

Treatment of olive mill solid wastes by chemical processes enhanced with iron rich materials

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Abstract

The main objective of the present study was to investigate the Fenton's process for the chemical stabilization of olive mill solid waste (OMSW). Three different iron-rich residues and synthesized nanoscale zero-valent iron (nZVI) particles were tested to evaluate their potential for replacing iron sulphate as catalyst. Neutralized acid mine drainage (AMD) sludge, Fenton's process sludge (FSW) and iron powder (IPW) from a metallurgical industry were the iron-rich wastes considered. nZVI particles were synthesized in aqueous solution through iron salts reduction using sodium borohydride. Iron-rich catalysts and OMSW were characterised concerning moisture, volatile solids, pH, electrical conductivity, chemical oxygen demand, iron content and *Kjeldhal* nitrogen. Besides, elemental analysis of C, N, H and S was also determined. Additionally, phytotoxicity tests were also performed for OMSW before and after treatment. nZVI morphology, size distribution, specific surface and zeta-potential were assessed, alongside with post-synthesis storage methods and aging. Fenton's process was carried out in a semi-batch system. Each catalyst (FeSO₄, AMD, FSW, IPW or nZVI) was added to an aqueous suspension of OMSW, using L/S 5, pH 3, under agitation for 15 min. The efficiency of the process was analysed through the amount of CO₂ released during oxidation.

All the iron rich wastes showed catalytic activity to promote peroxidation of OMSW. However, it is remarkable the efficiency obtained for IPW when compared with conventional Fenton's catalyst (FeSO₄). The results reveal the potential of integrating the management of two solid wastes in an environmental benign manner. Moreover, the catalytic potential of the raw iron rich materials is still being compared with nZVI prepared by the different procedures mentioned.

Keywords: chemical stabilisation, olive mill wastes; iron-rich wastes; Fenton's process iron nanoparticles

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1. Introduction

Despite environmental laws are becoming stricter regarding waste management, the excessive amount of wastes produced and their final destination is still a major concern faced by society nowadays. Waste valorisation strategies are being implemented and reinforced by European Commission in order to improve the current situation.

Olive oil industry is responsible for high loads of organic waste production in Mediterranean countries. Both olive mill wastewater (OMW) and olive mill solid waste (OMSW) are wastes produced during the extraction of olive oil, being often disposed of in soil for fertilization purposes (Nasini et al., 2013; Buchmann, 2015). However, not only disposal costs are increasing due to the high quantity produced, but also high organic load and phytotoxicity have a negative impact on soils, crops and groundwater (Morillo et al., 2009). OMSW is not easy to degrade biologically, due to refractory and toxic compounds such as polyphenols and fatty acids (Albuquerque et al., 2004; Azbar, 2004; Chowdhury et al., 2014). One of the conventional treatment processes consists on the combustion of the solid waste as fuel for heat recovering (Azbar et al., 2004; Cema et al., 2008). However, the incomplete combustion can lead to the production of gas emissions with toxic compounds, and the high water content (around 60% in a two phase process) may require high energy consumption, increasing the costs of treatment. Anaerobic digestion (Borja et al., 2003; Rincón et al., 2013) has becoming interesting for biogas production, but according to Rincón et al. (2013) for organic matter higher than $9.2 \text{ g COD L}^{-1}\text{d}^{-1}$, the process reveals instability. Composting (Filippi et al., 2002) brings other difficulties such as odors and extensive maturation time.

In this context, it is required the development of other treatment technologies able to reduce the impact of OMSW in the environment. Several iron wastes are produced by a wide sector of industries such as mining, chemical or metallurgical. In spite of some iron wastes have been recovered inside their industrial cycles, others have some industrial drawbacks, being challenging to handle when produced in high amounts, hindering their final disposal which is often landfill. On the other hand, iron has been used as a catalyst for environmental remediation due to their oxidizing and reducing properties. One example is the nanoscale zero-valent iron (nZVI) that has been gaining interest throughout the past decades (Crane and Scott, 2012; Yan et al., 2013). Zero-valent iron (ZVI) applicability is very wide encompassing treatment strategies for water and groundwater depuration (Dou et al., 2010; Hashim et al., 2011) and more recently for soil remediation (Gomes, 2015), either with organic or inorganic

contaminants. Pollutants such as azo dyes (Zhang et al., 2012), chlorinated organic compounds (Erto et al., 2014) or metal species (Rangsivek and Jekel, 2005) have been explored. In particular, metallic iron, Fe^0 , has been also used as a catalyst in the Fenton-like process to treat landfill leachates (Martins et al., 2012) as well as dyes (Shahwana et al., 2011) and other pollutants, like chlorinated compounds (Shen et al., 2013). In what regards to nZVI synthesis, even though several methodologies have been studied, chemical precipitation, based on the reduction of iron salts with sodium borohydride is the most used technique due to its simplicity (Wang and Zhang, 1997).

Fenton's process based on the oxidant capacity of hydrogen peroxide catalysed by iron, already revealed to be an interesting technology on the abatement of the pollutant character of cumbersome wastewaters (Martins et al., 2010). Nevertheless, more recently Fenton's reaction has aroused interest in semi-solid and solid matrixes. Erden and Filibeli (2010) performed Fenton's peroxidation in anaerobic sludge in order to increase the biodegradability of sludge. Hu et al. (2010) used a semi-solid system in order to remove hazardous compounds from swine sludge without water production, where the liquid/solid (L/S) ratio proved to be a crucial parameter. Beneduci et al. (2012) stabilized crops with Fenton's process in 6 h of treatment, and the final compost showed to be odourless and with low humidity. Also Quina et al. (2015) showed the benefits of using Fenton-like processes to stabilize digestate from anaerobic digestion of the organic fraction of municipal solid wastes. Therefore, this technology appears as a promising alternative for wastes stabilization. However, solid waste stabilization by Fenton's peroxidation seems to be few studied and the integration of iron solid wastes as a catalyst for the chemical stabilization of another waste may open a new path for waste recovering and valorisation (a good example of industrial ecology).

The carried research aims to study the chemical stabilization by Fenton's process as a treatment for OMSW, using iron wastes as catalysts and using nZVI for catalyst comparison purposes.

2. Materials and Methods

2.1 Materials

The olive mill solid waste (OMSW) considered in this study was collected from a Portuguese two-phase olive mill industry. In addition, three iron-rich wastes were selected as iron source, namely neutralized acid mine drainage (AMD) sludge, Fenton's process sludge (FSW) and iron powder (IPW) from a metallurgical industry.

2.2. nZVI preparation and characterisation

The synthesis of nZVI was performed by the reduction of FeCl_3 with NaBH_4 according to the methodology proposed by Wang and Zhang (1997). In 400 mL of distilled water (DI), 4.25 g of NaBH_4 (Sigma-Aldrich, 98%) were dissolved and then added at 6.8 mL/min to a 13.5 g/L $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Riedel-de Haën, > 99%) aqueous solution. The mixture was vigorously mixed at 200 rpm until all NaBH_4 was poured. After the synthesis, Fe^0 was collected by centrifugation (Nahita centrifuge, model 2655) at 3500 rpm for 5 min in falcon tubes with 45 mL of suspension. Following the discharge of the supernatant, the washing process relied on adding 15 mL of ethanol (Panreac, 99.5%) to each falcon tube and the process was repeated twice. Finally, Fe^0 was stored by adding ethanol (~15 mL) to the centrifuged sample.

Morphology and size distribution of nZVI were characterized using transmission electron microscopy (TEM), dynamic light scattering (DLS) and specific surface area of Brunauer Emmett and Teller (BET). TEM images were recorded by TECNAI G2-FEI operated at 200 kV. The preparation of samples consisted in the immersion of the carbon coated TEM grid onto 3 mL of ethanol slurry of Fe^0 particles, previously sonicated for 10 min with 2 drops of 1-butanol (99.7%), and drying in a vacuum-desiccator overnight. Chemisorption surface area analyzer Micromeritics ASAP 2000 was used to determine the specific surface area with the BET methodology, where samples were dried in a vacuum desiccator overnight, degassed at 90 °C for 1 h and then at 200 °C for 4 h. Particle size by DLS was measured with the Zetasizer apparatus mentioned above using the option of backscattering light (90°). Samples were prepared by diluting aliquots of Fe^0 slurry (after sonication) in DI water. Zeta potential, ξ , was measured by Laser Doppler Electrophoresis using a Zetasizer Nano-ZS - Malvern Instruments. Samples were prepared by adding 15 mg of dried particles to 500 mL DI water, with mechanical agitation and 10 min of sonication previous to sample withdrawal. The reactivity of Fe^0 was evaluated based on H_2 generation according to Eq. (1).



The procedure consisted of introducing 10 mg of powder Fe^0 into 10 mL glass vial and closed it with a rubber cap to avoid leakage of H_2 . Then HCl in excess (Panreac, 37%) was injected into the vial with a syringe. Hydrogen volume released according to Eq. (1) was measured in a graduate syringe, during 30 min of reaction. Since experiments were carried out under ambient conditions (25 °C, 1 atm), the amount of iron was estimated by the ideal gas law,

admitting the number of moles of zero-valent iron is equal to number of moles of H_2 released in the reaction.

2.3. Characterisation of wastes

Moisture content (MC) was determined by standard oven method (drying the sample at 105 °C until constant weight), and the percentage of total solids (TS) as 100-MC. Organic matter was assumed as volatile solids (VS) which were determined by drying the sample in a muffle furnace at 550 °C until constant weight (1 h). pH and electric conductivity (EC) were measured with Consort C863 Multi-parameter analyser, in a suspension of a liquid to solid ratio (L/S) of 10 mL/g. Chemical oxygen demand (COD) in solids (g O_2 /kg TS) was assessed based on the method developed by Noguerol-Arias et al. (2012). A suspension of 1.5 mg of sample and 398.5 mg of distilled water was prepared. Then, 3.6 mL of acid solution (90.4%w/v H_2SO_4 and 9.6%w/v $AgSO_4$) and 3.6 mL of 0.25 M K_2CrO_7 was added to this suspension. The calibration curve was obtained with potassium hydrogen phthalate ($C_8H_5KO_4$). The sample was in the Thermoreactor CR3000 (WTW), for 2 h at 150 °C, and after cooling the absorbance was measured at 605 nm in COD Photometer MPM 3000 (WTW). Soluble chemical oxygen demand (SCOD) was also determined for iron-rich wastes according to the 5220D Standard Method (Standard Methods, 1992). Liquid samples were also in this case digested with dichromate in the thermoreactor, during 2 h at 150 °C and COD was directly measured by the photometer at 605 nm.

Total Kjeldahl nitrogen (TKN) was quantified with Velp Scientifica equipment by digestion of the sample, distillation and titration with HCl. Total phenolic content (TPh) of OMSW was determined following the procedure indicated by Goldsmith et al. (2014), which involves the preparation of a suspension of 2 g of OMSW and 12 mL of methanol:water 80:20 (v/v). This sample was vortexed for 2 min, ultrasonicated for 15 min and centrifuged at 3000 rpm for 25 min. The extract was filtered and 300 μ L of Folin Ciocalteu's reagent was added to an aliquot of 300 μ L and equilibrated for 2 min. Finally, 2.4 mL of 5% of sodium carbonate was added and kept in dark conditions for 1 h. The absorbance at 760 nm was measured using a UV-Vis T60 spectrophotometer, and the results converted in mg of gallic acid equivalents (GAE) per g ST (dw).

The total content of iron in the wastes (AMD, FSW and IPW) was determined by flame atomic absorption spectrometry (Perkin-Elmer 3300) after acid digestion of 0.5 g of material with aqua regia. Elemental analysis using the EA 1108 CHNS-O-Fison equipment was conducted

to determine the C, H, N and S content of materials. Phytotoxicity bioassays were carried out to evaluate the potential for inhibition of seed germination. Garden cress (*Lepidium sativum*) seeds were used and germination index (GI) calculated by combining the percentage of germination and the percentage of radicle length in relation to blank tests (Trautmann and Krasny, 1997). The results were interpreted according to the Zucconi et al. (1981) classification.

2.4 Chemical oxidation procedures

Chemical oxidation of OMSW was based on Fenton's reaction conducted in batch mode using a three entrances reactor of 0.5 L. Thus, the treatment was applied in semi-solid phase. Firstly, the operating conditions were optimized varying the amount of catalyst (iron sulphate heptahydrate: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as well as the amount of H_2O_2 in aqueous phase between 5 and 50 g H_2O_2 kg TS⁻¹. The vessel was under stirring and two of the three entrances of the reactor were closed to avoid CO_2 leakages during oxidation, whereas the other entrance was connected to two scrubbers placed in series and partially filled with 0.5 M NaOH, where the CO_2 released was captured. About 20 g (dry basis) of OMSW, previously mixed with distilled water, were placed into the reactor with L/S 5 L kg⁻¹, and the pH was adjusted to 3 using 1 M H_2SO_4 . Preliminary tests showed that 15 min of peroxidation was enough in terms of reaction time. Finally, it was concluded that the best operating conditions were L/S 5, H_2O_2 (33% w/v) concentration of 25 g/kg TS, Fe(II) concentration of 5.45 g/kg TS in acidic medium (pH 3), atmospheric pressure and room temperature. Then, experiments were performed in these operating conditions by using as iron sources AMD, FSW and IPW and also nZVI.

The performance of the Fenton's method was assessed by capturing the carbon released as CO_2 , C- CO_2 , which was calculated according to:

$$C - \text{CO}_2 (\text{mg}) = \left(\frac{V_{\text{NaOH}} \cdot C_{\text{NaOH}}}{1000} - \frac{V_{\text{HCl}} \cdot C_{\text{HCl}}}{1000} \right) \frac{1}{2} \cdot 12 \times 10^3 \quad (1)$$

where V_{NaOH} and C_{NaOH} are the volume (mL) and concentration of NaOH (M) in the solution placed in the gas scrubbers, V_{HCl} and C_{HCl} are the volume (mL) and concentration of HCl (M) solution used in titration, 1000 is the conversion factor from mL to L, $\frac{1}{2}$ is related to the stoichiometry of the reaction, and 12×10^3 is the molar weight of carbon (mg mol^{-1}).

3. Results and Discussion

3.1 Characterisation of wastes and nZVI

3.1.1 Olive mill solid wastes (OMSW)

Olive mill solid waste (OMSW) was collected from a Portuguese olive mill that operates based on a two phase system. This waste is well known by its richness in organic matter and phytotoxicity due to polyphenols, organic acids and lipids that may lead to important environmental problems. Table 1 shows the main physic-chemical characteristics of this material and compares with others reported in literature.

As it can be observed, the waste composition is very variable depending upon the type of olive culture and oil extraction techniques. Nevertheless, some general remarks can be taken. In fact, OMSW shows a strong organic load as it is reported by the VS and COD values (98.9% and 4107 gO₂/kgTS). These values are coherent with the results presented in literature. For example, Fezzani and Cheikh (2008) report 97.5% and 1100 gO₂/kgTS for those parameters. However, Fernández-Rodríguez et al. (2014) refer a much lower COD value (331.1 gO₂/kgTS). According to the pH values determined (which are very similar to those found in literature), OMSW is a slightly acidic waste. Given its content in organic matter, inorganic nutrients (namely K) a common practice to manage of this kind of waste consists on its deposition in the farm land. Under specific conditions it has been used as soil amendment. In this context, it is of extreme importance to quantify the potential impact over plants growing. For this, phytotoxicity was appraised regarding germination of *Lepidium sativum* seeds. A GI index of about 68% (compared with the blank) was determined, being near the value reached by Aviani et al. (2010). This means that the waste is moderately phytotoxic (Trautmann and Krasny, 1997) and should not be directly disposed into the soil. These results highlight the relevance of investigating suitable technology able to minimize the potential impact of these wastes over the ecosystems.

Table 1 – OMSW main physic-chemical characteristics (mean±sd)

Parameter	This work	Fezzani and Cheikh (2008)	Aviani et al. (2010)	Fernández-Rodríguez et al. (2014)	Droussi et al (2009)
Moisture (%)	4.75 ± 0.27	-	-	-	26.2
VS (%)	98.9 ± 0.24	97.5 ± 0.5	-	23.5	97.27
pH	5.3 ± 0.01	-	5.6	4.9	5.88
EC(μS/cm)	996 ± 15	-	213	-	3330
TKN (g/kgTS)	8.6±0.9	12 ± 0.5	-	-	7.0

TPh (mg GAE/g TS)	0.45±0.07	-	-	-	0.35
COD (gO ₂ /kg)	4107 ± 89	1100 ± 5	-	331.1 ± 0.7	-
GI (%)	68	-	52.66	-	-

3.1.2 Iron-rich solid wastes

Three wastes were selected to be tested as catalysts in the Fenton's oxidation of OMSW due to their richness in iron. Neutralized acid mined drainage (AMD) is a waste for which still there is not a suitable valorization strategy. Fenton's sludge (FSW) is a solid by-product from wastewater treatment through Fenton's process. Iron powder (IPW) is a waste resultant from surface treatments processes. Table 2 summarizes the main characteristics of these materials.

Table 2 – Iron rich wastes main physic-chemical characteristics (mean±sd)

Parameter	AMD	FSW	IPW
Moisture (%)	4.46 ± 0.48	52.10 ± 2.33	0.71 ± 0.04
VS (%)	17.1 ± 8.3	52.8 ± 0.8	0.0 ± 0.1
pH	6.4± 0.4	7.0± 0.1	7.0± 0.3
EC(μS/cm)	4960 ± 10	2670 ± 19	160 ± 5
SCOD (mgO ₂ /L)	95.4 ± 5.0	2752 ± 56	96.6 ± 5.5
Fe (g/kgTS)	588.3 ± 6.2	343.1 ± 31.4	899.2 ± 43.0

As expected, FSW shows a strong organic load (VS = 52.8 % and SCOD = 2752 mgO₂/L). In fact, this waste is obtained from the treatment of liquid effluents through Fenton's process. In this technology, iron salts are dissolved in the wastewater to act as catalysts to promote hydrogen peroxide decomposition into hydroxyl radicals (HO[•]) that will oxidize organic matter. At the end of the process, for iron separation, an alkaline agent is applied to produce the insoluble Fe(OH)₃ that will precipitate. This surely leads to the coagulation of some dissolved organic matter that is dragged to the sludge increasing its organic load. The other two wastes, due to their inorganic nature show a much lower organic content.

All the wastes present a high load in iron which can be beneficial for the Fenton's process. However, it can be highlighted IPW has the highest iron content (899.2 ± 43.0 g/kg) followed by AMD (588.3 ± 6.2 g/kg) and FS (343.1 ± 31.4 g/kg).

3.1.3 Nanoscale zero-valent iron (nZVI) particles

Fig. 1 shows TEM images of the synthesized Fe⁰, which are mainly spherical as expected according the typical morphology of iron nanoparticles formed in solution (Sun et al. 2006). The nanoparticles are aggregated due to their magnetic properties (Jones et al. 2001), forming

big chain-like structures, whereas each nanoparticle is the base unit of the bulk structure attached to others nanoparticles.

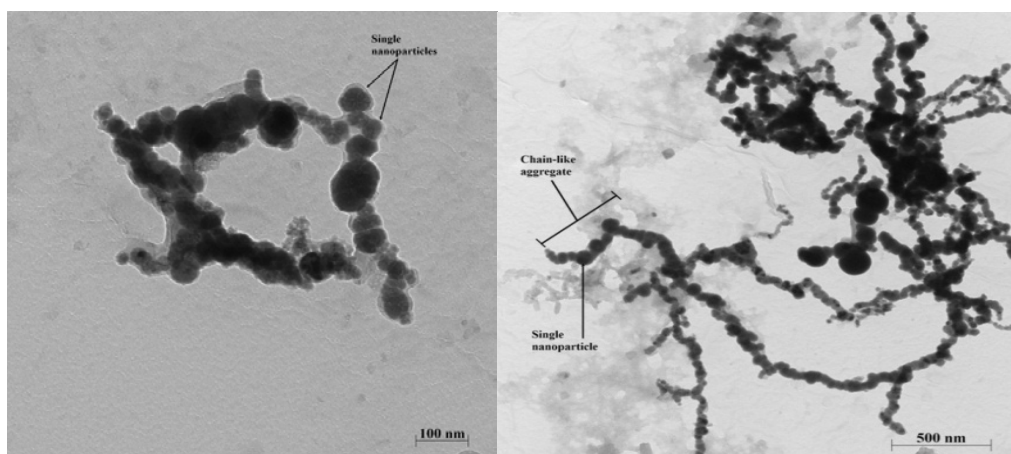


Figure 1- TEM images of the synthesized nanoparticles.

Nanoparticles were characterized according to their size distribution using three different techniques, TEM, DLS and BET surface area (Table 3). According to TEM results, nZVI has a large range of size distribution, which exceeds the nanoscale when approaching the upper limit. This is probably caused by the agglomeration associated with uncoated nanoparticles. However, 90% of the synthesized particles have diameters smaller than 102.5 nm (Fig. 2) and the mean particle size diameter, D_p , is 51.9 ± 33.2 nm.

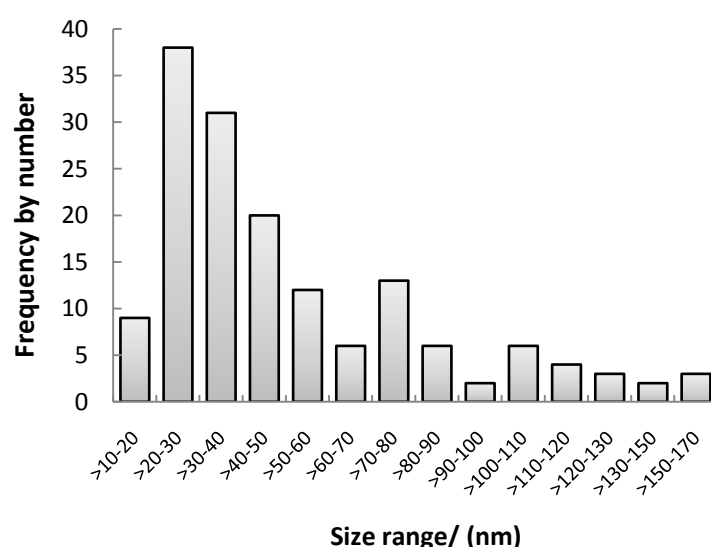


Table 3- Particle size and surface area according to different techniques.

TEM results		BET results		
n	D _p (nm)	S _{BET} (m ² /g)	D _{p-shell} (nm)	D _{p_nshell} (nm)
155	51.9 ± 33.2	46.94	19.1	16.4

The measure of the hydrodynamic diameter with the DLS technique proved to be challenging and despite several attempts the values obtained using DLS did not pass the quality criteria, hence are not presented. Domingos et al. (2009) observed that light scattering techniques need high particles density for the analysis, which in our case contributes to nanoparticle aggregation and sedimentation and makes measurements highly uncertain. Filtering the suspension prior to DLS determination has been reported to eliminate particles larger than 200 nm (Goldstein and Greenlee, 2012), well outside of the nanorange. However, results show that agglomeration occurs during analysis, as particles larger than 200 nm still show up in the DLS results. Thus, the results of the DLS technic should be used with care when used with magnetic Fe⁰, and it is likely that the size diameter measurements by TEM to be more reliable. An estimate of the particle diameter (D_p) can be made from the BET values using the density value. Since nanoparticles present a core/shell structure, a density of 6700 kg/m³ is used as the average density value between Fe⁰ and Fe₃O₄(Nurmi et al., 2005). The results considering the existence (D_{p-shell})and the absence (D_{p_nshell}) of a Fe₃O₄ shell are also reported in Table 3.

As nanoparticles age, a layer of oxides is formed on the surface. The smaller the amount of oxides, the more reactive nanoparticles are because more Fe⁰ is available at the surface to reduce pollutants. When the metallic iron reacts with HCl, the H₂ released is directly proportional with the zero-valent iron content in the nanoparticles (Eq. 1). Hence, by using the hydrogen generation test it is possible to quantify the reactivity of a suspension of Fe⁰ and its evolution over time, and estimate nanoparticle's behaviour during environmental applications. Fig. 2 shows the aging of the produced nZVI nanoparticles over time. The initial volume of H₂released was about 5 mL, which meansa ratio per mass of Fe⁰of 0.50 mL/mg. The gas released decreased about 40% in 44 days.

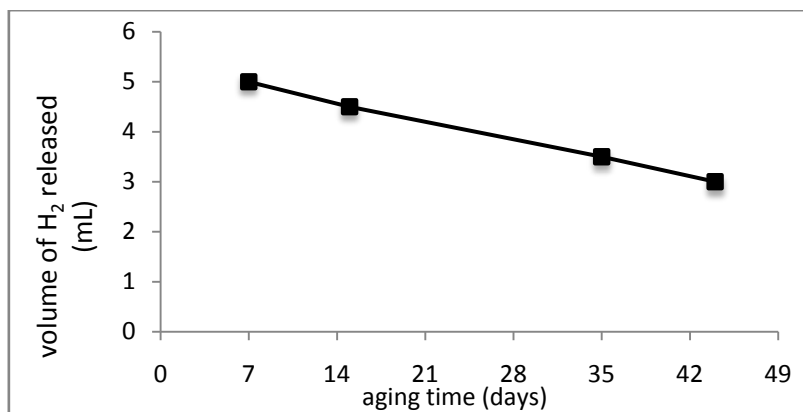


Figure 2. Volume of H₂ gas released in the reactivity test for nZVI for 44 days.

3.2. Optimisation of the chemical treatment

As referred in the introduction, it is increasingly important to implement the concept of industrial ecology to promote resources efficiency and environmental management. In this scope, this study tries to evaluate the possibility of using iron-rich wastes as source of iron to Fenton's process. In this first approach, the aim was to conclude about the impact of the key parameters (catalyst and hydrogen peroxide load) over the performance of Fenton's oxidation on the chemical stabilization of OMSW.

The iron source in these experiments was the classical Fenton's catalyst FeSO₄. The selection of the hydrogen peroxide and iron conditions were selected based on the optimal results reported by Neyens and Baeyens (2003). In their work, the best oxidation conditions were 25 gH₂O₂/kgTS and 1.67 gFe²⁺/kgTS. However, one should consider that the sludge applied in that work already presented some iron in its composition (which will also act as catalyst) while OMSW showed a negligible amount of that metal. In this context, the load of iron used was corrected bearing in mind this question. Table 4 summarizes the experiments performed and the conditions applied in which experiment.

Table 4- Experimental conditions tested for optimizing the chemical treatment

Operation parameter	Experiment							
	E1	E2	E3	E4	E5	E6	E7	E8
[H ₂ O ₂] (g H ₂ O ₂ /kg TS)	5	5	10	10	25	25	50	50
[Fe ²⁺] (gFe ²⁺ /kgTS)	5.5	8.2	5.5	8.2	5.5	8.2	5.5	8.2
L/S	5	5	5	5	5	5	5	5
pH	3	3	3	3	3	3	3	3
Reaction time (min)	15	15	15	15	15	15	15	15

To analyse the efficiency of the treatment process, the amount of organic carbon removed (measured by the carbon dioxide released), the solid COD and the VS were followed. Fig. 3 shows the amount of organic carbon ($\text{C-CO}_2/\text{gC}_{\text{org}}$) abated after 15 min of reaction as function of the hydrogen peroxide load at two different iron concentrations.

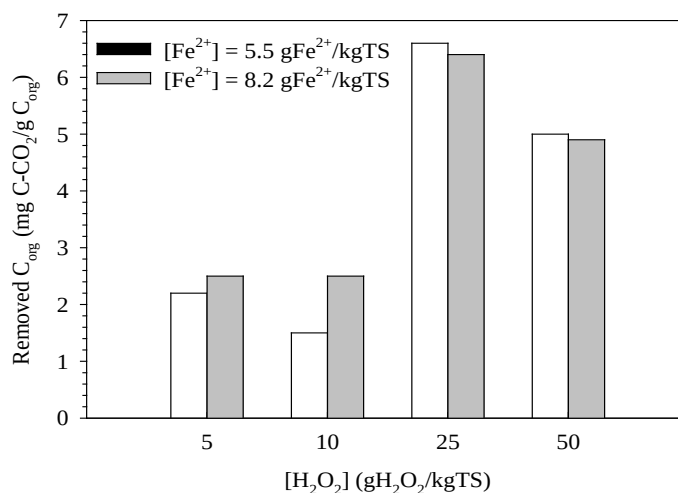


Figure 3- Effect of H_2O_2 concentration on the amount of organic carbon removed.

From these results it can be concluded that this waste presents a low load in oxidizable organic matter. In fact, the maximum CO_2 production achieved is about $6.6 \text{ mg C-CO}_2/\text{gC}_{\text{org}}$ while, in a previous work, a carbon dioxide release of about $20 \text{ mg C-CO}_2/\text{gC}_{\text{org}}$ was detected for the chemical oxidation of anaerobic digestate (Quina et al., 2015) using similar operating conditions. Moreover, it can be observed a similar degradation trend for both iron levels applied. In what regards the impact of hydrogen peroxide dose, the CO_2 production increases with the increase of oxidant applied until $25 \text{ gH}_2\text{O}_2/\text{kg TS}$. After this, the process efficiency decreases which must be related with the radical scavenger effect observed when hydrogen peroxide is in excess. This is related with the reaction of H_2O_2 with the produced hydroxyl radicals leading to the production of hydroperoxyl radicals with a much lower oxidation capacity.

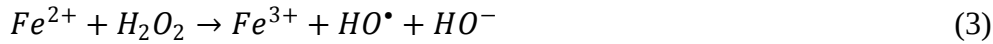
Thus, among the tested operating conditions, the best cost/efficiency ratio is obtained when applying $25 \text{ gH}_2\text{O}_2/\text{kgTS}$ and $5.5 \text{ gFe}^{2+}/\text{kgTS}$ since the increase on these parameters lead only to slight improvements on the treatment efficacy.

3.3. Screening of iron-rich catalysts for chemical treatment

Bearing in mind the best experimental conditions determined before, Fenton's process was now applied using as iron source the selected iron wastes. The amount of waste used corresponded to an iron load of 5.5 gFe²⁺/kgTS while hydrogen peroxide dose was fixed at 25 gH₂O₂/kgTS. Fig.4 shows the percentage of shows the amount of organic carbon (C-CO₂/gC_{org}) released after 15 min of Fenton's peroxidation using the different wastes as catalyst. For comparative purposes the results attained for the same conditions with iron sulphate are also shown.

Among the iron rich wastes applied, IPW revealed the best efficiency as catalyst on the removal of C_{org} (about 4 mgC-CO₂/ gC_{org}) from the OMSW with a similar behavior to the one observed for the traditional iron catalyst (iron sulphate).

The oxidation state of the iron is an important feature of the catalyst used in the oxidation. In fact, the hydrogen peroxide decomposition in hydroxyl radicals is promoted by Fe²⁺ according to Eq. (3) (Neyens and Baeyens, 2003).



Bremmer et al. (2006) verified that Fenton's peroxidation could be improved by using zero valent iron that at acidic conditions would generate Fe²⁺:



Moreover this strategy allows a faster recycling of the ferric iron into Fe²⁺ at the zero through zero valent iron without the waste of hydrogen peroxide molecules:



This may explain the efficiency of IPW in Fenton's process once this waste (due to its metallic nature) is mainly composed of zero valent iron.

The application of nanoscale zero valent iron (nZVI) further improved the process leading to about 7.1 mgC-CO₂/ gC_{org} removed in 15 min. It seems thus that the size range of the particles can play a key role on the treatment efficiency.

It should be, however, referred that further optimization tests are being performed namely to infer about the impact of the oxidation systems over the OMSW GI.

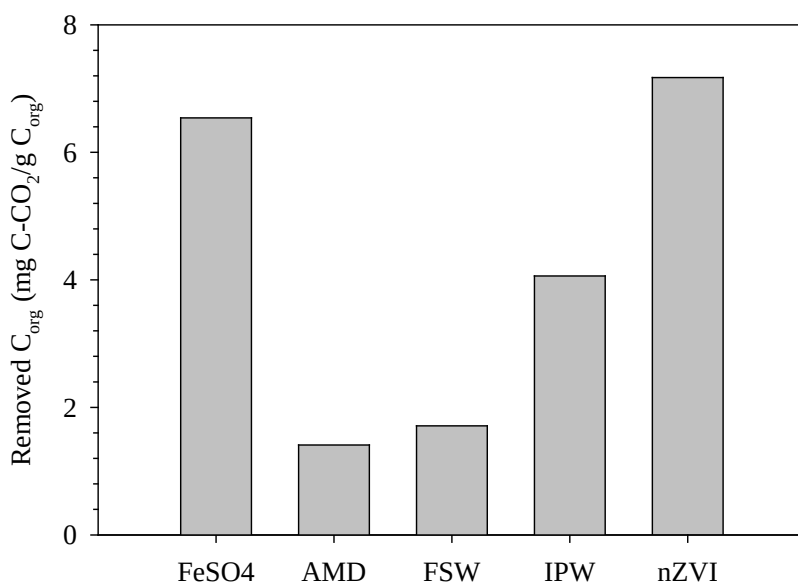


Fig. 4 – C_{org} removed using different sources of iron.

4. Conclusions

The aim of the present work was to analyse the behaviour of Fenton's peroxidation on the chemical stabilization of OMSW. The raw OMSW shows a strong organic load and some phytotoxicity associated with a relatively low GI.

The application of Fenton's process using its conventional catalyst (FeSO₄) was able to remove up to 6.6 mgC-CO₂/ gC_{org} when a hydrogen peroxide load of 25 gH₂O₂/kgTS was applied.

Some iron rich solid wastes were selected in order to identify the most promising to act as catalytic material in the OMSW stabilization. Among them, IPW revealed to lead to the highest C_{org} abatement (4 mgC-CO₂/ gC_{org}). This efficiency must be related with the fact that IPW is rich in zero valent iron that is known by its ability to improve the treatment process since it enhances Fe³⁺ reduction into Fe²⁺ leading to a faster catalyst recycling. In fact, the use of synthesized nanoscale zero valent iron particles (nZVI) showed the best OMSW degradation (7.1 mgC-CO₂/ gC_{org}).

The results obtained lead to the conclusion that the IPW and nZVI can be envisaged as potential catalysts for the chemical stabilization of OMSW. Nevertheless, further optimization studies are being performed, given particular relevance to the effect of the treatments over the waste GI. This is an important parameter since OMSW is likely to be applied as a soil amendment and, therefore, its impact over germination is a crucial issue.

Acknowledgments

This work is funded by the European Regional Development Fund (ERDF) through COMPETE – Operational Programme for Competitiveness Factors (OPCF), and by Portuguese National funds through the FCT – Fundação para a Ciência e a Tecnologia, under the Project PTDC/AGR-AAM/101643/2008 NanoDC. C. Dias-Ferreira gratefully acknowledges the FCT - Fundação para a Ciência e a Tecnologia for the financial support (SFRH/BPD/100717/2014). R.C. Martins gratefully acknowledges the FCT for the financial support under the IFCT contract (IF/00215/2014).

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