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Full length article

The sustainable recovery of the organic fraction of municipal solid waste by integrated ozonation and anaerobic digestion

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ABSTRACT

The organic fraction of municipal solid waste is commonly handled via biological processes, which enable the production of materials with potential fertilizer properties. When the biological process occurs under anaerobic conditions, the recovery of energy from biogas is also obtained. However, the sustainable recovery of organic solid waste implies the effective utilization of the biological treatment products, namely compost and digestate, which is often limited by the presence of organic contaminants. They enter the biological processes along with the organic waste and, due to their recalcitrance to the biodegradation, end up in either compost or digestate, posing the issue of their safe use on soil. The present study proposes ozonation as a possible strategy to reduce the presence of organic contaminants in the digestate originating from the organic fraction of municipal solid waste. In this view, digestate samples were collected from full-scale reactors operated at hydraulic retention time of 11 and 41 days and ozonated at 0.11 and 0.16 g_{O3}/g_{TS}. Experimental results, including the evaluation of the eco-toxicological potential of differently treated substrates, showed that the integration of ozone and anaerobic digestion can be pursued for the sustainable recovery of organic solid waste, but the identification of the combined process lay-out requires the evaluation of the digestate biological stabilization level.

1. Introduction

The management of the organic fraction of municipal solid waste (OFMSW) commonly relies on biological processes, namely composting and anaerobic digestion. The latter has been increasingly spread in Europe, with an installed treatment capacity continuously growing over time (De Baere and Mattheeuws, 2015). Such condition has been mainly driven by the possibility of converting residual organic substrates into a methane-rich biogas, which can be recovered for energy purposes (Riggio et al., 2017; Woon et al., 2016). The generation of this biogas comes along with the production of the anaerobic digestate, with potential fertilizer properties due to the significant content of both macro- and micro-nutrients (Owamah et al., 2014; Tambone et al., 2010; Tampio et al., 2016).

The potential recovery of the anaerobic digestion products makes it a suitable OFMSW management strategy to implement at full-scale the principles of the circular economy approach (Ghisellini et al., 2016; MacArthur, 2013), pursuing the full valorization of waste and the consequent reduction of residual streams.

In this regard, the optimization of anaerobic digestion yields plays a key role and different strategies have been identified over time (Jain et al., 2015; Paul and Dutta, 2018). Co-digestion processes can be applied to increase the organic load to the digesters, while creating a balanced environmental media, so as to increase methane production (Divya et al., 2015; Mata-Alvarez et al., 2014; Xu et al., 2018). Similarly, the separation of the hydrolytic and acidogenic steps from the methanogenic one represents a strategy for the optimization of the single biological reactions, which lead to improved methane conversion yields (Li et al., 2018). More recently, two-stage anaerobic systems, combining hydrogen and methane production, have been regarded as a promising technology to improve the energy recovery efficiency of the substrate (Ren et al., 2018).

The substrate processing prior to the anaerobic treatment is another option that has been largely investigated to enhance anaerobic digestion performances. A wide variety of chemical, physical or biological techniques have been proposed, with the main aim of promoting the solubilisation of the complex organic substrates, thus enhancing the amount of organic matter readily available for its biological conversion into methane (Ariunbaatar et al., 2014a; Cesaro and Belgiorno, 2014).

Among chemical pretreatments, the use of alkali reagents, often in combination with thermal processes, has been frequently studied (Abudi et al., 2016; Pellera and Gidarakos, 2018; Solé-Bundó et al.,

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2017). More recent trends focus on organic solvents. The use of alcohols (Amiri et al., 2014; Li et al., 2012; Mancini et al., 2018) as well as organic acids (Qin et al., 2012; Wang et al., 2012; Zhu et al., 2015) on lignocellulosic substrates has been studied to pursue the separation of high-purity cellulose from both the lignin and hemicellulose fractions (Zhang et al., 2016). These products can be differently recovered and reintroduced in the material cycle, boosting the principles of the circular economy.

Ozonation is a further chemical pretreatment method, relying on the high oxidant power of the ozone, which reacts with different organic substrates without producing residues (Carrère et al., 2010). Successful industrial applications have been implemented to treat sewage sludge prior to anaerobic stabilization (Sievers et al., 2004) and research studies have highlighted the potential of this technique in improving both the solubilisation and anaerobic biodegradability of organic solid waste (Adarme et al., 2017; Bakhshi et al., 2018; Somers et al., 2018). However, the extent of ozone effects was observed to depend on the relative presence of sugars, lipids and proteins in the substrate (Ariunbaatar et al., 2014b). Moreover, the need of operating with tightly low ozone doses (Cesaro and Belgiorno, 2013) makes this technology less competitive than other pretreatments when intended to be applied for the larger scale processing of solid substrates.

Conversely, such low ozone doses were observed to be effective in reducing the concentration of selected organic contaminants in both sewage and anaerobically digested sludge (Bernal-Martinez et al., 2009).

Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs) and pesticides are among the persistent organic contaminants most frequently detected in both compost and digestate originating from the OFMSW biological treatment (Brändli et al., 2006, 2007a, Brändli et al. (2007c)). These pollutants enter the biological treatment along with the waste (Bansal and Kim, 2015) and, due to their recalcitrance to the biological degradation, end up in the final products of waste recovery processes. Brändli et al. (2007b) pointed out a reduction up to 90% in the concentration of low molecular weight PAHs achieved during composting, while the anaerobic digestion did not provide any degradation of these pollutants, notwithstanding their molecular weight. Similar considerations can be drawn for the biological degradation of PCBs, whereas the assessment of pesticide degradation was found to be more complex due to both the wide number of existing compounds and the diverse physical-chemical and biological mechanisms they can undergo (Kupper et al., 2008).

The presence of these hazardous substances represents a limit to the safe use of OFMSW recovery products for agricultural purposes (Al Seadi et al., 2013). In this regard, it is worth pointing out that in most European countries, the use of organic waste recovery products on soil is legally established, with parameters and corresponding limit values defined for quality characterization. Nevertheless, a great heterogeneity in both formally identified properties and characterization procedures can be identified among the regulations enforced in different Member States. Recent studies pointed out that the quality assurance of waste-based fertilizer is fundamental to promote their successful integration into the marketplace (Dahlin et al., 2017; Vaneeckhaute et al., 2018). Nevertheless, the agricultural use of the digestate, as that of compost, is mainly referred to the concentration of impurities, metals and pathogens and only few States regulate the presence of persistent organic compounds in organic waste recovery products (Cesaro et al., 2015a; Wei et al., 2017a).

Such condition poses a severe issue related to the potential risk, for both environmental and human health, from the application of contaminated waste-based products on soil and boosts the need to propose adequate technical solutions.

In this context, the ozonation of OFMSW digestate could prove to be a valuable option if intended to pursue simultaneously the reduction of persistent organic compounds and the enhancement of its solubilisation. The pretreated digestate could thus be partially recirculated into the anaerobic reactor to improve methane recovery, while the residual portion could be destined to soil applications.

Aim of this work was in investigating the effects of ozonation on the digestate originating from the anaerobic treatment of the organic fraction of municipal solid waste. In order to achieve this aim, OFMSW digestate samples were collected at a full-scale plant, characterized by their chemical-physical properties and spiked with benzo[*a*]pyrene, as target compound for a polycyclic aromatic hydrocarbon contamination. The variation in solubilisation and biodegradability as well as the contaminant removal were monitored after ozonation, in order to discuss its possible integration with the anaerobic digestion for the sustainable recovery of OFMSW in a circular economy perspective.

2. Materials and methods

The experimental activity was carried out on digestate samples collected at a full-scale facility, treating 30,000 t/year of source sorted OFMSW through a wet anaerobic digestion process. Over the treatment line, fully described by Cesaro et al. (2015b), samples were obtained from two anaerobic reactors, ensuring a retention time of 11 and 41 days, respectively. The retention time of the collected samples accounted for their different biostabilization level, so as to investigate the ozone effects on differently composed organic pools.

2.1. The substrate: characterization and spiking procedure

Table 1 summarizes the main chemical and physical characteristics of the digestate samples. The presence of polycyclic aromatic hydrocarbons (PAHs) was quantified as well and the absence of these contaminants addressed the need for artificial contamination.

Benzo[a]pyrene (b[a]p), identified as one of the most recalcitrant PAHs (Brändli et al., 2007a), was assumed as the target compound and it was used to prepare a stock solution for digestate spiking.

The stock solution was prepared by dissolving 50 mg of b[a]p in 10 mL of dichloromethane and added to the digestate samples. Spiked samples were stirred for 24 h, at ambient temperature, so as to promote the controlled volatilization of the solvent used to prepare the b[a]p solution and to obtain a theoretical initial concentration of 100 mg/kg_{TS}, chosen for both experimental and analytical purposes.

Analytical results showed an average initial value of 82.93 ± 6.97 mg/kg_{TS}.

2.2. Experimental set up

2.2.1. Ozone device

A 10 L/min air flow was introduced into a UV generator (model Ozone - Procom srl) to produce ozone. The air stream containing ozone was then introduced at the bottom of a glass reactor containing the samples; exhaust gases were extracted on the top of this reactor and forced to pass through a Drechsel trap filled with 200 mL of 2% KI solution, in order to capture residual ozone and determine the ozone demand.

On the basis of previous studies performed on both the sludge (Bernal-Martinez et al., 2009) and organic solid waste (Cesaro and

Table 1
Characterization of the digestate samples.

Parameter	11 days digestate	41 days digestate
pH	7.2 ± 0.1	8.4 ± 0.2
TS [%]	4.59 ± 0.47	2.81 ± 0.19
VS [%TS]	58.04 ± 6.93	42.80 ± 1.98
COD [mg/L]	89,200 ± 20903	22050 ± 7000
sCOD [mg/L]	56,149 ± 8610	5985 ± 1182
BOD_5 [mg/L]	45,960 ± 5600	3700 ± 1838
PAH [mg/kg_{SS}]	n.d.	n.d.

Belgiorno, 2013) destined to anaerobic digestion, ozone doses of 0.11 and 0.16 g_{O3}/g_{TS} were investigated.

2.3. Analytical set up

2.3.1. Chemical - physical analysis

The pH of samples was measured by pHmeter model HI 99121 (Hanna Instruments).

Chemical Oxygen Demand (COD), total solid (TS) and volatile solid (VS) were evaluated according to Standard Methods (AWWA-APHA-WEF, 1998). The Biochemical Oxygen Demand in 5 days (BOD_5) was assessed via respirometric tests performed through the Oxytop system.

Both the soluble COD (sCOD) and the soluble BOD_5 ($sBOD_5$) were measured on each sample after centrifugation and filtration (< 0.45 mm) following the same Standard procedure. The ratio between $sBOD_5$ and sCOD served as an indicator of the biodegradability of the soluble organic matter.

COD_{NaOH}, representing the sample soluble COD obtained with 1 M NaOH digestion, as reported by Muller (2001), was assessed to estimate the maximum portion of organic matter that could be solubilized.

The concentration of polycyclic aromatic hydrocarbons (PAHs) was determined in accordance with the Standard Methods EPA 3550 C and EPA 8270 D.

The Standard Method 2350 US-EPA (Ozone Demand/Requirement, Semi-Batch Method) was used to determine the residual ozone, after the treatment of the digestate samples.

The anaerobic biodegradability was assessed through batch tests, carried out under mesophilic conditions and using digested sludge as inoculum. The sludge was sampled at the anaerobic digester of the conventional wastewater treatment plant in Salerno (Italy) and incubated at 35 °C until use. The daily biogas production was settled by a water displacement method, in order to assess the cumulative production in 21 days. The results of these tests are discussed in terms of variation of the specific biogas production of ozonated substrates out of the untreated ones.

All the analytical determination were performed, at least, in triplicate and average values were considered for discussion.

2.3.2. Ecotoxicological tests

The ecotoxicity tests were performed using an eluate (solid-to-liquid ratio 1:10 (v/v)) obtained from the solid digestate sample, in accordance with the technical standard UNI EN, 12457-2, 2004. Five different concentrations of the eluate, namely 10%, 25%, 50%, 75% and 100% (v/v), were defined for the ecotoxicological tests.

Aliivibrio fischeri strain NRRL B-11,177 was used for the test of luminescence inhibition (UNI EN ISO (2009) with Microtox® luminometer (Microtox Model 500; Microbics Corp., USA). The luminescence intensity in all cuvettes was measured before as well as after both 15 and 30 min exposition; a computer program for Microtox Acute Toxicity Test (Azur Environmental Ltd., UK) was used for the data elaboration.

Seed germination and root elongation assays were performed following the method UNICHIM 1651 (2003). Briefly, *L. sativum* seeds were placed in contact with different concentration of samples in controlled conditions. Germination and growth experiments were conducted at controlled pH, in a Petri dishes (90 mm diameter) with one sheet of Whatman No. 1 filter paper as support, in three replicate experiments. After the addition of 10 seeds and 3 mL of test solutions, Petri dishes were sealed with Parafilm to ensure a closed-system model. The seeds were placed in a growth chamber at 25 °C. Bioassays lasted 72 h and after this period, the number of seeds germinated was counted and the radical length was measured. The Index of Growth (IG) was calculated by multiplying the germinated seed number (G) and the length of roots (L).

The germination index (GI), indicating the inhibitory effects, was expressed as percentage with respect to the control:

$$GI = (IGc - IGs)/IGc^* 100$$

where IGs and IGc are the germination indices calculated for samples and control, respectively.

Daphnia magna, cultured at ERL-UNINA (Ecotoxicology Research Laboratory, University of Naples Federico II), was used for the immobilization test (UNI EN ISO 6341, 2012). The immobile daphnids were counted after 24 h of exposure.

3. Results and discussion

3.1. Ozone effects on the substrate biodegradability and b[a]p removal

The reactions of ozone with organic compounds can occur through either direct or indirect oxidation mechanisms: the direct oxidation relies on the molecular ozone itself and it is the prevailing reaction at very low pH; the indirect oxidation is provided by the hydroxyl radicals originating from ozone decomposition in aqueous solution and is predominant at high pH (Hoigné and Bader, 1977). In the basic pH range, the products of the ozone reaction with biorefractory or toxic aromatic compounds are more biodegradable (Delgenès et al., 2003). The average pH of the investigated samples was 7.2 and 8.4 for the 11 days digestate and the 41 days one, respectively. In these conditions, the radical action may prevail and, as it is not selective, oxidative reactions of both organic matter and b[a]p were expected to transform organic compounds into oxygenated intermediates, which are more soluble and more biodegradable (Gilbert, 1983). For this reason, the variation in soluble compounds was expressed as sCOD. Moreover, the quality of the solubilised fraction, in terms of biodegradability, was referred to the ratio between BOD_5/COD, evaluated on the soluble organic matter.

Fig. 1 plots the variation of both sCOD and $sBOD_5$/sCOD after ozonation for the digestate samples characterized by either 11 or 41 days retention time. In the former case (Fig. 1a), ozone determined a sCOD increase up to 24%, notwithstanding the applied ozone dose. Similarly the application of ozone doses up to 0.16 g_{O3}/g_{TS} did not affect the VS content, indicating the absence of mineralization phenomena. These effects came along with an enhancement of the soluble fraction biodegradability: the application of the higher ozone dose resulted in an average 23% enhancement of the ratio $sBOD_5$/sCOD of the digestate samples.

For the 41 days-digestate samples (Fig. 1b), ozonation determined a slight mineralization, with a reduction in VS content up to 10% for an ozone dose of 0.16 g_{O3}/g_{TS}. In this case, it can be also observed that neither the concentration expressed as COD or the biodegradability of the soluble fraction of the investigated samples varied significantly after ozonation.

The different solubilisation responses of the investigated digestate samples to the application of ozone reflected their different initial biostabilization level, which in turn was related to the retention time in the anaerobic digesters. Hydraulic retention time (HRT) plays indeed a key role in defining anaerobic process stability and performances, as the longer a substrate is kept in the digester, the more complete its degradation will be (El Achkar et al., 2018; Grosser, 2017; Wei et al., 2017b).

The study of anaerobic digestion optimization by the characterization of different organic substrate fractions clearly pointed out that the biodegradation process results in the reduction of the soluble fractions, which are the most readily accessible to microorganisms (Jimenez et al., 2014, 2015). The extent of sCOD reduction is, in turn, depending on its chemical composition, since the accumulation of non-biodegradable recalcitrant organics in the solubilised pools may also occur (Ma et al., 2018).

The chemical characterization of the residual organic material in anaerobic digestate confirmed that it was essentially composed of less accessible fractions (Maynaud et al., 2017). Teglia et al. (2011) reported that the organic matter non-extracted fraction represented a

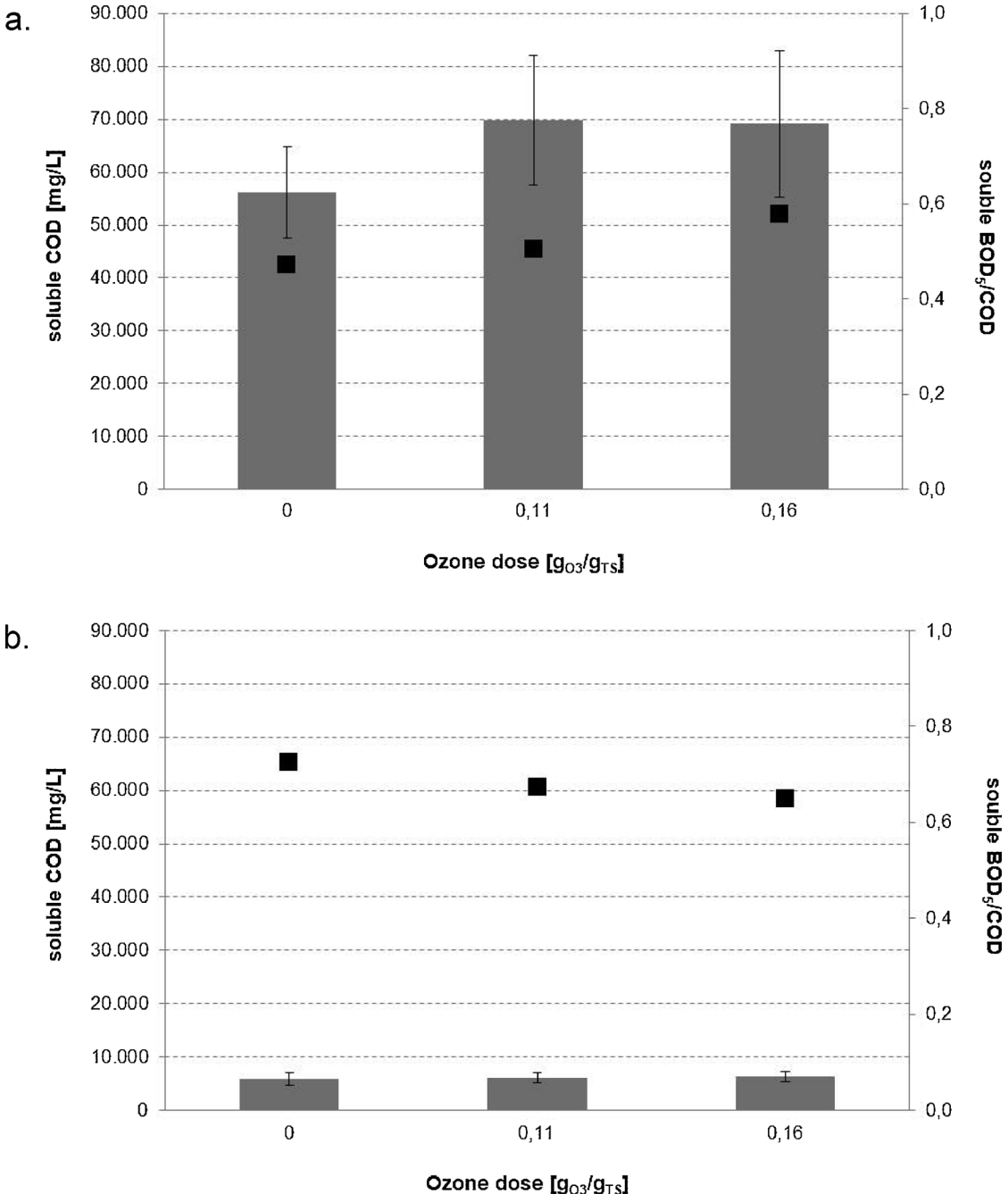

Fig. 1. Variation of both sCOD and $sBOD_5/sCOD$ ratio for increasing ozone doses in (a.) 11 days-digestate samples and (b.) 41 days-digestate samples.

large part of the total COD for most of the investigated kinds of digestate. Furthermore Lu et al. (2018) showed that the residual dissolved organic matter in digestate is dominated by humic-like substances, hydrophobic organic carbon as well as low molecular weight neutrals, including alcohols, aldehydes, ketones and mono-oligosaccharides. The same authors also pointed out that the majority of these compounds were refractory to either hydrolysis or biodegradation.

In the present investigation, digestate samples collected after 11 days of anaerobic processing were found to be characterized by an average sCOD value one order of magnitude higher than that of 41 days-samples, which is consistent with the trend reported by Ma et al. (2018). For these samples, sCOD was calculated to be approximately 95% of COD_{NaOH}. This outcome, reflecting the extent of the organic matter biodegradation process within the anaerobic digestion treatment line, could also account for the ozonation effects on the 41 days-digestate samples. It is indeed reasonable that during the overall digestion process the soluble organic matter had been biologically degraded in the digesters, so that the obtained digestate after 41 days was mainly composed of the less accessible fractions, either particulate and dissolved, that could not be effectively solubilised by the applied ozone doses.

It is also worth pointing out that the ozone action affects both the digestate organic portion and the spiked organic contaminant: Fig. 2 displays ozone effects towards the target contaminant, namely b[a]p.

In the 11 days digestate samples the b[a]p concentration was found to decrease for increasing ozone doses: approximately 10% and 50% removal were obtained for 0.11 g_{O3}/g_{TS} and 0.16 g_{O3}/g_{TS}, respectively. Conversely, in the 41 days digestate samples, an average 50% removal was obtained despite the applied ozone dose.

These results are in good correlation with previous studies

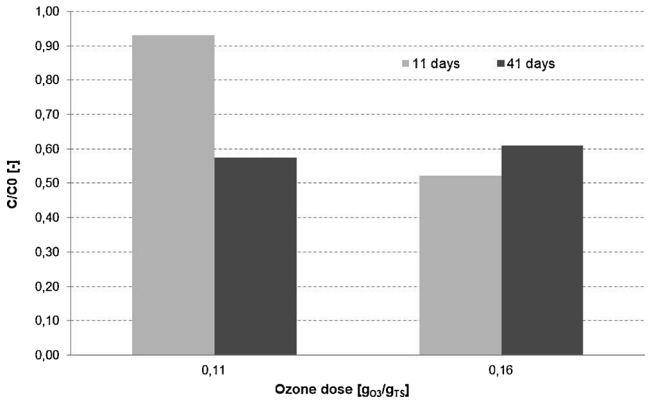

Fig. 2. Removal of the target contaminant for increasing ozone doses in both the 11 days-digestate and the 41 days-digestate samples.

performed on the sludge originating from wastewater treatment. (Bernal-Martinez et al., 2009) found that ozone doses comparable to those used in this study determined a decrease of b[a]p concentration ranging between 50 and 66%, according to the configuration of the combined ozone/anaerobic digestion process.

In a previous study, the same authors found that PAH removal yields depended on the competition between both PAH and organic oxidable matter towards ozone: the higher solubilisation occurred, the lower was the probability for ozone to react with PAH (Bernal-Martínez et al., 2005). This outcome explains the removal yields achieved in the present study. In the 11 days digestate samples, the improvement in sCOD hindered the reaction between ozone and b[a]p. Conversely, in the 41 days digestate samples the limited content of oxidable organic matter resulted in the prevailing reaction between ozone and b[a]p: the concentration of the target contaminant was indeed halved at the lower ozone dose and any further reduction was obtained for 0.16 g_{O3}/g_{TS}, but some mineralization was observed.

The effects of ozone positively influenced the anaerobic biodegradability of the pretreated substrates.

Specific biogas production increased up to 2.5-fold when increasing ozone doses were applied to the 11 days digestate samples (Fig. 3): this outcome was consistent with both the sCOD increase and the enhanced b[a]p removal. On the other hand, as increasing ozone doses did not significantly affect the organic matter quality but determined an average 50% b[a]p removal, comparable results in terms of biogas production were achieved from the 41 days digestate samples after pretreatment. In this case, as shown in Fig. 3, the variation was in the

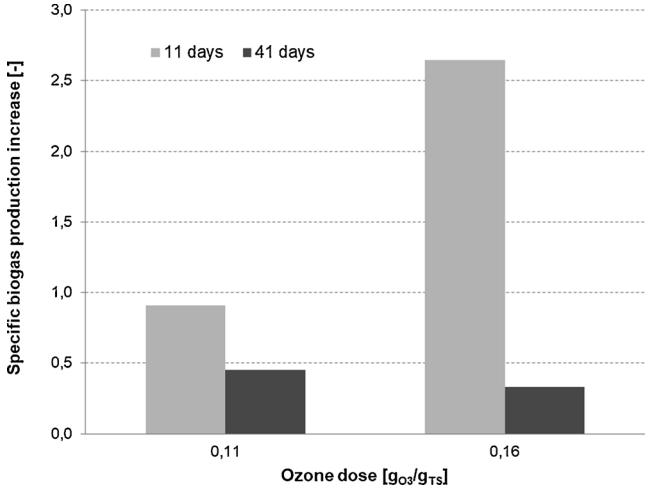

Fig. 3. Enhancement in specific biogas production after the ozonation of both the 11 days-digestate and the 41 days-digestate samples.

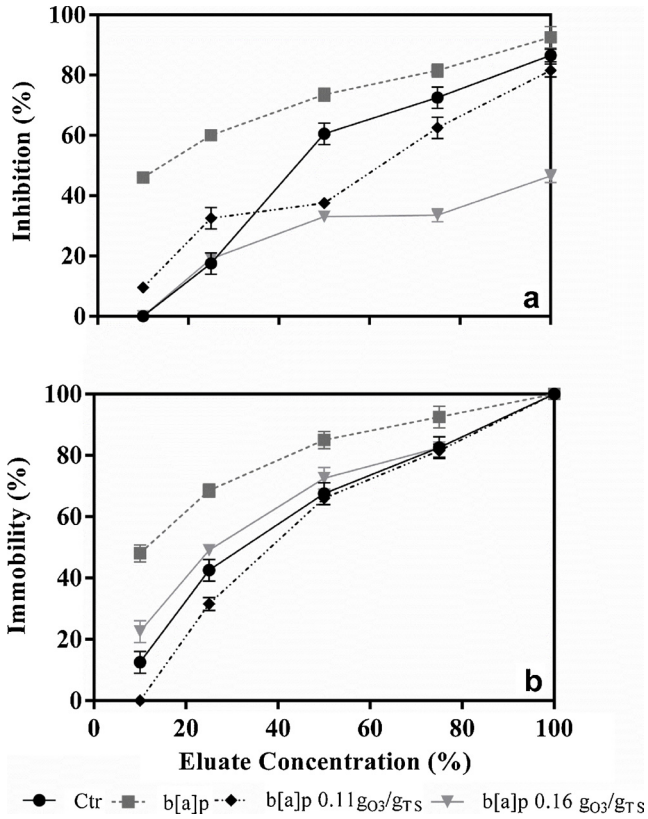

Fig. 4. Results of the test on *A. fischeri* (a.) and *D. magna* (b) for the 11 days digestate samples.

range 0.3-0.5 and it was in direct relation with the b[a]p removal yields.

The experimental activity pointed out the potential of ozonation and anaerobic digestion integration for the sustainable recovery of OFMSW. To this end, ecotoxicological tests were also performed, in order to address further analysis for the optimization of the combined process conditions.

3.2. Ecotoxicological response of ozonated substrates

Figs. 4 and 5 show the ecotoxicological results of bioassays with *A. fischeri* (A), *L. sativum* (B) and *D. magna* (C) performed on the eluate, obtained from the 11 and 41 days digestate samples, respectively. Ecotoxicological tests were performed on the eluate of samples spiked with b[a]p, collected before and after ozonation. Negative control was included in each testing run and it was carried out on the eluate of the digestate to evaluate the baseline toxicity. These data were also elaborated in order to calculate the EC50 and its confidence limits, as reported in Table 2.

The results plotted in Fig. 4a highlight that the samples spiked with b[a]p displayed higher toxicity on *A. fisheri* than the negative control ($p > 0.05$). Even at 10% dilution, a luminescence inhibition of 46% was observed, indicating the great toxicity of contaminated samples over the parent digestate ones. At the same dilution, the ozonated samples did not provide any toxic effect. It is also worth pointing out that higher ozone doses resulted in a significant decrease in the toxicity of undiluted samples: at 100% eluate concentration, the ozone dose of 0.16 g_{O3}/g_{TS} determined a 40% inhibition, lower than the one provided on the untreated samples as well as on that ozonated at 0.11 g_{O3}/g_{TS}. The EC50 (Table 2) of the samples treated with 0.16 g_{O3}/g_{TS} was estimated to be higher than 100% concentration, demonstrating a high reduction of the toxic potential.

The phytotoxicity tests performed with *L. sativum* (data not shown)

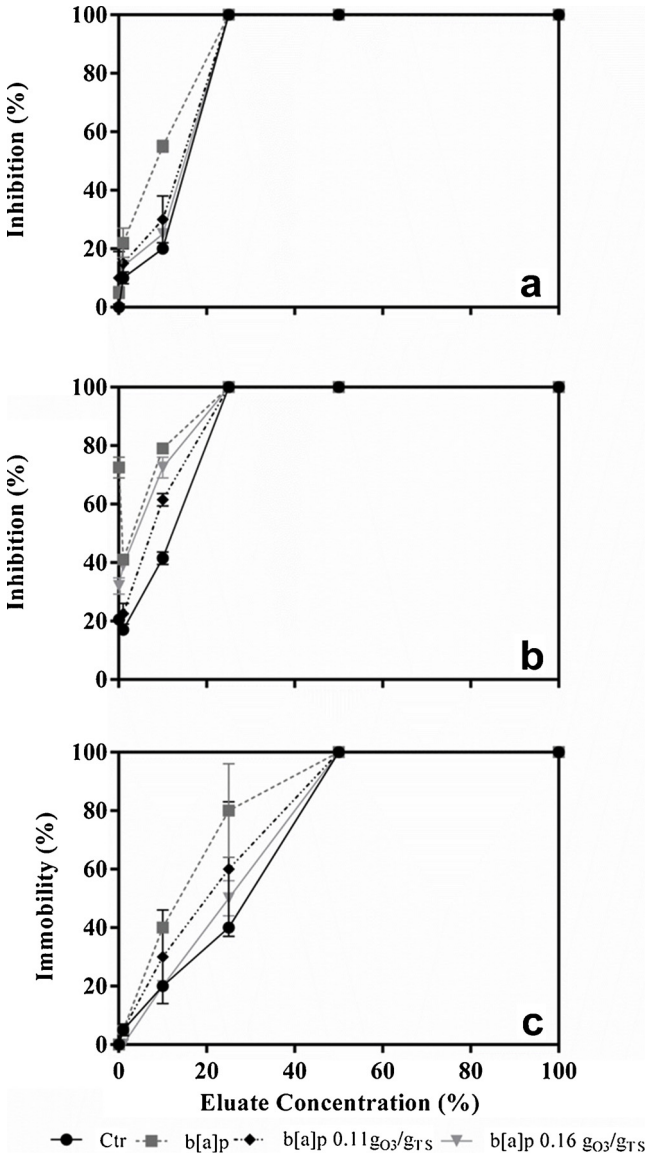

Fig. 5. Results of the test on *A. fischeri* (a.), L. *sativum* (b.) and *D. magna* (c.) for the 41 days digestate samples.

did not result in inhibitory effects. The not observed toxicity of root growth was already found by other authors and it can be ascribed to the presence of nutrients like the nitrogen as well as to the high content of total carbon that indicates the genetic adaptability of the plants (Tigini et al., 2016; Wang et al., 2010).

Different results were obtained on *D. magna* (Fig. 4b). The toxicity of untreated samples was observed to decline for decreasing eluate concentration: at 10% dilution, only 48% of immobilization occurred. Although an increase of the mobility was recoded, there were no statistical differences compared to negative control. In this case, the treatment with ozone did not lead to an improvement in the quality of the digestate showing similar toxicity to negative control. These results could be also related to the high sensitivity of *D. magna*, indicating that daphnids have a homeostatic response of the toxic effect of digestate (Calow and Forbes, 2014).

The toxic potential of the 41 days digestate samples, both untreated and ozonated, was found to be significantly higher than the one of the 11 days digestate samples, as plotted in Fig. 5.

A. fischeri was very sensitive towards the more biostable digestate and 100% bioluminescence inhibition was observed for concentrations higher than 10% (Fig. 5a). As expected, the most toxic samples were those spiked with b[a]p with an EC50 of 6.02% (Table 2). However, ozonation did not provide any reduction in toxicity, as comparable EC50 values were obtained for samples ozonated at both 0.11 and 0.16 g_{O3}/g_{TS}.

In *L. sativum* bioassays, 100% growth inhibition was observed at lower dilution, whereas at 1% and 0.1% eluate concentrations the toxic response was different for the investigated samples. This outcome can be ascribed to the sample salinity that, in previous study, was appointed as the main cause of inhibition in germination processes (Pivato et al., 2016).

Similar consideration can be drawn also for the *D. magna* assays (Fig. 5c). However, in this case, for eluate concentrations lower than 40%, increasing ozone doses resulted in reduced toxicity: in particular, at 1% eluate concentration the EC50 of the samples ozonated at 0.16 g_{O3}/g_{TS} was found to be in the same order of magnitude than the one of the control, highlighting the ozone potential in decreasing the toxicity of treated substrates.

4. Technical considerations

The experimental results seem to encourage the use of ozonation for the treatment of organic solid waste destined to anaerobic digestion, currently limited by the high operating costs associated to ozone generation. The possibility of enhancing biogas production, while posing a barrier to the spread of organic contaminants that could enter the anaerobic reactors along with the waste, would indeed make the

Table 2
EC_{50} values with 95% Confidence limits for the performed tests.

		A. fischeri	L. sativum	D. magna
11 days digestate	Control	45.38% (41.71% - 49.36%)	> 100%	30.15% (25.98% - 34.98%)
	Contaminated digestate	13.50% (10.46% - 17.43%)	> 100%	11.43% (9.33% - 14.00%)
	Contaminated digestate + 0.11 g_{O3}/g_{TS}	51.40% (41.84% - 63.13%)	> 100%	36.44% (32.64% to- 40.68%)
	Contaminated digestate + b[a]p 0.16 g_{O3}/g_{TS}	> 100%	> 100%	24.54% (20.66% - 29.15%)
41 days digestate	Control	16.40% (0.39% - 27.37%)	26.53% (23.56% - 29.87%)	23.83% (19.18% - 37.55%)
	Contaminated digestate	6.02% (1.53% - 23.71%)	12.09% (11.06% - 13.22%)	12.18% (9.83% - 15.11%)
	Contaminated digestate + 0.11 g_{O3}/g_{TS}	15.47% (1.80% - 32.40%)	18.45% (15.93% - 21.37%)	16.93% (10.67% - 26.86%)
	Contaminated digestate + b[a]p 0.16 g_{O3}/g_{TS}	16.19% (1.70% - 24.50%)	13.00% (11.34% - 15.08%)	22.03% (14.53% - 33.42%)

combined ozonation-anaerobic digestion processes more sustainable.

The promising outcomes of this study highlighted that ozonation can effectively improve the quality and anaerobic biodegradability of contaminated digestate. In this view, the integration of the ozonation with the anaerobic digestion processes of the organic fraction of municipal solid waste can provide a suitable strategy for its sustainable recovery in a circular economy perspective.

However, the extent of the ozone effects was observed to depend on its biological stability, which in turn is related to the retention time in the anaerobic digesters. The experimental results showed that ozone performed better on the 11 days digestate samples, suggesting that higher yields can be pursued when ozone is applied on partially biodegraded organic materials. In this view, the anaerobic digester retention time is a key operation parameter to consider when approaching the combination of the ozonation process with the anaerobic digestion.

Similarly, the ozone dose plays a fundamental role. The supplied ozone dose should indeed promote both the solubilisation of organic matter and the removal of target contaminants, while avoiding the formation of toxic by-products. In this study, the ecotoxicity tests pointed out that the higher ozone dose resulted in a sensitive reduction of sample toxicity, suggesting that the reaction intermediates generated during the ozonation of the 11 days digestate were less toxic than the parent compounds. However, the application of the same ozone dose to the 41 days digestate spiked with b[a]p made its toxicological behavior comparable with that of the control. It should also pointed out that the toxicity of these more biostabilised samples was found to be generally higher and very low eluate concentration had to be reached in order to find some differences in the response of the investigated samples.

The identification of the optimal combination of the anaerobic digestion retention time with the most effective ozone dose and supplying mode should come along with that of the amount of digestate to be ozonated for its further anaerobic treatment. The combined ozone-anaerobic digestion process is indeed expected to address the recirculation of the pretreated digestate into the anaerobic reactor. In this view, the optimal recirculation ratio needs to be defined, taking into account that the energy spent for ozonation should not exceed the benefit from the surplus of the biogas generated by the anaerobic processing of pretreated substrates.

5. Conclusions

The present study showed that ozonation can effectively improve the quality and anaerobic biodegradability of contaminated digestate. Ozone doses up to 0.16 g_{O3}/g_{TS} determined both the overall biodegradability enhancement as well as the reduction of benzo[*a*]pyrene concentration for the 11 days digestate samples; this condition, in turn, provided an increase of the specific biogas production. Conversely, ozone supply did not greatly influence the biodegradability of the 41 days digestate samples but determined an average 50% b[a]p removal. The ecotoxicity tests further support the evidence that ozonation can effectively improve the toxicological response of digestate samples, especially that of the less biostabilised ones.

These promising results promotes further studies to identify the optimal operating conditions as well as to assess the technical and economic feasibility of the integrated ozonation-anaerobic digestion process. The characterization of the ozone reaction intermediates should be also carried out, in order to better integrate the results of the ecotoxicological tests as well as to provide reliable data for the efficient scale up of the proposed combined process.

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