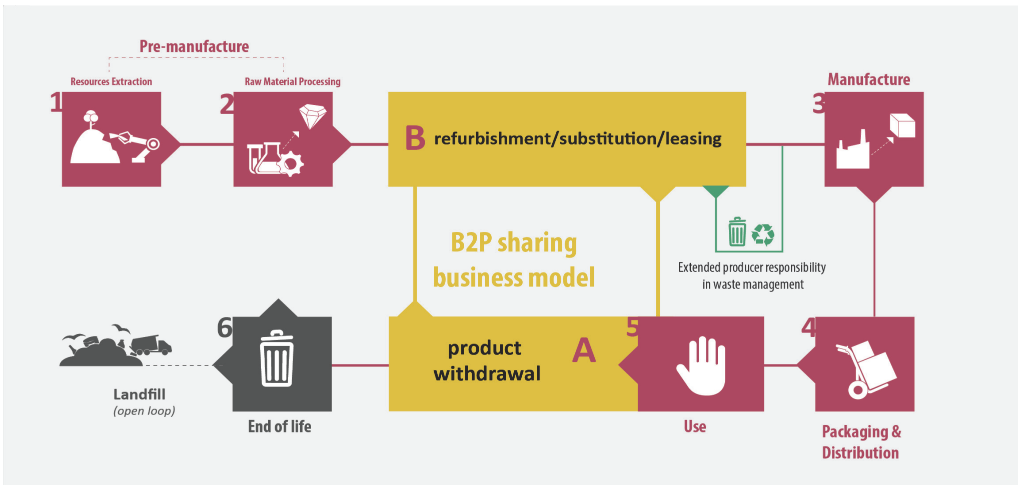

Fig. 4. Product life cycle scheme with the integration of B2P sharing business models (elaboration of the authors)

- **Usage and consumption stages (5):**

- *Direct impacts*: lower impacts related to products with better environmental and quality performance and lower consumptions (energy, resources, spaces, etc.) thanks to the shared use and the application of product – service system (PSS) which foresee a withdrawal and programmed updating.

- *Critical issues*: high frequency of usage may bring to a major obsolescence of the products.

- **End of life stages (6)**

- *Direct benefits*: The optimization of the underuse rate of the products and the extension of the materials cycle thanks to a longer useful life of the products, brings to a lower production of waste.

- *Potential benefits* (mostly for B2P): Waste management systems with extended responsibility to the producers. Thanks to the service/withdrawal system, the producers manage directly the disposal system with greater efficiency and regulation (i.e. through industrial symbiosis principals by re-introducing directly in other product cycles)

In the case of collaborative models **B2P**, there have to be outlined in particular the effects of two phases that become crucial in case of transition from products to services, in a product service system perspective:

✓ **in the withdrawal stage of the products (A):** potential impacts related to the transport and logistic. Greater impacts related to energy consumption due to digital platforms usage.

✓ **in the updating/maintenance stage of the product (B):** impacts related to consumption of resources and materials in the stages of updating, maintenance, regeneration and repair of the withdrawn products to reissue on the market.

6.2. Analysis of circularity potential of sharing economy in strategic sectors

In order to target the investigation to circular economy advantages of sharing economy, it has been chosen to analyse cases and sectors that have a greater impact in economic and environmental sustainability. For the identification of strategic sectors in a circular economy perspective, there have been analysed the following aspects: sectors with greater development potential through sharing models, critical sectors in terms of resources use, consumption and waste production, economics aspects and household expenditure.

According to this selection criteria the following sectors emerged:

- mobility sector;
- manufacture production sector;
- housing sector;
- agro-food sector.

For each sector, it has been realized an in-depth analysis considering previous issues and examples of successful sharing economy models, especially considering the environmental issues.

In the following tables, a synthesis of the much relevant data in terms of circular economy perspective/opportunity is provided for each sector.

6.2.1. Mobility sector

Mobility sector is contemporary the most inefficient one from a resources efficiency point of view, and one of the the most promising in terms of improvement through the application of sharing models. In a recent ENEA study (2014) it emerges that shared mobility has significantly reduced transport costs by allocating more travelers in less cars (fuel costs, tolls, parking, etc.). On the other hand, thanks to the reduction of vehicles in circulation, environmental benefits have also been produced.

6.2.2. Manufacture sector

Considering goods and products as a whole, it is difficult to present general data on related waste. Examples of critical environmental issues such as the use of precious materials, the use of toxic substances, polluting production processes or production of waste, vary from product to product in terms of quantity and triggers. However, the size of the problem can be intuitively understood.

6.2.3. Housing sector

Common spaces are popping up in new development projects across Europe. Many new buildings offer guest rooms, lounge areas for working and socialising, terraces with outdoor-kitchens, drying rooms for laundry – all shared by the owners of the flats. In 2012, an Ellen Mc.Arthur Foundation survey of 500 construction and building management CEOs predicted a 55% reduction through increasing of shared spaces and tele-working (staff-to-desk ratio). In Table 3, an analysis of **housing** sector and particularly the touristic services is provided.

6.2.4. Agro-food sector

The agro-food sector interacts with both, production and consumption. Production includes agricultural systems, supply chains and value chains, distribution and sales, while consumption includes the purchasing attitude of consumers.

These activities may be associated with two types of food waste (EC, 2010):

- Losses (foodlosses) which occur at the beginning of the food chain, mainly in the process of land use, growing, harvesting, processing, storage and processing of agricultural raw.

- Waste (foodwaste) that occurs during the industrial processing, distribution and final consumption.

The sharing platforms operating in the agrifood sector mainly intercept the second type of waste, also known as food waste.

Table 1. Mobility sector analysis

Losses, waste and resources consumption	- Typical European car is parked 92% of time. For the rest of the time there is: 1.6% looking for parking, 1% sitting in congestion, 5% driving. - Average European car has 5 seats but when the car is used, only 1.7 of its 5 seats are occupied. - 50% of most city land is dedicated to streets and roads, parking, service stations, driveways, signals, and traffic signs; road reaches peak throughput only 5% of time and, even at rush hour, cars cover only 10 percent of the average European road. - Less than 20 percent of the total petroleum energy is transformed into kinetic energy, and only 1/13 of that energy is used to transport people. (Ellen MacArthur Foundation, 2015)
Environmental Impacts	According the European Commission, cars are responsible for around 12% of total EU emissions of CO_2, the main GHG. Although these emissions have decreased by 3.3% compared to 2012, they are 20.5% more than in 1990. In the EU, transport is the only sector where GHG emissions continue to increase (EC, 2016). The road traffic exposes the 90% of city residents in Europe to air pollution levels considered harmful by the World Health Organization (WHO, 2016)
Examples of Sharing platform benefits	Among investigated platform in the **mobility** sector, a service of ridesharing like Blablacar optimizes the car use bringing important benefits especially from an environmental point of view. The occupation rate of cars shift from a European average of 1.7 to 2.8 passengers per car. This determines a reduction of the CO_2 emissions equal to a 500.000 oil savings per year and around 1.000.000 tones of CO_2 per year.

Table 2. Manufacture sector analysis

Losses, waste and resources consumption	- Considering all manufacture sectors, products are used on the average at 50% of their lifetime (for a drill, this percentage goes down to 5%). This estimate is much lower in the case of some electrical and electronic equipment which, while having durable hardware, they have a technological/aesthetic obsolescence much shorter. This means that despite the positive growth of innovation, the economic value associated with it disappears almost entirely due to the short life cycle (EC, 2015). - 77 % of European citizens declare to prefer repairing their goods rather than buy new ones, but frequently they have to replace or discard them because of the cost of repairs and the weak service provided. - Household waste (8,3%) and manufacturing waste(10,2 %) represent the 19,1% of total waste produced in EU (Eurostat 2014 – data updated in October 2018, (EC, 2016b)
Environmental impacts	As underlined by the European Sustainable Consumption and Production (SCP) policies, the need for a new generation of "green" products is essential to counter the environmental crisis we are experiencing. Manufacturing sector is responsible for most of the polluting emissions. Indeed, industrial processes and product use contribute with 8 % to EU-28 total greenhouse gas emissions (Eurostat, 2015) (EC, 2016b)
Examples of Sharing platform benefits	Concerning the **manufacture sector**, a study of the Italian sharing platform of new and used clothes "Subito.it", has estimated an annual saving of greenhouse emissions of 3.500.000 kg of CO_2e. In particular, most of the benefits can be associated to used cars trade. It has been calculated an emission cut of 2.664.260 kg of CO_2e. Furthermore, the reuse of goods and furnishing objects bring to 575.750 kg of savings and the second life of electronic devices avoids emissions for more than 250.000 kg of CO_2e.

Table 3. Housing sector analysis

Losses, waste and resources consumption	- EU-27 has 25 billion square meters of area, but most of these spaces remain empty or underused (i.e in housing rooms dedicated to entertainment or leisure activities, secondary school, stays, living rooms or rooms that are used very rarely as the guest rooms; in working sector meeting and waiting rooms, laboratories with equipment and services used sporadically) - Offices occupy some 1.4 billion square metres but the average European office is used only 35% – 40% of the time, even during working hours (Ellen MacArthur Foundation, 2015) - Construction sector contribute for 34,7% of total EU produced in EU (Eurostat 2014) (EC, 2016b) - According to the English Housing Survey (2014), 49% of houses in the UK are "under-employed", recording at least two bedrooms plus the declared needs.
Environmental impacts	According to ISO 21931-1 (2010), building sector in EU is responsable for: - 40% of total global emissions, - 40% of natural resources consumption, - 40% of global waste production.
Examples of Sharing platform benefits	Airbnb is the most famous platform offering sharing lodging. This service can also contribute to the greenhouse emissions reduction. According to Cleantech Group study (CTG, 2015), it has been estimated that environmental savings related to housing services offered by Airbnb platform in the North America, are equal to 67.500 m^3 of water and 9.5 millions of tonnes of greenhouse gasses.

Table 4. Agro-food sector analysis

Losses, waste and resources consumption	- FAO estimated that each year 1.3 billion tons of food are being wasted. It is equal to 1/3 of the total production intended for human consumption (FAO, 2013, 2016). - European average pro-capita waste production is 180 kg /year, of which: 42% in domestic waste and 58% in industrial system (39% production, 14% restaurants and 5% distribution) (EC, 2010). - Greenhouse gas emissions from agriculture contribute with 10 % to EU-28 total greenhouse gas emissions (Eurostat, 2015) (EC, 2016b)
Environmental impacts	- Food sector is the main responsible for changes in land use, loss of habitats and biodiversity, as well as for of climate change, water pollution and impoverishment of the soil (Tukker et al., 2006) - Current lifestyle combined with population increase will produce an important increase of emissions. According to Ellen MacArthur Foundation (2015), it is estimated that 18 billion of tons of CO_2eq (20% of total emissions) will arise from food sector by 2050. It is also estimated that more and by 2050 will be generated 1.9 to 2.5 billion of tons of CO_2eq per year due to food wastes for final consumption. The study shows therefore that about 14% of global agricultural emissions could be easily avoided through better management of use and food distribution. - According to the Save Food Initiative of FAO (2013, 2016), in developing countries the 40% of food waste take place in post-harvest and production phases while in industrialized countries the same percentage take place in the consumption and distribution phases. It follows that in the developing countries food losses are associated with a production system with inefficient agricultural infrastructure, whereas in industrialized countries such losses are more chargeable to inefficiency of the distribution and citizens behavior.
Examples of sharing platform benefits	A German sharing initiative, called Foodsharing platform, has had strong expansion. Currently it has registered 110.00 users in 200 cities in Germany, Austria and Switzerland, by realizing 270.000 collections in shops, restaurants, and supermarkets. The total saving in 3 years are 4 millions kg of food that otherwise would have been wasted. Other sharing initiatives for the food waste reduction are foodbanks. An example is the Italian association "Trentino Solidale" that estimates to have collected from the bins 7 tonnes of food every day (2.000 tonnes per year) for a monetary saving of 2.300.000 euro

4. Conclusions

The application of the sharing economy models to the productive system allows to overcome some barriers to innovation which are typical of the actual model of production and consumption. Considering the life cycle of the products and services, there are inefficiencies and environmental impacts in different sectors in all life cycle stages: raw materials extraction, production distribution, use and consumption, final disposal.

Sharing economy models offer the opportunity to overcome some barriers that cause these inefficiencies. From an economic point of view the adoption of sharing economy models will affect the final cost of the product which, being shared, is reduced sensibly. This phenomen has its own rebound effects in environmental impacts and resources consumption, but the paradigm could be a strategic market driver to boost the demand and consumption with high quality and environmental performances. On the other side, the difficulties of the companies to invest in research and development on eco-innovation of processes and products could be reduced. Moreover, the adoption of sharing economy models can become a strategy for companies to improve their market position towards circular economy approach.

Thanks to the increasing demand of high environmental performance goods and services, sharing economy business model based on the supply and assistance of products allows to achieve important results:

- Stimulate integration of eco-design strategies, particularly in the extension of usage phase and end of life phase by designing products that can be shared, collected and updated/replaced.
- Extend market share thanks to virtual communities. In the sharing economy, indeed, confidence is no longer between the company and the single customer, but between the company and a number of individuals connected in a virtual community. Through digital reputation system, the companies that invest in innovation and provide new systems and consumer models, may take advantage on a virtual "word of mouth" able to penetrate in wider market shares.

From a resource efficiency point of view, waste prevention and reduction, the sharing economy models offer significant opportunities, in particular the responsibility of the collection in charge of the companies (together with a rewarding regulation), may improve the waste management scenarios. This because there would not be dispersion of materials and resources at the end of life (re-issue through industrial symbiosis) and because this scenario would further stimulate the companies to design products that can be easily updated, maintained, and disassembled. The management strategies of post-consumer products, in a circular economy perspective, may also become a strategic market driver.

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CIRCULAR ECONOMY STRATEGIES FOR ELECTRIC AND ELECTRONIC EQUIPMENT: A FUZZY COGNITIVE MAP

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Abstract

A worldwide trend is leading the international community to explore the possible paths for the transition from a linear to a circular economic model. Recent studies identified the main enabling factors to facilitate this transition, among which closed loop logistics models and new service-based and function-oriented business models play a significant role. The diffusion of new business models relating to the use of a product rather than its ownership can indeed reduce material consumption and the related environmental impacts, while customer loyalty and company revenues are expected to increase. However, the overall impacts of such models on the environmental, economic and social perspectives are not clear, as several uncertainty factors arise with the implementation of non-ownership models. Therefore, the aim of this work is to evaluate impacts on sustainability dimensions due to the transition from an ownership-based to a product-as-a-service based model in direct and reverse supply chain of a large appliance product, i.e. washing machines. The analysis is carried out developing a fuzzy cognitive map model to quantify direct and indirect effects on the social, economic and environmental dimensions due to the adoption of a new business model. First, both the traditional and the leasing supply chain models are investigated. Then, the key drivers and their causal relationships affecting systems' performance are identified and discussed. Results stress out the great potential of such a change in the improving of the sustainable dimensions highlighting the enabling strategies viable by a policy maker to facilitate the transition to a product-as-a-service based model.

Key words: Circular Economy, closed-loop, fuzzy cognitive maps, product-service systems, sustainability

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1. Introduction

One of the biggest challenges for companies nowadays is decoupling economic growth from the environmental impacts related to resource depletion, pollutants emissions and waste management. In the last decades, the Circular Economy (CE) paradigm has become more and more popular as a possible path for a sustainable development, especially in the European and Chinese contexts (McDowall et al., 2017; Xiong et al., 2015). Several institutions and policy makers worldwide are encouraging the shift from a linear to a circular economic model, but this requires a deep change in the mindset of all the actors involved. In a CE perspective, every material flow entails a value, end-of-life outputs are not waste but a source of valuable materials and should be treated as such. The use of raw materials should be therefore minimized, and renewable sources should be preferred to non-renewable ones. The value of materials should be preserved over time, avoiding material losses and increasing their durability (Ellen MacArthur Foundation, 2013).

This radical change of perspective poses some challenges to manufacturing companies, while at the same time can represent an opportunity for business innovation and sustainable value creation (Park et al., 2010). However, a need for a redefinition of supply

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chain practices towards CE emerges. Zeng et al. (2017) show how a sustainable supply chain management can be the key to increasing CE capabilities, and it can be enhanced through institutional pressures.

Despite the increasing interest in CE, research about its implementation, including the economic and social advantages for companies and customers, is still lacking, as well as assessment tools to verify the effectiveness of circular strategies, although it is necessary for a successful implementation of circular models (Geng et al., 2012; Elia et al., 2017; Winans et al., 2017). Starting from these premises, in this work the authors analyze the implementation of a CE-oriented business model in the Electronic and Electric Equipment (EEE) sector through a case study, proposing an approach to identify the benefits and evaluate the effectiveness of an innovative circular model, based jointly on a product service system (PSS) proposition and on a closed-loop model. The analysis is carried out through fuzzy cognitive maps (FCM).

In Section 2, a literature analysis relating business model for circular economy is outlined and a description of the leasing-based Supply Chain (SC) is provided, as well as the Fuzzy Cognitive Map methodology and its application to the case-study. Scenarios analyses results are shown in Section 3, while conclusions and future development are in Section 4.

2. Materials and methods

2.1. Circular economy business models and closed loops in the EEE supply chain

The Ellen MacArthur Foundation (2013) reports that new PSS business models based on refurbishment and product life extension could be implemented with environmental benefits in several sectors, such as the automotive or the EEE. This last one, in particular, is considered crucial both for the volumes of e-waste generated annually, with a forecasted annual growth of 4-5 %, which often contain hazardous substances, and for the high value entailed in the materials used (Elia and Gnoni, 2015; Elia et al., 2016). For these reasons, policy pressures have been pushing the industry to search for sustainable solutions for the management of Waste from EEE (WEEE). As an example, the new European directive released in 2012 (2012/19/EU) prescribes a change in the collection target, which was so far of 4 kg/capita, switching to a floating target of 45% in weight of the EEE sold in the three preceding years. Reverse logistics models are already widely applied for the collection of WEEE, but collection rates are still pretty low: in 2014 the European countries' average was from 1.5 kg/capita in Romania to 14.9 kg/capita in Norway (Eurostat, 2016). Moreover, some major changes in the design are needed to allow easier recyclability and remanufacturing of the products (Ellen MacArthur Foundation, 2013). Several challenges related to reuse and remanufacturing of EEE have been identified in literature (Kissling et al., 2013; Kumar and Putnam, 2008). Some of them could be tackled through the implementation of new circular economy oriented business models, such as leasing (Ellen MacArthur Foundation, 2013). This solution involves two of the main pillars and enabling actions of CE: PSS use-oriented business models, contributing to the dematerialization of the offer (Mont, 2002), and closed-loop models, aiming at increasing products and materials recovery (Elia et al., 2017). In particular, the following barriers could be overcome through business model innovation:

- the need for sufficient volumes and quality of used products;
- the unpredictability of return rates;
- the uncertainty of demand;
- the competition from the informal sector and the illegal market;
- the uncertain economic profit;
- the lack of information systems to support take-back.

A leasing based business model, where the user has access to the product for a predefined amount of time (e.g. 5 years), would indeed allow the producer to decrease the uncertainties related to return rates and volumes, while the benefits of a maintenance service can increase the quality of the products collected at the end of the contract. At the same time, take-back would be guaranteed, decreasing the diversion to illegal market and informal sector. The economic profit for the producer should be deeply analyzed to ensure the viability of such a model. However, a deep analysis of customers' willingness to adopt new business models is also needed, since literature suggests that sustainable business models are not necessarily appealing to the user (Pérez-Belis et al., 2017).

Among the actions identified as enablers for the implementation of CE strategies, organizational changes are widely acknowledged to be a fundamental and critical step for successful CE strategies (De los Rios and Charnley, 2016), as a way to reduce the environmental burden related to the product, while extending the product and/or its components lifetime (Tukker, 2015). Despite the implementation of new business models – such as PSS – has been identified as an enabling factor for the transition to CE, a few studies have attempted to analyze the challenges related to business innovation oriented to circularity and its effective impacts for the companies.

Schulte (2013) identifies five key principles on which a circular business model should be based: waste minimization, understanding the total ecosystem of the business, maximizing flexibility through design, use of renewable energies, and energy efficiency maximization.

Some insights are present in literature about specific sectors. Despeisse et al. (2016) analyze the potential of 3D-printing to open CE paths, reviewing some of the main research questions on the topic, including considerations on the business model transformation. Johansson et al. (2016) give an example of business model conceptualization towards CE, exploring the main issue to address when designing a PSS for urban mining. Moreover, an analysis of business model innovation towards CE has been presented by Weissbrod and Bocken (2017), who started from the test case of a clothing retailer to understand how a company can build the necessary organizational capabilities to move from linear to circular model, summarizing their findings through nine key lessons.

On a more strategic level, De los Rios and Charnley (2016) focus on the transformation that CE requires for production and consumption systems, identifying the role of design as a key to tackle this challenge. Starting from some multinational enterprises case studies, they try to identify the main requirements and proficiencies necessary for successful design innovations.

Cohen and Muñoz (2016) investigate the implementation of Sustainable Production and Consumption (SPC) systems and sharing economy initiatives in cities, elaborating a typology of sharing SPC-oriented activities. On one side, the authors underline the potential of SPC and sharing economy for positive implication on sustainability and CE, on the other side, they point out the lack of empirical evidence to evaluate the actual impacts of these paradigms. Similarly, Witjes and Lozano (2016) propose a collaborative framework between sustainable public procurement and sustainable business models oriented to the transition to CE.

Finally, Pialot et al. (2017) explore the concept of upgradability as a way to contrast product obsolescence, combining it with the PSS business model. The result is a hybrid model called “Upgradable PSS”, in which optimized maintenance, refurbishment and offer servitization can open new perspectives for both businesses and customers, who would act in a continuous interaction, and facilitate the transition to a CE. The authors underline how the advantages of such an offer could push the customer to choose use-based models rather than ownership-based ones, helping the business to increase control over products and components flows.

Several other works can be found in literature analyzing the introduction of innovative business models for sustainability, although they do not explicitly refer to CE strategies. Mont and Tukker (2006) underline the growing importance and adoption of PSS, which is increasing knowledge and management capabilities of these business models. Guidat et al. (2014) propose a set of guidelines for the definition of innovative industrial

PSS for remanufacturing, with the aim of supporting the transition to the new business model. Gelbmann and Hammerl (2015) analyze an example of sustainable PSS based on reuse model, showing its positive impact on the three dimensions of sustainability, while Wells and Seitz (2005) highlight that business models based on closed-loop systems can contribute to reach sustainability goals.

Despite the interest shown towards the application of closed-loop and PSS as suitable ways for a transition to CE, none of the works analysed consider the joint effects of both tools on a supply chain level, and only a few of them attempt to evaluate the impacts of these actions on sustainability.

Moreover, although the high value of EoL materials from WEEE and the critical importance of this waste flow, research about business model innovation oriented to circularity in the EEE sector is lacking. The aim of this work is to contribute to fill the gap, proposing the joint application of two CE pillars to this sector: PSS and closed-loop models. To understand the viability and the benefits and challenges related to this business model proposition, an assessment of the impacts of this solution on all the actors involved in the EEE supply chain is needed. To do this, the test case of the washing machines segment is explored in the following sections.

2.2. The supply chain in analysis

Washing machines market is currently heavily dependent on product lifetime and prices. Similarly to other mass customized products, one main driver for product evaluation is the price: this forces towards entry-level machines usually characterized by short lifetime. In the long period, this economic advantage is completely inverted. Indeed, the user cost per washing cycle is 55 % lower for high-end machines (Ellen MacArthur Foundation, 2013). The transition to a leasing-based model allows overcoming high-end segment entry barriers constituted by the price and, due to a win-win strategy, to spread more benefits between producers and consumers. A recent study (Ellen MacArthur Foundation, 2013) has outlined several benefits due to this transition. For the producer point of view, moving from an ownership-based to a leasing-based business model will allow to optimize its supply chain due to a more high and stable product return rate along as well as a greater control over the time usage of products.

From an environmental point of view, the leasing-based business model ensures easier and higher value of the recovered materials in terms of both quantity and quality of flows, addressing one of the main criticalities of EEE remanufacturing related to the state of the returned product that also affects the cost-efficiency of the process (Nitkiewicz and Starostka-Patyk, 2017). From the consumer point of view, the transition to leasing-based model ensures an easier access to the high-end market products as well as time usage flexibility and increased service level due to a more simple extension of the warranty period.

Thus, a new supply chain model for washing machines is proposed based on the integration of leasing based model for the direct flow of materials and closed loop models for managing reverse logistics flows of waste. The main actors and processes are depicted in Fig. 1. The main actor of this supply chain is the Service Provider Company (SPC), which is directly involved in managing leasing contracts, as well as maintenances activities; it completely replaces the 'traditional' retailer, which is usually responsible only of sale activities. Since in the proposed SC no redemption of leasing agreements would be possible for both households and commercial users, the leased product is collected after the use phase. A third party Logistic Service Provider (3LSP) would be designated for transportation and collection processes. The collected products are then sent to refurbishment processes managed directly or indirectly from the SPC. Refurbishment processes usually relate replacement of the common break points (motor, pump, bearing etc.) or improvements in energy efficiency programs enabling the refurbished products leased for consecutive times. Indeed, the SPC is also responsible for managing the second-hand products leasing contracts too. When the refurbishment processes are not viable for technical or economic reasons, EoL washing machines are recycled. SPC is responsible also for secondary raw materials markets and scrap disposal.

2.3. The proposed Fuzzy Cognitive Maps model

To overcome the current literature gap, the authors propose a Fuzzy Cognitive Map (FCM) to quantitatively asses how multiple tools of the CE paradigm could contribute to increase the overall effectiveness of the Electric and Electronic Equipment (EEE) supply chain from a sustainability point of view. The FCM methodology allows evaluating interrelated impacts due to multiple sources of factors: this is the case in analysis where the simultaneous presence of leasing based business model and a closed loop reverse logistics model are jointly applied to transform the traditional EEE supply chain in a more circular one.

FCMs are a modelling methodology based on exploiting knowledge and human experience to both design and control complex and dynamic systems, drawing a causal picture to represent the model and the behavior of a system (Groumpos, 2010). Originally introduced by Kosko (1986) as an extension of the forerunner cognitive maps proposed by Axelrod (1976), FCMs are directional diagrams to represent causal reasoning. FCMs fuzziness allows the forward and the backward direct and indirect systematic causal propagation assessment (Glykas, 2010; Henly-Shepard et al., 2015).

As depicted in Fig. 2, FCMs consist of three main elements:

- concepts (*n*): they represent the *i*-th nodes of the graph C_i and stand for variables describing features and behavioral characteristics of the analyzed system (Stylios and Groumpos, 2004);
- arcs: the directed arcs stand for causal interactions between C_i and C_j concepts;
- relative weights, w_{ij}: each w_{ij} varies from [-1; 1]; it represents the degree of influence that the value of C_i has on the value of C_j (Papageorgiou and Stylios, 2008). Three possible interaction exist: *positive causality* ($w_{ij} > 0$), i.e. the increase of the concept C_i causes the increase of the concept C_j; *negative causality* ($w_{ij} < 0$), i.e. the increase of the concept C_i causes the decrease of the concept C_j; and, finally, *no influence* if $w_{ij} = 0$.

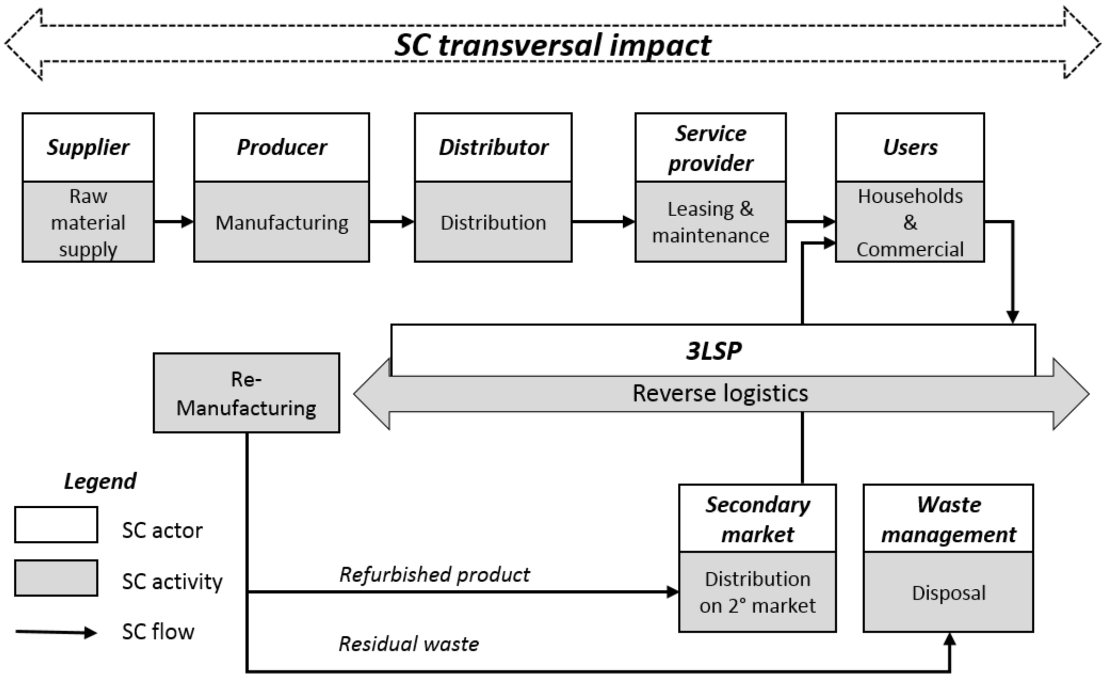

Fig. 1. Leasing based SC

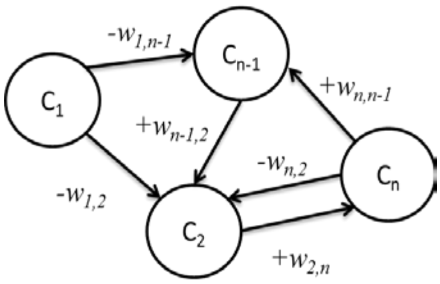

Fig. 2. Example of an FCM representation

Thus, the first step of the proposed FCM model has been to outline the concepts that compose the FCM. By analyzing the literature review about the specific supply chain and the two CE tools applied, i.e. leasing based and closed loops models, four main concepts categories have been outlined for each levels of the analyzed supply chain: economic, environmental, social and technical ones. The consistency of the overall concepts has also been checked through an experts' analysis. Data are reported in Table 1.

Once the concepts have been identified, the causal relations and relative weights between concepts have to be determined, thus constructing the map in Fig. 3.

Starting from the total number of both components (29) and connections (72) identified, the density index is evaluated showing how connected or sparse is the map (Hage and Harary, 1983). The map density is 0.09 consistent with values observed in literature (Klein and Cooper, 1982; Malone, 1975). The complexity score, calculated as the ratio between receivers and transmitters (Gray et al., 2014; Özesmi and Özesmi, 2004), is an indicator of how the system is perceived to be complex. The complexity index for the developed map is equal to 2.5, as well as the average number of connections per component.

Table 1. FCM Components based on SC level and impact category

SC level	*FCM Concepts*	*Impact category*	*References*
Suppliers	Suppliers' orders generation rate (C1)	Economic	-
Producer	Raw materials flow mass rate (C2)	Environmental	Baines et al. (2007); FORA (2010)
	Remanufacturing processes cost (C3)	Economic	Mont (2002)
	Net recovered materials rate (C4)	Economic	Mont (2002)
	Landfilling cost (C5)	Economic	consequence of waste generation
	Producer profit (C6)	Economic	Baines et al. (2007)
	Refurbishment products volume (C7)	Technical	consequence of leasing
	Recycling rate (C8)	Environmental	Mont (2002)
	Extension of product lifetime (C9)	Technical	Mont (2002)
	Production outputs rate (C10)	Technical	consequence of lifetime extension
Distributor	Traceability and take-back forecasting effectiveness (C11)	Technical	consequence of leasing
Service provider	Leasing contract rate (C12)	Economic	-
	Service provision and maintenance rate (C13)	Technical	consequence of leasing
3LSP	Reverse logistics rate (C14)	Technical	Baines et al. (2007), Mont (2002)
	3LSP commissions generation rate (C15)	Economic	consequence of reverse logistics service
Secondary market	Refurbished products sold rate (C16)	Economic	
User	Illegal market size (C17)	Economic	consequence of traceability
	Ownership product rate (C18)	Technical	Baines et al. (2007) Demyttenaere et al. (2016), FORA (2010)
	Customer cost (C19)	Economic	Fora (2010)
	Customer service level (C20)	Technical	Baines et al. (2007)
	% of products used for an efficient time period (C21)	Technical	-
	Availability rate of high-end machines (C22)	Social	Baines et al. (2007), FORA (2010)
	Spread rate of technologically updated products (C23)	Technical	FORA (2010)
Waste management	Waste generation rate (C24)	Environmental	Baines et al. (2007)
Transversal impacts	Tax incentives (C25)	Economic	FORA (2010)
	Emissions reduction rate (C26)	Environmental	Baines et al. (2007)
	Public consciousness and involvement in CE (% of people) (C27)	Social	-
	Leasing public acceptance (% of people) (C28)	Social	consequence customer cost, equity
	Normative compliance (C29)	Technical	consequence of recycling

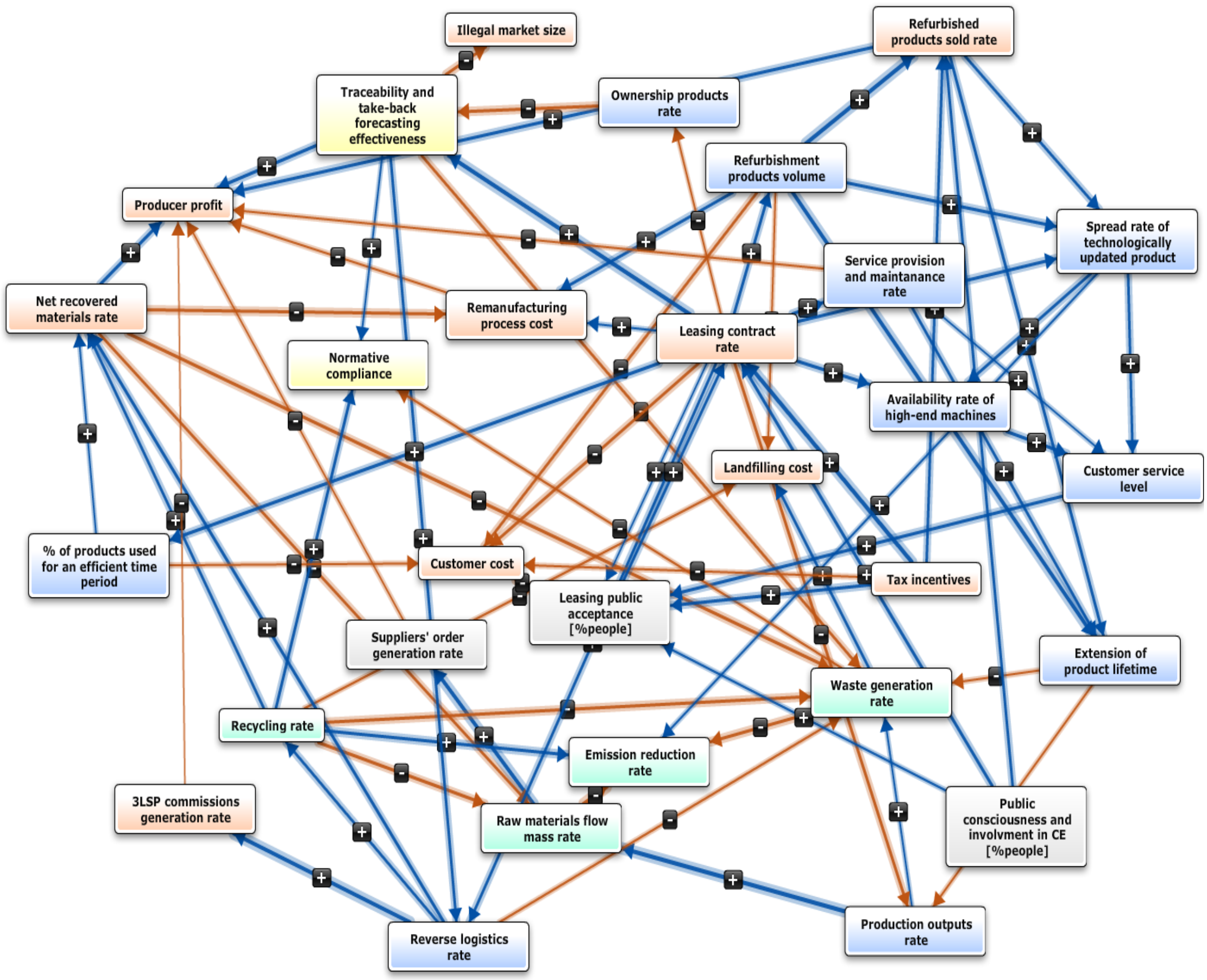

Fig. 1. FCM: identification of causal relations and relative weights

According to graph theory, FCM can be converted into a *(n* x *n)* square matrix 'W', where both the rows and the column represent the *i*-th concept and each cell represents the weighted influence existing between concepts (Özesmi and Özesmi, 2004). Weight values are assigned to each arc by following the membership functions explained in (Stylios and Groumpos, 2000). As an example, in our map $w_{3,6}$ is posed equal to -0.80 since when the 'Refurbishment Process Cost (C3)' decreases, the 'Producer Profit (C6)' increases. According to membership functions, the casual influence by which the 'Refurbishment Process Cost' influences the 'Producer Profit' is negatively very strong meaning an influence below to -75 %. The FCM related adjacency matrix W is reported in Table 2. In a FCM, concepts could be classified as transmitter (also called drivers, forcing functions, sources), receiver (or utilities, ends, sinks) and ordinary variables by evaluating their outdegree and indegree values (Harary et al., 1965; Özesmi, 1999). The outdegree value shows the cumulative strength of connections exiting the concepts, while the indegree shows the cumulative strength of connections entering the concept (Özesmi, 1999). Consequently, transmitter concepts have a positive outdegree and zero indegree. On the opposite, receiver concepts have a positive indegree and zero outdegree. A positive indegree and outdegree characterizes the ordinary concepts. The centrality index, calculated as the sum of indegree and outdegree, represents the contribution of a concept in the map and how strongly it is connected to other concepts. The indegree and the outdegree have been evaluated to identify drivers, receivers and ordinary variables as well as to establish the centrality for each component (Table 3). Two transmitter concepts have been identified:

• Tax incentives (C25): it represents a 'user incentive-scheme' to foster the adoption of a new business models based on leasing contracts.

• Public consciousness and involvement in CE (C27): it jointly represents policy measures aiming at increasing awareness and commitment of users in CE milestones, influencing their inclination to the adoption of the new business model.

These variables are the policy variables as they could be modified by policy makers with the aim of improving the economic, environmental, technical and social performance of the analyzed supply chain.

Table 2. Adjacency matrix ‘W’

	C1	***C2***	***C3***	***C4***	***C5***	***C6***	***C7***	***C8***	***C9***	***C10***	***C11***	***C12***	***C13***	***C14***	***C15***	***C16***	***C17***	***C18***	***C19***	***C20***	***C21***	***C22***	***C23***	***C24***	***C25***	***C26***	***C27***	***C28***	***C29***
C1	0	0	0	0	0	-0.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2	0.88	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.85	0	0	0
C3	0	0	0	0	0	-0.4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C4	0	-0.5	-0.55	0	0	0.6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.75	0	0	0	0	0
C5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C7	0	0	0.8	0	-0.4	0	0	0	0.85	0	0	0	0	0	0	0.88	0	0	-0.53	0	0	0	0.65	0	0	0	0	0	0
C8	0	-0.6	0	0.65	-0.43	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.8	0	0.8	0	0	0.75
C9	0	0	0	0	0	0	0	0	0	-0.43	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.38	0	0	0	0	0
C10	0	0.85	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0	0	0	0	0
C11	0	0	0	0	0	0.6	0	0	0	0	0	0	0	0.7	0	0	-0.8	0	0	0	0	0	0	-0.55	0	0	0	0	0.43
C12	0	0	0.45	0	0	0	0.8	0	0	-0.5	0.88	0	0.83	0.78	0	0	0	-0.48	-0.6	0	0.7	0.5	0.68	0	0	0	0	0.43	0
C13	0	0	0	0	0	-0.2	0	0	0.7	0	0	0	0	0	0	0	0	0	0	0.43	0	0	0	0	0	0	0	0	0
C14	0	0	0	0.7	0	0	0	0.75	0	0	0	0	0	0	0.85	0	0	0	0	0	0	0	0	-0.45	0	0	0	0	0
C15	0	0	0	0	0	-0.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C16	0	0	0	0	0	0.7	0	0	0.725	0	0	0	0	0	0	0	0	0	0	0	0	0	0.65	0	0	0	0	0	0
C17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C18	0	0	0	0	0	0	0	0	0	0	-0.63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.68	0
C20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.65	0
C21	0	0	0	0.38	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.35	0	0	0	0	0	0	0	0	0	0
C22	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.8	0	0	0	0	0	0	0	0	0
C23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.8	0	0.65	0	0	0	0.35	0	0	0
C24	0	0	0	0	0.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.65	0	0	-0.45
C25	0	0	0	0	0	0	0	0	0	0	0	0.85	0	0	0	0.6	0	0	-0.4	0	0	0	0	0	0	0	0	0.8	0
C26	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C27	0	0	0	0	0	0	0	0	0	0	0	0.6	0	0	0	0.5	0	0	0	0	0	0	0	0	0	0	0	0.28	0
C28	0	0	0	0	0	0	0	0	0	0	0	0.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C29	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Receiver variables reflect the totality of causal relations between ordinary variables and of strategies implemented for transmitter variables; five receiver concepts have been also identified:

• Landfill cost (C5): It represents the cost incurred to dispose of not recyclable products/components.

• Producer profit (C6): It represents the producer earning due to the production and the sell/leasing of the washing machines.

• Emission reduction rate (C26): It represents the emissions cuts due to recovered and recycled materials flows, as well as to improved energy efficiency programs.

• Normative compliance (C29): it represents the compliance with European directives.

• Illegal market size (C17): it represents an economic and social measure of illegal phenomena affecting the EEE market.

The more central concepts are the '*Leasing contract rate'*, '*Waste generation rate*' and the '*Net recovered material value*'. Full data about each concept are in Table 3.

Next, the mathematical resolution of the map is developed. In detail, the column matrix A^t represents the value of each concept at each iteration step *t* within the range [-1; 1]. It is calculated through equation (1) where *f* is the threshold function.

$$A^t=f(A^{t-1}+A^{t-2}W) \quad (1)$$

Usually, two kinds of threshold function are employed, depending on the methods used to describe the concepts (Stylios and Groumpos, 2004). The mathematical modeling of FCM refer to Papageorgiou and Salmeron (2014) and Papageorgiou and Kontogianni (2012).

3. Results

The developed FCM has been digitized in the software Mental Modeler (Gray et al., 2013) and used to explore different scenarios, in order to evaluate the impact of some possible strategies on the sustainability dimensions all along the supply chain. Two scenarios have been considered:

• Scenario 1: it refers to the baseline scenario where the new business model based on leasing contracts has been introduced without any incentives;

• Scenario 2: it differs from the previous one only due to the adoption of tax incentives and policies oriented to increase public consciousness and involvement in CE issues (C12, C25 and C27) for supporting the new business model.

The results obtained for both the scenarios are shown in Fig. 4.

Table 3. FCM inference: Initial steady state and indexes

COMPONENTS	*INDEGREE*	*OUTDEGREE*	*CENTRALITY*	*TYPE*
C1	0.88	0.20	1.08	ordinary
C2	1.95	1.73	3.68	ordinary
C3	1.80	0.40	2.2	ordinary
C4	1.73	2.40	4.13	ordinary
C5	1.58	0	1.58	receiver
C6	2.80	0	2.80	receiver
C7	0.80	4.11	4.91	ordinary
C8	0.75	4.03	4.76	ordinary
C9	2.28	0.81	3.09	ordinary
C10	0.92	1.25	2.17	ordinary
C11	1.51	3.08	4.59	ordinary
C12	1.95	7.61	9.56	ordinary
C13	0.83	1.33	2.16	ordinary
C14	1.48	2.75	4.23	ordinary
C15	0.85	0.10	0.95	ordinary
C16	1.98	2.08	4.06	ordinary
C17	0.80	0	0.80	receiver
C18	0.48	0.63	1.10	ordinary
C19	1.88	0.68	2.56	ordinary
C20	2.03	0.65	2.68	ordinary
C21	0.70	0.73	1.43	ordinary
C22	1.15	0.80	1.95	ordinary
C23	1.98	1.80	3.78	ordinary
C24	3.33	1.85	5.18	ordinary
C25	0	2.65	2.65	trasmitter
C26	2.65	0	2.65	receiver
C27	0	1.38	1.38	transmitter
C28	2.83	0.50	3.33	ordinary
C29	1.63	0	1.63	receiver

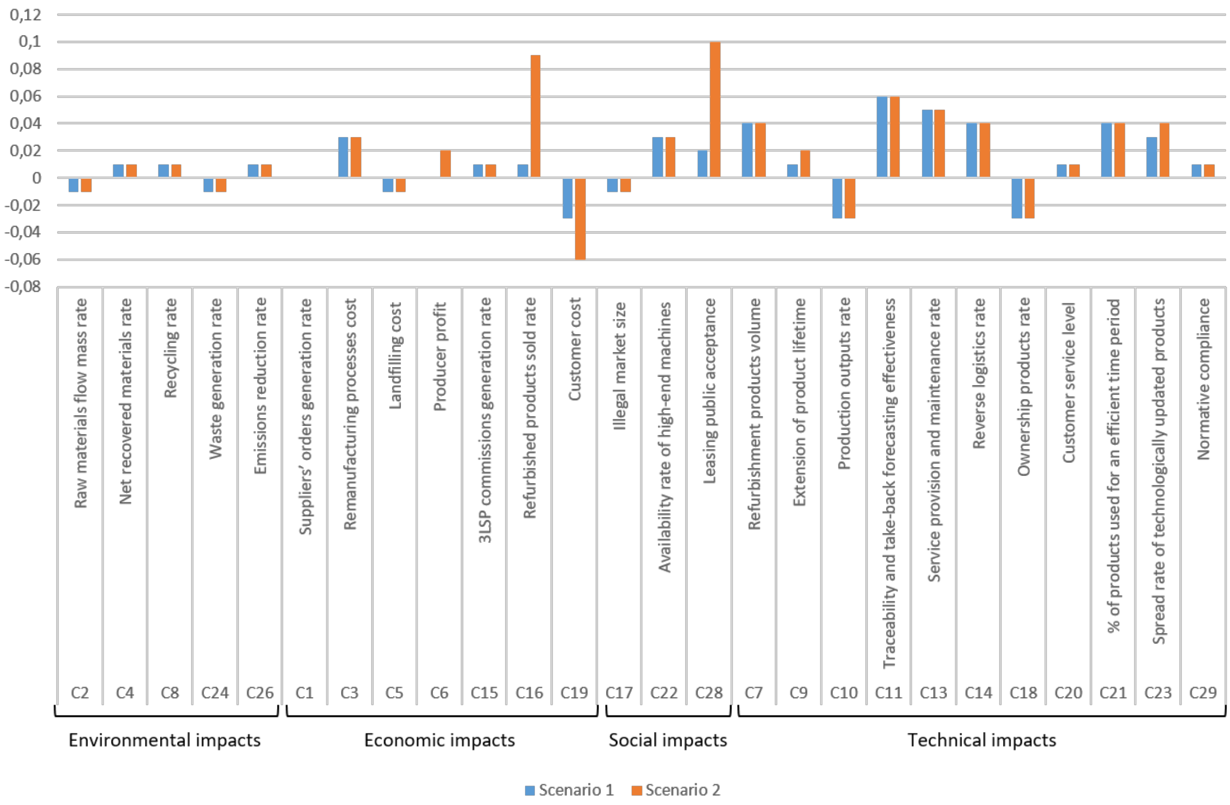

Fig. 2. Scenario analysis results

The introduction of leasing contracts in scenario 1 is compliant with four of the five objectives introduced as a performance measurement, causing a decrease of landfilling costs and illegal market size, while increasing the emission reduction rate and the normative compliance. This is mainly due to a lower waste generation rate. The combination of a more efficient reverse logistics with an increase in traceability effectiveness allow to divert the used products from the illegal market, increasing, at the same time, the recycling rate and the net recovered material rate. On the economic side, we notice that the producer profit does not change a lot by introducing the new business model; this is mainly due to increased costs to remanufacturing and service provision, which compensate for the lower production volumes and the sales of refurbished products.

Differently from scenario 1, in scenario 2 financial and social measures to support the introduction of the new business models have been evaluated. On the social side, the wider access to high-end machines allows even low-income customers to benefit from good quality products thus saving costs. Thus, we can notice how the introduction of tax incentives and public awareness oriented policies can support better the economic feasibility of the new business model. Due to a huge increase of the refurbished products sales compared to scenario 1, the producer profit increases thus amplifying benefits of the new business model.

At the same time, the customer cost decreases. Two other components are affected by the policy measures introduced: the extension of the products lifetime and the spread of technologically updated products, due to the increase of refurbished products sold.

While most of the technical, social and environmental impacts are confirmed in both scenarios, the introduction of incentives in scenario 2 seems to boost the economic sustainability of the business model, at least in the starting phase. Both the cost for the customer and the producer's profit would benefit from the measures considered, increasing the market profitability and the public acceptance of the model. Considering the complexity of the innovation at the supply chain level and according to these results, we can suggest that a policy oriented to financial and motivational support could increase sensitively the effectiveness of the model proposed.

Summarizing, on one side, this analysis confirms the positive benefits expected from the implementation of a PSS closed-loop model in the washing machine segment on the four dimensions considered. On the other side, it outlines quantitatively the potential contribution of such policy measures and how they could significantly be used to support the transition to use-based business models.

4. Conclusions

In this paper, the authors analyze the effects on economic, environmental, social and technical performance due to a shift from a traditional ownership-based business model to a leasing-based business model for washing machines. For this purpose, a FCM is developed.

Results obtained witness the robustness of the developed FCM in the evaluation of the forward and the backward systematic causal propagation for the circular economy strategies detection. Starting from the transmitter variables identified in the map (*'Tax Incentives'* and *'Public consciousness and involvement in CE'*), two different scenarios have been evaluated. Simulation solutions stress out the great potential of the leasing-based model since the sustainable performances tend to improve in the scenarios analyzed.

Allowing a better flows traceability, the introduction of leasing contracts enables the reduction of the illegal market size and increases the recycling rate. These in turns influence (increasing their value) the normative compliance, the net recovered material rate and consequently the emissions cut. Additional improvements affect the economic aspects: decreasing of both the incurred landfill cost and of the customer cost. The latter could be further improved by introducing targeted policies to improve user awareness and commitment in CE issues, fostering the adoption of the leasing model and considerably increasing the sales of refurbished products. In this case, the producer profit increases too. The lower cost perceived by the users increases their acceptance of the new business model triggering a very 'virtuous cycle'.

The wider access to high-end machines also contributes to increase the social sustainability of the model. This work shows the potential benefits of PSS, closed-loop based business models on the sustainability performance of supply chains in the washing machines segment. It is a business model that initially requires auxiliary policies to facilitate its development and to ensure the economic viability for companies.

Supportive measures identified are the introduction of tax incentives and investment to increase public awareness and involvement. Future developments should address the quantification of flows managed in both direct and reverse logistics and relative costs and revenues for each actor involved in the system for a better prediction over the time of the system performance.

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ORGANIC WASTE VALORIZATION THROUGH COMPOSTING PROCESS: A FULL-SCALE CASE STUDY IN MAXIXE, MOZAMBIQUE

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Abstract

Organic solid waste and the current lack of sound treatment for its valorisation are of high priority for decision makers in developing countries. Despite the remarkable use of composting processes in those areas, an appropriate scientific literature as well as databases are still lacking, hampering the sustainable implementation of composting process. This paper contributes to cover this gap, presenting a full-scale case study in Maxixe, Mozambique. Technical characteristics and detailed operational data (e.g.: process duration, frequency of pile turning, pile temperature trend) of the composting plant represent useful information that can support technicians interested in designing and operating composting plants in developing countries.

Key words: Composting, developing countries, Mozambique, organic waste, waste recovery

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1. Introduction

The organic fraction of municipal solid waste (OFMSW) is assuming an increasing interest in the last 15 years, especially in urban and peri-urban areas (Vaccari et al., 2013; Zurbrügg et al., 2014). This is due to the introduction of the Integrated Solid Waste Management (ISWM) concept (van de Klundert, 2001; Wilson et al., 2013), which entails an organized and sustainable waste management system towards the waste recycling and environmental impact minimization (Di Bella and Vaccari, 2014). The valorisation of organic waste through composting process is widely applied in developing countries (Charisiou et al., 2016; Harper et al., 2004; Yhdego, 1994; Zurbrügg et al., 2012). This is because composting is regarded as a sustainable way to manage organic waste: it helps solving the problem of waste disposal and produces organic fertilizer (or compost) as an end product (Lim et al., 2016; Wu et al., 2014; Zhao et al., 2016).

The scientific literature includes mainly laboratory and pilot scale experiences, pointing out different aspects and findings about the composting process, such as kinds of bacteria involved into the degradation process, chemical quality of the produced compost, alternatives for compost utilisation, reduction of greenhouse gas emission (Cabañas-Vargas et al., 2013; Friedrich and Trois, 2013; Oberlin and Szanto, 2011; Pebler and Barkdoll, 2016; Van Fan et al., 2016). Nevertheless, all those data are not enough to support field practitioners who will to start-up and manage a composting plant in a low or middle-income country. Very often, chemical and biological laboratories able to assess compost quality or to analyse the biomass involved into the composting process are not available in those contexts, therefore it is difficult to use the literature data as a reference. Moreover, the lack of environmental laws and guidelines hampers further the sustainable implementation of the composting process and the final compost utilization (Zurbrügg et al., 2004).

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Technicians and operators who want to start-up and operate appropriately a composting plant in developing countries look for basic information based on full scale experiences and referred to simple parameters that can be easily measured in those areas. Unfortunately, the literature on composting process usually does not include those kinds of information; this paper contributes to cover this gap, presenting data regarding a full scale composting plant placed in Mozambique. Specifically, this work presents the characteristics of that plant and its operating data collected thorough a specific monitoring campaign.

2. Materials and methods

2.1. Maxixe city background

Maxixe city is located on the coast of the Inhambane province; according to the Mozambican national institution of statistics (INE, 2013), the resident living population is equal to 125,208 inhabitants. A number of 21,767 people live in the Chambone neighborhood, where waste collection is insufficient as in many other African cities (The worldbank, 2012). As a result, the solid waste is abandoned along the streets or burned inside the municipal street container, where present. CeLIM, an Italian NGO, has implemented a project to reduce the environmental and sanitary problems caused by the inadequate waste management in Maxixe district.

To achieve the project goals, new street containers were introduced in order to increase the volume of collected waste and at the same time to reduce the uncontrolled dumping along the streets.

Moreover, a centralized composting plant was built near Maxixe dumpsite to treat the OFMSW produced in Chambone neighborhood, which represents 40% of the total produced waste (Fernando and Carmo Lima, 2012). CeTAmb LAB (Research laboratory on Appropriate Technologies for Environmental Management in resource-limited Countries) of the University of Brescia) was involved in the starting-up and monitoring of the composting plant in order to improve its treatment capacity and operational performances.

2.2. Plant description

The Maxixe composting plant (Fig. 1) includes one area for the OFMSW selection and grinding, 18 covered cells for the biological process, one area for compost refining and two water tanks. Moreover, an office, a compost storehouse, a toilette with shower and a plant nursery complete the facility. The base of each composting cell is perforated and raised above the ground to favour compost aeration and possible leachate leakage.

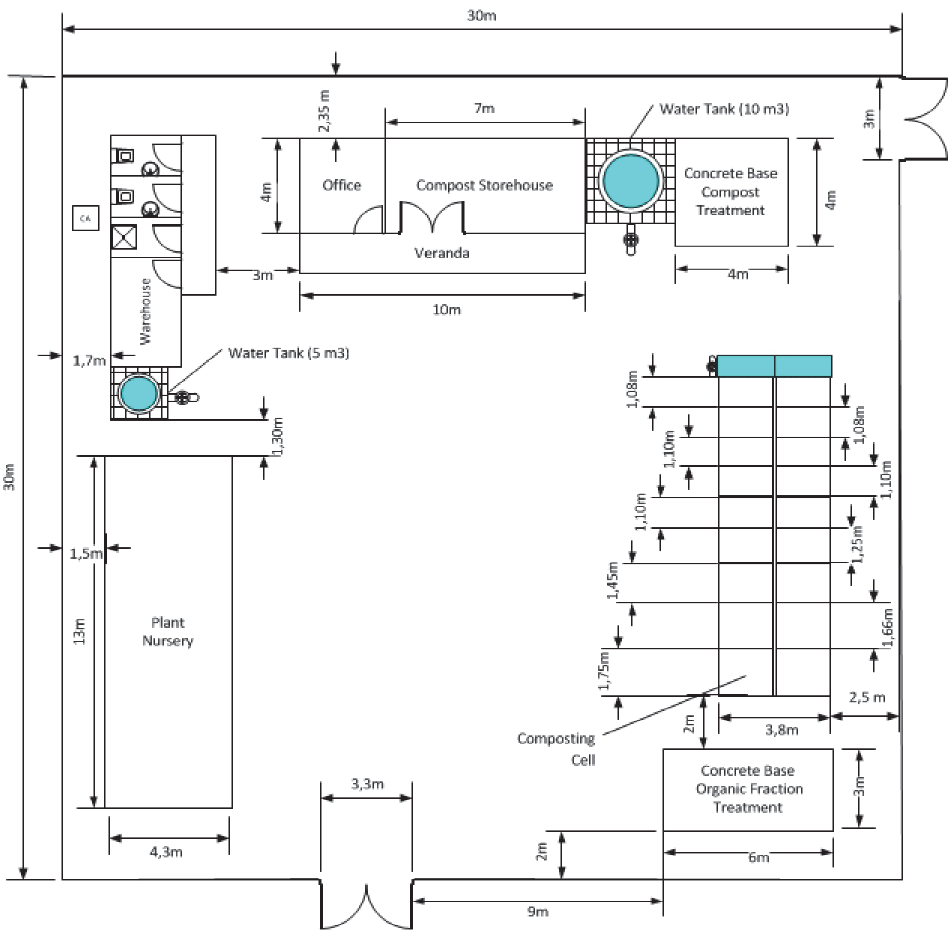

Fig. 1. The composting plant scheme

Three operators work in the composting plant. The composting plant receives mainly food left overs, leaves, tree branches, grass and sawdust. Approximately, 80% of the organic waste is manually collected directly at the close dumpsite; the remaining part is represented by organic waste collected at local markets and restaurants. The plant operators check the waste, remove manually the undesired materials (e.g. plastic, metal, glass), grind coarse organics (as tree branches) and put the mixed waste in the first composting cell. The volume of the first pile is about 3.5 m^3. The pile is usually moved by shovels into the second cell after 7 days, then into the third cell after further 7 days and so on. Since the cells are 18, the composting treatment lasts about 4 months. This is in line with the results obtained by Awasthi et al. (2014), who observed that weekly turning regime led to a significant increase in aerobic bacteria populations in compost piles.

The process temperature and the moisture content are monitored to verify the biological process is not inhibited. Moisture content is evaluated by means of the squeeze test described by Rothenberger et al. (2006). Water is added by the operators when the pile moisture is lower than 40%.

At the end of the composting process, the compost is extracted and air-dried on a concrete base for 24 hours. Finally, the dried compost is sieved using a manual 10 mm mesh sieve; the coarse material is recirculated at the beginning of the process, whereas the compost is stored and used in the plant nursery or sold at a price of 5 Mozambican metical per kg (i.e. about 0.05 €/kg).

2.3. Plant monitoring

The monitoring was carried out by the plant operators, conveniently trained and supervised by the authors. The following data were collected:

- date when a new heap was made up;
- mass of each different kind of organic waste used to build a new heap, measured by a mechanical balance;
- date and volume of water dosed, measured in a graduated bucket;
- date and heap temperature, measured by a 1 m long temperature probe;
- date when compost heap was moved from a cell to the following one;
- date and mass of compost removed from the last cell;
- mass of compost after 24 hour sun drying;
- mass of final compost after sieving.

Data elaboration allowed to calculate:

- total mass and percentage of different organic waste treated into the composting plant;
- the temperature trend for each heap;
- heap overturning frequency;
- the entire process duration;
- volume of water dosed per kg of organic waste treated;
- percentage of recirculated material after the final sieving;
- mass of final compost produced and process yield referred to the initial mass of waste.

2.4. Compost characterization and analytical methods

Samples of compost were taken from piles C27 and C28 at the end of the treatment in order to evaluate their properties. The compost analysis was carried out in an Italian laboratory, since a chemical laboratory was not available in Maxixe city. The parameters investigated were: organic carbon, total nitrogen, organic nitrogen, humic and fulvic acids, pH, moisture, copper, zinc, cadmium, nickel, mercury, hexavalent chromium, *Salmonella*, *Escherichia Coli*. The analyses were performed following the analytical methods published by the Italian Environmental Protection Agency (ANPA, 2001) and the Italian Ministry of Agriculture and Forestry (Italian Ministry of Agriculture and Forestry, 2000).

The phytotoxicity of compost extracts was evaluated by the seed germination technique. Cress (*Lepidum sativum L.*) was selected for this bioassay due to having a good response to toxic materials and also its rapid and easy germination (Zucconi and de Bortoli, 1987).

Cress seeds were surface sterilized by immersion in 75% alcohol for three minutes followed by transferring in 0.001 $HgCl_2$ solution for two minutes with periodical agitation and finally thoroughly washed with sterilized distilled water to get rid of toxic chemicals. 10 ml of water compost extract was applied to filter paper in a Petri dish and 10 seeds were then placed on the filter paper. All experiments were run in triplicate. The Petri dishes were sealed with tape to minimize water loss while allowing air penetration and then were incubated in the dark for 24 hours at 27°C, the seed germination percentage and root length of the plants in the extracts were determined. The seed germination in distilled water was used as control. The germination index (GI) was calculated according to Zucconi et al. (1981) as follows:

$$GI(\%) = (SG_{compost} \times RE_{compost}) / (SG_{control} \times RE_{control}) \times 100 \quad (1)$$

where:

$SG_{compost}$ = Number of seeds germinated in compost extract
$RE_{compost}$ = Mean root length in compost extract
$SG_{control}$ = Number of seeds germinated in control
$RE_{control}$ = Mean root length in control

3. Results and discussion

3.1. Plant monitoring and mass balance

A number of 64 compost heaps were started from July 2013 to August 2014, i.e. approximately 4 heaps per month. Fig. 2 shows the initial composition of heaps started between January and August 2014. It can be observed that heaps always contained grass and hay (12%-42%), screening material (7%-27%) and coconut sawdust (3%-18%). Food leftovers, which represent the faster degradable organic fraction, were present in all the heaps (between 9% and 51%) except in C28; leaves and pruning were present in all the heaps (between 5% and 49%) except in C35 and C36. In 10 heaps, 5%-16% of papaya branches was present. Overall, in the considered period heaps were made of 30% of leaves and pruning, 23% of food leftovers, 22% of grass and hay, 15% of screening material, 7% of coconut sawdust and 3% of papaya branches.

Fig. 3 shows the monthly mass of organic waste treated in the plant and of compost produced from January to August 2014. The average organic waste treated by the composting plant and the average compost production were equal to 3,953 kg/month and 1,314 kg/month, respectively. During the process, 2,178 L/month of water were added as an average, which means about 0.54 L of water per kg of treated waste.

Fig. 4 shows the temperature trend of some compost piles. A couple of days after the process start-up the temperature reached a peak between 60 and 70 °C, then it gradually decreased to the ambient temperature (25-35 °C) after about 125 days. The 'up-and-down' behaviour of the temperature is typical of a composting process, as found in several studies (*inter alia*: Kumar et al., 2010; Tatàno et al., 2015; Manu et al., 2017), since the exothermic activity of microorganisms is highly influenced by aeration and moisture. In fact, the pile revolving brings new oxygen to biomass, promoting the biological activity and consequently leading to a rise in temperature. On the other hand, when the moisture of the compost is too high (i.e. greater than 60% in case of excessive water dosages) or when it decreases excessively (lower than 40%), the aerobic degradation of the organic matter is limited leading to the temperature decrease (Storino et al., 2016).

The high pile temperatures (50-70°C) maintained in the first 30 days process could provide the necessary pathogen deactivation (Gajalakshmi and Abbasi, 2008; Koné et al., 2007; Pandey et al., 2016). As previously mentioned, the raw compost taken from the last cell is air dried before being sieved. Air drying is necessary to avoid sieve clogging during the sieving phase. In the monitored period, the raw compost removed by the last cell varied between 1,624 and 3,327 kg/month (Fig. 5).

The water lost during the following drying phase was 11.9 %. The coarse material and the final compost were equal to 31.7% and 56.4% of the undried compost mass, respectively. The high fraction of sieved material was due to the high percentage of lignocellulosic material received by the plant (Fig. 2). In terms of mass, the final compost produced monthly varied between 880 kg (in May) and 1992 kg (in February).

3.2. Compost quality

Table 1 shows the results of the analyses carried out on the two compost samples taken from compost piles C27 and C28. The values obtained are compared to standards for compost quality set by the Italian legislation since the Mozambican regulation is lacking.

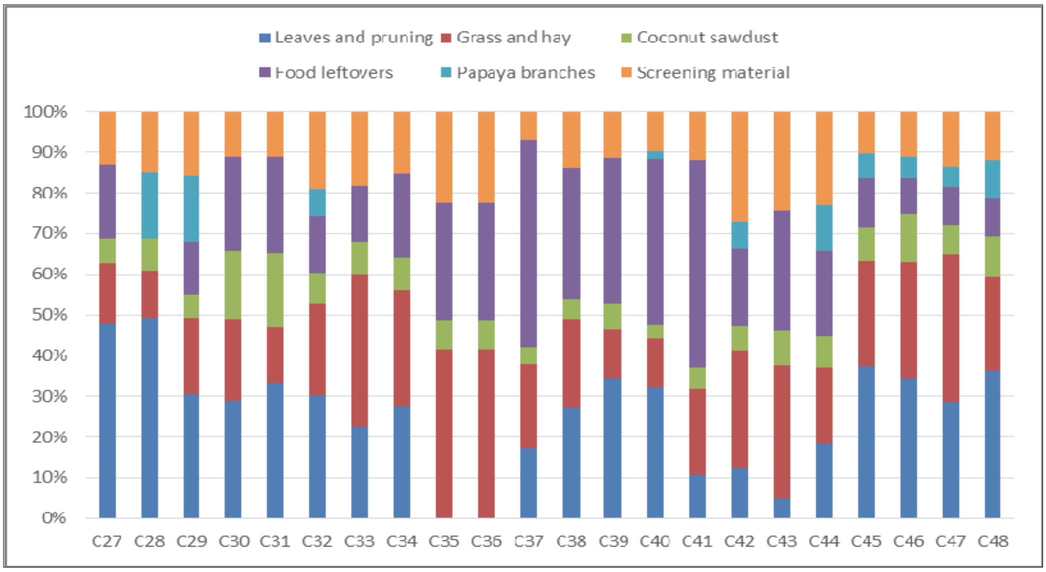

Fig. 2. Initial mass composition of heaps formed between January and August 2014

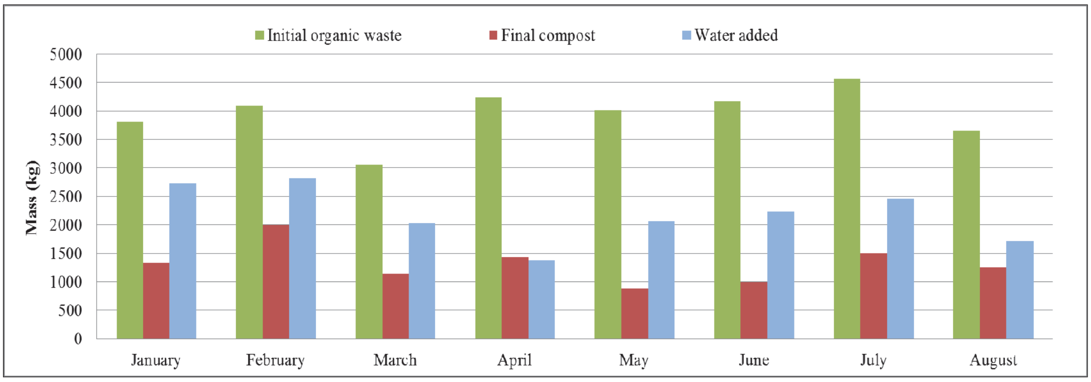

Fig. 3. Mass of waste treated and compost produced monthly (period: January-August 2014)

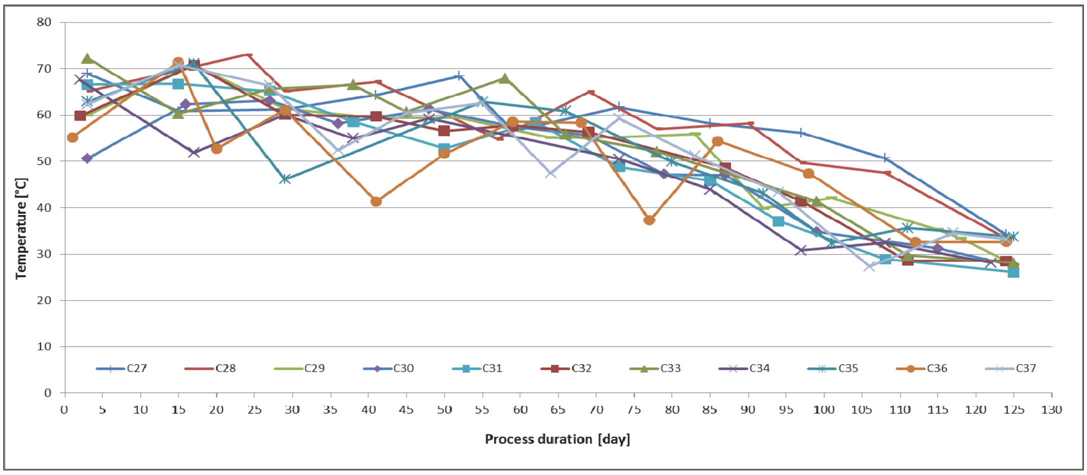

Fig. 4. Temperature trend of some compost piles

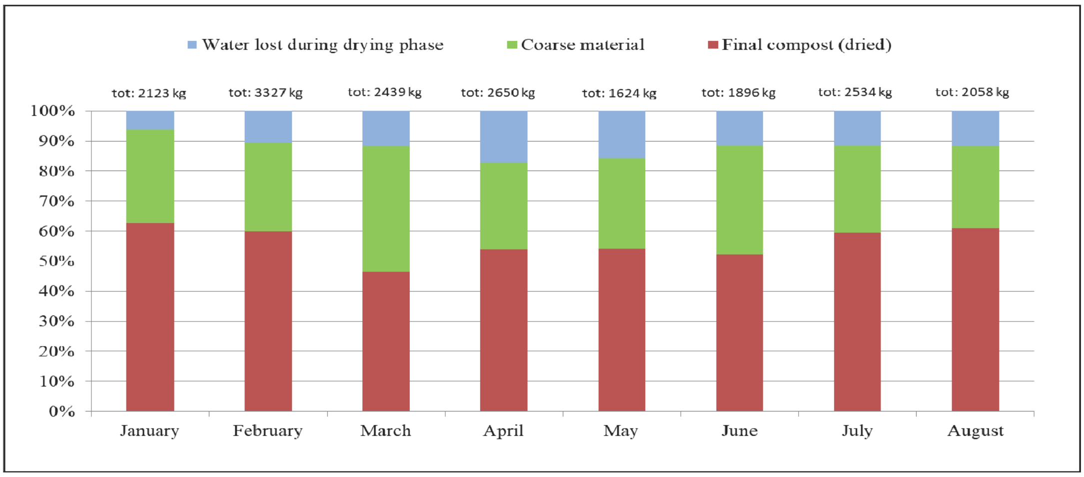

Fig. 5. Composition of raw compost (period: January-August 2014)

All the parameters complied with the Italian law, with the exception of organic carbon and humic and fulvic acids, which were lower than Italian standards, and carbon-nitrogen ratio (C/N) and pH, which were higher than the prescribed values.

Nevertheless, the slightly high pH values found in the heaps C27 and C28 are not of great concern. In fact, Rich and Bharti (2015) noted that pH is not a key factor in evaluating the stability of the compost; moreover, they noted a pH of 6.7-9 supports good microbial activity during composting. During the initial stage of composting, the pH of the system reduces to 4 or 5 because of the production of organic acids; then, the decomposition of organic acids is followed by a rapid increase of pH caused by the transformation of organic nitrogen into ammonium nitrogen (Bech-friis et al., 2001). Thereafter, the pH generally increased sharply to 8 or 9. Zhu (2007) and Kumar et al. (2010) observed pH around 9 at the end of the aerobic composting.

Table 1. Characteristics of the final compost

Parameters	*Units*	*C27*	*C28*	*Italian standards*[a]
Organic carbon	% DM[b]	23.9	16.5	> 20
Total nitrogen	% DM	0.7	0.4	-
Organic nitrogen	% N tot	87.35	90.64	> 80
Humic and fulvic acids	% DM	4.11	2.44	> 7
C/N ratio	-	33.7	39.2	< 25
pH	-	8.6	8.7	6-8.5
Moisture	%	38.1	22.9	< 50
Cu	mg/kg_{DM}	9.1	8.1	< 230
Zn	mg/kg_{DM}	80.2	59.6	< 500
Cd	mg/kg_{DM}	0.5	0.1	< 1.5
Ni	mg/kg_{DM}	5.8	8.7	< 100
Hg	mg/kg_{DM}	0.2	0.2	< 1.5
Cr^{IV}	mg/kg_{DM}	0.3	< 0.1	< 0.5
Salmonella	MPN/g	Absence	Absence	Absence
Escherichia Coli	CFU/g	Absence	Absence	< 1000
Germination Index	%	94.1	72.0	> 60

[a] *Italian standards are set by Legislative Decree 75/2010 (LD 2010)*
[b] *DM: dry matter*

Initial C/N ratio between 20/1 and 40/1 is suggested to obtain good composting yield (Pace et al., 1995); lower starting C/N ratios give a malodorous characteristic in the compost feedstock (Mohee et al., 2015), meanwhile, higher ratio means that there is inadequate N for optimal growth of microorganisms and, as a consequence, decomposition advances at a slow rate (Chen et al., 2011). The heaps C27 and C28 were made of mainly pruning waste (48-49%) and grass and hay (12-15%), whose C/N ratio is respectively 122 (Nikaeen et al., 2015), 42-57 (Rahman et al., 2017; Zahan et al., 2017). Moreover, those heaps contained also coconut sawdust (6-8%), whose C/N ratio is 100 (Thomas et al., 2013). Only C28 contained food waste (18%), whose C/N ratio is 10-18 (Li et al., 2017). The initially high C/N values of C27 and C28 caused, as demonstrated in previous studies (*inter alia:* Storino et al., 2016; Tatàno et al., 2015), low organic matter decomposition rates and low final humification levels; that is the reason why the final values of C/N ratio in heaps C27 and C28 were still high. Suitable C/N ratio at the end of the process as well as higher concentrations of humic and fulvic acids can be obtained in Maxixe plant through a more balanced mixing of different organic wastes at the beginning of the process. In particular, food waste should be between 40% and 60%, whereas pruning waste and sawdust should be 20-40% as a sum.

The above improvement should guarantee the production of a high quality compost since the data in Table 1 shows the complete absence of *Salmonella* and *Escherichia coli* as well as low concentrations of metals and good germination tests. Moreover, as already mentioned, the compost produced in Maxixe plant is partially used in the internal plant nursery to cultivate acacia and mango plants and, even though phytotoxicity tests were not performed, adverse effects due to compost application have never been observed in those plants.

4. Conclusions

The organic waste entering the Maxixe composting plant has a very high lignocellulosic component, about 75%, and the food waste represents only a quarter of the total.

The biological process is controlled simply monitoring compost temperature (by a thermometer) and moisture (by the squeeze test). The final product, obtained after 4 months treatment, represents one third of the organic waste treated in the plant; the final compost is hygienised, uncontaminated and is effectively used in the plant nursery.

Finally, the quality of the compost produced could be further improved by increasing the percentage of food waste at the beginning of the process to 40-60% in order to have a starting C/N ratio between 30 and 40.

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BIOGAS PRODUCTION FROM WHEAT STRAW PRE-TREATED WITH HYDROLYTIC ENZYMES OR SODIUM HYDROXIDE

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Abstract

Lignocellulosic residues are relatively recalcitrant to bioconversion during anaerobic digestion (AD) for biogas production. Pre-treatments with cellulolytic enzymes or diluted alkali can facilitate biomass hydrolysis and enhance the process. Both pre-treatments require low energy and chemical inputs, without accumulation of inhibitor. Milled wheat straw was pre-treated with hydrolytic enzymes or with diluted NaOH before AD. The pre-treatments were performed on sterilized, stabilized with formic acid or not sterilized wheat straw to evaluate the effect of straw indigenous microorganisms on the sugar concentration before AD. Anaerobic digestion was carried out in batch reactors, at 35 °C, for 3 months. The maximum cumulated methane production (Mmax) and the daily rate of methane accumulation (R) were estimated by a modified Gompertz equation. The NaOH pre-treatment was the most effective, with average increases of 23 and 85 % for Mmax and R, respectively, in comparison with no pre-treatment. The enzymatic pre-treatment only increased Mmax by 14 %. However, the same increase was observed with heat-inactivated enzymes, thus it was merely caused by the bioconversion into methane of the organic compounds contained in the enzymatic preparations. Moreover, all the pre-treatments determined a holocellulose conversion into reducing sugars lower than 4 %. In particular, the sugar concentration from not sterilized or stabilized with formic acid straw was lower than from sterilized straw, probably due to straw indigenous microorganisms activity. In conclusion, hydrolytic enzyme addition does not seem to provide a real advantage in terms of methane yield from wheat straw, differently from alkali pre-treatment.

Key words: alkaline pre-treatment, cellulose, enzymatic hydrolysis, formic acid, lignocellulosic biomass, methane

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1. Introduction

Biogas production from lignocellulosic biomasses is gaining an increasing interest for its high sustainability considering either the utilization of low input and highly productive dedicated crops or the exploitation of agricultural residues, as wheat straw. The use of such materials would benefit of a pre-treatment step able to increase holocellulose accessibility and thus facilitate anaerobic digestion (AD). Different pre-treatment types and strategies have been proposed, like physical (grinding), thermo-physical (steam explosion), chemical (diluted acid or alkali), biological (ligninolytic fungi), biochemical (lignocellulolytic enzymes) as well as combinations of some of them (Cianchetta et al., 2014; Reilly et al., 2015; Singh et al., 2015; Zheng et al., 2014). Mild pre-treatments are preferable, in order to minimize the consumption of energy and chemical inputs, reduce environmental pollution and decrease the production of inhibitors for the subsequent steps of digestion (Isroi et al., 2011).

Among biochemical pre-treatments, the addition of hydrolytic enzyme blends, containing mainly fungal cellulase, xylanase and β-glucosidase, represents an interesting strategy to promote biogas production from lignocellulosic biomasses. These enzymes can be applied prior to or directly during

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AD (Romano et al., 2009). In the latter case additional reactors are not required. Positive results have been reported, mainly regarding industrial, municipal, food-processing wastes or silages (Akao et al., 1992; Higgins and Swartzbaugh, 1986; Mshandete et al., 2005; Quiñones et al., 2012; Sonakya et al., 2001; Ziemiński et al., 2012). Increases in biogas yield up to 60 % were reported in the case of enzymatic pre-hydrolysis of paper sludge in pilot scale trials (Davidsson et al., 2007).

With specific regard to lignocellulosic agricultural residues, like straw, the literature about the effectiveness of enzyme addition is scarce and controversial. A positive effect of enzyme addition is expected, since hydrolysis of cellulose and hemicellulose is believed to be a rate-limiting step in AD. Positive practical results were reported by Gerhardt et al. (2007) in a commentary about the direct addition in biogas plants of an enzyme mix specifically designed for the AD of untreated energy crops and plant residues. Increases of biogas ranging from 4 up to 35 % were reported, without indicating the enzyme dosage. Recently a statistically significant increase in methane yield from particular wooden species after addition of high doses of cellulolytic enzymes was reported (Matsakas et al., 2015). Other authors only found yield increases from wheat straw at some time-points within 30 days, after enzyme addition directly during AD, without observing statistically significant increases in the daily rate of accumulation of methane (Reilly et al., 2015).

Other studies on lignocellulosic residues reported not significant benefits to final methane potential yields or to rates of release. Binner et al. (2011) added commercial enzymes directly during the AD of corn silage, without significant increases in final yields. Also Romano et al. (2009) did not found significant increases in biogas yield from *Jose Tall* wheat grass, after pre-treatment with various cell-wall hydrolyzing enzymes. These enzymes affected the rate of biogas production only when used prior to AD or when added to the hydrolysis stage of a two stage digester (Romano et al., 2009). The high cost of commercial enzyme production, however, still limits application of enzymatic hydrolysis in full-scale biogas production plants, although production of low-cost enzymes and genetic engineering are addressing this issue (Parawira, 2011).

Thus, the effectiveness of an enzymatic pre-treatment of agricultural lignocellulosic residues should be further investigated, also in comparison with well-established chemical methods. Among these, dilute alkali pre-treatments have been reported to be effective on different lignocellulosic biomass for biogas production enhancement, including wheat straw (Sambusiti et al., 2012). Dilute alkali enhances the porosity of the lignocellulosic materials by saponification of intermolecular ester bonds, with the removal of cross-links among xylan, lignin and other hemicelluloses and by the removal of acetyl groups, with a low production of inhibitors (Chang and Holtzapple, 2000; McIntosh and Vancov, 2011; Sun and Cheng, 2002). Low capital costs are required since alkaline pre-treatments are usually carried out at lower temperatures and with less specialist equipments than acidic alternatives (Sun and Cheng, 2002). A further advantage is represented by the creation of a high pH feedstock, which can counteract anaerobic digester acidification due to fermentation end-products (Massanet-Nicolau et al., 2013). A high pH environment also helps in maintaining sterile conditions during pre-treatment, avoiding the consumption of carbohydrates (Massanet-Nicolau et al., 2013). If neutralisation is required, this can be performed cost-effectively by recycling waste CO_2 streams (Reilly et al., 2014). NaOH has commonly been the preferred among alkaline pre-treatments (He et al., 2008). $Ca(OH)_2$ has also been used, with some advantages like the lower costs per tonne, recoverability for re-use and its better ability to maintain pH during pre-treatment (Fernandes et al., 2009; Hendriks and Zeeman, 2009). NaOH and $Ca(OH)_2$ can be also used in combination, reducing chemical input costs and stabilizing pH during the process (Xu et al., 2011).

To add information on the controversial topic about the usefulness of adding hydrolytic enzymes to increase biogas production from agricultural lignocellulosic biomass, this study investigated the effect on biogas production of a pre-treatment with hydrolytic enzymes of a relatively recalcitrant lignocellulosic residue like wheat straw, in comparison to a pre-treatment of proven effectiveness, according to literature, like diluted NaOH. Straw indigenous microorganisms can consume the sugars released during enzymatic pre-treatments (Quéméneur et al., 2012) indirectly affecting the subsequent AD process (yield and rate). The addition of organic acid, like formic acid, to silage crops, in order to suppress the indigenous microflora, is a widespread commercial practice in silage-making (Castle and Watson, 1970). Thus, sterilized and stabilized with formic acid wheat straw were used in comparison to not sterilized straw to also investigate the possible impact of indigenous microorganisms of the straw on the sugar concentration after hydrolysis and on the final biogas yield.

2. Materials and methods

2.1. Feedstock

Air-dried wheat straw, provided by the CREA experimental farm at Budrio (BO, Italy), was used as lignocellulosic substrate. The values of selected composition parameters are reported in Table 1. Moisture content (7.5 % w/w) was determined by maintaining a sample at 105 °C for 3 days. The wheat straw was ground by a mill (Fritsch type nr 455, Germany) and sieved to pass through 5, 2 and 1 mm screens.

Table 1. Selected composition parameters for the wheat straw used as substrate in the experiment. Standard deviation in parentheses (N=3). FM: fresh matter

Composition parameter	***Mean (sd)***
Total solids, TS (g kg^{-1} FM)	923 (13)
Volatile solids (g kg^{-1} FM)	808 (18)
Volatile solids (g kg^{-1} TS)	875
Organic C (g kg^{-1} TS)	450 (5)
Total N (g kg^{-1} TS)	9.1 (1.4)
C/N	49.5
pH in water (1.5:50 w:v)	7.92 (0.24)
Lignin (g kg^{-1} TS)	125 (4)
Hemicellulose (g kg^{-1} TS)	345 (4)
Cellulose (g kg^{-1} TS)	371 (11)

The two most abundant fractions, A (1–2 mm) and B (2–5 mm), were collected and stored at room temperature in plastic bags. Pre-weighted glass jars of 430 mL were prepared (Bormioli Rocco s.p.a., Novara, Italy), containing 10 g of sieved wheat straw (5 g of each fraction A and B).

2.2. Experimental design

The sieved wheat straw was stabilized (sterilized, stabilized with formic acid or non-sterilized) (3 levels). Then, chemical or enzymatic pre-treatments were performed (active enzymes, heat-inactivated enzymes, diluted alkali, no treatment) (4 levels), with 3 replicates, prior to inoculation and biogas production monitoring, according to a randomized complete block design with antimicrobial stabilization (AS) and pre-treatment as factors, for a total of 36 experimental units. Antimicrobial stabilization and pre-treatments were carried out as described below.

2.3. Wheat straw stabilization

Sterilized (ST), stabilized with formic acid (FA), and non-sterilized (NS) wheat straw were prepared as follows: sterilized wheat straw was obtained by adding 22 mL of tap water into the glass jars, that were closed and sterilized at 121 °C for 30 min. After autoclaving, few millilitres of sterilized water were added to restore 70 % moisture w/w. Wheat straw stabilized with formic acid was obtained by adding into the jars 22 mL of a water solution containing formic acid and HCl (the final formic acid and HCl contents were 65 and 27 μmol g^{-1} dry wheat straw respectively). Non-sterilized wheat straw was hydrated by adding 22 mL of tap water into the glass jars containing 10 g of sieved wheat straw, 3 h before use (70 % moisture, w/w). The jars were left at room temperature for 12 h, then the pH was measured and resulted equal to 4.0. Three jars were prepared for each thesis, and stored at −20 °C for further treatments and analyses.

2.4. Pre-treatments

The following pre-treatments were all carried out in 100-mL glass reactors closed with rubber stoppers, each containing 1 g of volatile solids (VS) of ST, FA or NS wheat straw, and then incubated overnight (16 h) at 50 °C, with 3 replicates, including untreated ST, FA and NS wheat straw used as controls.

2.4.1. Enzymatic pre-treatments

Seventeen mL of an enzyme mix in sodium acetate buffer (23.5 mM pH 4.8) including 120 μL of commercial cellulase (C2730, Sigma-Aldrich), 5 μL of xylanase (NS22083, Novozyme), 5 μL of an enzyme complex, composed by arabinase, pectinase and other carbohydrases (NS2219, Novozyme), and 15 μL of β-glucosidase (Novo188, Novozyme), were added into the wheat straw-containing reactors (final 5 % w/w slurry on a dry basis). The reactors were incubated as described above.

Cellulase activity of the enzyme mix was checked before use, according to Cianchetta et al. (2012), to obtain a final cellulase load of 10 FPU g^{-1} d. w. of substrate. The same enzyme mix was heat-inactivated (95 °C, 10 min) and used to pre-treat ST, FA and NS wheat straw in the reactors as described above. The residual cellulase activity after heat-inactivation resulted less than 3 % of the initial activity.

2.4.2. NaOH pre-treatment

The wheat straw in the reactors (1 g VS) was wetted with 15 mL of an alkaline water solution (NaOH 75 mM) to obtain 50 mg NaOH g^{-1} d. w. of wheat straw. At the end of the incubation period (16 h, as described above), 2 mL of sodium acetate buffer 200 mM (pH 4.8), corresponding to 23.6 mg of acetate ion, were added into each reactor to equalize the acetate content with respect to the enzymatic pre-treatments.

2.5. Anaerobic digestion

After the pre-treatments, the reactors were inoculated for the AD and the biogas production and composition were monitored during a 3-month period.

2.5.1. AD inoculum preparation

The inoculum was prepared using pig slurry as raw material. Specifically, the clarified fraction of pig slurry collected from the storage tank of CREA–ZA experimental farm at S. Cesario sul Panaro (MO, Italy) was utilized for AD in laboratory batch reactors, and digestate was used as the inoculum source. The inoculum was prepared following a laboratory consolidated procedure (Vasmara et al., 2015). Briefly, pig slurry was withdrawn from the farm storage tank collecting the liquid fraction of pig manure after solid separation. Two hundred mL of slurry were mixed with 200 mL of sterilized Phosphate Buffered Basal Medium without energy sources (Hydration Medium, HM) in 500-mL serum bottles, in a N_2-CO_2 (80:20) atmosphere. This mixture was left to incubate at 35 °C, in strictly anaerobic conditions, and the headspace composition was analysed for gas accumulation. The inoculum was considered as ready for use when gas production had stopped, indicating the complete exhaustion of endogenous energy sources. It was centrifuged, the pellet was resuspended in 200 mL HM, in anaerobic conditions, and used for the inoculum of all reactors.

2.5.2. AD experiment

AD was carried out in the same reactors containing differently pre-treated wheat straw as described above. Controls were also included (untreated wheat straw). After pre-treatment, 33 mL of sterilized HM and 5 mL of inoculum were added. The initial pH of the mixture was checked and resulted on average equal to 6.9 ± 0.2. The headspace of the reactors was gassed with N_2-CO_2 (80:20) throughout the preparation steps before inoculation. Reactors were plugged with butyl rubber stoppers and aluminum seals and they were incubated at 35 °C for 90 days. During the incubation period they were randomly distributed on the incubator shelves. Methane production was checked also for reactors containing 23.6 mg of acetate ion dissolved in 50 mL of HM, in order to measure the CH_4 production from the same amount of acetate included in the pre-treatment mixtures.

2.5.3. Biomethanation tests

The biogas production (volume and composition) was measured according to Owen et al. (1979), 2 days after the start of the incubation and then weekly for 3 months. Biogas was collected by means of 100-mL glass syringes, as previously detailed (Vasmara and Marchetti, 2016). The incubation period was completed when there was no more biogas production in any of the reactors. No methane production was detected in the control reactors where the inoculum had been suspended in HM. Methane concentration in the biogas was determined by means of a MicroGC Agilent 3000 gas-chromatograph, equipped with 2 columns: Molsieve and Plot U; detector: TCD. Carrier gas: argon.

2.5.4. Parameters of the cumulative methane production curves (Gompertz parameters)

The parameters of the cumulative CH_4 production curves were evaluated by means of a modified 3-parameter Gompertz equation (Eq. 1):

$$M(t) = M_{\max}\, exp\left\{-exp\left[\left(\frac{e\,R_{\max}}{M_{\max}}\right)(\lambda - t) + 1\right]\right\} \quad (1)$$

where *M(t)* (*mL* $CH_{4(STP)}$) is the total amount of CH_4 produced at the culture time *t (d)* in standard conditions (STP) of temperature (273 °K) and pressure (101 kPa); *e* is exp of 1; *Mmax* (*mL* CH_4 *g*) is the maximum cumulative CH_4 production; *R* (*mL* $CH_4\, d^{-1}$) is the daily rate of CH_4 accumulation; and λ is the lag time duration (d), that is the time of microbial adaptation before exponential CH_4 production. This function is often utilized for interpolating growth curves, in general, and microbial growth curves, in particular (Zwietering et al., 1990). The time (d) necessary to reach Mmax was estimated by calculating the *Mmax / R* ratio and adding to the quotient value the lag time duration.

2.6. Analytical methods

Total solids (TS), volatile solids (VS), organic C, total N concentrations and pH were determined on the straw (APHA, 1992). Total solids were determined gravimetrically by thermal treatment at 105 °C at constant weight. Volatile solids were determined as the difference between TS and ashes. Ashes were determined by incineration in a muffle furnace at 550 °C for 10 hrs. Analyses of the straw were conducted on samples dried at 65 °C at constant weight and milled at 1 mm. Organic C was determined by dichromate oxidation with external heating and reflux condenser. Total N was determined with the Kjeldahl apparatus. The pH was determined after suspension, 2-h stirring and sedimentation of 1.5 g dry matter in 50 mL distilled water. Fiber fractions (neutral detergent fiber, NDF; acid detergent fiber, ADF; and lignin, ADL) were determined on wheat straw according to Van Soest et al. (1991). The hemicellulose content was estimated as the difference between NDF and ADF; cellulose as the difference between ADF and ADL.

For the determination of total reducing sugars, samples of 200 μL were withdrawn from the reactors at the end of the incubation period (immediately prior to the AD experiments), kept in ice during manipulation and centrifuged at 1000 rpm for 3 min. Supernatants were stored at −20 °C before assays. Sugar equivalents released after the different pre-treatments in comparison to control were quantified by the 3,5-dinitrosalicylic acid (DNS) method (Miller, 1959), adapted for 96-well microplates (Cianchetta et al., 2010) with two replicates.

2.7. Statistical analysis

All the statistical analyses were performed using the SAS package procedures (SAS Institute, 1987). Fitting of the Gompertz model to measurements was performed using the PROC NLIN; measurements from 3 replicates were merged for the parameter value estimation. The parameter values were estimated according to the Gauss-Newton method. The PROC MIXED procedure (Littell et al., 1996) was used to test the significance of the treatment effects on AD parameters. Multiple comparisons of the means were carried out using the SAS LSMEANS statement. Factors and factor interaction effects were considered significant at $P < 0.05$. The Tukey Honestly Significant Difference (HSD) at $P = 0.05$ was used to compare treatment mean values. In the case of total reducing sugar concentrations, PROC GLM was used for two-way analysis of variance (ANOVA) and the Fisher Least Significant Difference (LSD) test at P = 0.05 was used for mean comparison.

3. Results and discussion

3.1. Effects of the pre-treatments on anaerobic digestion

Biogas production started immediately after inoculation (Fig. 1), as lag phase (λ) was not significantly affected by the different pre-treatments, irrespective of the AS levels (Table 2). This suggests that neither the enzymatic preparations (10FPU and 0FPU) nor alkali pre-treated straw contained inhibitory compounds (enzyme preservatives or lignin-derived compounds) affecting the start of AD.

The maximum CH_4 production was achieved in about 37 days, on average, for the control and for both the enzymatic pre-treatments, whereas it required only 27 days, when the wheat straw was pre-treated with NaOH. The time to join Mmax was 34 days as average of the AS levels (Fig. 1).

The pre-treatments significantly influenced methane production in terms of Mmax, irrespective of the AS levels of the wheat straw (ST, FA, NS) (Fig. 2a, Table 2).

Table 2. Significance of the effects of pre-treatment (PRETR), antimicrobial stabilization (AS) and their interaction (PRETR*AS) on the Gompertz parameter values λ, R and Mmax

Parameter	*Factor effect*	*F value*	*Pr > F*
λ	PRETR	2.01	0.1436
	AS	0.13	0.8777
	PRETR*AS	0.09	0.9963
R	PRETR	111.17	<0.0001
	AS	9.54	0.0011
	PRETR*AS	3.12	0.0240
Mmax	PRETR	33.55	<0.0001
	AS	2.05	0.1535
	PRETR*AS	0.98	0.4624

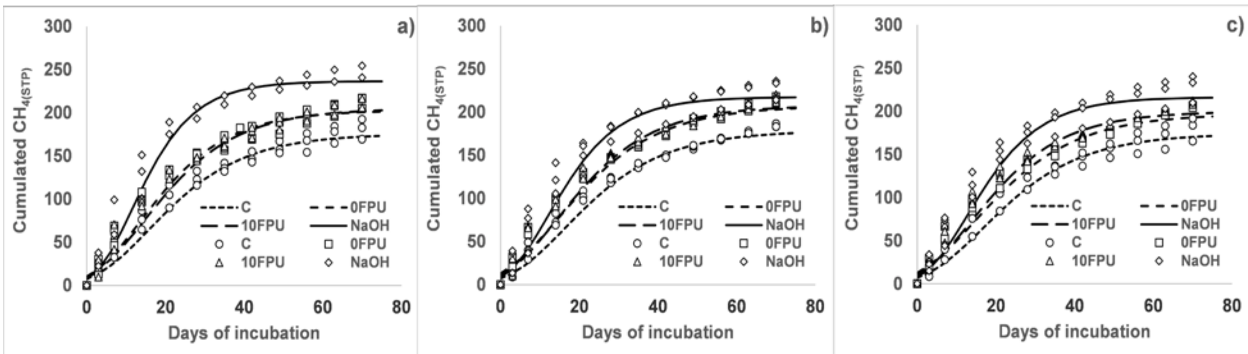

Fig. 1 Gompertz-estimated curves of methane production from wheat straw pre-treated with active enzymes 10 FPU g^{-1} d.w. (10FPU), heat-inactivated enzymes (0FPU), NaOH 5 % w/w (NaOH) and from untreated wheat straw as control (C). Before pre-treatment, straw was sterilized by autoclaving (a), stabilized with formic acid (b) or not sterilized (c).

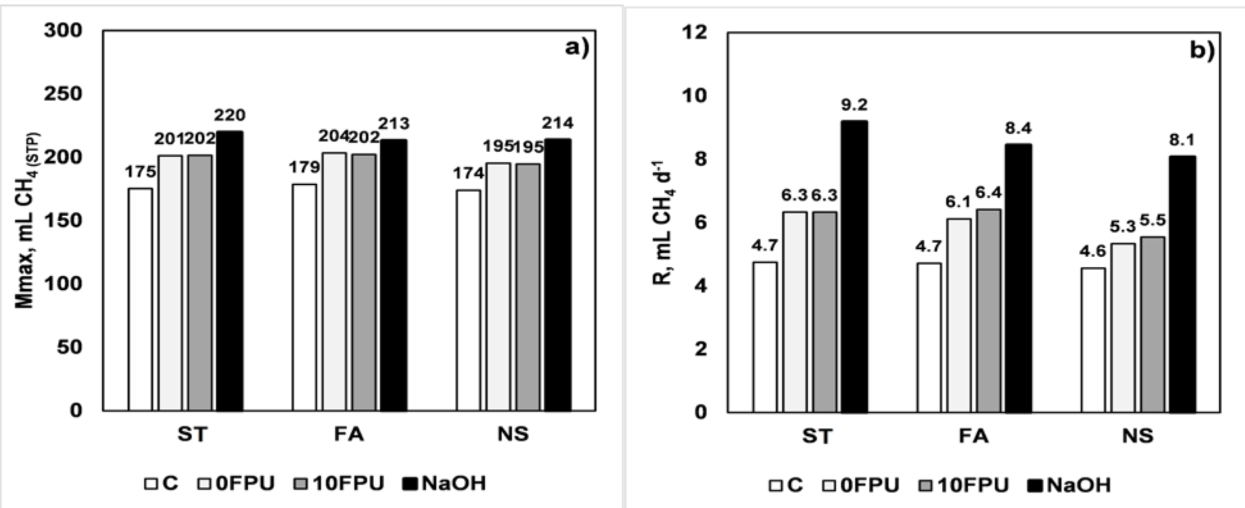

Fig. 2. Mean values of a) the maximum cumulative CH_4 production, Mmax and b) the daily rate of CH_4 accumulation, R, relative to the anaerobic digestion of wheat straw pre-treated with active enzymes 10 FPU g^{-1} d.w. (10FPU), heat-inactivated enzymes (0FPU), NaOH 5 % w/w (NaOH) and untreated wheat straw as control (C). The pre-treatments were carried out on sterilized (ST), stabilized with formic acid (FA) or not sterilized (NS) straw. The Tukey Honestly Significant Differences at P = 0.05 are 30.6 and 10.6 mL CH_4 for Mmax; 1.4 and 0.5 mL CH_4 d^{-1} for R, for pre-treatments and antimicrobial stabilization levels respectively.

The NaOH pre-treatment gave the highest Mmax values (216 mL CH_4, on average) and increased biogas yield by 23 % in comparison with no pre-treatment (C) (176 mL CH_4, on average) (Fig. 2a). Both the enzymatic pre-treatments (10FPU and 0FPU) gave Mmax values of 200 mL CH_4, on average, lower than NaOH but higher than the control, with an increase of the methane yield by 14 % (Fig. 2a).

The pre-treatments significantly affected also methane production in terms of R and a significant effect was also observed for the AS level (Table 2). In particular, the enzymatic pre-treatments did not produce any significant effect on R, while NaOH was the only effective pre-treatment (Fig. 2b). The highest R value was observed for ST wheat straw pre-treated with NaOH, with a 96 % increase compared to the not pre-treated control (9.2 vs 4.7 mL CH_4 d^{-1}, respectively) (Fig. 2b).

The increase of methane yield observed with the enzyme pre-treatments compared to the not pre-treated controls (+14 %) cannot be explained in terms of wheat straw hydrolysis since the same level of methane yield has been achieved both with active and with heat-inactivated enzymes. The heat-inactivation was actually effective since the cellulase residual activity was checked, resulting less than 3 % of the original activity. Also the active enzymes were carefully checked before use.

A possible explanation for the observed increase could be provided considering that the main commercial preparation used (C2730) contained about 166 mg mL^{-1} of proteins and 280 mg mL^{-1} of not reducing sugars (mainly sorbitol) as stabilizers (Nieves et al., 1997). These amounts are not negligible and could account for a large portion of the observed yield increases. In fact, the enzyme mixtures add biomass which is digested as well (Quiñones et al., 2012).

The lack of differences between active and heat-inactivated enzyme treatments could be also interpreted considering the relatively high recalcitrance to hydrolysis of wheat straw, even if milled at 2-3 mm. According to Taherzadeh and Karimi (2008) the enzymatic hydrolysis of recalcitrant lignocelluloses requires chemical-physical pre-treatments to be effective. At this regard, hydrothermally pre-treated wood species benefited of high doses of enzyme addition (15-30 FPU) both before and during AD to enhance biogas yield, depending on the species, while untreated samples showed only modest increases (Matsakas et al., 2015). It should be noted that most of the positive effects of enzyme addition on biogas yield reported in literature are mainly related to industrial or municipal waste materials, like paper sludge or pulps, which were previously processed (Davidsson et al., 2007; Lin et al., 2010; Mshandete et al., 2005; Ziemiński et al., 2012) and thus they could be considered somehow already pre-treated. For this reason, it should be better to compare our results with those reported by other authors for untreated lignocellulosic materials, like agricultural residues (straw, stalks etc.). In this context a lack of effectiveness of enzyme addition was already previously reported by Romano et al. (2009), working on milled wheat grass (not chemically pre-treated), even if it should be noted that these authors used a very low dose of hydrolytic enzymes (about 1.6 FPU g^{-1}) in a separated step of hydrolysis before AD. In the current study a 5-fold higher dose (10 FPU g^{-1}) of the same enzyme mix was used, enriched with other accessory enzymes, but no effect was obtained on production, even in terms of daily rate of accumulation (R).

More recently also Reilly et al. (2015) reported that the enzyme addition (Accellerase®-1500) at a relatively high dose (0.2 mL g^{-1} VS) during the AD of milled wheat straw did not significantly increase the rate constant k_{bmp}, an indicator of hydrolysis speed, even if increases in biogas yields up to 15 % were observed at defined time-points (5, 15 or 30 d). It should be considered that a loss of activity can occur with the enzyme addition during AD, as observed by Binner et al. (2011), who studied the stability of different commercial hydrolytic enzymes in presence of soluble fractions from different AD plants and demonstrated that externally added enzymes were mostly degraded in about 10 min. Moreover, digester pH and temperature can be sub-optimal for some commercial enzymes like Accellerase®. Thus pH, temperature and enzyme dose should be carefully controlled when evaluating enzyme effects on the biogas production from lignocellulosic biomasses. In fact, high doses of enzymes (up to 30 FPU g^{-1}), combined with temperature and pH near to optimal for the enzymes (55 °C and 5.5 pH) produced improvements in the biogas yield from a particular untreated lignocellulosic material (birchwood), but the same conditions proved to be still ineffective on other untreated wood species (Matsakas et al., 2015).

Overall, our results indicate that the addition of holocellulose hydrolytic enzymes to an untreated lignocellulosic material like wheat straw in a separate step prior to AD provides modest increases in the methane yield, mainly due to the bioconversion of organic compounds carried along with the enzymes themselves.

On the other hand, our results confirmed the efficacy reported in literature for alkaline pre-treatments. In fact, the pre-treatment at 50 °C with NaOH at low dosage (5% w/w) improved biogas production in terms of Mmax (Fig. 2a).

Our results are in good accordance with those reported by other authors for similar lignocellulosic materials: NaOH and $Ca(OH)_2$ at 4 % w/w for 24 h at 55 °C raised the methanation potential yield by 35 and 26 %, respectively, from milled (2-3 mm) sunflower stalks (Monlau et al., 2012). Extruded grass treated with 5 % w/w $Ca(OH)_2$ at 51° C for 24 h produced an increase in methane by 14 %. Higher doses (7.5 %) increased yields up to 37 % (Khor et al., 2015). Finally, milled (2-3 mm) wheat straw treated with 7.5 % w/w $Ca(OH)_2$ at 20 °C for 48 h produced an increase in methane by about 15 % after 30 days (Reilly et al., 2015).

In the present study wheat straw pre-treated with NaOH also produced a significant increase in the R value (+85 %, on average) compared to the control. Comparable increases (+69-96%) were observed by Reilly et al. (2015) for the rate constant k_{bmp} calculated for milled (2-3 mm) wheat straw pre-treated with $Ca(OH)_2$. The observed R increase suggests that a reduction of the AD duration can be obtained in biogas plants loaded with alkali pre-treated lignocellulosic materials.

3.2. Effect of the antimicrobial stabilization level on sugar concentration

The indigenous microorganisms of the straw can have a strong impact on the actual sugar concentration after enzymatic pre-treatments, due to the possible exploitation of the sugars released as carbon source (Quéméneur et al., 2012) and thus their effect on the subsequent AD process can be substantial. In order to verify the effect of the different AS level of the wheat straw (ST, FA, NS), the reducing sugar concentration after the pre-treatments (10FPU, 0FPU, NaOH) was checked before the AD, in comparison with the untreated controls (C). The results were analyzed by ANOVA and a significant interaction pre-treatment x AS level was highlighted (P = 0.0175). Statistically significant greater concentrations of reducing sugars were observed after 10FPU pre-treatment on ST and FA wheat straw in comparison with NS wheat straw (1.3, 1 and 0.4 mg mL^{-1}, respectively, Fig. 3), meaning that in absence of sterilization or AS, a bacterial growth occurred at the expenses of the sugars released by the enzymes. The value obtained with 10FPU on NS wheat straw was not statistically different from that of the control (C) and from that obtained with all the other pre-treatments (0FPU and NaOH), which were not expected to affect sugar concentration, meaning that the sugars released were almost completely removed by microorganisms. Thus in the case of a separate hydrolysis phase before AD, an AS treatment compatible with AD, like formic acid, would be required in order to reduce sugar exploitation by indigenous microorganisms.

Moreover, the active enzyme mix was only able to partially hydrolyze the wheat straw, reaching at maximum 1.3 mg mL^{-1} of reducing sugars, corresponding to a holocellulose conversion by about 4 %. This low value could be a further explanation of the lack of differences in terms of Mmax and R in the AD phase observed among enzymatic pre-treatments (0FPU and 10FPU), confirming the need for a chemical-physical or biological pre-treatment prior to enzyme addition in the case of recalcitrant lignocellulosic biomass (Cianchetta et al., 2014; Taherzadeh and Karimi, 2008).

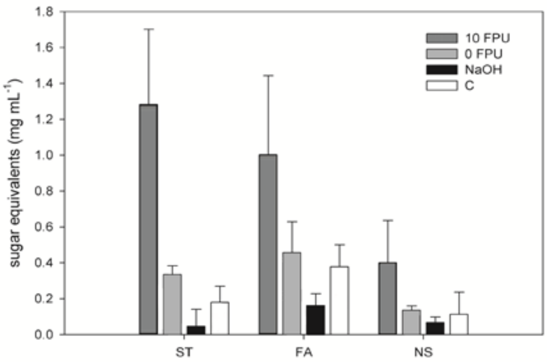

Fig. 3. Total reducing sugars for sterilized (ST), formic acid stabilized (FA) and not sterilized (NS) wheat straw after pre-treatment with active enzyme 10 FPU g^{-1} d.w. (10FPU), heat-inactivated enzymes (0FPU), NaOH 5 % w/w (NaOH) in comparison with untreated wheat straw (C). Columns represent mean values (n = 3) and bars represent standard deviations. Fisher Least Significant Difference value = 0.334 mg mL^{-1}, at P = 0.05.

4. Conclusions

Our results indicate that the pre-treatment prior to AD with hydrolytic enzymes of a relatively recalcitrant lignocellulosic material like milled wheat straw, provides modest increases in the methane yield, mainly due to the bioconversion of organic compounds supplied with the enzymes themselves. On the contrary, low dosage alkaline pre-treatment of wheat straw can provide significant advantages for the AD process, by improving both methane yield and daily rate of accumulation. Thus, in order to optimize methane yields and daily rate from wheat straw, a mild alkaline pre-treatment, that partially solubilizes lignin, followed by holocellulose hydrolytic enzyme addition, could be appropriate. In this way the enzymes can more effectively convert holocellulose into simple sugars, potentially leading to an even higher increase of the daily rate of methane production.

Moreover, a mild alkali pre-treatment prior to the enzyme addition would overcome the need of an AS of the lignocellulosic materials, to avoid the sugar consumption by indigenous microorganisms of the straw in the hydrolysis reactor.

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THE SMART-GREEN RECYCLING

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Abstract

This paper describes shortly some outcomes of a project aiming to apply a scientific research directly to industry, passing through a system that wants to promote an economic "Pact" in relation to the new construction and renovation projects of energy, according to its fundamental guidelines of the moment: renewable energy and energy efficiency. The key point is to produce energy from recycled materials that become functional to dwellings (from the garden shed to furnishings, etc.), which are combined with the latest technology. The photovoltaic paint,vertical gardens, trees with Silicon cells.
During the day these furnishings will remain open, incorporating heat and sunlight; in the evening the huge Silicon cells of the trees will close, creating picturesque lampposts with gradual release of heat, which will be retrieved for the production of thermal energy to heat houses.

Key words: green energy, recycling, sustainability

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1. Introduction

The problem this paper tries to solve through a field trial, because this is a real problem, is to face not so much the theme of energy through recycling, but first of all how to frame the concept of energy in respect of recycling.

The concept of "recycling" linked to the word "energy" cannot be used without having the slightest rethinking of the idea of energy and the idea of what today it can be called civilization (Robins et al., 2010). First of all it is important to underline what the term energy means in reference to a society that has already set in motion the process of optimization in respect of the production. Energy, originally a capacity of people and things to perform a job (eg. a man pushing a cart in antiquity), then was used to satisfy basic needs, through the mechanization of certain processes and produce energy to transform immediately (interaction things-man), thereupon it served to facilitate more and more abundant production for today daily lives. So: jobs, production, processing and distribution. That is, when man understood that alone could not cover the needs of their own tribe, he started to look around and find a way to produce energy from various sources. Over time, the energy was used to operate the industries to transport goods, lighting houses, offices and so on; it was used to heat the rooms in winter or cool them in summer; it was used to move cars, ships, trains or aeroplanes; it was used to communicate at a distance or send tv signals: today everything is powered by the energy and technically everyone has a much higher amount of it than what objectively serves. From here onwards it was realized that the energy could also be produced differently and you could also use the most "dangerous" part of it, which was typical of fossil fuels. Here the root node of the history of energy, as Gladwell (2000) exposed.

The controversy between fossil fuels and renewables starts. Year 1973: the first oil crisis (Marchetti and Nakicenovic, 1979). The Arab States had entered the war against Israel, that won thanks to the help of the West. So the Arab countries of Opec (Organization of the Petroleum Exporting Countries) halted oil exports to US and Europe, as Maugeri (2006) demonstrated. Oil prices quadrupled and even those of electricity, in that time produced from oil and natural gas. Consequently, increased fuel prices, reduction of more than 40% of all kinds of lighting called "unnecessary". See public lighting, closing of public places by midnight, decrease of the speed on the highway, turning on appliances only at night and so on. Synthetically all measures that make independent from oil for power generation, as indicated by Martin-Amouroux (2009). The first international energy-saving campaign began, defining efficiency standards for appliances, automobiles and construction. Rising prices of oil and fossil fuels developed between 1973 and 1985 and began tending to increase energy efficiency and reduce energy intensity. In the USA energy efficiency measures were created that allowed, despite the growth of 50% of the population, an increase of only 26% of energy consumption, as Carollo (2009) demonstrated.

In the mid-1980s the energy-saving and nuclear development allowed Western countries to bring down the price of oil. 44 years have passed by the oil crisis of the 1973, during which the importance of the concepts of efficiency and energy saving have never produced a serious and consistent policy that could be essential to find solutions to the financial and economic crisis, as well as to ensure the reduction of CO_2 emissions that are destroying our planet (Fattouh and Stern, 2011).

From that day to today, in one of the longest and toughest financial crises of the modern world, an urgency to reduce consumption in the round is wreaking quite unexpected effects. The revolution, if it can be defined it as such, then began in 1973, and there was no real news in the recent COP 21 and 22. So why do people talk about revolutionary event? Simply because after so many years, almost all countries have approached in a more or less sensible to the concern, which, evidently, in addition to having accumulated tensions on climate data always fluctuating over the years, shook some financial pillar, implying that intervene on the climate meant also create new models of development consistent with a financial growth, as indicated in Gao (2007).

Then so we can talk about awareness and change the term “revolution” with the term “awakening”. An awakening from the dogmatic sleep, quoting the philosopher Kant referring to Hume. In other words, marrying the changes already under way in the energy sector, have been highlighted the prospects and potential of energy with low emissions of greenhouse gases, that is from renewable source, giving credibility to the implementation of effective action against climate change by developing new models of development and, as a result, production conditions in the areas of energy efficiency and resource optimization, as Stern (2005) explained.

Ergo, in other words, any COP can make sense talking about the union of intentions on new models of development and production conditions then, as showed previously (Knight et al., 2010). Otherwise it has no right to be. First of all it is necessary to manage and run a new transformation of the energy sector, responsible for at least two-thirds of greenhouse gas emissions. To do this, it is important to understand the energetic phenomenon, study and finally create new professions, studying mainly and primarily the story. Going back again to the past, with proper contextualization, the Energy Charter of 1994 gives the trusted servant to understand totally the two focus on which the project is concentrating. At the Dublin European Council (June 1990) the Prime Minister of the Netherlands suggested establishing cooperation in the field of energy with the countries of Eastern Europe and the former Soviet Union to accelerate their economic recovery and improve security of supply in the community. The Commission, which had been invited by the Council to study how best to implement this cooperation, proposed in 1991 the idea of a European Energy Charter, that led to the Energy Charter Treaty, on energy efficiency and related environmental aspects, intended to promote East-West industrial cooperation by providing legal guarantees for investment, transit and trade and to establish a legal framework to promote long-term cooperation in the energy sector, based on the principles set out in the European Energy Charter, as exposed in World Energy Council (2010).

The objectives of the Protocol were: 1) the promotion of energy efficiency policies compatible with sustainable development; 2) creating framework conditions which induce producers and consumers to use energy in an economical, efficient and environmentally friendly way as much as possible; 3) encouraging cooperation in the field of energy efficiency. These 3 points led to the creation in 2005 of the so-called "20-20-20 climate and energy package" of 1997, defined the Kyoto Protocol (COP 3).

This package is part of the negotiations prior to the Conference of the UN Framework Convention on climate change in which it reaffirmed the position to reduce unilaterally the emissions by 20% by 2020 and, in the case of international agreement, to undertake progressively to the 2030 and 2050 to reduce 30% and 50% respectively of its emissions, compared to the 1990 levels. Full approval of the climate and energy package should have taken the start officially on the occasion of the 15th Conference of the Parties (COP15) held in Copenhagen in December 2009, as showed by Iea (2010a).

But even today the good intentions of Kyoto (according to many the true and serious event devoted to these themes) have not produce all the desired results, as indicated by Iea (2010b). The climate and energy package is a set of implementing measures greenhouse gases emission reduction to regulate key sectors effectively, as Barbier (2010) explained.

To reach the goal of keeping the global average temperature growth on land and on the surface of the oceans to a maximum of +2 degrees

Celsius by the end of the century, compared with preindustrial levels, as established in the recent COP, we need to distribute it among the various States, as seen in Ren21 (2010).

In this context nobody used the criterion of credibility (see differences in incentives worldwide on boosting renewables) or the policy of economic expectation of resources for the implementation of interventions. In general an unconditional development of technologies was preferred in countries (therefore also in their hometowns) that maybe needed more high-impact daily applications in the single reality than technologies that make smart shapes that do not solve a big problem. See the two examples of intelligent traffic lights that didn't solve the traffic problem and see the intelligent streetlights, that in a large part don't work. Hence the real international problem. If you read the abstracts of the research framework programmes (EU Member States with those non-Member States) the first thing you notice and that is required is precisely the replicability of the technologies and of the project. Here is the second failure. One example of this attitude to be edited is the tale of smart cities, as Yergin (2008) demonstrated.

The trend is to export innovations, discoveries and various applications that work "well" in some cities in other with different geography, people, roads, streets, cars, etc. With all these meetings, a sense of the best practices indexing, the contextualization of interventions and their genius were lost. Dulcis in fundo: in schools and universities, where they should act with a real common protocol, to create a truly global approach competences and an exchange of the appliances, there are so many divisions, that the discrepancy between the Italian school system and the American one results very deep. It is important to shift the focus from a trade management of affairs in the hands of a few to an international free trade agreement. With this one on one hand the energy quota rates (that is what it must be paid in bills as consumption) decrease, on the other hand fixed costs could be reduced because the environmental standards and safety regulations would regulated better. Another inspiration could be producing electricity by sharing in grid parity (putting in equality the real demand and consumption) the distribution of the energy in excess producing even more jobs for management regulation.

De Paoli (2012) in the encyclopedia Treccani explains the energy nowadays. That is, today energy has conquered two ephocal "dimensions", that collide every day: one derived from stock sources and the other derived from flow sources. The first ones are extracted and are immediately available. This category includes fossil fuels (oil, gas, coal) and uranium, as De Paoli (2012) demonstrated.

Flow sources regard the renewable sources. The Sun or the wind are energy flows that may not be available when needed. The first ones need of maintenance and management and the second ones of trasformation technologies which create economic and energy wastes. So, beyond the debates as to which of the two modus is right or not, that is not the aim of this paper, the focus is, as mentioned at the beginning, the idea of energy and on this historic itinerary. Before talking about recycling energy, talk about rationalization. A process that brings together the two moments through lack of culture of waste, that is "recover", "fix" and "recycle".

This project wants to bring together innovation with the real needs of the people who, more often, are tied to tradition. Along this road, the house can become efficient, taking advantage of the latest technologies, environmentally-friendly and intelligent, as Varvelli (2008) showed.

This project focuses in particular on the following main objectives:

- Building requalification with bio-ecological criteria, as Woollaston (2014) wrote.
- Creation of a "Smart" Small Community"
- Sustainable energy planning
- Development of technologies for on-site energy production from renewable sources
- "Zero Waste" objective

2. Materials and methods

2.1. The Cube Project

The project wants to bring together innovation with the real needs of the people who, more often, are tied to tradition. Along this road, the house can become efficient, taking advantage of the latest technologies, environmentally-friendly and intelligent, as Friedman (2012) explained.

Make smart a dwelling implies the planned and intelligent use of human and natural resources, properly managed and integrated with numerous ICT technologies already available, to create an ecosystem capable of making the best use of resources and to provide increasingly intelligent and integrated services. The actions of the project develop on these axes: mobility, environment and energy, building quality, economy, tenants' safety and infrastructure.

Cradle of the project is the Cube, a palace of 7 apartments, which will be terminated at the end of 2017. In the approach to this new system, that consists in drawing power from recycled materials, first of all materials found on site were scaled according to the construction needs. In other words, neither raw materials were produced, nor the environment was ransacked, nor renewable materials were used. A calculation in terms of energy (with sustainable impact for the future), a business plan on the real requirements of the potential buyers of the apartments and a list of materials ready on site considering were done as first step, then, their lowest cost on transport and transformation. For example, wood, plastic materials, everyday objects, earth products were recovered to outline an initial architectural design of the building.

Everything that concerned the production of electricity was detected in two steps: the first step, for the geothermal energy, related to the heat of the earth, with a so-called "ring" transformation technology, i.e. the Earth's heat is radiated through the tubes, made with recycled plastic materials found on site, which radiate the plates, whose task is to release heat through a cavity that is placed under the flooring made with wood or recycled materials.

The second step, for electricity, was to use some techniques that serve to produce electricity through solar Spectra, which in turn distribute energies through a technological infrastructure related to wireless power transmission (patent n. 722016000085159, integration to the patent BiroRobot n. 102015000044214), as Delle Piane (2016) explained, and a system based on an energy accumulator. The off grid technology, through the use of smart grids, offers a maximum 2500 kWh yearly for the apartments and a maximum of 6000 kWh for the attic, available energy throughout the year. There won't be traditional meters or electric bills. No counter installation is required, there will be only a "current meter" which is called, technically, "Wattametro". The Wattametro, born from the BiroRobot scientific project, reports not only the actual consumption in Watts, but also the relative economic consumption in terms of euro spent on the livelihood of the individual appliance and evaluates the exceeding of the free threeshold.

Starting from a requirement that fluctuates between 11.000 kWh/year and 19.000 kWh/year, and declaring the possibility to manage efficiency through the implementation of energy-saving technologies at every stage, from production to transmission and to the distribution to the final customer, a recovery flow of 80% of the needs that accumulates and falls into the internal network can be definitely guaranteed, giving users the ability to move not in off grid way (out of the national network), but in board grid (in their proper network). The technological tool with its physical function is the Smart Grid Player, as Gariboldi (2017) showed.

In addition to lowering consumption, the smart grid player will be able to reduce demand peak levels through a more efficient breakdown of consumption over the course of the day and throughout the year. In this way, it is possible to limit the amount of resources maintained in stand-by to ensure maximum levels of consumption and make sure that the plants are sufficiently flexible to manage sudden changes in energy delivery, through an expanding portfolio of renewable energy-based plants and the little stability of the network that comes downstream from the building.

2.2. Calculation

With the calculation of consumption, taking into account of 4,5 kW available for each apartment, the annual requirements of the building is about 80.000 kWh in energy and thermal energy:

Average 4 components family consumption: 220 kWh

Average consumption in 12 months = 2.640 kWh per apartment/annum

In 7 apartments = 18.480 kWh of electricity

In 1000 m^3 of thermal energy of a family = 12.000 m^3/annum

3. Results and discussion

The analyses on the project Cube to reach energy efficiency through recycling have led to the following solutions, which will apply to the building.

Small antennas, that use grids with patented algorithm MSK, will transmit wireless power, will regulate the intensity of light scattering, based on the approach of people at night, will be on-demand and will activate a security alert.

The innovative algorithm for the energy assessment records the real time energy (lighting/thermal) consumption data and compares them with historical energy consumption data to provide new tools to reduce wastes and to improve users awareness and pro-active energy management, as Santarelli (2017) underlined.

Currently the innovative algorithm has been developed and validated in relevant (lab level) and real household environment, allowing a reduction of above 10-30% in energy consumption and related costs, which results from the cross-reference between different statistical data detected from Italian and European families' samples and Support Vector Machine and from specific families' pilot cases: in particular about 250 Italian families and about 150 among German, Austrian and Swiss families.

The innovative algorithm describes the operation of the network, elaborates the registered data and it is able to self-adapt to specific external and internal conditions. This algorithm also elaborates specific advices and potential measures to be performed.

Fig. 1. Building basis

There will be columns for the charge of electric cars and bikes and services arising from the energy produced (bistros, restaurants and bars with zero impact).

A "raw" area will become the new epicenter of attention to ecology for citizens, through virtuous behaviour and anti waste.

Fig. 2. Building under construction

Fig. 3. Rendering

4. Conclusions

The goal is to break down totally energy consumption through these radiant surfaces, using also roof gardens, natural air ventilation systems, steam cooling systems, refreshing sheets and panels with darkening and shading effect of the external facades.

Automatic sensors will activate or not ad hoc features and functions, in conjunction with the flow that it will be created. So the launch of a smart-green ecological system, which recycles its natural resources. From the ground will emerge a city of the next millennium with energy, water and gas at km 0.

Energy is strongly linked to Infrastructures. In this context, the development, the security and the quality of life in the industralized countries increasingly depend on a system of infrastructures, that operate in a continuous and coordinated way, called Critical Infrastructures. The expression "Critical Infrastructure" refers to a system, a resource, a process, a totality, whose distruction, interruption or partial or temporary unavailability has the effect of weakening the efficiency and the normal operation of a country in a significative way and also on its security and financial, economic and social system, including central and local administration. The ad hoc algorithm studied first of all analyses the context and doesn't make a system replicable on a large scale, when the reference conditions are different. The prevision calculus for the critical infrastructures, that is:

R place, V, E(t) = place M (2); V (2); E (P)

R (risk): the risk linked to a particular attack in a specific place.

M (threat): the probability of trying a particular attack (1… N) in a specific place in 2 ways, one as prevention and the other as crisis.

V (vulnerability): the probability that a threat has success in order to a weakness (1… T) in the defense of an objective and in other two aspects: a preexisting aspect and a probable one.

E (exposure): the potential damage of the attack and corresponds with the portion of the objectively quantifiable "MOTEFF" categories: present infrastructural goods, population.

The calculus describes also sociological aspects:

- Actualization difficulties (relevant to the attacker):
  - technique availability,
  - costs,
  - logistical difficulties,
  - know how,
  - motivation;
- Attractiveness of the objective.

The world is totally projected in a deep transformation. Connecting systems are replacing isolated ones.

We usually call this trend "Internet of Things" or IoT. This is a modified reality, driven by the concept of "convergence" through devices always connected, but in a decentralized way. This change is generating unprecedented opportunities that could increase the productivity and the efficiency, improve the crisis prevention process, crisis management and crisis communication in real time, solve problems and develop new and innovative user experiences.

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