Zero valent iron (ZVI) mediated Fenton degradation of industrial wastewater: Treatment performance and characterization of final composites

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HIGHLIGHTS

- Cost-effective technology for the treatment of a wastewater generated by a drug manufacturing plant.
- 60% TOC mineralization and a remarkable enhancement of the biodegradability.
- Different iron/hydrous oxides cover the metallic ZVI final composite.

ARTICLE INFO

ABSTRACT

A heterogeneous advanced Fenton process (AFP) based on the use of zero valent iron (ZVI) has been investigated for the treatment of a real industrial wastewater, generated from a drug manufacturing plant. The effluent consists of a complex mixture of organic substances which are refractory to conventional treatments. The concentration of ZVI and oxidant (H_2O_2) were studied. The use of moderate concentrations of oxidant and ZVI commercial catalyst led to total organic carbon (TOC) reductions of 70% and 55% of diluted (TOC_0 0.1 g L^{-1}) and as-received pharmaceutical wastewater (TOC_0 5 g L^{-1}), respectively, with a remarkable enhancement of the biodegradability in all cases. Apart from that, it was demonstrated a notable effect of the magnetic agitation system (speed and size of the stir bar) on the catalytic performance of the ZVI/H_2O_2 system. The aggregation of ZVI particles on the magnetic stir bar surface, due to its intrinsic magnetic properties makes that the availability of active ZVI particles was somewhat controlled by the size of the magnetic stir bar. For the best operation conditions, a higher TOC conversion was accomplished during the first minutes of reaction, slowing down afterwards, probably due to passivation of the ZVI catalyst. The different stratified layers of iron/hydrous oxides covering the metallic ZVI surface formed under the different reaction conditions were studied by XRD, TPR and XPS characterization techniques.

1. Introduction

Over the last century vast quantities of industrial wastewater have been directly discharged to surface water causing negative effects to the ecosystems and human's life. Each industrial sector produces its own particular combination of contaminants, so the treatment of those effluents must be designed specifically for the particular type of effluent produced. Pharmaceutical waste is one of the most complex and toxic industrial wastes [1].
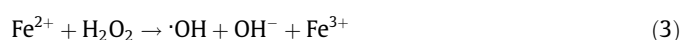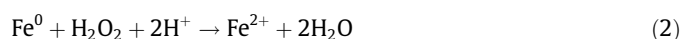
Although biological processes are commonly used for the domestic and industrial wastewater treatment due to its simplicity and because efficiently mineralize different types of organic constituents, the treatment of industrial wastewaters by conventional biological process is difficult due to the presence of toxic, persistent and inhibitory organic compounds [2–4]. Then, different pre-treatment technologies, including Advanced Oxidation Processes (AOPs), have been extensively reported in literature [5]. The AOPs have been found to be successful for the abatement of those organic pollutants in water and wastewater, being mostly used in combination with conventional biological and chemical methods [6]. Various pre-treatment technologies for enhancing the biodegradability in wastewater have been reported including Fenton [7,8], ozonation [9,10] or photocatalysis [11]. However, most of the AOPs are cost intensive operations and the time of treatment is a limiting factor in the overall cost. Fenton processes are

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considered as a viable solution for the removal of a great variety of organic pollutants [12]. Nevertheless, the major drawbacks of the conventional Fenton process are that it operates at the optimum pH of 3 and uses amounts in excess of ferrous ions. Therefore, alternatives such as the heterogeneous zero-valent iron (ZVI) particles have been lately evaluated [13,14]. In the ZVI/O_2 process, dissolved oxygen (DO) was continuously activated by ZVI to produce reactive oxygen species (ROS) at ambient pH, temperature and pressure. Although the nature of ROS (reactive oxidant species) is still unclear, their production most likely involves the three steps: ZVI oxidation, formation of H_2O_2 and Fe(II), and reactive oxygen species production through Fenton-like chemistry. Hydrogen peroxide is formed on the surface of ZVI by two-electron reduction of O_2 (Eq. (1)). The hydrogen peroxide so produced is either reduced to water by another two-electron transfer from ZVI (Eq. (2)), or is converted into reactive oxidants such as hydroxyl radical ·OH (or ferryl ion) by reaction with Fe(II) (Eq. (3)):

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{1}$$

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow {\cdot}OH + OH^- + Fe^{3+} \tag{3}$$

The ZVI/O_2 is an interesting system that can remove a variety of organic and inorganic chemical compounds and bacterial indicators. However, the low yields of reactive oxidants can limit the application of this system, especially for the treatment of real wastewater [15]. The loss of hydrogen peroxide by two-electron reduction (Eq. (2)) is the cause and the passivation of ZVI surfaces and the co-precipitation of Fe(II) and Fe(III) species at neutral pH are also partially responsible. Therefore, in order to improve the oxidant production, several approaches such as the addition of iron chelating ligands [16] and the introduction of secondary metal [17] have been attempted. Also, the addition of hydrogen peroxide to the system increases the ROS production.

Although the ZVI systems have been successfully applied for water treatments, only a few studies have been carried out using real industrial wastewater [18]. The majority of the reported literature deals with simulated effluents or model pollutants such as heavy metals, formic acid, phenol or dyes [19,20], and the results may, or may not, be reproduced for real industrial applications. To the best of our knowledge, the characterization of the final ZVI composite obtained after the treatment of real industrial wastewaters has also been barely investigated. The aim of this work is to bring new insights into the degradation of a highly organic-loaded industrial effluent using ZVI, evaluating the experimental parameters not only in terms of TOC removal but also the characterization of the ZVI final composite.

2. Materials and methods

2.1. Regents

Hydrogen peroxide (Scharlab, 30% pure) and iron metal powder ZVI (Sigma–Aldrich, 97% pure) were used as purchased. ZVI specific surface area and particle size were 5 m^2/g and 4.5–5.5 μm, respectively.

2.2. Experimental set-up

In a typical experimental set-up, a cylindrical glass vessel was filled with 0.5 L of the pharmaceutical wastewater (PWW). The wastewater was previously diluted 1/50 until initial TOC of ca. 0.1 g L^{-1}, unless otherwise specified. Thereafter, appropriate amounts of hydrogen peroxide and zero-valent iron (ZVI) were added in the presence of aeration with a flow rate of 5 L min^{-1}. The temperature was controlled at 22 ± 2 °C during the reaction. The pH was kept uncontrolled during all the experiments. The amount of initial hydrogen peroxide was equivalent to the stoichiometric amount, half or twice (coded as 100%, 50% or 200%, respectively) for the complete mineralization of the carbon content present in the wastewater to CO_2 and H_2O, following Eq. (4):

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O \tag{4}$$

The reaction medium was agitated in a cylindrical glass vessel of 12 cm diameter using magnetic stir bars of 1, 4 or 6 cm length coded as small, medium or big size, respectively. The total organic carbon (TOC) content, the hydrogen peroxide conversion, the iron dissolved and the pH of the wastewater were monitored throughout the reaction time. Samples were filtered through 0.22 μm nylon membranes prior to analysis. TOC was measured using a combustion/non dispersive infrared gas analyzer model TOC-V (Shimadzu). Hydrogen peroxide concentration was determined by iodometric titration and the iron dissolved in the filtered solution after reaction was quantified by ICP-AES analysis using a Varian Vista AX spectrometer. The pH of the solution was measured using a Metrohm pH meter.

2.3. Characterization techniques

The ZVI powder before and after the treatments were characterized by X-ray powder diffraction (XRD) and temperature programmed reduction (TPR) in order to evaluate the crystalline phases and the oxidation state of the iron species formed. XRD recorded in the 2θ range from 10° to 70° were obtained with a Philips X-Pert diffractometer using Cu Kα radiation. Temperature programmed reduction (TPR) was performed in a Micromeritics Autochem 2910 instrument. The samples were heated from 50 to 900 °C (heating rate 10 °C/min) under a hydrogen–argon mixture (10% H_2) with a flow rate of 40 mL/min. X-ray photoelectron spectroscopy (XPS) analyses were performed in a VG Escalab 200 R spectrometer provided with Mg Kα radiation (1253.6 eV) source, a hemispherical electron analyser and a five channeltron as detection system. Photoelectrons were probed at a takeoff angle of 45°, while the analyser was opened with constant pass energy of 50 eV. Under these conditions, the resolution as measured by the full width at half maximum (FWHM) of the Au4f7/2 core level was 0.86 eV. The binding energies were referenced to the C1s peak at 284.8 eV due to adventitious carbon. This reference gave binding energies values with accuracy of ±0.1 eV. The spectra were decomposed with the least square fitting routine using Gaussian/Lorentzian lines and after subtracting a Shirley background. Atomic fractions were calculated using peak areas normalized on the basis of sensitivity factors [21].

3. Results and discussion

3.1. Characterization of the pharmaceutical wastewater

The drug manufacturing plant located in Toledo (Spain) is dedicated to producing different active drugs for heart-diseases, osteoporosis and anti-depressive compounds. Various types of waste streams are generated by this plant depending upon the manufacturing process. All mixed streams were firstly treated in the pharmaceutical plant to recover volatile solvents.

The resulting effluent was collected to be studied herein. It contains ca. 5 g/L of TOC and 15 g/L of COD with low biodegradability as the BOD_5/COD was 0.18 (Table 1).

Table 1
Physico-chemical characteristics of the industrial wastewater.

pH	6.50 ± 0.5
BOD_5 (mg L^{-1})	2700 ± 150
COD (mg L^{-1})	$15,000 \pm 100$
BOD_5/COD	0.18
TOC (mg L^{-1})	4700 ± 100
Turbidity (NTU)	267 ± 1
Conductivity (mS cm^{-1})	70.0 ± 1

3.2. Preliminary blank experiments

The efficiency of the ZVI/H_2O_2 system was initially studied under acidic pH (3), 2.4 g/L of ZVI and stoichiometric amount of the hydrogen peroxide (100%) for the treatment of diluted pharmaceutical wastewater (0.1 g/L of TOC). This system was evaluated by comparing the catalytic performance of the $Air/ZVI/H_2O_2$ system with several blank experiments: (i) only aeration in order to check the possible stripping of volatile pollutants (without H_2O_2 nor ZVI), (ii) aeration in the presence of ZVI without H_2O_2, in order to evaluate the oxidizing power of the Air/ZVI system, and (iii) aeration in the presence of H_2O_2 without ZVI, in order to determine the oxidizing potential of H_2O_2 in a non-catalytic Air/H_2O_2 system.

All the experiments were carried out using a magnetic stirring at 500 rpm. Those blank reactions were compared to the results obtained for the ZVI/H_2O_2 system under the same conditions, with and without aeration. Table 2 shows the TOC and hydrogen peroxide conversions, the pH values and concentration of dissolved iron for the above mentioned conditions after 2 h of treatment. It must be noted that experiments of the $Air/ZVI/H_2O_2$ system and the other blank reactions were performed in triplicate in order to evaluate the reproducibility of the experiments. The standard errors of the monitoring parameters were of ca. 10% for the TOC and H_2O_2 conversions and 4% and 6% for the pH and the iron dissolved of the aqueous solution, respectively.

The aerated blank experiment in the absence of H_2O_2 and ZVI revealed no significant reduction of the TOC content with only 8% removal after 120 min. In fact, these results were expected as the pharmaceutical effluent was previously treated by stripping within the pharmaceutical plant, to recover volatile organic solvents. It was also remarkable that no significant differences were obtained in terms of TOC for the aerated blank experiments when using only ZVI (without H_2O_2) or H_2O_2 (without ZVI), obtaining 7% and 11%, respectively after 120 min. Regarding the oxidant conversion, 83% after 120 min was reached when using Air/H_2O_2 system, indicating a non-efficient use for the mineralization of the organic matter. These results demonstrated the negligible effects of the hydrogen peroxide as oxidant and ZVI alone under aerated conditions for the wastewater treatment, unlike the promising results reported in literature for the Air/ZVI system in the degradation of model pollutants [22]. However, when the $Air/ZVI/H_2O_2$ was applied, TOC degradation of almost 50% was obtained, in contrast to the ca. 34% TOC mineralization in the ZVI/H_2O_2 system without aeration. Moreover, the $Air/ZVI/H_2O_2$ system showed a total conversion of the oxidant, being more efficiently used according to

the TOC reduction. Likewise, the iron dissolved in the wastewater from the ZVI was relatively low for the $Air/ZVI/H_2O_2$ system (10 mg/L) taking into account the residual iron content of the own wastewater (3 mg L^{-1}) as revealed the iron concentration of the blank experiments when ZVI was not used (Table 2). Note also that the aeration does not affect the leaching of ZVI with non-additional increase of the iron concentration in the wastewater. It is also important to remark the evolution of pH values. They kept acid throughout time for the Air/H_2O_2 (without ZVI) and aeration (without ZVI nor H_2O_2) systems with final values of 2.9 and 3.1 after 120 min, respectively. However, in the presence of ZVI, the pH increased up to 6.0 and 6.1 after 120 min for the Air/ZVI and $Air/ZVI/H_2O_2$ systems, respectively, as hydrogen peroxide is consumed. The increase of pH along the reaction is the main reason of the precipitation of oxidized iron species to iron oxy-hydroxides leading to low iron leaching from ZVI in the wastewater after the treatment.

3.3. Influence of the initial oxidant and ZVI catalyst concentrations

The influence of different initial oxidant dosages and ZVI concentrations was studied for the treatment of 0.1 g L^{-1} TOC with the aim of obtaining maximum degradations in terms of TOC conversions and reducing costs of treatments.

It is shown that the TOC removal was enhanced as the concentration of ZVI increased from 0.6 to 1.2 and 2.4 g/L (Fig. 1a) obtaining TOC conversions of 35%, 47% and 50%, respectively, after 2 h of treatment. This is in agreement with data found in the literature, where it is stated that increasing the ZVI dosage increases the amount of released Fe^{2+} and therefore the efficiency of the degradation [23]. However, it should also be taken into account that due to the magnetic properties of the ZVI material, it aggregates on the surface of the magnetic stirring bar used for agitation. Regarding the hydrogen peroxide conversion, the hydrogen peroxide (100% of the stoichiometric amount) was completely consumed after 2 h of treatment in all cases, but following different consumption rates. When using the highest ZVI concentration (2.4 g L^{-1}), the H_2O_2 was depleted after 40 min of reaction. For the intermediate and the lowest ZVI concentration (0.6 and 1.2 g L^{-1}, respectively), the hydrogen peroxide was still present in both cases at that reaction time. It must be pointed out that the TOC conversion increased from 40 to 120 min and from 60 to 120 min when using 2.4 g/L or 1.2 g/L of ZVI, respectively, and the hydrogen peroxide was completely consumed.

While the exogenous hydrogen peroxide is still present, the generation of hydroxyl radicals through Fenton reactions (Eqs. (2) and (3)) are considered the primary oxidizing species. The initial acid pH (3.0) increased when the hydrogen peroxide depleted, reaching values up to 5.5–6.0. When the hydrogen peroxide is consumed, the low increase of TOC conversion is attributed to another reactive oxidant species (ROS), such as the ferryl species [22,24,25]. The oxidation power of ferryl ions (Fe_{aq}^{4+}) have been reported in the literature as a less reactive but more selective oxidant than hydroxyl radicals (only able to degrade oxidized compounds such as carboxylic acids), being stable at circumneutral pH values [26].

Table 2
TOC and H_2O_2 conversions, pH (initial and final) and iron concentration of blank experiments and $Air/ZVI/H_2O_2$ system after 2 h. *Experimental conditions:* TOC_0 0.1 g L^{-1}, acid pH (3), ZVI (2.4 g L^{-1}), H_2O_2 (100%), 500 rpm, medium magnetic stir bar and 5 L min^{-1} air flow.

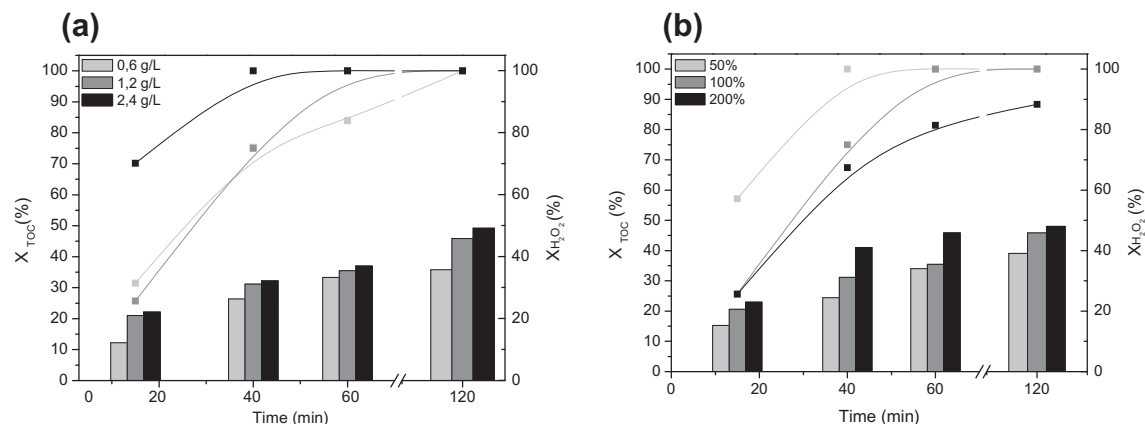| Reactions	TOC%	H_2O_2%	pH_0	pH_f	$Fe_{dissolved}$ (mg L^{-1})
Air (without ZVI nor H_2O_2)	8.3	Non-used	3.0	3.1	3
Air/ZVI (without H_2O_2)	6.8	Non-used	3.0	6.1	5
Air/H_2O_2 (without ZVI)	10.8	83	3.0	2.9	3
ZVI/H_2O_2	33.8	79	3.1	3.2	8
$Air/ZVI/H_2O_2$	48.9	100	3.0	6.0	10

Fig. 1. Effect of (a) the initial catalyst concentration and (b) the initial oxidant dosage on the TOC (columns) and hydrogen peroxide (lines) conversions. *Experimental conditions:* TOC$_0$ 0.1 g L^{-1}, acidic pH (3), H$_2$O$_2$ (100%_a)), ZVI (1.2 g L^{-1}_b)), 500 rpm stirring speed, medium-sized magnetic stirrer and 5 L min^{-1} air flow.

Thus, as the effectiveness of Fenton-like ZVI treatment mainly depends on oxidizing species produced by decomposition of hydrogen peroxide [27], the influence of H$_2$O$_2$ concentration ranging from 50% to 200% was studied for the treatment of 0.1 g L^{-1} TOC using 1.2 g L^{-1} of ZVI and initial pH of 3. The increase of the hydrogen peroxide (Fig. 1b) showed a clear enhancement of performance reaching almost 50% TOC conversions when the highest oxidant loading (200% H$_2$O$_2$) was used. However, once the hydrogen peroxide was consumed, the TOC removal rates dramatically decreased. It is well-known that when one of the Fenton reactants, Fe^{2+} or H$_2$O$_2$, is added in excess, the organic degradation can be inhibited by radical scavenging reactions. Such inhibition was not observed as the hydrogen peroxide increased until an excess of 200% of the stoichiometric amount under the experimental conditions studied herein. Thus, according to the results of the influence of the initial ZVI and H$_2$O$_2$ concentrations, 2.4 g L^{-1} ZVI and 200% H$_2$O$_2$ were used as the best operation conditions to further study the effect of the magnetic agitation on the modification of the ZVI final composite.

3.4. Influence of the magnetic agitation: the stirring speed and magnetic stir-bar size

Magnetic stirring systems are commonly used for catalytic batch experiments of advanced Fenton processes based on ZVI at lab-scale [28–30]. However, it is important to highlight the magnetic properties of the iron employed as a catalyst. The ZVI particles get stuck on the magnetic bar employed for agitation, so the ZVI available for reaction and its corrosion depend on the magnetic surface and consequently by its size.

For this reason, the influence of the magnetic stirrer size was investigated using three diameters of 1, 4 and 6 cm (coded as small, medium and big) under the same experimental conditions (200% H$_2$O$_2$, 2.4 g L^{-1}).

Fig. 2 shows the influence of the stirring speed in terms of TOC and the hydrogen peroxide conversions. When the stirring velocity increased from 250 to 500 and 1000 rpm, the TOC conversions increased from 34% to 57% and 68%, respectively. With regards to hydroxyl peroxide conversion, when using the highest stirring speed (1000 rpm), all the hydrogen peroxide was consumed after 40 min.

At lower speeds, hydroxyl peroxide conversions increased over time, resulting in 75% and 90% conversions after 120 min of reaction at 250 and 500 rpm, respectively. These results prove the influence of stirring speed on the mass diffusion and reaction kinetics due to a higher turbulence in the reaction medium. Values
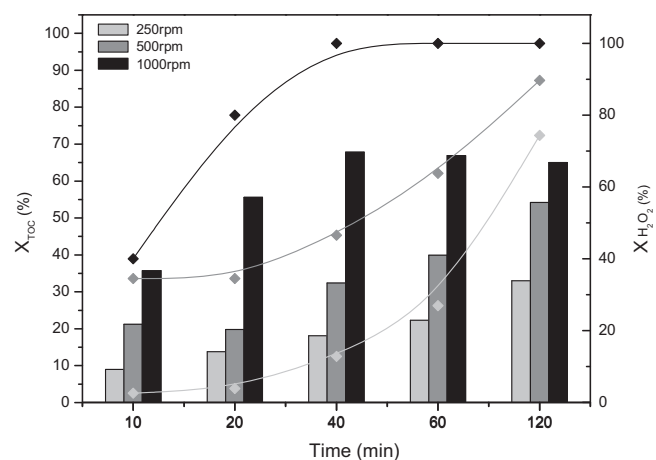

Fig. 2. The effect of the mixing velocity employed on the TOC (columns) and hydrogen peroxide (lines) conversions. *Experimental conditions:* TOC$_0$ 0.1 g L^{-1}, acidic pH (3), medium magnetic stir-bar, ZVI (2.4 g L^{-1}), H$_2$O$_2$ (200%) and 5 L min^{-1} air flow.

of pH increased upon H$_2$O$_2$ depletion towards neutral, obtaining values of 3.0, 4.8 and 5.6 after 120 min of reactions using 250, 500 and 1000 rpm. Concentration of iron leached were almost negligible obtaining less than 10 mg L^{-1} in all cases.

Fig. 3 shows an enhancement of the TOC conversion as the size of the magnetic stir bar increased, in particular for the initial reaction times of 10 and 20 min.

The small size evidenced a progressive increment of the TOC conversion up to 62% after 2 h of reaction, whereas the medium and the biggest magnetic sized-bars achieved a constant TOC conversion of ~68% and 70% at 40 and 20 min, respectively. Values of pH increased upon H$_2$O$_2$ depletion towards neutral values, obtaining values of 3.0, 5.5 and 5.6 after 120 min of reactions using small, medium and big magnetic stir-bar sizes, respectively.

The increase of TOC conversion by increasing the size of the magnetic stirrer was also accompanied by an increment of the hydrogen peroxide conversion. The oxidant consumption was low when using small magnetic stirrer (20%, 45%, 70%, 85% and 100% after 10, 20, 40, 60 and 120 min, respectively), whereas using the biggest size, the hydrogen peroxide conversion increased from 85% at 10 min to a total consumption after 20 min. These results of the TOC and hydrogen peroxide conversions can be attributed to different hypotheses. One the one hand, the energy applied into the reaction medium is proportional to the size of the stir-bar.
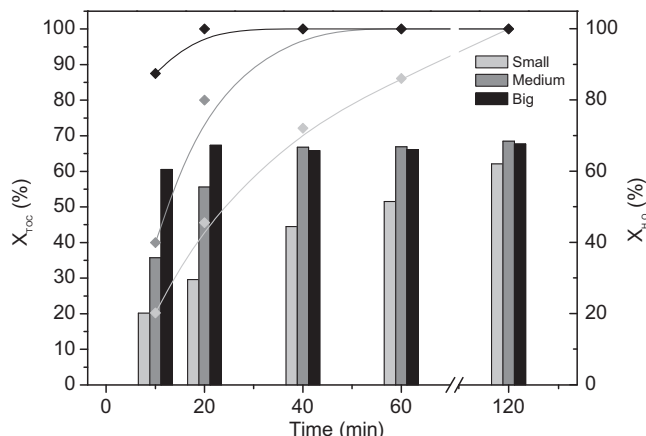
Fig. 3. Effect of magnetic stir bar size on TOC (columns) and hydrogen peroxide (lines) conversions. *Experimental conditions:* TOC_0 0.1 g L^{-1}, acid pH (3), ZVI (2.4 g L^{-1}), H_2O_2 (200%), 1000 rpm and 5 L min^{-1} air flow.

Thus, as the size of the stir-bar increased, the energy supplied to the aqueous solution is higher, enhancing the mass transfer and the reaction kinetics of TOC degradation. On the other hand, the ZVI particles are attracted and aggregated to the magnetic stir-bar surface during the treatment. It must be pointed out that most of the ZVI particles are attached to the magnetic stir-bar, regardless of its size, leaving a very small proportion of particles in suspension as slurry reactor. In this sense, the use of bigger sizes leads to a higher covering surface of active ZVI particles available for the catalytic degradation of TOC. Therefore, both hypotheses seem to fairly support the higher catalytic performance of ZVI when using a larger magnetic stir-bar.

3.5. Influence of the magnetic stir-bar size in the resultant ZVI composite

The activity of ZVI in the advanced Fenton processes is associated to previous corrosion of the metallic surface to generate ferrous species and following modified-ZVI/iron oxide composites that are formed during the oxidation treatment. In order to demonstrate a plausible relationship between the catalytic performance of the ZVI/H_2O_2 system and the resultant ZVI/iron oxide composite, several samples were recovered from the experiments carried out with different stir bar sizes for characterization by XRD, TPR and XPS techniques.

XRD patterns (Fig. 4) of the ZVI composite after the treatments demonstrated the clear formation of new diffraction peaks related to crystalline mixed iron oxide phases and the total disappearance of Fe^0 (readily indexed as a cubic phase $2\theta = 44°$ (intense peak) and 65°) in the catalyst used with the biggest stir bar (Fig. 3c). The crystalline iron oxide phases are the results of the superficial oxidation of the ZVI surface [31]. Crystal phases observed are a mixture of lepidocrocite (L), magnetite (M) and wüstite (W) (Fig. 4b and c). These findings support the remarkable role of the magnetic stir bar size employed. It is shown that the biggest size provided a major availability of powder ZVI to be exposed to the reaction medium with a more rapid corrosion, unlike the small and medium sizes, where less iron oxide phases were formed and where the presence of Fe^0 was still obvious, especially when the smallest size was employed (Fig. 4a and b).

Temperature programmed reduction (TPR) analyses of these samples were also performed (Fig. 5). As expected, TPR of fresh ZVI did not exhibit any reduction peak (data not shown). The TPR profiles of composite obtained after using the small magnetic stir-bar (1 cm) show a reduction peak centered at ~470 °C assigned to the presence of magnetite ($FeOFe_2O_3$).
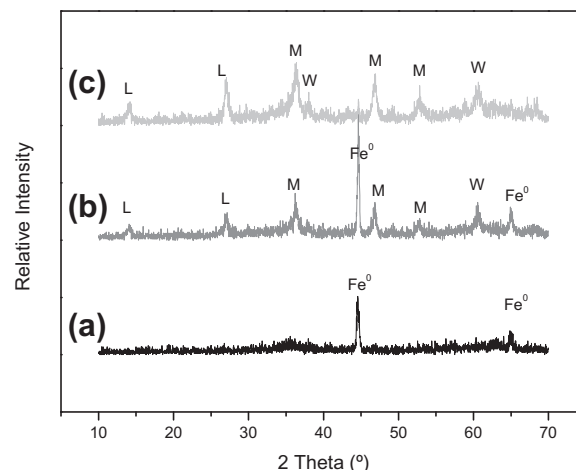

Fig. 4. XRD patterns of ZVI composites after treatment using (a) small, (b) medium and (c) big magnetic stir bar sizes. *Experimental conditions:* TOC_0 0.1 g L^{-1}, acid pH (3), ZVI (2.4 g L^{-1}), H_2O_2 (200%), 1000 rpm and 5 L min^{-1} air flow (L: lepidocrocite, M: magnetite, W: wüstite).
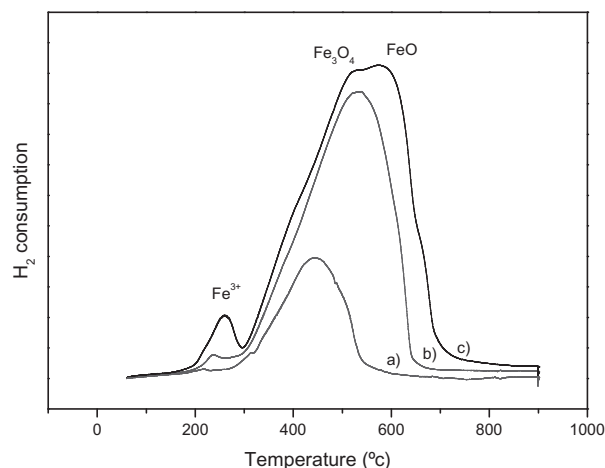

Fig. 5. TPR profiles of ZVI composites after 2 h reaction employing using (a) small, (b) medium and (c) big magnetic stir bar sizes. *Experimental conditions:* TOC_0 0.1 g L^{-1}, acidic pH (3), ZVI (2.4 g L^{-1}), H_2O_2 (200%), 1000 rpm and 5 L min^{-1} air flow.

TPR profiles obtained when using the medium (3 cm) magnetic stir bar shows an intense reduction peak centered at ~500 °C assigned to the presence of magnetite ($FeOFe_2O_3$) and a small peak at ~250 °C that could be assigned to lepidocrocite (γ-FeOOH); likely due to reduction of a shell of the Fe_2O_3 phase. When using the biggest stir-bar (6 cm), the TPR profile shows a more intense reduction peak centered at ~500 °C and ~580 °C which are attributed to magnetite and wüstite (FeO), respectively. The low H_2 consumption obtained when using the small magnetic stir-bar is consistent with the mainly metallic core–shell structure previously observed by XRD. These results confirmed a more oxidized composite obtained when the biggest magnetic stir-bar was employed as qualitatively revealed the higher intensity of iron oxide phases obtained.

X-ray photoelectron spectroscopy (XPS) was further used to study the surface chemical compositions of the samples after the ZVI-Fenton experiments. It is emphasized herein that the escape depth of photoelectrons in the solid is only about 3 nm, therefore the region of the solid probed by this technique is confined to a few atomic layers which not necessary coincides with the bulk of the solid.

Fig. 6a and b show the Fe2p and O1s core-level spectra, respectively, of the samples used in the Fenton process, and the binding energies of the Fe2p$_{3/2}$ and O1s photoelectrons are summarized in Table 3.

The two Fe2p$_{3/2}$ and Fe2p$_{1/2}$ spectra of the Fe2p doublet of all samples appear at binding energies of 710.7–710.8 and 724.4–724.5 eV, with a shake-up satellite lines at ca. 719.1 eV and 732.8 eV, respectively. These binding energies and the observation of satellite lines, that are the fingerprint of Fe^{3+} ions, indicate unambiguously that Fe^{3+} are the only iron ions present on the surface (3 nm) region of the catalyst particles [32].

The precise knowledge of the oxygen species surrounding Fe^{3+} ions is obtained from the O1s core level spectra (Fig. 6b). The O1s spectra show two components: at 529.6–529.7 eV, associated to lattice oxygen (O_2^-) and at 531.0–531.3 eV, typical of OH species [33]. These spectra indicate that both O_2^- and ^-OH species are present around the Fe^{3+} ions. Besides this, the O/Fe surface ratio and the oxo-hydroxide formula have been determined. The trend observed indicates that the proportion of O_2^- increases from the small to the big stir bar sample whereas the OH groups follow the opposite trend.

3.6. Influence of the organic loading

In order to evaluate the feasibility of the Fenton-like ZVI system for as-received pharmaceutical wastewater, TOC loadings of ca. $0.1 \, g \, L^{-1}$ were compared to more concentrated loadings of ca. $5 \, g \, L^{-1}$ under the same experimental batch conditions namely, $2.4 \, g \, L^{-1}$ ZVI, acid pH, medium-sized magnetic stirrer and 200% H_2O_2 and agitation velocity of 1000 rpm.

Fig. 7 shows that, the TOC conversion decreased for treatment of the as-received wastewater, obtaining 55% TOC conversion as compared to ca. 70% when 1/50 diluted wastewater was used. Regarding the hydrogen peroxide conversion, the initial rates also decreased, although total consumption was achieved after 40 min of reaction, with no further TOC reduction. Leached iron concentration obtained for the reaction systems conducted with an organic load of $0.1 \, g \, L^{-1}$ did not exceed $\sim$10 mg L^{-1}, while for the treatment of $\sim$5 g L^{-1} the iron leached obtained was $\sim$70 mg L^{-1}. In all cases, the pH increased when the initial hydrogen peroxide depleted, obtaining values of 6.0 after 120 min of reaction.

Table 3

Binding energy (eV) of core levels and O/Fe surface atomic ratios of iron samples using small, medium and big stir-bar in the ZVI Fenton reaction (between brackets peak percentages).

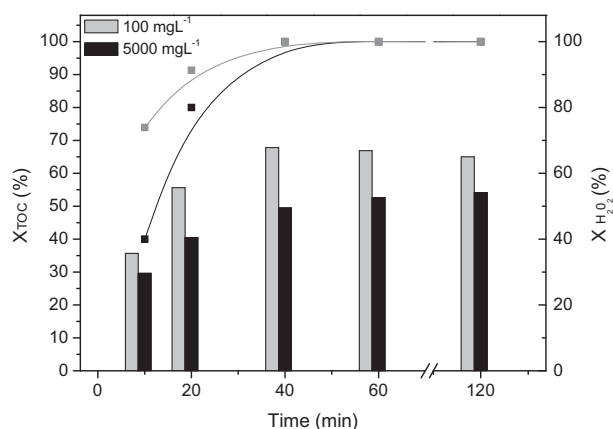| Sample	Fe2p$_{3/2}$	O1s		O/Fe atom	Assignment
Small	710.7	529.6 (42)	531.1 (58)	2.707	$FeO_{1.14}(OH)_{1.57}$
Medium	710.8	529.7 (54)	31.3 (46)	2.441	$FeO_{1.32}(OH)_{1.12}$
Big	710.8	529.6 (55)	531.0 (45)	2.935	$FeO_{1.61}(OH)_{1.32}$

Fig. 7. Effect of initial TOC loadings of 100 and 5000 mg L^{-1} in terms of TOC (columns) and hydrogen peroxide (lines) conversions. *Experimental conditions:* acidic pH (3), ZVI (2.4 g L^{-1}), H_2O_2 (200%), 1000 rpm and 5 L min^{-1} air flow.

It should be pointed out that the ZVI/TOC concentration ratio for the treatment of the as-received wastewater was significantly lower than the used for the treatment of the diluted wastewater (0.5 and 24, respectively). The catalyst passivation therefore, can occur faster. As previously mentioned, the formation of iron/hydrous oxides covering the surface of the ZVI material decreases at some stage the activity of the generation of Fe^{2+} and consequently reduces the oxidizing radical species formation.

However, this implies that during the reaction, the concentration of Fe^{2+} and OH^- increases, so the precipitation $Fe(OH)_2$ or $Fe(OH)_3$ occurs [34]. As a result, the release of dissolved iron is
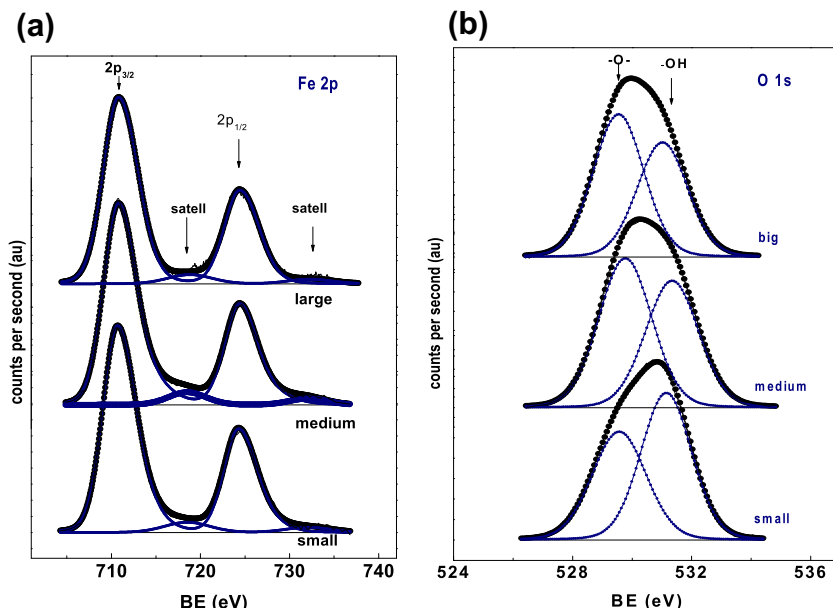

Fig. 6. Fe2p (a) and O1s (b) core level spectra of the ZVI samples used in the PWW using ZVI Fenton processes.

slower at higher pH values that occur when the H_2O_2 depleted (after 60 min of reaction). This means that the final effluent contains very low concentrations of iron dissolved, 10 mg L^{-1}, which is within the limit of legal industrial discharge [35]. Moreover, the efficacy of the treatment was also evaluated in terms of biodegradability of the treated wastewater. After all Fenton ZVI/H_2O_2 treatments studied herein, the biodegradability (in terms of BOD_5/COD ratio) was greatly enhanced, obtaining in all cases values higher than the initial 0.18 value of the as-received wastewater. The biodegradability increased up to 0.35 and 0.25 after treatment of diluted (0.1 g L^{-1} TOC) and as-received wastewater (5 g L^{-1} TOC), respectively. This indicates that treated PWW by ZVI/H_2O_2 could be afterwards treated by a conventional biological system [36], being a cost-effective pre-treatment step considering the moderated concentrations of oxidant and catalysts employed. According to other monitored parameters such as turbidity and conductivity, Fenton like-ZVI treatments also yielded remarkable performances. The turbidity was lowered to 0.71 and 4.55 NTU for diluted and as-received PWW compared to the value of 267 NTU in the initial wastewater. The conductivity decreased down to values of approximately 0.4 and 7.9 mS cm^{-1} (0.1 and 5 g L^{-1}, respectively) compared to the initial value of 70 mS cm^{-1}. The final effluent was visible clear.

4. Conclusions

This study shows the effectiveness of the ZVI/H_2O_2 system for the removal of the organic pollutants present in a wastewater generated by a drug manufacturing plant. The use of moderate concentrations of oxidant and ZVI commercial catalyst led to TOC reductions of 70% and 55% of diluted and as-received pharmaceutical wastewater, respectively, with a remarkable enhancement of the biodegradability in all cases. The use of magnetic stirring devices can play an important role in the catalytic performance. ZVI particles are majorly aggregated around the magnetic surface reducing significantly the suspension of particles in the aqueous medium, and therefore, the availability of the metallic sites for degradation of TOC on the ZVI/H_2O_2 system. Thus, the use of larger magnet stir-bars enhanced significantly the TOC and H_2O_2 conversions, although the contribution of the increased turbulence as the diameter of the stir bar increases cannot be discarded. The different ZVI composites formed under the different batch reaction conditions were evaluated by XRD, TPR and XPS characterization techniques. In all cases, ferric iron oxides were present on the more superficial part (3 nm) of the composite. However, the corrosion proceeded differently by forming stratified layers of iron/hydrous oxides covering the metallic ZVI surface.

Acknowledgements

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