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Procedia Environmental Science, Engineering and Management

22nd International Trade Fair of Material & Energy Recovery and Sustainable Development, ECOMONDO, 6th-9th November, 2018, Rimini, Italy

Selected papers (1)

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Aims and Scope

Procedia Environmental Science, Engineering and Management (P - ESEM) is a journal focusing on publishing papers selected from high quality conference proceedings, with emphasis on relevant topics associated to environmental science and engineering, as well as to specific management issues in the area of environmental protection and monitoring.

P - ESEM facilitates rapid dissemination of knowledge in the interdisciplinary area of environmental science, engineering and management, so conference delegates can publish their papers in a dedicated issue. This journal will cover a wide range of related topics, such as: environmental chemistry; environmental biology; ecology geoscience; environmental physics; treatment processes of drinking water and wastewater; contaminant transport and environmental modeling; remediation technologies and biotechnologies; environmental evaluations, law and management; human health and ecological risk assessment; environmental sampling; pollution prevention; pollution control and monitoring etc.

We aim to carry important efforts based on an integrated approach in publishing papers with strong messages addressed to a broad international audience that advance our understanding of environmental principles. For readers, the journal reports generic, topical and innovative experimental and theoretical research on all environmental problems. The papers accepted for publication in *P – ESEM* are grouped on thematic areas, according to conference topics, and are required to meet certain criteria, in terms of originality and adequacy with journal subject and scope.

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GUEST EDITORS

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 140 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 Italian Representative in the "Working Party on Biotechnology, Nanotechnology and Converging Technologies" at OECD (Organization 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) Horizon2020 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.

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ASSESSMENT OF THE ENERGETIC VALUE OF ANCIENT SICILIAN WHEAT IN THE INDUSTRIAL SYMBIOSIS PERSPECTIVE*

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Abstract

In recent years, the European Union has promoted several strategies to support the transition from a linear economy to a circular economy without waste. In this context, industrial symbiosis plays a fundamental role, that is, by the process of company interaction aimed at obtaining competitive advantages from the transfer of resources between dissimilar industries. In this regard, Sicilian farmers and agronomists have recently rediscovered ancient Sicilian wheat, re-evaluating the local agricultural sector. It has been long time since the latter was outclassed by modern wheat substantially accountable for food allergies. Due to hot, dry weather conditions and to a low gluten index, this wheat keeps its special healthy benefits that makes it ideal for combating digestive disorders. The project studies the Company "F.lli Vescera S.r.l. – bakers and pasta makers", situated in Carlentini (Sicily). The aim of this research is the analysis of agri-food companies' potentialities to produce energy from biomass which comes from ancient Sicilian wheat.

Keywords: industrial symbiosis, circular economy, biomass, energy efficiency, ancient Sicilian wheat

1. Introduction

The transition to a circular economy mainly involves the agricultural sector, which must be up to this challenge through a sustainable management of natural resources. For this reason, in many agri-food companies, the production and the use of biomass as a new source of renewable energy in the manufacturing process has emerged. The circular economy,

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according to the definition given by the Ellen MacArthur Foundation, is a generic term widely used to define an economy designed to regenerate itself. It is, therefore, a system that organizes all the activities - from the extraction to the production. In the linear economy, however, once consumption has taken place, the cycle of the product ends too and it becomes waste, forcing the economic chain to continuously follow the same extraction, production, consumption, and disposal scheme. The circular economy provides for a massive use of renewable energy sources (central element of sustainability), a large transfer of information among economic actors, a strong capacity for technological innovation and products that are totally or partially recyclable or reusable. This phenomenon could bring with it the end of one of the mechanisms that underlies the linear economy: the programmed obsolescence of products. The incentives to produce on the model of a circular economy would be essentially a saving on production costs and the acquisition of a competitive advantage, as a consumer prefers to buy a circular consumer product rather than a linear one. This new approach also entails a significant decrease in the company's environmental impact. It is therefore advantageous to apply the concept of circular economy to all the activities linked to the primary sector, in particular to livestock farming. The improper waste disposal risks negative effects being produced both from an economic and environmental point of view: diffusion in the environment of pathogens; production of harmful elements for soil, plants and man himself; eutrophication of water (Chen et al., 1994).

In July 2018 the EU outlined some fundamental strategic guidelines in which industrial symbiosis is identified as a particularly useful policy tool for achieving this innovation. This new field of interdisciplinary research, aiming at sharing resources between companies in traditionally separate sectors, wants to avoid that a company's by-products, potentially used for production purposes by other companies, can become waste. The transition to a circular economy model is a relevant matter, especially for the agricultural sector. In fact, even if traditional agriculture already incorporates cyclic reuse of its products, industrial agriculture that has developed recently, has become much more linear, consuming materials and disposing of more waste. In fact, it is necessary to highlight how this new approach can contribute to a more efficient use of natural resources and, at the same time, to encourage an increase in the competitiveness of agricultural enterprises. The way agri-food companies implement circular economy processes to make sustainable activities has been widely discussed. What is significant is certainly the re-use of resources available to create something new to reduce waste through biomass production. For a part of the planet, a high level of satisfying food needs has been reached (food security), but the industrialization of the food production processes has led to a flattening of the features of production. In short, a lowering of safety (food safety), has been demonstrated by the large numbers of emergencies caused by contamination and food quality. In very recent times, various Sicilian agronomists have rediscovered ancient wheat for its extraordinary beneficial properties. The scientific definition of the Mediterranean diet is owed to the American scholar Ancel Keys, who studied the eating habits of people when heart disease or strokes were still unknown. Durum wheat is certainly the most important of southern Mediterranean cereals and bread and pasta are the main foods derived from processing. These constitute the essential elements of the Mediterranean diet which, as well as a beneficial health food system, defines a model of endogenous, integrated and sustainable development (Saia et al., 2015; Scheer, 2006).

The objective of this research is to analyse agri-food companies to understand how they can achieve energy efficiency while maintaining a proactive behaviour towards the environment. This can happen, in fact, in different ways depending on the resources that the company makes available. So, this includes investments in plants aimed at using renewable energy, or recovering waste materials, especially with the creation and use of biomass energy.

The industrial symbiosis, in this perspective, plays a fundamental role because it could represent an opportunity for those companies that do not have the proper resources to adapt to the new environmental necessities that nowadays are increasingly urgent.

2. Materials and methods

The food industry and food farming sectors in Italy are mainly composed by small-average firms. To innovate means to equip the company with the basic tools that allow the Italian enterprises to reduce their own energy requirements. The production of renewable energy from agricultural sources is an articulated challenge. Zootechnical are organized for origin (agricultural enterprise, agroindustry, forest, biomasses of the management of the public green or the wooded areas) and for typology (grassy crops, woody biomasses, by-products, outflowing zootechnic). Besides, the techniques of transformation of these raw materials are constituted by a multitude of physical, chemical and biological processes. An agricultural enterprise, to exploit the opportunities offered by the sector of the renewable sour-energies, must proceed in different ways: first, the agricultural enterprise can produce different raw materials (like biomass) that can be converted in energy through different technologies of transformation. The agricultural enterprise can produce biomass from annual vegetable species (sorghum, corn, kenaf), from long-time ones (thistle, Miscanthus, reeds, poplars) or from pruning waste. These raw materials can be transformed through a thermochemical conversion, in fuel (bio-oil, coal, gas, combustible gas) or heat, which in turn produce electric energy. A second possibility is that the agricultural enterprise can produce ethanol or combustible gas through fermentation and digestion of the biomass. Otherwise, it produces an oleaginous oil (as that of the sunflower) and, through a process of physical-chemistry conversion - called pressing - and get combustible oil or biodiesel, turned into electric energy or heat (Bartolazzi, 2006).

The biomass in the form of plants, trees, grass, leaves, manure and animal waste can be a valid source to produce alternative fuels that can replace combustible fossils. Recently, the ancient wheats have been rediscovered: they contribute to the production of biomass through the recycling of some inedible components, as the stem. One of the most innovative approaches, undertaken by a food-farming firm, could be the investment in new equipment in order to transform biomass to produce biogas. Systems and machinery available in agriculture, such as combine harvesters, with models of various power and dimension, carry out the processes of harvest and transformation.

Biomass energy is, perhaps, one of the most controversial typologies of alternative energy used today. The advantages of energy coming from biomasses are different. First, biomass energy is a renewable resource. Secondly, it reduces the dependence from the fossil fuels, and it is a carbon neutral resource: that is to say, it does not produce carbonic anhydride in excess during its transformation. Besides, the organic waste in the form of leaves, grass and trees, but also carcasses of animals and their excrements are available in abundance and they can be used to produce energy. This is a possible way to use waste because if it was not used to produce electricity, it would increase the quantity of waste in dumps. It helps therefore to reduce waste and the management of the waste. Continually enormous quantities of solid waste are created which can be classified as biodegradable, recyclable refusals, but also dangerous toxic ones. Finally, the biomass can be useful to create different products coming from different forms of organic material: it can be used for producing gas methane, biodiesel and other biofuel or directly in the form of heat or electricity (Scheer, 2006). The interest in renewable energies emerged in 70's, following the first great world oil crisis of the 1973. In 1974 the report "A Time to Choose" by David

Freeman was published, commissioned by the Ford Foundation, which addressed the opportunities given from the use of the renewable energies and on the possible energetic savings thanks to the new productive technologies. It was not about climatic changes, the main issue concerned atmospheric pollution and the overcoming of economic and political risks determined by the dependence toward the importations of energy. The American government stimulated the production and the use of the so-called "green energies" (Raj and Antil, 2011).

Table 1. Renewable resources in European countries (QualEnergia.it) – primary production by energy type, 2013

Country	***Total primary production (Mtoe)***	***of which (shares):***					
		Solid fuels %	***Oil %***	***Gas %***	***Nuclear %***	***Renewable sources %***	***Wastes (nonrenewable) %***
EU	**789.7**	**19.7**	**9.1**	**16.7**	**28.7**	**24.3**	**1.5**
Belgium	14.6	0.0	0.0	0.0	75.2	20.0	4.8
Bulgaria	10.5	45.4	0.3	2.1	34.8	17.3	0.1
Czech Republic	29.9	59.0	0.9	0.7	26.6	12.2	0.7
Denmark	16.6	0.0	52.3	25.8	0.0	19.5	2.4
Germany	120.6	37.4	3.1	7.4	20.8	27.9	3.4
Estonia	5.7	78.3	0.0	0.0	0.0	19.9	1.9
Ireland	2.3	56.9	0.0	6.8	0.0	33.7	2.5
Greece	9.3	72.3	0.8	0.1	0.0	26.7	0.2
Spain	34.2	5.1	1.1	0.1	42.7	50.5	0.4
France	135.1	0.0	0.9	0.2	80.9	17.1	0.9
Croatia	3.6	0.0	16.8	41.6	0.0	41.4	0.2
Italy	36.9	0.1	15.9	17.2	0.0	63.7	3.1
Cyprus	0.1	0.0	0.0	0.0	0.0	100	0.0
Latvia	2.1	0.1	0.0	0.0	0.0	97.1	0.2
Lithuania	1.4	1.7	6.2	0.0	0.0	91.1	0.1
Luxembourg	0.1	0.0	0.0	0.0	0.0	76.4	23.6
Hungary	10.1	15.9	8.5	15.3	39.3	20.5	0.5
Malta	0.0	0.0	0.0	0.0	0.0	100	0.0
Netherlands	69.7	0.0	3.1	88.7	1.1	6.2	0.9
Austria	12.1	0.0	7.2	9.3	0.0	78.2	5.3
Poland	70.5	80.5	1.4	5.4	0.0	12.1	0.6
Portugal	5.8	0.0	0.0	0.0	0.0	97.5	2.5
Romania	26.1	17.8	16.3	32.9	11.5	21.3	0.3
Slovenia	3.6	30.3	0.0	0.1	38.5	30.2	1.0
Slovakia	6.4	9.1	0.2	1.6	64.1	22.9	2.1
Finland	18.0	9.4	0.4	0.0	33.8	55.2	1.2
Sweden	34.7	0.5	0.0	0.0	49.4	48.4	1.7
United Kingdom	109.5	6.7	38.3	30.0	16.6	7.7	0.7
Norway	**193.9**	**0.6**	**43.5**	**49.3**	**0.0**	**6.4**	**0.1**
Montenegro	0.8	48.9	0.0	0.0	0.0	51.1	0.0
FYR of Macedonia	1.4	77.9	0.0	0.0	0.0	22.1	0.0
Albania	2.0	0.0	57.9	0.7	0.0	41.4	0.0
Serbia	11.4	67.4	10.8	3.7	0.0	18.1	0.0

3. Case study: F.lli Vescera S.r.l.

Ancient wheats, after being rediscovered by local farmers, are considered fundamental for the realization of the circular economy within the agri-food companies. Thanks to their different physiognomy and their longer stem, as compared to the modern grains, the production of greater biomass is possible.

Spelt has a very different bran compared to soft wheat because this fiber is largely made up of non-cellulosic polysaccharides that our intestinal flora can transform into short-chain organic acids. These are the primary sources of energy for the epithelium of the colon and stimulate cell turnover, blood flow and intestinal motility. Spelt has easily digestible, non-allergenic proteins and starches with slow release of sugars. This allow the sick organism to restore the organic functions compromised by incurable diseases such as chronic disease, celiac disease, diabetes mellitus or even cancer. In reality, what has changed recently is not the quantity of gluten of the wheats but the "Gluten Index", which is linked to the rheological properties of gluten. The study focused on 8 modern wheat varieties (Adamello, Simeto, Preco, Iride, Svevo, Claudio, Saragolla, PR22D89) and 7 ancient wheat varieties (from 1900 to 1949 Dauno III, old Saragolla, Rusello, Timilia, Capelli Garigliano, Grifoni 235) to investigate the different composition of gluten. Gluten is deposited in a grid and, with a centrifugation; it is observed how much of the gluten comes out of the grill. The amount of gluten that remains in the centrifuge grid in relation to the total weight of the wet gluten compared to the Gluten Index (De Santis et al., 2017).

Table 2. Ancient and modern grains in comparison

Groups	***Genotypes***	***Pedigree***	***Year of release***
Old	Dauno III	Landraces from south Italy	1900
	old Saragolla	Landraces from south Italy	1900
	Russello	Landraces from Sicily, Italy	1910
	Timilia (R.B.) “reste bianche”	Landraces from Sicily, Italy	1910
	Cappelli	Selection from Tunisian population Jean Retifah	1915
	Garigliano	Tripolino x Cappelli	1927
	Grifoni 235	Cappelli x *Triticum aestivum*	1949
Modern	Adamello	Valforte x turkish line 7116	1985
	Simeto	Capeiti 8 x Valnova	1988
	Preco	(Edmore x WPB881) x Selected line 3	1995
	Iride	Altar 84 x Ionio	1996
	Svevo	Cimmyt line x Zenit	1996
	Claudio	(Cimmyt selection x Durango) x (IS1938 x Grazia)	1998
	Saragolla	Iride x PSB 014 Line	2004
	PR22D89	(Ofanto x Duilio) x Ixos	2005

According to ISTAT, the area sown with durum wheat in Italy in 2017 amounts to 1.28 million hectares following a marketing campaign carried out in 2016. For centuries Sicily was considered a "granary" of Italy. The ancient Greeks and Romans contributed significantly to the cereal cultivation on the island. It was during the period of Greek domination that the trimenaias, quarterly cycle wheat, sown in March (more commonly known as timilia) began to be cultivated. Among the most important centres where the cultivation obtained immediately excellent results were the fields of Lentini, a production that has been carried out over the years up to the present day. From 1890, in Carlentini the Vescera family has carried out their activity as bakers: today, with Franco Vescera, they have reached the eigth generation. The company philosophy is aimed at the recovery of ancient Sicilian grains such as Russello, Tumminia and Margarito Persicane (grains that still follow the traditional grinding techniques) to make the typical bakery products of the territory.

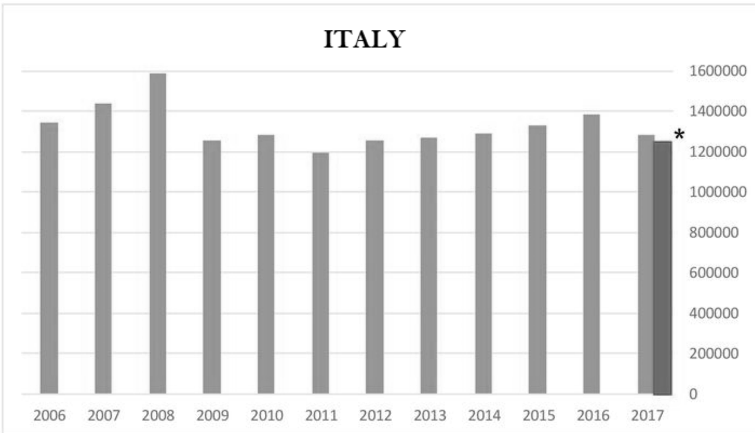

Fig. 1. Chart of durum wheat sowing in Italy (source: ISTAT)

Grinding at low speed prevents the cooking of flour due to overheating: in this way the ground product maintains taste, aromas and beneficial properties that would otherwise be lost by industrial grinding. In fact, the ancient grains favour a better digestive action and are particularly suitable for those who suffer from gluten intolerance. This is combined with the use of sourdough and of course the art of bakers in processing and baking in a wood oven, resulting in a nostalgic reappearance of the ancient Sicilian breads.

The company alternate the grains of Timilia, which occupy 50% of the land (used for sowing cereal for their high versatility), with the grains of Russello to produce bread: both products are varieties available for many years with their fragrance and organoleptic properties are a clear example of the Sicilian tradition handed down over the centuries. Tumminia and Russello bread, obtained from integral re-milled durum wheat semolina, has a higher antioxidant content than that obtained from red grapes. The grinding is done in stone mill at low speed, and cooking is done in a wood oven. This is how the wholemeal semolina bread is made, obtained from the indigenous wheat grains of timilia, rich in fiber, easily digestible and long-lasting.

Recently, other varieties of bread, pizza dough and bronze-drawn pasta in various shapes, including lasagne, linguine and macaroni have been produced. The company obtained the BIO certification, defined at Community level through the EC Regulation 834 (2007) and nationally by the Ministerial Decree 220/95, and, of course, HACCP according to the European Directive 43 (1993) (implemented in Italy with the Legislative Decree n.155 of 1997). Since the Expo in Milan in 2015, remarkable results have been obtained. The company is also the main figure at many trade fairs and markets that take place annually throughout Europe to promote and make them known internationally.

4. Results and discussions

The "F.lli Vescera" company is considered a leader in the circular economy sector, since it reuses everything produced during the production process. Always attentive and respectful of the surrounding environment, it represents a combination of efficiency and quality, tradition and innovation. The company produces biomass from anything that could be considered waste: waste from olive groves, citrus groves and straw. An efficient use of biomasses is their carbonization in stone ovens, from which the ash is obtained that is very popular with farmers to fertilize their plants. Since 2000 the company, in close collaboration with the Experimental Consortium of Granicoltura for Sicily located in Caltagirone, has begun to carry out research to deepen and analyse the sources of provenance of the wheat used.

The company intends to introduce photovoltaic panels on all the roofs of their buildings within the next two years. In this way solar power will be used to produce electricity. This is possible thanks to the fact that Eastern Sicily is the sunniest area in Europe. Another important initiative is to install water facilities throughout the structure to collect rainwater and not waste even a single drop. The water collected can be useful in all stages of processing, from upstream to downstream: for example, it is useful for the irrigation of plants and therefore their photosynthesis, it can be used in the cleaning and rinsing of plants and tools. Once filtered and purified, it could also be used in the processing of products.

The proposal offered to the company is to introduce biomass transformation plants to create energy. Careful analysis allowed the most suitable biomasses for biogas yield in animal escrement, crop residues, organic waste from agri-industry and energy crops through anaerobic digestion. For biomass to become biogas the action of different types of specialised microorganism is required. A first group of bacteria starts the degradation process, transforming the organic substance into intermediate compounds such as hydrogen, acetic acid and carbon dioxide. A second group of bacteria, made up of metanigenic microorganisms, completes the work producing methane. The biogas production process takes place inside specific "digesters", where the introduced biomass (the so-called "substrate") is divided in variable percentages between 40% and 60%. The anaerobic digestion technique can be dry or wet, in mesophilic conditions (about 35 ° C) or thermophilous (55°C). Once the biogas is obtained, before its use, it must be purified by desulphurization and dehumidification. Then, it is ready for the realization of energy. This can be done by:

- direct combustion in the boiler, with the production of only thermal energy
- combustion in engines that drive generating sets to produce electricity
- combustion in co-generators for the combined production of electricity and thermal energy
- for automotive use as 95% methane

Another product obtained from the anaerobic digestion of biomass is the digestate, which can represent an exceptional fertilizer rich in nutrients. The latter can be separated by centrifugation in a liquid and a solid phase. The solid phase is sent to the production of compost, while the liquid phase can be reused as an inoculum in the production cycle or be distributed in the field by special machines or directly by fertigation.

The environmental advantages deriving from an anaerobic digestion plant are certainly significant. First, it is possible to produce energy from a renewable source; secondly, there are less greenhouse gas emissions and, consequently, better management of emissions into the atmosphere; finally, it leads to a marked improvement in the economy of livestock and/or farms that can point to a new revenue from a secondary activity (Cocozza, 2013). Productivity (in terms of the quantity of wheat per hectare) in a company that decides to grow ancient grains in a biological way is reduced by about 50%. Nevertheless, profit margins are not reduced; on the contrary, they increase thanks to two elements:

1) Cost reduction: to produce the local wheat the grower does not have to turn to any supplier: the seed is on the farm; it does not need to be fertilized chemically, not to be defended by herbicides. This results in a significant reduction in costs.

2) Premium Price: given its quality, ancient wheat can be sold at a higher price than modern wheat. The premium price can more than offset the revenue losses generated by lower productivity. The company's revenues are not reduced. Given its characteristics, ancient wheat does not need the many inputs (fertilizers) and the processing that conventional (or modern) grain requires; moreover, it is better able to resist the negative effects of the weeds because it is possible to obtain more biomass (the modern grain is just 90 cm tall, while the local wheat is between 1.5 and 2.2 meters) (Ruggiero, 2014).

Ancient wheat has a capacity to root more than modern grains because it must support a taller stem; which allows it to access micronutrients normally not accessible to modern grains. The straw obtained from the wheat is destined for 40-50% as litter for animal shelter, 10% for animal feed, and the remaining 30% is burned in the field. With the entry into force of the Kyoto Protocol, the research and use of renewable energy sources has become necessary, thus reducing the emissions of greenhouse gases into the atmosphere: biomass represents a concrete and current possibility in this sense.

5. Conclusions

It has been written how the industrial symbiosis in the agri-food sector proposes a new vision of the circular economy, a model which today is increasingly widespread and rooted in the thinking of companies replacing the old linear model. Thanks to this premise, the italics company has decided to embark on this path that will lead to an improvement of effectiveness and efficiency of the input/output ratio, becoming a proactive company using solar-energy.

The creation of new structures aimed at exploiting biomass as a source of biogas represents an important starting point for obtaining other certifications, such as those of the ISO 9000 family. This conclusion considers the increasing needs of the modern consumer who demands technological innovations and respect for the environment. It emerges how the market, in the last 20 years in constant ferment, increasingly seeks "green" companies that are careful about their emissions. The companies, through an intense environmental marketing activity, will have a wide competitive gap that the competitors will necessarily have to fill.

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TECHNOLOGIES TO OBTAIN HEAVY AND PRECIOUS METALS FROM HAZARDOUS WASTE INCINERATION ASHES *

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Abstract

Fly ashes from hazardous waste incineration contain high concentrations of several heavy metals, and due to the potential leaching of these heavy metals and other toxic components. The speciation of heavy metals in fly ashes and other combustion residues is highly influenced by the metal's behavior and fate during the combustion process. More volatile metals, as for instance Cd, may vaporize during combustion and subsequent condense out on the surface of fly ash particles when the flue gas cools down downstream of the boiler. Thereby, the fly ash becomes enriched in volatile elements whereas the bottom ash is depleted in these elements. Non-volatile elements, on the other hand, are highly retained in the bottom ashes. Cd, Pb and Zn have all been found to be enriched in the fly ash fractions due to initial volatilization whereas Cu and Cr to a great extent are retained in the bottom ashes. Every firm operating in the field of the circular economy should adopt an industrial approach based on resource efficiency and the use and supply of sustainable raw materials, which can be achieved through innovative technologies, innovative methodologies and new business models. GE.S.P.I, one of the most innovative firms in Sicily, has become a leader in the sector of hazardous industrial waste disposal, adding value to waste through a groundbreaking technology. The result of the process is the production of energy, as well as the creation of ash, treated in order to separate dangerous heavy metals from the ash through the technique of eddy currents. Metals and purified ash can be then put on the market. The aim of this paper is to strictly analyze ashes coming from the process of incineration of hazardous industrial waste, and all the possible treatments to be implemented to extract heavy and precious metals from them.

Keywords: incineration, industrial symbiosis, precious metals, special waste

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1. Introduction

This paper is focused on the experimental phase of the thesis: by analysing datas and information it will be definitely found an efficient treatment for ashes from incineration. Fly ashes from hazardous waste incineration contain high concentrations of several heavy metals, and due to the potential leaching of these heavy metals and other toxic components (Pedersen and Ottesen, 2003). The speciation of heavy metals in fly ashes and other combustion residues is highly influenced by the metal's behaviour and fate during the combustion process. More volatile metals, as for instance Cd, may vaporise during combustion and subsequent condense out on the surface of fly ash particles when the flue gas cools down downstream of the boiler. Thereby, the fly ash becomes enriched in volatile elements whereas the bottom ash is depleted in these elements. Non-volatile elements, on the other hand, are highly retained in the bottom ashes. Cd, Pb and Zn have all been found to be enriched in the fly ash fractions due to initial volatilization whereas Cu and Cr to a great extent are retained in the bottom ashes (Chandler and Eighmy, 1997).

Every firm operating in the field of the circular economy should adopt an industrial approach based on resource efficiency and the use and supply of sustainable raw materials, which can be achieved through innovative technologies, innovative methodologies and new business models. GE.S.P.I, one of the most innovative firms in Sicily, has become a leader in the sector of hazardous industrial waste disposal, adding value to waste through a groundbreaking technology. Its core business focuses on an incineration plant, where waste from ports, healthcare, pharmaceutical companies and the petrochemical industry is brought. The result of the process is the production of energy, as well as the creation of ash; this ash is then treated in order to separate dangerous heavy metals from the ash through the technique of eddy currents. Metals and purified ash are then put on the market. The aim of this chapter, and of all the thesis, is the analysis of incoming waste and of ashes, intended as output of the production cycle, in order to implement Circular Economy's principles. A similar waste management of special waste represents a significant source of profit for companies, but above all it represents an environmental advantage, because incineration constitutes the last alternative before dumping (Baglio et al., 2017).

The outcome of the incineration process by burning a ton of waste is: 230kg of dry bottom ash, 20 kg filter ash and a lot of energy. The energy amount is about 500 kWh of electric energy. The 230kg bottom ash will receive further treatment, while the filter ash gets landfilled. The energy, which is created when the oven heats up secondary water, becomes steam and turns a turbine, is basically green electricity. Ashes resulting from the process of incineration can be dry or wet depending on the treatments chosen by firms. Dry ashes are preferred because they are less expensive to be disposed and transported. Another advantage of using dry ashes instead of wet ashes is they are safer for the environment (Böni, 2012).

2. Materials and methods

Ashes resulting from the process of incineration can be dry or wet depending on the treatments chosen by firms. Dry ashes are preferred because they are less expensive to be disposed and transported. Another advantage of using dry ashes instead of wet ashes is they are safer for the environment. The investment needed to buy technology capable of obtaining dry ashes from wet ashes is quantified in 3 million Euros. Ashes are composed in different percentages of metals and an inert material; inert material is used in sectors like the construction industry, and it has an almost insignificant price. Instead, metals like

Aluminium, Copper, Silver, Gold and Palladium, but also Iron, Calcium and other heavy metals, in higher percentages than precious ones, depending on the source of waste; metals can be extracted from either dry and wet ashes, have a significant market value; for this reason, they can represent a way of obtaining a competitive advantage for a firm in the sector which has decided to use a specific technology.

In the incineration plant it could result 200 kg of dry ash per ton of waste. A burning process that does result in dry ash is recommended for at least two reasons:

- as a rule, the amount of wet ash resulting from the burning of the same amount of waste is about 35-40% higher than in the case of dry ash;
- dry ash is more suitable for extracting heavy metals than wet ones;
- dry ash is easier and cheaper to dispose of than wet ash.

These are some reasons why this type of treatment was initiated by GE.SPI in 2016.

Ashes from the incineration plant can be classified into two groups depending on the particle diameter:

- the first group includes particles larger than 8 mm in diameter,
- the second group contains particles having the diameter less than 8 mm and may represent 75% of the ashes from the incineration process

For example, 200 kg of ash would contain 150 kg of ash made up of particles smaller than 8 mm. From this quantity a 4% fraction of heavy and precious metals (about 6 kg) could be extracted, while the other 96% is composed of an inert material that can be used in other sectors such as the construction sector and whose price is too low to be considered relevant. The group consisting of ash with particles larger than 8 mm represents 25% of all ash (almost 50 kg). Analyzing this latter group, it can be seen that it includes 20%, so about 10 kg of iron and the remaining 80% (40 kg) of inert material.

3. Experimental

GE.S.P.I. SRL was founded in 1960 as a cooperative firm of local families, situated in the port of Augusta. Its initial role was to gather and burn waste coming just from ports. After the incineration of waste was legalized, GE.S.P.I. started to work with other market niches of waste, that is to say waste coming from other production activities, in the field of special and hazardous waste. For special waste incineration is the last possibility of disposal before dumping, it is more expensive than other activities but it is preferred when there are no other chances of recycling. Now GE.S.P.I. is a multitasking, family run business, in form of a limited liability company. After the Presidential Decree n°915/1982 [264] was approved, the main plant moved to its current position. Its core business focuses on an incineration plant, where waste from ports, healthcare, pharmaceutical companies and the petrochemical industry is brought. In particular, GE. S. P. I. S. r. l. offers services of:

- classification, management, transport and disposal/recovery of hazardous and non-hazardous special waste
- inboard collection and port waste disposal services within the roadstead
- emergency evacuation assistance service for oil jetty personnel
- transport service and inboard delivery of lubricating oils
- consultancy in the environmental field for reclamation and/or safety works on contaminated sites
- cleaning and decontamination of plant and equipment
- management of mobile and/or fixed plants for the disposal, recovery and/or volumetric reduction of waste
- plant design, construction and maintenance

– consultancy for quality, environment and safety

All collection, transport, transfer and subsequent incineration operations carried out by GE.S.P.I. Srl are supported in compliance with all current environmental, health and safety legislation and according to company procedures (Fig. 1). Compliance with these procedures is ensured by:

- Technical Director of the Thermodestruction Plant
- Incineration Plant Manager
- Responsible for the Prevention and Protection Service
- Environmental Responsible

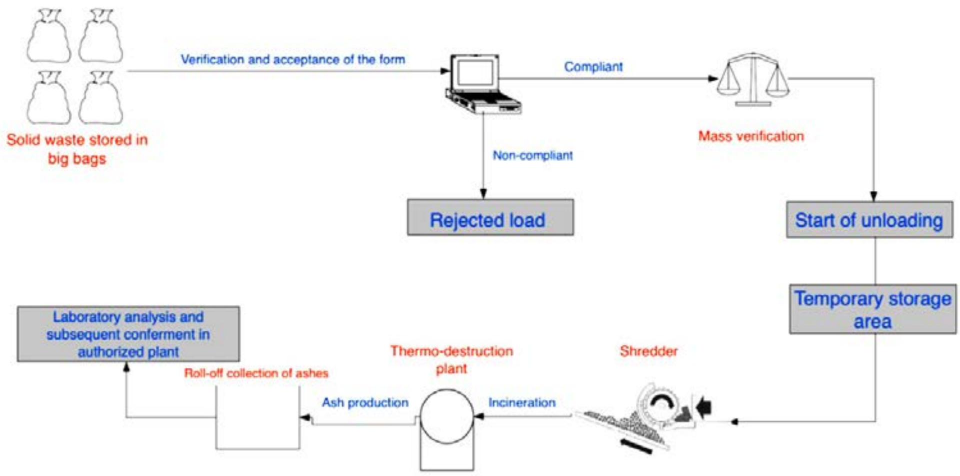

Fig. 1. Scheme of transfer of solid waste stored in big bags

The managers, within their competences, supervise the entire disposal process following the objective of continuous improvement of their performance in terms of customer satisfaction, environmental protection and protection of the health and safety of workers. The waste delivery and disposal activity at the plant is divided into the following phases:

Documental verification: the acceptance office checks the authorisations relating to waste transport activities, the correct compilation of the W. I. F. (Waste Identification Form) and any other complementary documentation (chemical analysis, safety data sheets, ADR, etc.).

Verification of packaging: the person responsible for waste disposal checks that the waste complies with what is described in the W. I. F. and that the packaging is intact and complies with the provisions of the regulations in force.

Mass verification: The vehicles are weighed using a weigh bridge system certified by the Metrology Office.

Once the above checks have been carried out and the appropriate safety instructions have been communicated to the personnel, the vehicle is taken to the areas dedicated to waste disposal when the results are positive. The process of unloading and subsequent disposal takes place according to the physical properties of the waste and the type of packaging following one of the schemes described below:

Liquid waste transported by tanker truck is transferred into temporary storage tanks. In the temporary storage area, in fact, there are 2 reservoirs with a total capacity of 56 m3 located inside a special containment tank. The liquid waste is then pumped directly into the combustion chamber of the furnace. Incineration operations shall normally start within 24 hours of delivery. Pumpable liquid and sludge waste is usually stored in drums with a capacity of 200 litres. Once unloaded from the vehicle, the drums are stored in the temporary storage area and then slinged with special equipment, poured into the loading pit of the volumetric pump that will feed the oven. Empty drums, if any, are shredded to facilitate disposal and then sent for thermal destruction. Incineration operations shall normally start within 24 hours of delivery. Solid waste stored in big bags usually has a capacity of about 1 m3. The big bags are stored in the temporary storage area and then shredded before being sent to the destruction hall. Incineration operations shall normally start within 24 hours of delivery.

Solid waste transported in bulk is discharged directly into temporary storage pits. They are then ground to facilitate better combustion in the oven. The shed where the pits are located and where the crushing is carried out is kept in a vacuum in order to protect the external environment. Medical waste with an infectious risk is unloaded from vehicles and placed directly on the conveyor belt, which will start it up directly in the oven without further handling. Incineration operations shall normally start within 24 hours of delivery.GE.S.P.I’s core business focuses on an incineration plant, where waste from ports, healthcare, pharmaceutical companies and the petrochemical industry is brought. Its waste management activities include: gathering waste coming from ships passing through Augusta’s port, land reclamation and commercial brokering with other local firms, consisting mainly in waste management. Until some year ago, another activity was the transport of hazardous waste from other structures to the incineration plant. Today this secondary activity has been replaced by security and supervision of oil terminals.

Among other activities, the company also makes innovative use of storage: differently from the other firms in the sector, it works as a logistic support for the core business. This type of storage is useful in case of the quantity of waste that the firm has to deal with is higher than the quantity that can be daily treated on the basis of the plant’s capacity. The stock prescription of waste is of 48 hours. GE.S.P.I is also involved in financial services , making agreements with seven different financial institutes , in order to improve the distribution of risk. GE. S. P. I. Srl owns a plant for the thermodestruction of hazardous and non-hazardous port and special waste. The plant of the company GE. S. P. I. Srl is authorized by Ordinance of the Commissioner Delegate for the Emergency Waste of the Sicilian Region No. 83 of 09/02/2005 and AIA Sicily Region of D. D. G. No. 634 of 15/11/2012.

The objective of incineration is to treat waste, in order to reduce its volume, its hazardousness and at the same time capture and destroy potentially hazardous substances that are released during the process (Table 1). The waste entering the plant consists of highly heterogeneous material consisting of organic substances, minerals, metals and water. During incineration, gaseous effluent is produced which will contain most of the energy available as heat.

The plant is located on an area of about 17,000 m^2 in the port area. The covered area is about 2,000 m^2 and consists of two industrial sheds used for waste storage (1,400 m^2), an office building (300 m^2) and a building used as a control room and instrumentation. The plant, authorized by Commissioner's Order no. 83 of 09/02/05, consists of 2 independent lines, one of which was built and is in an advanced start-up phase and the other is under construction and is developed in about 2500 square meters for structural foundations and 300 square meters for the building containing the technological systems and utilities (Matarazzo et al., 2018).

Table 1. Operating conditions for thermal treatment of waste

Operating temperature (°C)	850-1450
Pressure (bar)	1
Atmosphere with presence of:	Air
Stoichiometric ratio	>1
Treatment products: Gases	HCL, CO, NO_X, SO_2, VOC, Dust
Treatment products: Solids	Slag and Ash

The plant is suitable for treating hazardous and non-hazardous waste and has a disposal capacity of about 4 t/h. For each line, the system is equipped with an energy recovery section consisting of a boiler capable of producing 15 t/h of steam at a maximum pressure of 40 bar and a maximum temperature of 365 °C. The thermal cycle is completed by a Siemens ST110 steam turbine with a maximum power output of 2,540 kW and an expected annual electricity production of 8,000÷10,000 MWh. Of the above electricity production, about 1,800 MWh per year will be used for internal consumption, the remainder being fed into the grid at the best market conditions. The plant consists of:

- a section for the storage of incoming waste;
- a section for combustion and recovery of thermal energy through the production of steam;
- a section of demi water production;
- a smoke depuration section;
- an evacuating chimney to discharge the purified fumes into the atmosphere;
- systems for monitoring and controlling combustion, concentrations of pollutants (downstream of the smoke purification equipment and also used for regulating the dosage of reagents) and fumes leaving the chimney (Leanza et al., 2017).

4. Data and results

From an analysis of the production cycle during the month of November 2017, the purpose of this work is to create an evidence of the concentration of different metals in ashes from every kind of waste which GE.S.P.I. srl has to deal with (Table 2).

Table 2. GE.S.P.I. waste production in 2017

C.E.R	***Mass (kg)***	***Mass (%)***	***C.E.R description***
190102	469940	4.50%	Ferrous materials extracted from bottom ashes
190107	1485920	14.23%	Solid waste from gas treatment
190111	4579540	43.86%	Bottom ashes and slags containing dangerous substances
190112	1740720	16.67%	Bottom ashes and slags other than those mentioned in 19 01 11
190114	3851	0.04%	Fly ashes other than those mentioned in 19 01 11

Although solid waste incineration has many advantages, including detoxification, volume reduction, and resource recovery, residues contain some toxic elements that require special attention. The composition of the ash depends both on the type of waste treated and on the operating conditions of the furnace, e. g. combustion temperature, excess oxygen in the combustion chamber, quantities introduced per hour, dwell time, gas speed, etc. Bottom ashes, which can be reused as a secondary building material, should generally contain a low concentration of heavy metals, particularly volatile ones such as Pb, Cd and Zn (Chimenos et al., 2011)). Generally, the vaporized fraction from the combustion bed - 40% for Pb, 82% for Cd, 50% for Zn and 10% for Cr - is based on the thermodynamic study. The presence of heavy metals in incineration residues may have been the combination of several factors including the type of furnace, the capacity and the temperature, as well as the composition of the waste. In general, a large furnace has an advantage in that it results in uniform combustion because of its relative insensitivity to fluctuations in the amount of waste entering. Therefore, the volatilization of metals increases with the increase in furnace temperature and may directly affect the concentration of bottom ash elements (Jung et al., 2004). Ashes coming from the incineration plant can be divided into several categories on the base of the diameter of the particles. Categories which are expressed and can be analyzed in appropriate grading tables.

The main objective of this work is to establish a precise correlation between the different categories of waste which go through GE.S.P.I's production cycle and the achievement of heavy and precious metals, in terms of quantities and quality. In order to reach this purpose, a sample of incoming waste has been analysed in order to elaborate information about their quantity and chemical composition (Fig. 2).

By analyzing this date, it can be definitely said that industrial waste, which are disposed in a higher quantity in term of mass (Table 3). This scientific approach goes on with a chemical analysis of the samples of waste, the same one of the previous analysis of waste typology. Table 4, as an evidence of this research, shows the chemical composition of some incoming waste, dated 24/11/2017, in order to lastly define the strict correlation between industrial waste and heavy or precious metals (Table 5).

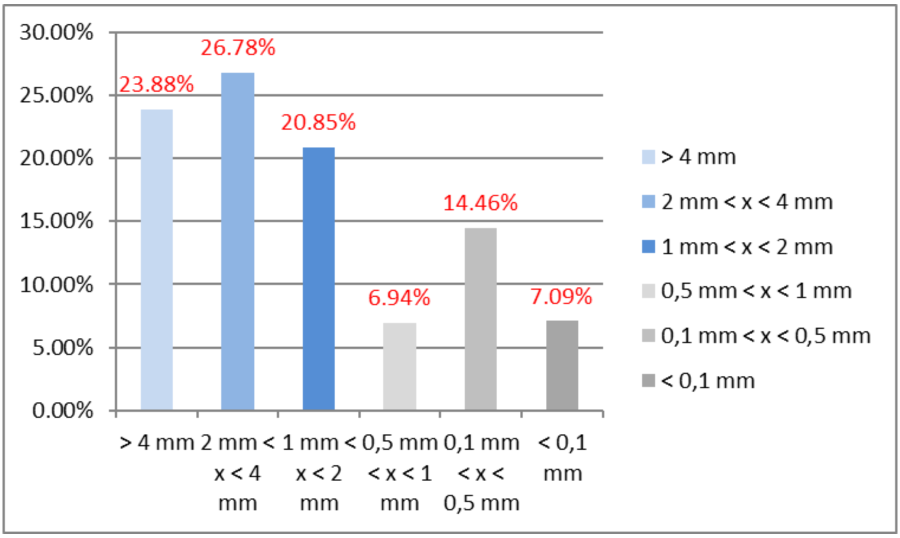

Fig. 2. GE.S.P.I ashes grading tables *(Source: GE.S.P.I. srl)*

Table 3. Grading tables

> 4 mm	23.88%
2 mm < x < 4 mm	26.78%
1 mm < x < 2 mm	20.85%
0.5 mm < x < 1 mm	6.94%
0.1 mm < x < 0,5 mm	14.46%
< 0.1 mm	7.09%

Table 4. An extract of incoming waste of the day 24/11/2017

C.E.R.	***Mass (kg)***	***Mass (%)***	***C.E.R Description***
190304	433070	18.14%	Wastes marked as hazardous waste partially stabilised other than those mentioned in 19 03 08
070501	325180	13.62%	Aqueous washing liquids and mother liquors
180103	199061.982	8.34%	Wastes whose collection and disposal is subject to special requirements in order to prevent infection
170503	146493	6.14%	Soil and stones containing dangerous substances
050106	138660	5.81%	Oily sludges from plant and equipment maintenance
191211	118790	4.98%	Other wastes (including mixtures of materials) from mechanical treatment of wastes
050109	100760	4.22%	Sludges from on-site effluent treatment containing dangerous substances
070510	70720	2.96%	Other filter cakes and spent absorbents
050103	66860	2.80%	Sludges from tank bottoms
070504	61860	2.59%	Other organic solvents, washing liquids and mother liquors
160303	60945	2.55%	Inorganic wastes containing dangerous substances
190207	55630	2.33%	Oils and concentrates from separation processes
070208	47580	1.99%	Other still bottoms and reaction residues
190204	43340	1.99%	Premixed waste containing at least one hazardous waste
150110	28543	1.20%	Packaging containing residues of or contaminated by dangerous substances
161002	26760	1.12%	Aqueous liquid wastes other than those mentioned in 16 10 01
161001	26380	1.10%	Aqueous liquid wastes containing dangerous substances
080312	26100	1.09%	Waste ink containing dangerous substances

As it can be noticed, sample n.1, which represents an industrial waste, rather than the other two, which represent waste from pharmaceutical and healthcare sectors, is composed of a higher quantity of heavy or precious metals, in different percentages (especially Nickel, Copper, Vanadium and Zinc) (Zhang et al., 1998) (Table 5).

Table 5. Metallic composition of sample of waste (period 24/11/2017)

	Sample n.1	***Sample n.2***	***Sample n.3***
Acceptance date	***24/11/2017***	***24/11/2017***	***24/11/2017***
Metals in the unaltered state			
Antinomy (sb) (mg/kg)	83.00	7.50	39.40
Arsenic (As) (mg/kg)	340.00	18.30	73.00
Beryllium (Be) (mg/kg)	<1	<1	<1
Cadmium (Cd) (mg/kg)	<1	<1	1.22
Cobalt (Co) (mg/kg)	1,790.00	<1	87.00

Total chromium (Cr) (mg/kg)	750.00	34.80	77.00
Manganese (Mn) (mg/kg)	1,670.00	109.00	460.00
Mercury (Hg) (mg/kg)	<1	<1	<1
Molybdenum (Mo) (mg/kg)	279.00	127.00	188.00
Nickel (Ni) (mg/kg)	9,700.00	129.00	1,210.00
Lead (Pb) (mg/kg)	204.00	27.40	219.00
Copper (Cu) (mg/kg)	2,310.00	151.00	1,060.00
Selenium (If) (mg/kg)	<1	<1	<1
Pond (Sn) (mg/kg)	109.00	8.60	44.60
Thallium (Tl) (mg/kg)	94.00	<1	<1
Tellurium (Te) (mg/kg)	3.42	<1	<1
Vanadium (V)	40,500.00	740.00	5,600.00
Zinc (Zn) (mg/kg)	7,500.00	980.00	2,130.00
Tot.	65,332.42	2,332.60	11,189.22

5. Discussions

The main advantages of a similar technology are: economic (cost-saving) and environmentally friendliness (for the same amount of waste there is a significant reduction in the amount of ash obtained so that a small quantity is stored). Given the costs of implementing a similar technology, an initial investment of EUR 3 million is proposed for switching from a wet ash treatment system to one for the production of dry ash (adding a maintenance of the 300,000 euro for facility). It should be noted that in 2016 the cost of removing wet ash was about 210 euro / ton at a total price of 84 euros (considering 400 kg of wet ash). By implementing the new technology, the price will be about 42 euros, half of the initial price. This analysis demonstrates how the new technology's profit-sharing in terms of cost reduction can affect the firm's overall profit. Moreover, since the inert material removal cost is about 80 euro / ton and the heavy and precious metals can be extracted in different combinations, it can be asserted that it would be useful to implement this technology in the GE.SPI installation. The implementation of a similar technology, which consists in the extraction of wet ash at dried ash near the incineration plant, would be advantageous in two directions:

1. for the environment, since the same amount of incinerated waste results in less dry ash production (about half of the wet ash), facilitating transport due to the significant reduction in volume and weight transported. Decommissioning is also easier due to the reduced dryness of dry ash due to the absence of water, and successive sequential treatments are relieved by choosing dry ash.
2. for generating profit by reducing costs: profit from the sale of heavy and precious metals from dry ash could be used to cover initial technology investment, and then, in a few years, the sale of precious metals could significantly influence the profit, making the firm a competitive advantage.

6. Conclusions

Overall, the results of this paper may be useful from several points of view. First, the low content of solid waste suggests that if recovery of these precious and rare metals would be possible, there would be only a small potential for economic and environmental benefits. In order to solve the problem of diminishing economic resources, it is necessary to develop an integrated perspective of the economy, applying the principles of circular economy. Other firms in the sector, even if they have the same basic activity as GE.S.P.I, treat urban waste with relevant consequences on the different percentages of metals that can be extracted from the ashes.

Therefore, a new perspective has been proposed for achieving sustainable growth and treating waste as a useful economic resource and it implies the conventional concept of resources and products in the market, named Circular economy. These advantages have been obtained by other leading firms in this sector, thanks to investments in modern technologies like eddy current separators, capable of adding value to ashes, letting firms obtain competitive advantages in the long-term. The eddy current separator system could be an innovative way of giving value to ashes, intended as waste of a production cycle, according to the principles of CE.

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SMART AND CIRCULAR ECONOMY APPLIED TO A SICILIAN COMPANY AS A SEWAGE TREATMENT MODEL*

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Abstract

The Circular Economy is a term used to define an economy able to regenerate independently where there is no trace of waste, every element is produced, consumed and then used in the cycle itself. The following paper deals with a reality which is particularly pertinent to this theme: farm holiday company in the province of Enna, inland Sicily. The company stands out thanks to the adoption of various techniques which make it a real closed-cycle business. The objective of this paper is to highlight how the analysed company, applies different methods to achieve its sustainable goals: the wastewater phyto-depuration, the composting technique, the use of solar panels and photovoltaic panels, the biocalce for the walls. Moreover, the company could be considered as a role model for the territory's enhancement, acting as a driving force for the local economy, in particular for the towns of Troina, Cerami, Nicosia by following the green economy principles.

Keywords: circular economy, phyto-depuration, sustainable tourism

1. Introduction

The concept of circular economy is based on the never-ending idea of every productive process circle which looks for better technologies to reuse some or all of materials which otherwise would be simply disposed of, thus to extend the life cycle of the products (which are not wastes anymore), to which a new use is guaranteed. The Circular Economy, according to the Ellen MacArthur Foundation definition, is a generic term for defining a new type of economy designed to regenerate itself. Therefore, it is a system in

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which all of the activities, (starting from the extraction and the production), are organized that waste is reused. In the linear economy, on the other hand, once the consumption has ended, the cycle of the product that becomes waste ends too, forcing the economic chain to continually resume the same scheme: extraction, production, consumption, disposal.

There are two essential reasons to produce on the model of the circular economy: a saving on production costs and the acquisition of a competitive advantage, as a consumer prefers to buy a circular consumption product rather than a linear one (Lucchetti and Jirillo, 1989). This new approach also entails a significant decrease in the company's environmental impact, therefore it is advantageous to apply the concept of circular economy to all those activities linked to the primary sector, in particular to the agri-food sector, where an incorrect disposal of waste risks to produce negative effects both from an economic and environmental point of view. Specifically, the company "Le Querce di Cota" undertakes to promote sustainable tourism in the territory of Troina, located in the Sicilian hinterland.

The term “sustainable tourism” has come to represent and encompass a set of principles, policy prescriptions, and management methods which mean that an area’s environmental resources are protected for future development (including natural, built, and cultural features) is protected for future development (Lane 1994). However, this paradigm has recently been criticized as being too limited or tourism-centric, in so far as it fails to provide a conceptual framework policy formulation which explicitly connects the concerns of tourism sustainability with those of sustainable development more generally (Hunter, 1997).

The objective of this paper is to highlight how a company which operates according to the principles of circular economy, using techniques including: phytodepuration of wastewater, solar and photovoltaic panels, biocalce buildings, composting techniques, crops of organic products and zero kilometer, can obtain both a competitive advantage and represent a strength for the valorization of the local economy.

2. Material and methods

Among the various techniques that can be adopted by a company that operates favoring the principles of circular economy there is certainly the treatment of wastewater. First of all, waste water refers to all those waters whose quality has been impaired by human action after their use in domestic, industrial and agricultural activities, thus becoming unsuitable for their direct use as they are contaminated by different types of organic and inorganic substances dangerous for health and the environment.

Three different types of waste water can be classified: the "domestic waste water" are those deriving from residential settlements and service deriving mainly from human metabolism and domestic activities"; the second important definition concerns the discharge of "industrial waste water". The law, as amended by Legislative Decree 4, (2008), states that this discharge is characterized by "any type of wastewater discharged from buildings or plants where commercial activities or production of goods are carried out, different from domestic wastewater and rainwater runoff... " (Article 74, paragraph1, letter h). Finally, a third concept concerns "urban waste water", which, after the amendment referred to in Legislative Decree 4, (2008), are defined as "domestic waste water or the mixture of domestic wastewater, industrial wastewater or run-off meteorites conveyed in sewage systems, also separated, and coming from agglomeration" (Article 74, paragraph 1, letter i). Wastewater treatment is the process of converting wastewater into bilge water that can be discharged back into the environment. It is formed by a number of activities including bathing, washing, using the toilet, and rainwater runoff. Wastewater is full of contaminants including bacteria, chemicals and other toxins. Its treatment aims at reducing the contaminants to acceptable levels to make the water safe for discharge back into the environment. There are two different wastewater treatment plants: one chemical or physical, the other biological. Biological plants use biological matter and bacteria and are ideal for wastewater treatment from families and business premises. The physical waste treatment plants use chemical reactions and physical processes to treat wastewater and are mostly used to treat wastewater produced by industries, factories and manufacturing companies. Wastewater treatment is divided into some specific phases:

- The initial step of the wastewater treatment process of this invention is to provide, in the recirculation tank, a desired concentration of biologically active particulate material (Pirbazari and Shorr, 1990). The waters are directed to a treatment plant using underground drainage systems; it is very important that certain hygienic conditions are respected, that the pipes or tracks are leak-proof and that the workers wear protective clothing.

- Odor control is the first real process of the wastewater treatment plant and is very important. The waste water contains a lot of pollutants that cause a bad smell. To ensure that the surrounding areas are free from bad odor, treatment processes are initiated at the treatment facility and in doing so all sources of odor are contained and treated with chemicals substances.

- Screening of all the sewage flow in to remove non-biodegradable solids (Bhardwaj, 2013) such as diapers, plastic, broken bottles or bottle tops that in one way or another can damage the machine. Neglecting this phase can cause constant as well as numerous problems. The solid waste found and removed from the wastewater is then transported and disposed of in landfills.

- The primary treatment involves the separation of macrobiotic solid matter from the wastewater and is realized by pouring the waste water into large tanks. The sludge, the solid waste deposited on the surface of the tanks, are removed and pushed into the center of the cylindrical tanks and then pumped out of the tanks for further treatment. The remaining water is then pumped for secondary treatment.

- The secondary treatment phase involves the addition of sludge to waste water. The air is first pumped into huge aeration tanks that mix the waste water with small amounts of mud, causing the growth of bacteria and other small microorganisms that consume the organic residue. The major part of bacteria in activated sludge use organic carbon in the form of small organic molecules as substrate, and some bacteria which are essential to biological nutrient removal, use inorganic carbon as substrate (Jeppsson, 1996).

- During the treatment of bio-solid substances, the solid matter deposited after the primary and secondary treatment phases is directed to the digesters. The digesters are heated to room temperature and the solid waste are then treated for a month where they undergo anaerobic digestion. During this process, methane gases are produced and there is a formation of nutrients rich in bio-solids that are recycled into local businesses. Methane gas formed is usually used as an energy source at treatment plants.

- The tertiary treatment phase can remove up to 99 percent of impurities from wastewater. This produces water with a quality close to that of drinking water. Unfortunately, this process tends to be a little expensive as it requires special equipment, highly skilled workers, chemical products and a constant supply of energy.

- After the primary treatment phases, the waste water still has some imperfections and to eliminate them, it must be disinfected for at least 20-25 minutes in tanks containing a mixture of chlorine and sodium hypochlorite. The disinfection process is an integral part of the treatment process because it protects the health of animals and local populations that use water for other purposes.

- The sludge that is produced and collected during primary and secondary treatment processes requires further processing. The thickened sludge layer left in the bottom of the treatment tanks is pumped to a mechanical dewatering device, usually a filter press, where water is mechanically squeezed out leaving the modified, dewatered sludge in the form of a filter cake (Smith and Brown, 2003). Instead, the remaining water is collected and sent back to the huge aeration tanks for further treatment.

In short, it is evident that the wastewater treatment process is one of the most important environmental conservation processes and that it should be encouraged and increasingly implemented all over the world. Compared to traditional sewage treatment methods, it can be stated that 'green technologies' are more appropriate for water clean-up (Schroder et al., 2007). There are numerous advantages related to it and in particular, the treatment of wastewater ensures that the environment is kept clean, there is no water pollution in fact, an American study pointed out that numerous compounds found in sewage plants will consequently also be present in potable-water supplies and, hence, represent a public health problem of increasing concern (Stackelberg et al., 2004), it avoids the proliferation of waterborne diseases and even more, it ensures the presence of sufficient water for purposes such as irrigation.

3. Case Study: Le Querce di Cota

Le Querce di Cota agritourism is located in Troina, a town in the province of Enna (EN) with an extension of Ha 20.98.00. It is the remaining part of a large fiefdom divided and then sold, located in a valley about 650-700 meters above sea level. Le Querce di Cota is just a slice of Sicily, a small magical corner of the late 1800, the classic place with beautiful landscapes, including one of the main slopes of Etna.

Fig. 1. Landascape from “Le Querce di Cota”

The renovation work began in 1999 and it was completed in 2001, the year in which the agritourism activity was inaugurated; so, today, the “Baglio” a typical Sicilian rural structure, is built around the two-storey manor house, with rooms for the peasants and stalls for the animals. They include sheep, ducks, hens, dogs, cats, and horses used for guided excursions. The structure also has nine rooms, two suite and an independent apartment. The olive press, the palm grove for the wine, the granary and the provisions for foodstuffs can be seen as evidence of total self-sufficiency. One of the peculiarities of “Le Querce di Cota” is undoubtedly the kitchen: it prepares traditional dishes from its rural heritage using the strong and genuine flavors of local products. From the love for genuine products comes the production and the subsequent sale of organic products to the public, such as oil, jams, aubergines, mushrooms, peppers, bread, wine and pasta.

A recognition of organic agricultural production is evidenced by the Certificate of Conformity issued by Ecocert Italia. Added to this is the success in November 2009, at the sixth edition of the Peasant Cooking Championship held in Arezzo on the occasion of AgrieTour, thanks to its most famous dish, “seasonal puff pastry”, “Le Querce di Cota” won the first prize. The natural conditions for renewable energy sources differ widely across Europe. Countries leading in renewable energies are countries with good conditions concerning rainfall, distribution of rainfall over the year and inflow which in turn make a high production of electricity from hydropower possible (Reiche and Bechberger, 2004). In Enna, the climate is warm and temperate, although there is significant rainfall throughout the year, with showers also in the driest month. Specifically, the company has exploited these circumstances by installing solar panels and photovoltaic panels. So, in a proactive way, sustainable development and economic growth have been sought together with the surrounding territory, trying to revitalize local tourism accordingly.

The concept of sustainable development need not be in conflict with the notion of economic growth. Supporters of sustainable development accept that economic vitality is essential in order to combat poverty, improve the quality of life and drive the process of environmental protection. However, balances have to be struck in order to ensure that growth does not make excessive demands on natural resources. (Owen et al., 1993).

4. Results and discussions

The company “Le Querce di Cota” driven by an innate vocation towards the principles of circular economy adopts the technique of phyto-purification for wastewater management. Phyto-depuration is an eco-compatible depuration process well inserted within the environmental reclaim context, directed to save energy, cut the costs, and to allow a reduction of water waste. There is a natural system for the depuration of sewage water projected to reproduce the natural depuration processes in a controlled setting. The first phyto-depuration plant in Europe dates back to 1952, but it took about twenty years of research to arrive at the realization of the first full-scale phyto-depuration plant, built in Germany. In Europe, there are currently thousands of plants of various types, widespread mostly in Germany and the United Kingdom. In Italy an incentive came from Legislative Decree 152/06 and subsequent modification (Legislative Decree 258, 2000): introducing the concept of "appropriate treatment". From the aforementioned Legislative Decree: "The appropriate treatments" must be identified with the aim: to make maintenance and management simple; to be able to adequately withstand strong hourly variations in the hydraulic and organic load minimize management costs.

The company analyzed, taking advantage of these recent incentives, in recent years has ventured into this activity with a significant investment of €36 thousand euros. The project hypothesis foresees the realization of a Phyto-depuration plant with horizontal sub-superficial flow (H-SSF) and a further surface flow Phyto-depuration basin (FWS). In particular, upstream of the existing septic a degreaser will be installed, while downstream of the tanks a connecting weel will be installed, with the function of equalization tank, and from here the water, by gravity, will be introduced into the Phyto-depuration plant.

The waters treated by the Phyto-depuration plant will be conveyed into a well where a small submersible pump will be installed to raise upstream the wastewater in a well, located upstream of the existing sub-irrigation system, and disposed of in the ground through the sub-irrigation system already at the service of the company.

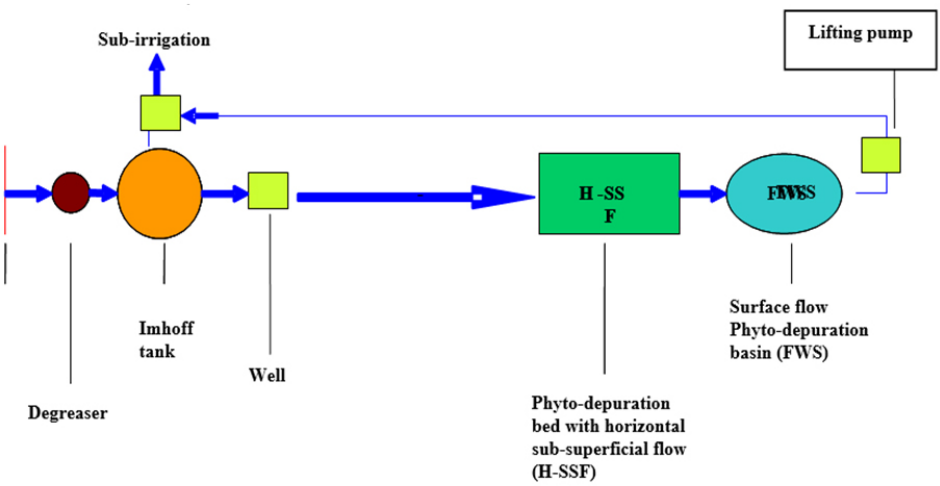

Fig. 2. Scheme of the waste water treatment plant at the "Le Querce di Cota" farm.

During the design phase various parameters were taken into consideration, including the inlet and outlet pollutant concentrations, the inlet flow rate, the surface area of the basin, the height of the water column and the porosity of the system, the surface area, the average daily flow, the slurry temperature, the height of the bed, the permeability. The meteoric influences on the system must not be neglected. The elements that characterize the phyto-depuration plant are plants, microorganisms, soil and waste water. One might think that the main role within the purification process is covered by plants, but in reality, it is not like that: they simply create the most suitable habitat for microorganisms to proceed with the biological purification of the water.

In the specific case, on the surface of the bed of phytoremediation cyperus papirus var siculus will be planted for the measure of four plants per square meter. The reasons that led to such an investment are mainly of environmental nature: for example, for a lower production of carbon dioxide compared to a classic purifier and a reduction of eutrophic risks in the discharge receiving bodies, with an erosion control, an air purification and an improvement of the microclimate. Other reasons are: energy saving, as it achieves the same level of efficiency of classical purifying technologies with reduced energy consumption, and the aesthetic appearance because the area that surrounds the purifier, normally degraded and abandoned, has a better appearance after the interventions.

On the other hand, there is no real economic saving at least in the present, but the company proposes in the immediate future to increase the size of the plant, consequently seeking to obtain economic advantages. Moreover, thanks to this Phyto-depuration plant and to numerous particularly innovative technologies including biocalce restorations and 0-kilometer crops, “Le Querce di Cota” has become the forefather of the revaluation and relaunch of sustainable tourism in the area, with particular reference to municipalities of Troina, Cerami and Nicosia.

The term sustainable tourism emerged in the late 1980s and has become firmly established in both tourism policies and strategies and tourism research (Hall, 2011). At the same time in the last two decades sustainability has emerged as a force in the tourism industry. There have been a number of institutional initiatives in this respect, and they have shaped a framework for both theoretical and applied development and have helped extend the paradigm of sustainability as a general feature of contemporary tourism (Torres-Delgado and López Palomeque, 2012).

5. Conclusions

Through the following studies it has been observed that in Italy there are examples of companies that act in compliance with the principles of sustainability: the main advantages are related directly to tourism and the environment. It is sincerely hoped that “Le Querce di Cota” can be observed as a model in the local scene, encouraging other similar companies in the search of sustainable tourism.

In the same way there are many positive effects for the environment, first of all reducing the withdrawal of natural resources and the waste to be disposed, making possible to prolong the use of most of the products and making everyday life concepts such as reuse and recycling.

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STUDY ON THE RELEASE CONDITIONS OF THE METALS PRESENT IN THE ZINC FERRITE *

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Abstract

The present research examines zinc ferrite, an industrial slag deriving from the zinc working process. In this slag, as is known, there are several metals that can be easily released.
The purpose of this work was to study the release variations, for specific metals present in the zinc ferrite, as a function of two variables: the pre-treatment temperature of the ferrite and the pH of the system in which the latter is inserted.
The release of the following metals was analyzed: Fe, Zn, Al, Cd, Co, Mn, Cu, Ni, Cr, Na, K, Cs, Mg, Ca, Ba, Bi, Ga, In, Li, Rb, Sr, Tl, U. In particular, zinc ferrite was pre-treated at different temperatures such as: 200 °C, 400 °C, 600 °C, 800 °C e 1000 °C. Subsequently the different calcined samples were placed in distilled water or in acid solutions (of hydrochloric acid, nitric acid and aqua regia at pH=1) or in basic solution (of ammonium hydroxide at pH=11). The systems were prepared in a ratio of 1:10, respectively, of grams of calcined ferrite and mL of the selected solution and stirred for one hour.
At the end of the test, each system was filtered and the obtained solution was analyzed by Plasma Mass spectrometry (ICP-MS). The results obtained defined the release conditions for each single element according to the two variables used. It is possible to say that tending to release the elements is more favored in an acid environment and above all in aqua regia. In general, it has been identified, for each element, the characteristic calcination temperature which favors' its release.

Keywords: heavy metals, industrial waste, slag, zinc ferrite

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1. Introduction

The industrial wastes generally contain a large quantity of pollutants of different nature depending from the type of production process. In industrial wastewater there are often present heavy metals (Giusti, 2009). These metals can be released into the soil and consequently into aquifers with serious damage to the environment and to human health. To reduce the level of pollutants, inorganic and organic, released into the aquifers, various methods such as ion exchange, adsorption, photocatalysis o phyto-depuration are used. To accomplish this propose différent materials are used such as: zeolites o zeotypes (Candamano et al., 2017; Choi et al., 2006; De Luca et al., 2009; De Luca et al., 2015; De Raffaele et al., 2016; Frontera et al., 2013; Turta et al., 2008; Vuono et al., 2014; Wang et al., 2010) photocatalytic agents (De Luca et al., 2011; Di Paola et al., 2012), nano materials (De Luca et al., 2018; Logar et al., 2006 ; Policicchio et al., 2015), plants for phytodepuration (Ghori et al., 2016).

The main purpose of this research is to study a particular industrial waste, called zinc ferrite, which derives from an industrial process of zinc extraction. This waste is dangerous owing to the presence of many metals inside it (Youcai et al., 2000). In particular, the release condition, for each specific metal present in the zinc ferrite, was studied as a function of two variables: the pre-treatment temperature of the ferrite and the nature of the system in which the latter is inserted.

2. Material and methods

The studied zinc ferrite is an industrial slag coming from a zinc production plant located in Southern Italy. The analyses were carried out using Perkin-Elmer Elan DRC instrument ICP-MS and for this analysis several isotopes were used for the same element ^{27}A, ^{138}Ba, ^{9}Be, ^{209}Bi, ^{44}Ca, ^{114}Cd, ^{59}Co, ^{52}Cr, ^{53}Cr, ^{133}Cs, ^{63}Cu, ^{56}Fe, ^{57}Fe, ^{54}Fe, ^{69}Ga, ^{115}In, ^{39}K, ^{7}Li, ^{24}Mg, ^{55}Mn, ^{23}Na, ^{58}Ni, ^{208}Pb, ^{85}Rb, ^{88}Sr, ^{205}Tl, ^{238}U, ^{64}Zn, ^{66}Zn.

In order to research the conditions of release of the metals present in the zinc ferrite, different systems were prepared by dispersing 10 grams of zinc ferrite, both as such and calcined at different temperatures, in 100 mL both of distilled water and of different solutions for nature and for pH values. In particular, the different samples of zinc ferrite were obtained by calcining in muffle for two hours at different temperatures such as: 200 °C, 400 °C, 600 °C, 800 °C, 1000 °C, while the used solutions were ammonia at pH: 11, nitric acid at pH: 1, hydrochloric acid at pH: 1 and aqua regia at pH: 1. After the test, each system was filtered and the solution obtained was subsequently analysed by ICP-MS to study quantitatively the concentration of released metals.

3. Results and discussion

The concentrations of the elements (μg/L) released by the zinc ferrite, obtained through ICP-MS analysis, are discussed as a function of the calcination temperature and the nature of the solutions (Tables 1-5). Table 1 shows that in water, the major element released from non-calcined ferrite (25 °C) is zinc, followed by manganese, sodium and calcium. Lead release in all samples of calcined ferrite at different temperatures is not found. Most element concentrations undergo variations as a function of calcination temperature. These variations are not always linear according to the calcination temperature although, as we will see later, these behaviours are repeated for the same element also for the other systems considered below.

Table 1. Concentration of the elements (µg/L) released from 10 grams of zinc ferrite in 100 mL of water, after one hour, under stirring and at room temperature

Element	***Calcination temperatures***					
	25 °C	***200 °C***	***400°C***	***600°C***	***800°C***	***1000°C***
Fe	45.10	119.92	254.33	/	/	19.29
Na	234400.04	21633.82	250916.34	269289.57	262157.88	67160.53
K	6421.21	1555.97	78219.46	104257.93	140892.26	33323.51
Cs	7.08	10.10	55.81	171.72	1012.89	6.48
Mg	69598.28	17171.52	170731.60	241582.84	119457.36	1413.74
Ca	201762.95	38446.99	374206.61	397378.08	408657.14	332533.01
Ni	270.22	95.94	1031.22	694.38	80.89	57.47
Cu	141.32	87.67	41040.15	75343.87	272.89	11.63
Zn	2077158.69	201600.59	3093533.11	3276532.51	67557.52	3946.15
Co	582.30	134.78	1537.55	2215.92	39.61	83.36
Mn	544382.77	52540.56	709814.95	971659.33	26427.50	164.74
Cr	/	/	/	/	/	/
Cd	14940.05	4777.20	57889.68	97631.46	38118.17	359.01
Al	/	/	421.77	155.98	24.22	8.84
Ba	5.27	1.97	2.59	24.30	92.64	133.80
Bi	/	6.51	164.99	203.94	55.35	/
Ga	6.33	1.07	15.40	16.88	6.31	1.34
In	/	/	/	/	/	/
Li	90.93	12.54	491.22	327.80	375.15	21.69
Pb	/	/	/	/	/	/
Rb	16.58	4.16	195.69	298.67	577.83	50.57
Sr	1684.46	332.57	333.57	4511.50	21535.71	26204.55
Tl	29.39	0.67	25.96	136.11	214.00	21.06
U	0.02	/	/	/	/	0.05

Table 2 shows the data relating to systems containing NH_3 solution, which shows how the situation changes compared to the previous one. In this system, characterized by a strongly alkaline pH, the most abundant element released from the non-calcined ferrite at (25 °C) is manganese followed by calcium and sodium. Another important fact is that in this system, the lead is released from both the ferrite as is and calcined at 200 °C. For higher calcination temperatures there is no evidence of Pb release. Futhermore, in this system there are variations of concentrations for the single elements, as a function of the calcination temperatures that are not always linear but often have peaks in the concentration that are repeated for specific calcination temperatures.

Table 3 shows the concentrations related to systems prepared with nitric acid solutions characterized by a strongly acid pH. In this system the most abundantly released element, from the non-calcined ferrite is zinc at higher concentration with respect to the system prepared with water. This leads to the assertion that zinc release is favoured by an acidic pH. Morover the release of Pb is not favoured.

Table 4 shows the data relating to systems prepared with hydrochloric acid. As expected, the situation is similar to the previous system (Table 3) prepared with nitric acid. The most influential parameter is the pH value rather than the nature of the acid. Table 5 shows the data relating to systems prepared with aqua regia. The solution is very aggressive compared to the last two previous systems (Table 3 and 4) and in this case, in addition to the zinc also the iron is released abundantly.

Table 2. Concentration of the elements (μg/L) released from 10 grams of zinc ferrite in 100 mL of NH_3 solution at pH:11, after one hour, under stirring and at room temperature

Element	***Calcination temperatures***				
	25°C	**200 °C**	**400 °C**	**600 °C**	**800 °C**
Fe	35.35	35.12	/	61.75	/
Na	197392.15	20698.44	24772.53	261569.66	224861.65
K	10290.45	11035.31	8180.60	51471.71	120566.44
Cs	167.53	138.48	16.18	124.11	272.13
Mg	67053.37	74710.43	17025.54	92730.80	156222.81
Ca	208693.64	207402.94	33652.21	172159.38	356609.93
Ni	86.53	95.39	62.36	171.20	33.18
Cu	9.93	15.83	95.09	191.68	314.43
Zn	50763.46	71001.32	140162.35	199135.86	14192.62
Co	189.16	262.00	104.66	788.83	1.93
Mn	390634.62	480260.80	69023.64	923995.36	275.70
Cr	/	/	/	/	/
Cd	7282.35	7538.11	4774.88	22069.44	3746.75
Al	33.97	7.65	/	7.16	/
Ba	10.75	15.78	1.00	1.69	41.48
Bi	107.81	69.71	17.77	/	7.76
Ga	0.86	1.09	0.73	2.32	2.97
In	/	/	/	/	/
Li	88.37	97.69	25.92	155.23	237.21
Pb	112.55	72.48	/	/	/
Rb	57.73	61.19	31.07	126.86	473.23
Sr	3004.22	2786.15	81.39	1986.51	26777.35
Tl	151.96	149.86	7.52	/	211.53
U	/	/	/	0.00	/

Table 3. Concentration of the elements (μg/L) released from 10 grams of zinc ferrite in 100mL of pH HNO_3 solution: 1, after one hour, under stirring and at room temperature

Element	***Calcination temperatures (°C)***					
	25 °C	**200°C**	**400°C**	**600°C**	**800°C**	**1000°C**
Fe	114472.05	134805.07	337545.28	18375.04	28596.07	43210.51
Na	203575.20	194052.18	280355.22	276310.73	293261.46	133140.46
K	6761.95	7112.63	108433.09	38873.62	173764.40	60251.87
Cs	38.96	38.51	131.33	122.19	340.24	25.68
Mg	67032.85	63035.18	197993.18	76484.46	226532.56	14169.41
Ca	220341.01	231228.81	588920.22	191816.87	1167921.51	1032647.6
Ni	371.10	342.22	1196.55	1229.67	339.03	3095.18
Cu	10487.35	14573.58	179442.02	28177.64	24493.65	3570.87
Zn	3032273.41	2908209.04	4313626.06	3763455.28	436384.49	240307.84
Co	481.80	581.15	1991.72	5208.81	221.73	9010.01
Mn	533825.12	559434.53	844504.04	1039092.38	177815.26	4973.53
Cr	323.34	348.92	161.72	20.19	27.95	41.14
Cd	14797.90	13753.13	66663.27	25588.14	130809.27	7439.51
Al	24089.60	26667.47	84859.81	9774.05	5300.51	12263.36
Ba	15.08	5.25	12.10	20.18	14.37	13.37
Bi	/	/	261.79	/	278.29	217.64
Ga	148.49	194.78	507.07	26.45	15.65	27.91

In	299.91	473.21	12835.92	6595.82	9965.83	1347.45
Li	69.93	311.48	347.30	132.14	452.42	119.54
Pb	/	/	/	/	/	/
Rb	48.36	49.30	310.41	136.56	545.30	120.11
Sr	1496.88	1356.31	734.87	938.11	2523.87	20879.78
Tl	120.66	130.49	79.59	/	253.26	13.68
U	36.27	39.31	/	44.17	/	/

Table 4. Concentration of the elements (μg/L) released from 10 grams of zinc ferrite in 100mL of HCl solution at pH: 1, after one hour, under stirring and at room temperature

Element	***Calcination temperatures (°C)***					
	25 °C	**200°C**	**400°C**	**600°C**	**800°C**	**1000°C**
Fe	133870.56	151389.33	372827.48	13403.75	29630.90	38333.07
Na	96447.04	90906.22	274923.84	284173.89	299636.78	127438.94
K	7183.26	7245.52	103660.33	39380.67	169915.15	59062.04
Cs	34.24	35.05	130.63	112.13	342.90	38.99
Mg	61231.21	57580.27	195737.23	70843.87	218518.66	14420.13
Ca	226334.54	241434.41	596079.11	195913.81	859645.29	1068005.27
Ni	319.76	260.83	1129.15	309.76	289.96	470.09
Cu	9723.59	13376.54	173982.43	26574.72	24540.24	4712.42
Zn	3164030.39	3010702.44	4302735.79	3884429.61	427167.06	236115.32
Co	431.43	383.40	2212.91	1272.07	240.82	926.89
Mn	562038.37	580279.17	844124.84	1075200.18	166072.98	6140.08
Cr	291.36	320.08	176.93	/	20.05	455.03
Cd	13757.14	12627.76	66580.41	24059.11	133329.93	8807.77
Al	22182.02	25392.01	83395.71	8908.65	5007.57	19531.79
Ba	6.86	6.09	8.63	9.47	10.40	18.32
Bi	/	/	338.22	/	358.18	374.59
Ga	129.52	179.92	515.52	23.09	14.32	54.59
In	328.71	474.61	13824.30	7562.78	12397.58	1696.34
Li	67.01	66.17	325.29	121.39	447.33	122.81
Pb	/	/	/	/	/	/
Rb	40.90	44.57	306.35	121.86	554.68	134.52
Sr	1409.94	1375.10	708.52	851.53	2442.24	16711.01
Tl	136.04	149.83	88.26	/	250.75	15.64
U	38.53	41.14	/	46.93	/	/

From the set of data reported in the previous tables, it is clear how the release of the different elements that characterize the zinc ferrite are affected by the pH of the system, but also by the calcination temperature of pre-treatment of zinc ferrite. The variation of the release concentration for the single elements does not follow a linear trend, but it is possible to identify for each individual element the calcination temperature and the optimal solution that favour its release.

Subsequently, in light of the previous considerations, the variations of the released elements concentrations, according to the variables considered, have been shown in graph. These graphs make it possible to identify, for each individual element, the characteristic conditions that favour its release. Given the abundance of data, in this context, the trends only for some elements, considered most representative, are reported, although it is possible to extend the graphic representation of the data also to the other elements. In particular, the following diagrams show the trends of the release concentrations of the following elements, such as Fe, Zn, Al, Cs, Co, Cu. The reported graphs show that the release conditions change according to the element considered.

Table 5. Concentration of the elements (μg/L) released by 10 grams of zinc ferrite in 100mL of aqua regia at pH: 1, after one hour, under stirring and at room temperature

Element	***Calcination temperatures***					
	25 °C	**200°C**	**400°C**	**600°C**	**800°C**	**1000°C**
Fe	3027074.11	7499509.44	3537220.86	1720918.01	1670172.72	12923.66
Na	119139.54	232988.44	136724.05	164094.36	180541.74	67638.82
K	46831.98	129877.44	71436.89	68907.20	97862.24	2763.97
Cs	119.75	214.52	88.10	85.11	165.55	64.47
Mg	85866.25	176368.29	88978.65	144356.76	111194.28	0700.03
Ca	471032.92	706376.55	158870.94	202337.13	517481.32	14561.65
Ni	13348.86	9548.32	15961.42	40908.39	33987.12	7070.10
Cu	101959.43	207615.30	107563.43	93468.80	53797.85	1407.81
Zn	3057038.01	5478466.37	3063945.54	2974098.94	1539617.89	44749.00
Co	23002.56	2637.57	31523.72	83439.92	60341.95	580.61
Mn	430048.64	859951.58	461209.47	600593.79	253452.35	58572.09
Cr	939.33	13400.39	/	1828.81	/	1263.34
Cd	27133.26	60081.35	28165.95	65644.40	79168.45	7733.64
Al	95657.84	193001.95	95745.02	87512.39	80378.94	8868.84
Ba	364.80	405.44	81.81	138.58	157.81	1537.87
Bi	/	4366788.74	/	/	/	88502.58
Ga	1510.08	3044.37	1587.10	587.10	589.90	524.94
In	10806.51	18665.10	12753.83	18036.51	10243.11	3780.43
Li	97.67	265.63	1241.74	238.14	321.60	242.12
Pb	/	/	/	/	/	/
Rb	187.93	369.06	179.30	154.51	275.43	172.81
Sr	9604.62	15110.45	5281.44	6983.77	44552.18	11643.91
Tl	1449.89	229.87	1864.29	1241.48	1834.66	26.94
U	54.21	/	79.48	89.65	113.76	/

Iron release is favoured through a pre-treatment of zinc ferrite at a temperature between 200-400 °C and in an acidic environment. The peak of release occurs in the aqua regia.

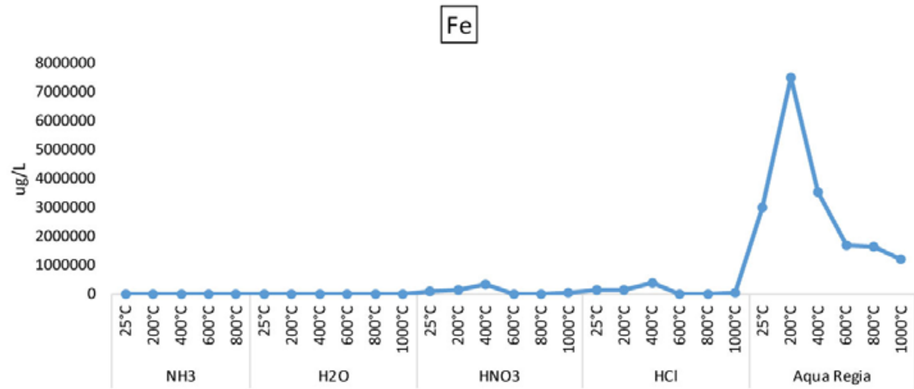
Zinc is released in greater concentration for a treatment between 400 and 600 °C and in a neutral or acid environment. In a basic environment there is no release while in the aqua regia there is the greatest release and also for lower calcination temperatures.

Aluminum present in the zinc ferrite is released in an acid environment and for a calcination treatment around 400 °C. In the presence of aqua regia it is also released at lower temperatures around 200 ° C.

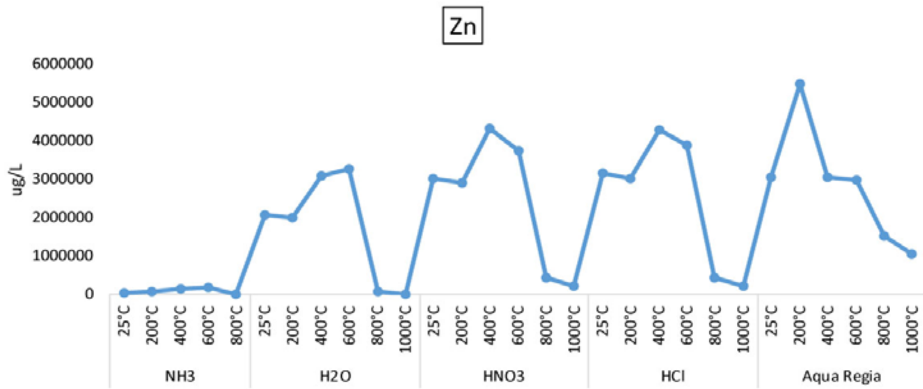
Cesium is released both in acidic, basic and neutral environment and mainly for a calcination temperature around 800 °C.

Cobalt is mainly released with a treatment at 600 °C and in water.

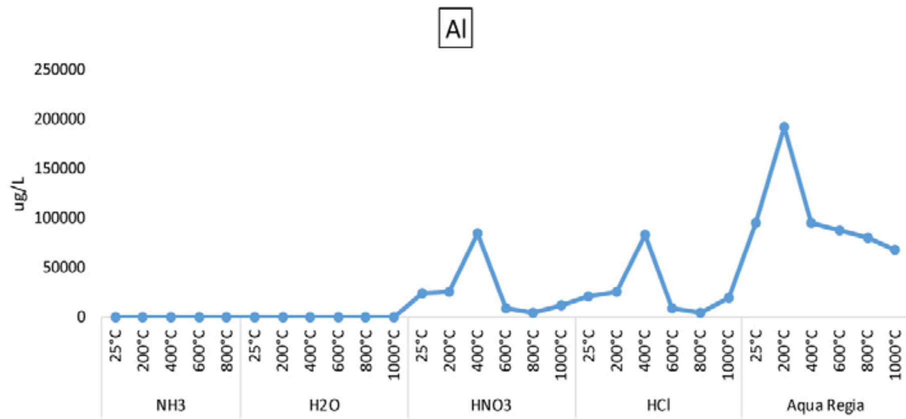
Copper is released in both a neutral and an acid environment, although the concentrations are higher in an acidic environment and for a calcination treatment around 400 °C. In the presence of aqua regia the calcination temperature is lowered.



(a)



(b)



(c)

Fig. 1. Concentration of the (a) Fe, (b)Zn and (c) Al released by the zinc ferrite as a function of the calcination temperature and the nature of the contact solution

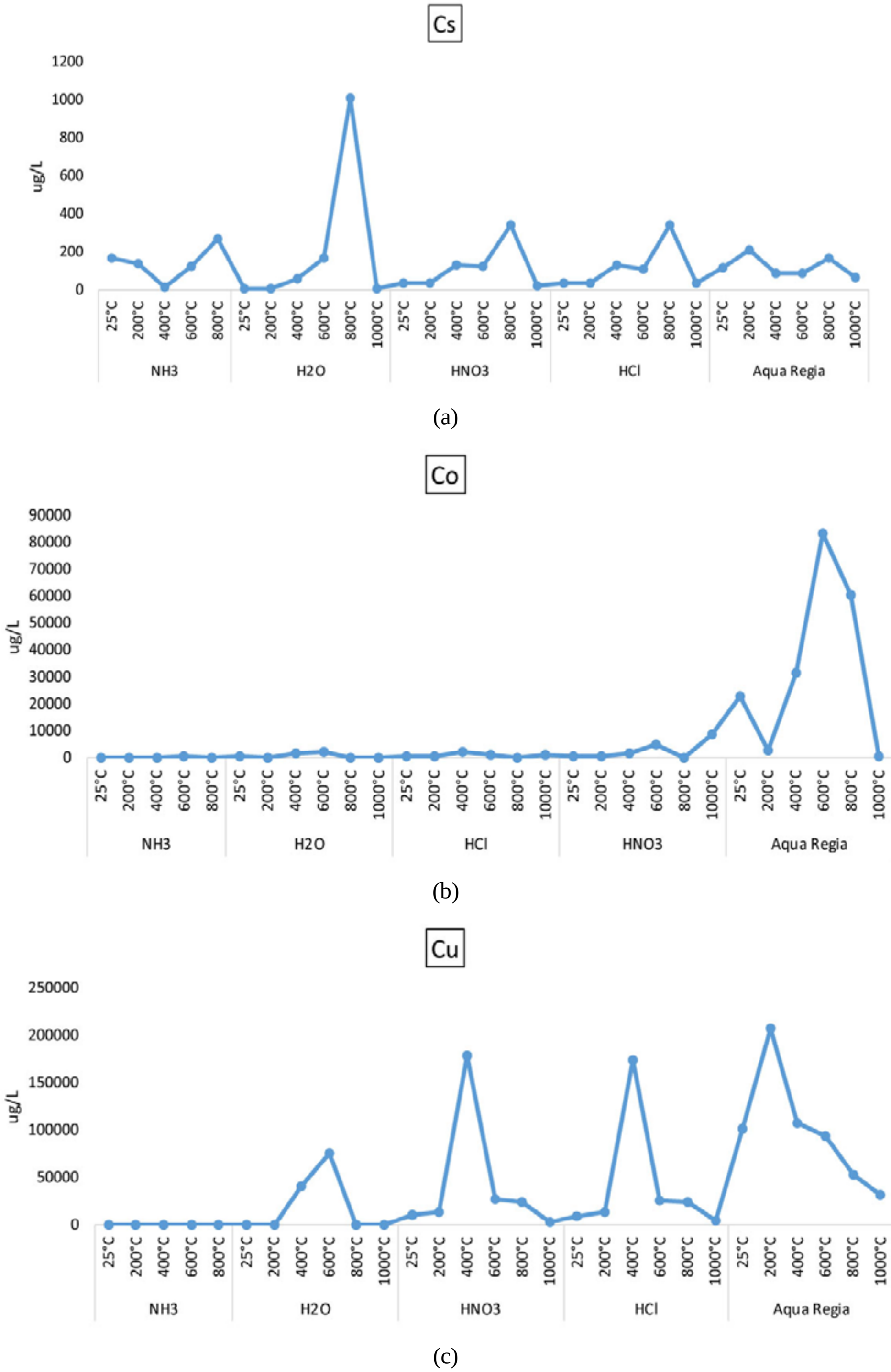


Fig. 2. Concentration of the (a) Cs, (b) Co and (c) Cu released by the zinc ferrite as a function of the calcination temperature and the nature of the contact solution

4. Conclusions

The results obtained from the present study allow us to have a mapping conditions of release of the single metals present in the zinc ferrite. These graphs, which can be immediately used, make it possible to identify the specific treatment to be carried out on the zinc ferrite according to the element to be recovered. These data can represent a valid support, for example, when ion exchange methods are used for the recovery and removal of metals.

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SUSTAINAIBILITY OF THE MANAGEMENT OF DIGESTATE FROM BIO-WASTE: COMPARISON OF TWO OPTIONS*

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Abstract

The sustainability of two different options for managing the digestate from the anaerobic digestion (AD) of the organic fraction of the municipal waste was investigated. The first option was its treatment in wastewater treatment plant (WWTP). The second was its use on land. The analyzed scenario refers to the amount of organic fraction currently processed via AD in Italy. The sustainability assessment was performed taking into account environmental, social and economic aspects. Results showed that the use on land gives lower environmental impact and has lower costs but on contrary showed the higher impact on human health, considered as social indicator.

Keywords: anaerobic digestion, cost, digestate, environmental impact, organic fraction, social impact, sustainability

1. Introduction

Anaerobic digestion (AD) is strongly encouraged by EU legislation (EC, 2014-2017a,b) for the treatment and the recycling of bio-waste. Recycling concept is based on the use of waste materials for replacing and/or avoiding the consumption of raw materials. In the specific context recycling concepts is related to the effective use on land of the digestate but this activity represents also one of the main obstacles for a full implementation of AD in this sector. In fact, currently about 10% of the whole bio-waste generated at EU level is processed by AD, about 50% is composted for organic fertilizer production and the remaining part is equally shared by landfill and incineration (ISPRA, 2017). Digestate use on land is not currently supported by EU legislation by specific end-of-waste criteria (EoW)

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able to assess when a waste ceases to be a waste and can be considered again a product. This entails a legal gap that represents among the most serious obstacle for both the authorization and management of bio-waste AD facilities. This means that digestate still remain a waste and has to be managed according to the specific legislation of the sector. In practice its use on land can be authorized according to the R10 – "Land treatment resulting in benefit to agriculture or ecological improvement" - recovery operation as reported in the Annex II of the waste EC framework directive (WFD, 2008). But in the majority of cases further processing at least of the liquid fraction in wastewater treatment plants (WWTP) could be requested by legal authorities.

Currently many studies have already been performed for assessing the environmental consequences of the use on land of the digestate. Main approach used was based on life cycle assessment (LCA) (Bernstad and la Cour Jansen, 2011; Di Maria and Sisani, 2017; Di Maria et al., 2018). All this indicated that there still remain a lack of research based on the assessment of the sustainability of different options for digestate management.

The main objective of this study was to analyze the sustainability of two different options for the management of the digestate from the organic fraction of municipal solid waste from separated collection: use on land; treatment in biological WWTP. This was assessed by the quantification of three main aspects: environmental; social; economic.

This work is divided in three main parts:

- selection of case study: Amount of organic fraction processed by AD in Italy;
- definition of sustainability indicators for comparing the two options based on LCA, social LCA and costs;
- analysis of results, drawing conclusion and formulation of recommendations for policy and decision makers in the sector of AD of waste.

2. Materials and methods

The assessment of environmental impacts was performed by Life Cycle Analysis (LCA) following the recommendations reported in ISO 14040 (2006), ISO 14044 (2006) and in the ILCD Handbook (EC, 2010, 2012). Calculations were performed by the SimaPro 8.2 software (Goedkoop et al., 2016) (Fig. 1). Midpoint of the ILCD 2011+ impact assessment method were used for the LCA (Table 1). These were successively aggregated using the EDIP 2003 procedure (Hauschild and Potting, 2003) for having a comprehensive unique indicator for environmental impact. According to UNEP/SETAC (2009), well-being of identified stakeholders is a central concept in promoting improvement in social conditions through a life cycle of a product or service. Human health (HH) (DALY) end point indicator was used for this aspect (Table 1).

Cost for use on land and WWTP were retrieved from literature data. For spreading operation of sludge Milieu (2008) reported comprehensive costs ranging from 96 to 225 €/tonne TS. For use on land of sludge with 20% TS Colivignanelli et al. (2015) reported an average cost for the EU of 44 €/tonne. Similar costs were also reported by Gebrezgabher et al. (2010). This indicates that the costs of use on land of the liquid fraction of the digestate (i.e. about 1%TS) ranges from about 1 €/tonne to about 2.5 €/tonne. Co-treatment with civil sewage in WWTP is another options largely exploited (ISPRA, 2017).

In general treatment fees are calculated on the basis of COD of the digestate. Based on Italian market price detected in the last 10 years of similar high polluted wastewaters the fee ranged from about 18€/tonne up to 35€/tonne including transports (Di Maria et al., 2018) even if in some cases prices up to 60€/tonne have been also detected.

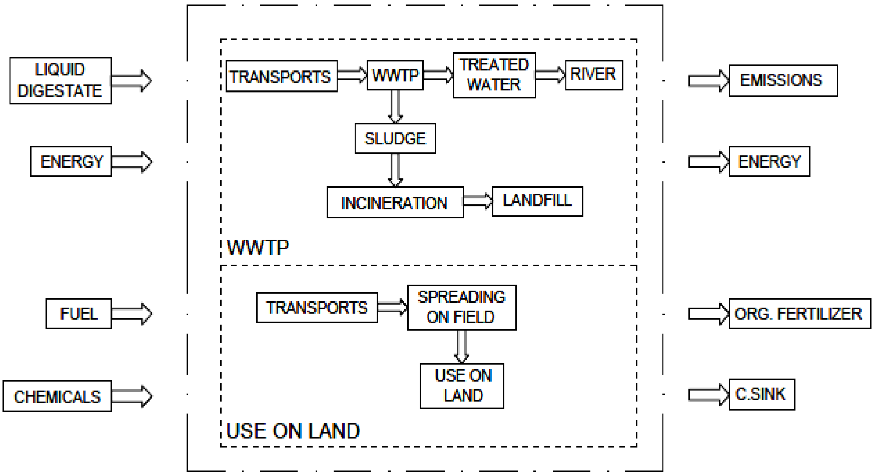

Fig. 1. System boundaries.

Table 1. Impact assessment indicators

Impact category	***Unit***
Midpoint ILCD 2011+	
Global Warming Potential, GWP	kgCO_2 eq.
Particulate Matter, PM	kgPM2.5 eq.
Photochemical Ozone Formation, POF	kgNMVOC eq.
Acidification, A	molc H^+ eq.
Fresh Water aquatic Ecotoxicity, FWE	kg P eq.
Abiotic Depletion, RD	kg Sb eq.
Endpoint IMPACT 2002+	
Human health, HH	DALY

5. Results and discussion

Concerning the environmental impact, the study highlights that there are some conflicting results (Fig. 2). In fact WWTP showed lower impact concerning GWP and A whereas use on land showed lower impact for the other indicators. Social impact quantified by HH resulted lower for the WWTP. For comparing the different indicator adopted for the assessment of the sustainability of the two options a normalization procedure was used related to the higher value assumed by each indicator. In particular, before doing this normalization, the environmental indicators (Table 1) were aggregated by using the procedure proposed by the EDIP 2003 method (Hauschild and Potting, 2003).

Results were reported in Fig. 3. According to this methodology use on land performed better than WWTP for the environmental and costs indicators. Opposite result was detected for the HH indicating that WWTP results able to reduce the negative consequences on the human health. By the way considering the limited values detected for HH characterization (Fig. 2) this can suggest that in any case the use on land can give larger global benefits considering the high values assumed by the environmental and costs indicators.

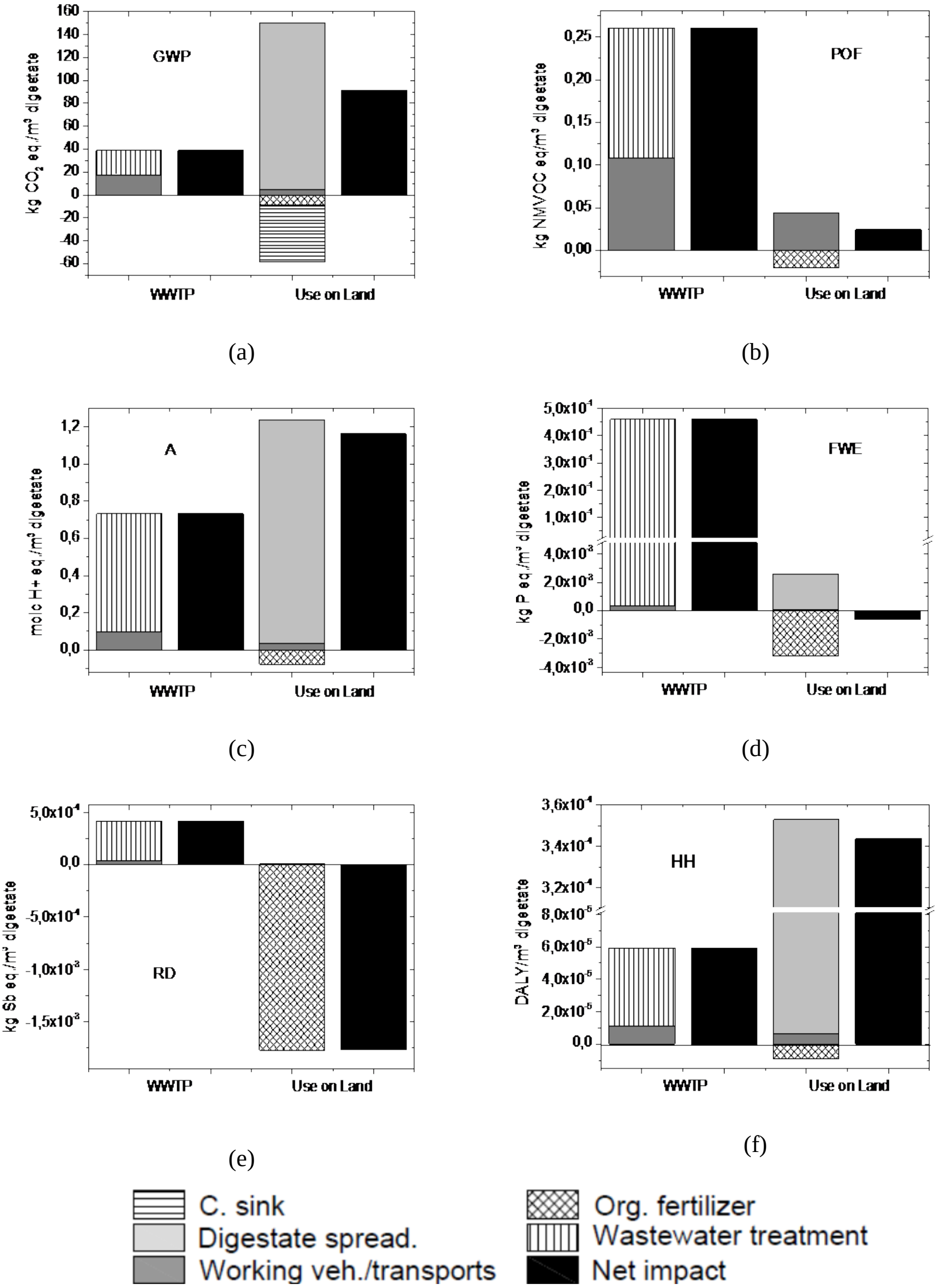

Fig. 2. Characterization of the impact indicators: (a) GWP, (b) POF, (c) A, (d) FEW, (e) RD, (f) HH

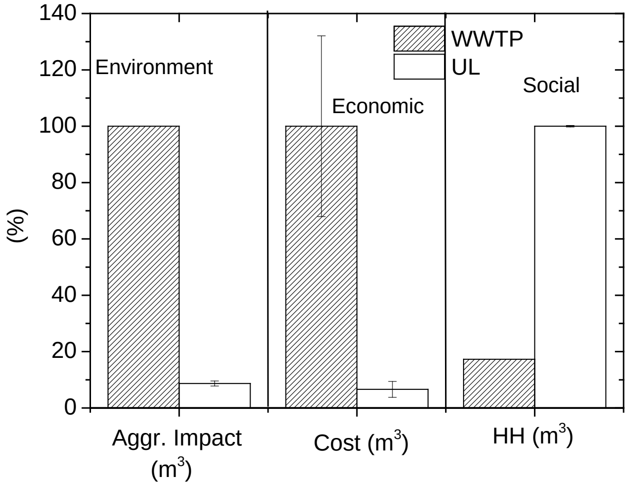

Fig. 3. Normalized indicator used for the assessment of the sustainability

6. Concluding remarks

The evaluation of sustainability requires the quantification of indicators able to assess at least the environmental, social and economic aspects. The management of digestate from bio-waste is a relevant topic for the sector and the present analysis showed that its use on land is more sustainable that processing in wastewater treatment plant at least for the environmental and economic point of view.

Social aspect quantified by the impact on human health showed opposite results. This open the floor to a successive aspect in sustainability analysis that is the weighting procedure to adopt for achieve an unique indicator able to assess all these information. This aspect represents another interesting topic to be investigated in future works.

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WASTEWATER STORAGE BASINS FOR IRRIGATION REUSE AND P/N REMOVAL: FINISHING LAGOONS IN IMOLA, BOLOGNA, ITALY*

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Abstract

Water scarcity has become more prominent in the last decades so since the '70 many studies focused on the use of natural basins both for treatment and storage of wastewater for irrigation. Afterwards, interesting projects of lagoons for reuse have been implemented in all Mediterranean countries. The irrigation water requirements depend on different factors as crops typology, soil structure, environmental features, seasonal variations etc. Consequently, the key point for a correct irrigation management is the possibility to store the proper water volume in storage basins where it is always available on demand.
In this context the aim of the present paper is to study the natural finishing processes occurring in lagoon basins in order to optimize the management policies. Those policies must take into account three main features: 1) respect of the legal thresholds for wastewater reuse, 2) satisfy the irrigation needs with an appropriate water volume 3) set the finishing capacity of the basin to regulate the best ratio Phosphorus/Nitrogen (P/N) in output in relationship with the amount requested by the different crops for their growth. The study focuses on the data collected in the first basin of the natural finishing part of the Santerno wastewater treatment plant. The plant is located in Imola (Bologna, Italy) and can be divided in two main parts: primary/secondary treatment and natural finishing treatment. The second part of the plant consists of five natural treatment basins. The monitoring campaigns focuses on the first basin called Basin 1 as the plant management company, HERA S.p.A., intends to destine the outlet of this basin to irrigation reuse. The Hydraulic Retention Time and wet surface area of Basin 1 are 2 days and 14000 m^2 respectively.

Keywords: irrigation, Lagoon, Phosphorus, Nitrogen, reclamation

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1. Introduction

Water scarcity has become more prominent in the last decades. It is mainly due to increasing population and intensive agricultural production. Moreover, in the next future water scarcity and drought events will increase as quantity and frequency, exacerbating the problem (Communication on Water scarcity and Droughts, 2007). Consequently, many recent studies focused on the use of non-conventional water resources to address the increased demand (Almuktar et al., 2018).

In this context wastewater reuse is a well kwon alternative for water resource conservation and use for irrigation. Finishing lagoons are recently studied as natural wastewater treatment for irrigation reuse because they can permit to achieve both of those important objectives: treatment and storage. Indeed, interesting projects of lagoons for irrigation reuse have been implemented in all Mediterranean countries (Liran et al., 1994). Anyway, the most important barrier to the development of wastewater reuse in Europe is the lack of a unique regulation. Indeed, there is not a specific directive on wastewater reuse but several environmental directives at member states and regional levels. Regulations are thus highly heterogeneous, especially in terms of intended uses, analytical parameters and permitted threshold values. Anyway, on May 2018 the European Commission (EC, 2007) published a "Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on minimum requirements for water reuse" (EC, 2018) in order to overcome this regulation heterogeneity.

The Regulation proposal comes from the Joint Research Centre (JRC) technical report for water reuse in agricultural irrigation published as final version in June 2017 (Alcalde-Sanz and Gawlik, 2017) and the additional study of the Technical University of Munich published as complete report in October 2017 (Drewes et al., 2017). Table 1 shows the legal limits comparison between Italian and proposed by EC for same parameters.

Table 1. Italian and EC Regulation proposal legal limits

	Italy (DM 185/2003)	***EC Regulation proposal***
BOD (mg/l)	20	10-25**
COD (mg/l)	100	-
TN (mgN/l)	15	-
TP (mgN/l)	2	-
NH_4^+ (mgNH_4/l)	2	-
E. coli (CFU/100ml)	10*	10-10^4**

** It is the limit for 80% of the samples while 100 CFU/100ml is the maximum limit for all cases. The limit is higher using natural systems (phyto-depuration or lagoons) becoming: 50 for 80% of the samples while 200 CFU/100mL is the maximum limit for all cases*

***The limit depends on the Classes of reclaimed water quality: A, B, C, D*

The main difference in those regulation is that the EC Regulation proposed does not foresee thresholds for Total Nitrogen (TN), Total Phosphorus (TP) and Ammonium (NH_4^+). In any case, those parameters must be considered because are crucial for the plant growth. For instance, high concentrations of Nitrogen and Phosphorus discharged in the soils can reduce the crops quality due to overstimulation, lodging or maturity delay (Lazarova and Bahri, 2005). Indeed, Nitrogen and Phosphorus compounds could be already present in the soil due to addition as fertilizer. Besides, eutrophication phenomena could be produced by high Nitrogen concentration discharged in water bodies (Mancini, 2004). Moreover, Phosphorus and Nitrogen compounds discharged by real scale urban Wastewater Treatment plants (WWTP) are very variable in concentration so to monitor those parameters is crucial for irrigation reuse.

In this contest the aim of the present paper is to study the natural finishing processes occurring in lagoon basins in order to optimize the management policies. Those policies must take into account three main features: 1) respect of the legal thresholds for wastewater reuse, 2) satisfy the irrigation needs with an appropriate water volume 3) set the finishing capacity of the basin to regulate the best ratio Phosphorus/Ammonium Nitrogen (P/N) in output in relationship with the amount requested by the different crops for their growth.

The study has been developed in the frame of a partnership project between the Department of Civil, Chemical, Environmental and Materials Engineering (DICAM) of the University of Bologna and the multiutility HERA S.P.A., responsible of the water and wastewater management in Bologna region.

2. Materials and methods

The study is based on the data collected on the natural finishing part of the Santerno wastewater treatment plant located in Imola (Bologna, Italy). The monitoring campaigns focuses on the first basin called Basin 1 because the plant management company, HERA S.p.A., intends to destine the outlet of this basin to irrigation reuse.

Basin 1 follows the secondary treatment phase of the plant which is continuously fed on urban wastewater coming from the city of Imola (Bologna, Italy). The influent flow rate and load are respectively 25000 m^3/day and 75000 Population Equivalent. Currently, the treated water is discharged in the Santerno River, after the natural tertiary treatment taken place in five lagoons.

In a first step, Basin 1 has been divided into four sections perpendicular to the main flow direction. Then, the samples have been collected in the middle of each section. The sampling points have been named L1A, L1B, L1C, L1D where L1 indicates the lagoon 1 and the following letter indicates the section (Fig 1). Moreover, samples were collected at the outlet of the secondary phase of the WWTP.

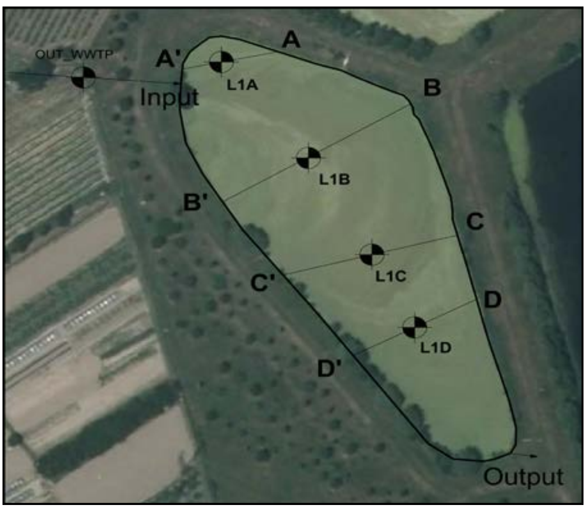

Fig. 1. Aerial view of Basin 1 with sampling points (OUT_WWTP, L1A, L1B, L1C, L1D) marked with black/white dots

The samples have been collected from 2016/05/25 to 2017/06/21 during four monitoring campaigns. The samples have been transported to the laboratories of the Department DICAM of University of Bologna and analyzed in the same day or not later than two days after the samples collection. For each sample have been measured Ammonium Nitrogen (NH_4^+-N), Total Nitrogen (TN) and Total Phosphorus (TP). NH_4^+-N has been measured using the Ion Selective Electrod Crison 9663C, TN and TP according to the APHA methods for water and wastewater (APHA, 1998).

3. Results and discussion

The monitoring results concerning Ammonium Nitrogen, Total Nitrogen and Total Phosphorus are grouped in Table 2 for each monitoring campaign in each sample point. The two last columns show the ratios TN/TP and NH_4^+-N.

Table 2. Basin 1: Ammonium Nitrogen (NH_4^+-N), Total Nitrogen (TN), Total Phosphorus (TP) and ratios TN/TP and NH_4^+-N /TN data in the middle of the sections A-A', B-B', C-C' and D-D'

Sampling Date	***Sample Name***	***NH_4^+-N [mgN/l]***	***TN [mgN/l]***	***TP [mgP/l]***	***TN/TP [mg/l]***	***NH_4^+-N/TN [mg/l]***
2016-05-25	OUT_WWTp	2.3	10.5	2.3	4.59	0.22
	L1A	4.4	13.4	2.4	5.57	0.33
	L1B	3.8	12.7	2.4	5.34	0.30
	L1C	4.3	13.6	2.4	5.67	0.32
	L1D	3.4	12.8	2.4	5.32	0.27
2016-11-30	OUT_WWTp	1.4	10.2	1.9	5.14	0.13
	L1A	0.9	12.0	2.0	5.92	0.08
	L1B	1.0	11.9	1.9	6.04	0.08
	L1C	1.0	11.1	1.9	5.58	0.09
	L1D	0.9	11.2	2.0	5.49	0.08
2017-03-22	OUT_WWTp	1.5	12.5	4.2	2.96	0.12
	L1A	1.5	12.7	4.2	3.00	0.12
	L1B	1.7	14.5	5.2	2.78	0.12
	L1C	2.2	13.7	4.9	2.79	016
	L1D	2.4	13.5	4.8	2.78	0.18
2017-06-21	OUT_WWTp	6.3	9.9	1.7	5.76	0.64
	L1A	5.9	10.3	2.0	5.11	0.58
	L1B	5.3	10.2	2.1	4.83	0.52
	L1C	4.4	8.8	1.9	4.41	0.51
	L1D	4.4	9.3	2.0	4.62	0.48

Observing at the plant outflow data (OUT_WWTp), we note that NH_4^+-N concentration is generally in the range 1.3 – 2.3 mgN/l except in the last monitoring campaign (2017-06-21) when it is 6.3 mgN/l. This variation is due to the management policies adopted in secondary phase of the plant. More in details, the secondary treatment is made by a predenitrification followed by a nitrification so the higher NH_4^+-N concentration measured in the last case was probably due to a plant management oriented to reduce the nitrate concentration by the Denitrification. This is also confirmed by the TN concentration values that are very similar to the values of all the other periods.

It is very interesting to compare the behavior of Basin 1, in terms of treatment capacity, under different influent concentrations.

To this aim we compare the values of the ratio TN/TP and NH_4^+-N/TN. In wider terms, we note that those ratios are similar in all cases under different influent concentrations. Those data show that the Basin 1 is able to handle changes in input condition. This feature is very important in case of the outlet wastewater should be reused in agriculture when stable TN and TP output concentrations are crucial. To better understand the variations along the lagoon section from input to output, we reported the data in two graphs shown in Fig. 2 and Fig. 3.

Analyzing Fig 2, the output values are in the range 4.5-5.5 that can be considered good values for the irrigation needs (Craine et al., 2008). This shows a good capacity of the Basin to reach the irrigation needs. Anyway, we also note a case in which this value is very low (2017/03/22) mainly due to the inlet anomaly (high TP concentration) and unfavorable environmental conditions for the biological phenomena (water temperature).

Observing the trend from Basin 1 input to its output, we note that the ratio is not so different even if there is a slight decrease of TN in same cases (Fig 2). This is due to the probable presence of anoxic zones in the lagoon and consequently denitrification conditions even if Basin 1 is an aerobic lagoon. This feature is typical of aerobic lagoon where anoxic conditions up to 10% of the water volume are possible.

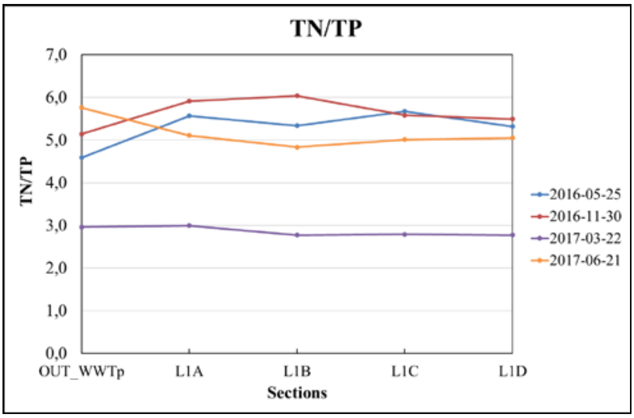

Fig. 2. TN/TP in basin 1 sections

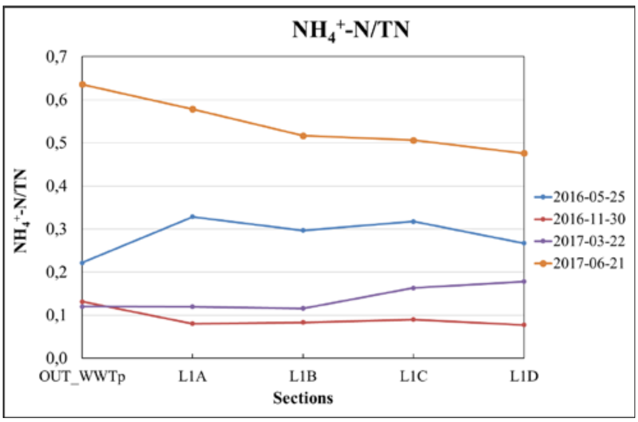

Fig. 3. NH4+-N/TN (b) in basin 1 sections

Fig. 3 trends show three different conditions based on NH_4^+-N/TN ratio. In case of NH_4^+-N/TN ratio essentially constant, it means that nitrification and denitrification efficiencies are comparable. In case of NH_4^+-N/TN ratio decrease along the basin sections, it means that nitrification efficiency is higher that denitrification (2017/06/21). Finally, in case of NH_4^+-N/TN ratio increase, it means that of NH_4^+-N increase due to production by cell lysis is higher than nitrification reduction. In any case, the ammonia reduction due to nitrification has been registered.

4. Concluding remarks

This paper aims to study the natural finishing processes of the lagoon basins to respect the needs for irrigation reuse in terms of the legal threshold and Phosphorus and Nitrogen required by plants. The results from four measurement campaigns in different seasonal conditions on the first natural finishing basin of Santerno plant (Basin 1) have been analyzed in comparison with the legal thresholds from the Italian regulation for wastewater reuse (DM 185, 2003).

Basin 1 shows a good capacity to handle changes in input conditions in terms of TN/TP as the values are in the range 4.5-5.5 that can be considered good values for the irrigation needs. Anyway, those values are not reached up by the Basin when the influent concentrations are very low and/or the external condition (water temperature) do not promote the biological processes.

Even if the main process occurring in the basin is nitrification, as expected for an aerobic lagoon, anoxic conditions (denitrification) are possible in some cases. Therefore, we conclude that the management policies must consider different phenomena occurring in the basin that contribute to the TN and TP output values.

Comparing the output concentrations with the legal thresholds of the DM 185 (2003) we conclude that are easier to achieve for Nitrogen than for Phosphorus compounds. This is due to the different treatment processes involved. Indeed, nitrogen compounds reduction can be achieved by nitrification and denitrification while Phosphorus only by biomass extraction. In the studied case, there is not a management policy for biomass extraction aimed to irrigation reuse and it is to be hoping to reach. Moreover, this extraction will reduce Phosphorus and Nitrogen compounds at the same time.

Acknowledgements
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IMPLEMENTATION OF THE WATER FOOTPRINT AND CARBON FOOTPRINT IN THE STEEL INDUSTRY*

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Abstract

The steel industry is a fundamental driving force of development for the Italian economy. It has been the focus of political and the media as well as public opinion attention for a long time. Certainly, steel production processes have had a significant impact on the environment. It is necessary to handle the productive processes with a different, careful attitude to pollution problems and its consequences for public health and future generations. Two new labels have been introduced in the Green Economy field: the Water Footprint and Carbon Footprint. They represent the new environmental accounting frontier. This case study examines the company "Acciaierie di Sicilia s.p.a." belonging to the group "Alfa Acciai", located in Catania.
The aim of this paper is to carry out an analysis of the water and carbon footprint, to optimise productive processes with a view to the safeguarding resources.

Keywords: Acciaierie di Sicilia, carbon footprint, public health, steel industry, water footprint,

1. Introduction

In recent decades, steel production has grown considerably, becoming today one of the cornerstones of the world economy. The most important aspects are those linked to emissions into the atmosphere, waste management and energy consumption.

A ranking of steel makers places China first, followed by Japan and the US. In this group of steel producing countries we can find Turkey, ranked eight among the steel-

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producing countries in the world, with a 34.7 million tons production meaning a share of 2.1% of the total world production in 2013 (WSO, 2014). In Europe, Turkey ranks second, after Germany (Olmez, 2015; WSO, 2014).

Achieving ‘‘sustainable development’’ requires methods and tools to help quantify and compare the environmental impacts of providing goods and services (‘‘products’’) to our societies (Rebitzer, 2003). The major challenge for industry is to demonstrate its contribution to the welfare and well-being of the current generation without compromising the potential for a better quality of life for future generations (Singh, 2006). The old, underperforming technologies in the iron and steel industry are energy-intensive. This situation is particularly common in developing countries and countries with economies in transition (Guo, 2009).

Today it is particularly important to analyze the relationship between environment and health to have better returns. Separating the problems related to the environment, health and economy and identifying solutions that solve all the problems is a very complex undertaking, that is why the health impact assessment (VIS), considering the uncertainties and the use of the principle of prudence, can be valuable tools for the minimization of their direct and indirect impacts and for the sustainable management of the plants (Ranzi, 2012).

In 2011, UNEP presented a report for a global green economy (Towards a Green Economy - Pathways to Sustainable Development and Poverty Eradication), which defined a green economy as an improvement in wellbeing human equity and social equity, able to ensure at the same time a significant reduction of environmental risks and ecological scarcity (Minambiente.it). The current levels of consumption mean that the average resources available on the planet are consumed in the first two thirds of each year, causing an improper use of resources which will be passed on to future generations in the last four months (Frey, 2013).

In its simplest form, a green economy can be conceived as an economy with low carbon emissions, efficient and socially inclusive. Therefore, the green economy does not appear as an abstract concept, but rather something that can be applied to every global citizen, and which is easy to become part of. According to the UN Environmental Program, the green economy is an economy in which the growth of income and employment are driven by public and private investments that aim to reduce pollution, increase renewable energy, efficiency resources and to avoid biodiversity loss. These investments must be supported by both political and institutional reforms.

The solution of environmental problems can also contribute to making economies more solid thanks to the creation of new businesses and jobs, laying the foundations for the green transformation of the economy (Cianciullo, 2010). For this reason, two new labels have been introduced in the green economy: the Water Footprint and Carbon Footprint. They represent the new frontier of environmental accounting.

The steel industry is certainly among the most important sources of CO_2 and other pollutants in the environment and in industrialized countries, owing to efficiency improvements and structural changes, has made reductions in CO_2 emissions during the past 40 years. Many countries, including Italy, have in fact massively outsourced their water footprint, importing from other places goods that require a large amount of water to be produced. The total water footprint of production in Italy amounts to around 70 billion m^3 of water a year. This equates to 3,353 liters per capita per day (Antonelli and Greco, 2014; Raimondi, 2013).). This paper is focused on the analysis of CO_2 emissions and on the water consumption of the analyzed company. They represent the fundamental basis from which Carbon Footprint and Water Footprint can be calculated.

2. Description of the investigated system: Acciaierie di Sicilia S.p.A.

Since its establishment in 1998 as part of Alfa Acciai Group, Acciaierie di Sicilia is the reference point of this company for the southern Italian market and for export to other Mediterranean countries, being the only steel producer in operation in Sicily with a favorable geographical position, located in Catania's industrial park. With a high production capacity and equipped with state-of-the-art technology, Acciaierie di Sicilia mainly produces bars and bobbins for reinforced concrete using EAF technology and ferrous scrap collected from all over Sicily. The company has created a very effective relationship with customers and suppliers, but also with employees, providing jobs for hundreds of people.

Acciaierie di Sicilia has implemented an important investment plan to ensure productive and organizational efficiency of production, as two of its main development objectives in the context of today's industrial development by eco-compatibility and sustainability. The company awards a great importance to the issues addressing environmental sustainability and product quality, and that's why its B450C S Sustainable Steel production is valued as providing excellent antiseismic performance of building structures. In this context, the company has obtained environmental certifications EN ISO 14021, ISO 14025 EPD, LCA and SUSTSTEEL which prove that sustainable environmental objectives are being achieved successfully. It has also wanted to improve its environmental impact associated with its processes also through the installation for the new smelter furnace suction system and dust abatement and the new fume hood in 2010. In 2012 an activated carbon plan was installed. The company provides a good example of circular economy by using scrap metal as a raw material and subsequently transforming it into a finished product (rebar).

3. Materials and methods

3.1. Goal of the case study

This case study aims to quantify CO_2 emissions and water consumption volumes associated with the investigated industrial system.

The Carbon Footprint and the Water Footprint calculation consists of a considerable element in the industrial sector. For this reason, this case study aims to quantify the analysed company's trend to understand and to highlight its behaviour towards the environmental mainstreaming. The calculation of these indicators represents one of the strategies which can be implemented to safeguard the environment and to obtain satisfying environmental performance. Moreover, this case study has been carried out to verify if the strategies implemented by the company and the large number of certifications have been able to reduce CO_2 emissions and the water wasted in the production process. This analysis can be a valid support for the company to value and eventually modify aspects of the production which produce excellent results in terms of Carbon Footprint and Water Footprint. Such purpose makes us define two labels introduced in the green economy context.

The Carbon footprint is an indicator which expresses in equivalent CO_2 the total amount of greenhouse gases emissions associated directly or indirectly with a product, an organisation or a service. In conformity to the Kyoto Protocol the greenhouse gasses to be considered are: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFC), sulphur hexafluoride (SF_6), perfluorocarbons (PFC). The measurement of the Carbon Footprint requires the identification and quantification of raw materials and energy consumption in the selected phases of the life cycle of the same (V et al., 2009; Minambiente.it). The Water Footprint, introduced in 2002 by Hoekstra (Chapagain, 2004), is an indicator of fresh water consumption used directly or indirectly by a customer or a producer. The Water Footprint of a person, a community or a company is defined as the total volume of fresh water used to produce goods and services, measured in terms of wasted water (incorporated or evaporated in a product).

The Water Footprint global statement is the result of three components:

- *Blue Water*: referred to the use of surface and underground water used for domestic, industrial and agricultural purposes.
- *Green Water*: it is the volume of rainwater which does not contribute to the superficial run-off and is referred to the evaporated water for agricultural uses.
- *Grey Water*: it is the volume of polluted water, quantified as the necessary water volume to dilute the pollutants so that the water quality achieves the quality standards.

(certiquality.it)

3.2. Phases of the process

Steelmaking starts from the scrap storage area and extends through the entire production department to the platform for the evacuation of billets for rolling. The plant is divided into an EAF melting furnace, representing the true core process of the steelworks. The steel is refined in a bath and the metallurgical parameters are established. The billet casting process is handled by two 4-strand continuous casting machines. The operating parameters of casting are managed by a complex automated system, which optimizes them in real time and allows their modification whenever necessary.

The Acciaieria products are billets with sides 120 mm and lengths 12 meters. The plant is engineered so that the production process is closely linked to a series of satellite facilities, including a modern off-gas system for furnaces which was built to high environmental safety standards: standards constantly improved, as in the recent intervention where the permanent monitoring of dioxins has been introduced, application of a technology that is now the prerogative of the waste-to-energy plants.

4. Results and discussion

In order to quantify the Carbon Footprint, the company has monitored the levels of carbon dioxide emissions concerning the years 2014-2015-2016-2017 and the partial ones about 2018 (until 31/06) by carrying out the synthesis under Directive 2003/87/CE. The total amount of emissions obtained from the plant arises from the sum of the emissions coming from the sources stream: Gaseous- natural gas; Material- scrap iron, Iron ores, Ferro-alloys; Solid- coking coal, anthracite, other coals; Materials-carbon electrodes for electric arc furnaces, other scums; Waste- industrial waste, fume suppression dust; Material- steel, steel produced by EAF (Electric Arc Furnace), purchased cast iron, HBI (Hot Briquette Iron)/DRI (Direct Reduced Iron), CaO, Mortar.

Table 1 and the histogram from Fig.1 show the total amount of CO_2 emissions in a year expressed in tons scaled to the total quantity of steel produced. As shown, Acciaierie di Sicilia has been able to reduce CO_2 emissions scaled to its production, recording a constant improvement of environmental performances during the examined years.

Regarding the quantification of the Water Footprint, the company makes use of the laboratory “Sias s. r. l.” which provides chemical analysis services and advice thanks to sampling technicians. In Table 2 sampling benchmarks, values and standard threshold are shown thanks to the data obtained by “Sias”. The test has been carried out for industrial waste water, the presence of colourless and odourless suspended particulates expressed in MOL. As for the quantity of water used during the productive cycle, it remains constant through the years as the company develops a closed process. Table 3 and the histogram from Fig. 2 show the quantity of wasted water in relation to the quantity of steel produced during the year.

Table 1. Indicator of CO_2 emissions

	2014	***2015***	***2016***	***2017***
CO_2 emissions $t\ CO_2/t\ p$	0.097	0.093	0.086	0.075

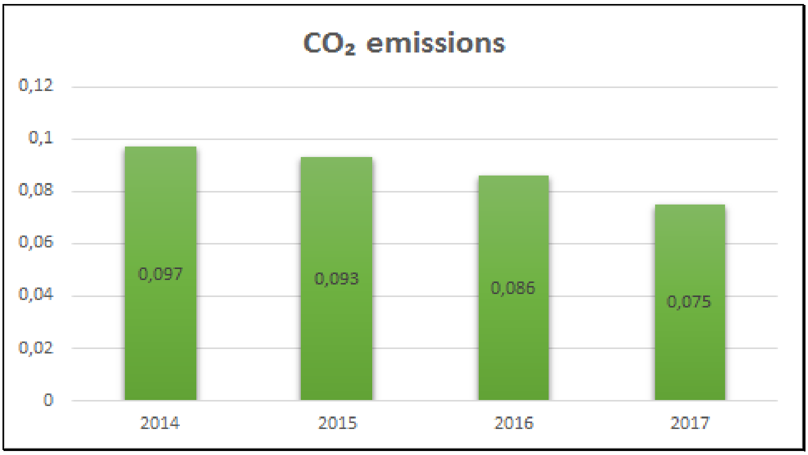

Fig.1. CO_2 emissions

Table 2. Sampling parameters

Parameters	***Value***	***DL***	***U.M***	***Limit***	***Method***
Temperature	21.8	_	°C	_	APAT CNR IRSA 2100
Ph	7.9	_	UNIT	5.5/9.5	APAT CNR IRSA 2060
Total suspended particulates	<1	1	mg/L	80	APAT CNR IRSA 2090

Table 3. Indicator of wasted water

	2014	***2015***	***2016***	***2017***
Wasted water t w/ t p	1.138	1.120	0.947	0.811

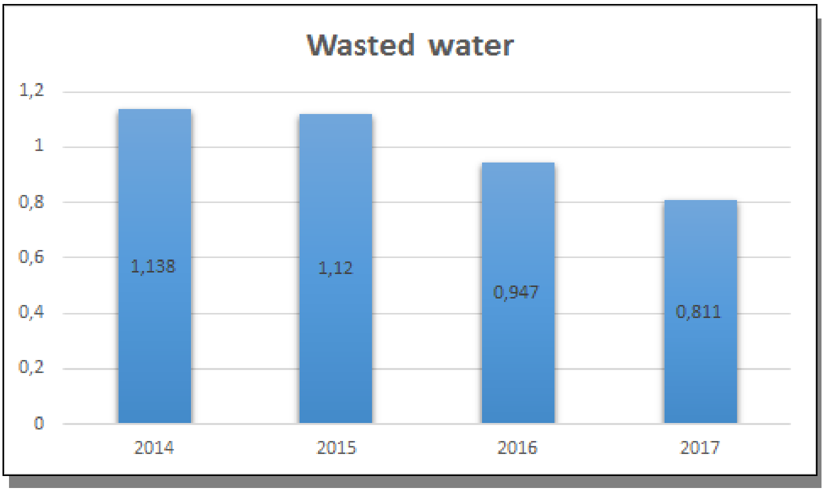

Fig.2. Wasted water

As can be seen, the company has been able to keep high environmental performances thanks to a reduction of water use compared to the production during the years. As to both CO_2 emissions in the atmosphere and to the water use, the registered trends show a reduction although the production increase during the examined years. The excellent result comes not only form the company's pro-active commitment towards the environment through the numerous obtained certifications, investments in modern technologies and, above all, the use of raw materials waste. These, once cleaned up, are used as second raw material reducing in this way water use, emissions and waste into the environment.

From the results obtained from this analysis arise a particularly active company towards the environmental protection, careful to remain coherent with its growth goals and ready to accept new environmental accounting instruments. This implies a growing commitment during the years to reduce anything dangerous for the environment as much as possible. Thus, the company has the possibility to use of this advantage to move forward its competitive environment. In this way it will be able to overcome all those companies which did not realize the importance of these sensible subjects.

5. Conclusions

The calculation of the Carbon Footprint and the Water Footprint are today considered as the new frontier of environmental accounting, an evolution of the company environmental policies also in relation to the growing awareness about the problem of climate change. The Carbon Footprint is a valid tool for the quantification and identification of emission sources, providing the company with the ability to manage and monitor greenhouse gas emissions. This tool therefore allows the company's carbon intensity to be identified and allows the opportunities for improvement to be analyzed. It also provides the company with data and information to support the strategic choices which conform to the requirements and the improvement of the image of the company towards customers and investors.

The analysis of the Water Footprint allows the impact on the water sector caused by a product, a process or an organization to be measured, using the methods indicated in the ISO 14046 standard, "Environmental management - Water Footprint - Principles, requirements and guidelines". The advantages deriving from the use of this tool are essentially: better management of resources that reduces the risks caused by over-exploitation of water sources, with greater availability and quality; the identification of the impacts on the natural environment and the identification of the modalities for their reduction. Moreover, the analysis based on the life cycle allows transparent information to be provided to consumers and producers, also improving its image.

From the analysis of the Italian economic system, there is a significant improvement in the economic sustainability indicators related to industrial production in terms of both the productivity of the use of natural resources and the environmental performance of production processes, thanks to investments for environmental protection. The companies most involved in the initiatives of the green economy are, in fact, more success driven in the international field (high retirement in exports) and to increase company skills through the recruitment of highly qualified personnel and the training of new recruits.

In conclusion, from monitoring the company's performance, it is shown that it has become a relevant reference point for the Sicilian territory. It aims to make people aware of environmental issues and to respect the surroundings by carrying out its work and by improving its image towards the stakeholders.

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