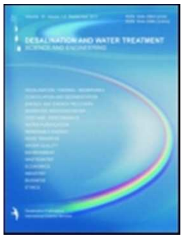

Catalytic wet peroxide oxidation of phenol using nanoscale zero-valent iron supported on activated carbon

Journal:	*Desalination and Water Treatment*
Manuscript ID:	TDWT-2014-1270.R1
Manuscript Type:	Original Paper
Date Submitted by the Author:	05-Dec-2014
Complete List of Authors:	Messele, Selamawit Ashagre; University of Rovira i Virgili, Chemical Engineering Bengoa, Christophe; University of Rovira i Virgili, Chemical Engineering Stuber, Frank; University of Rovira i Virgili, Chemical Engineering Fortuny, Agusti; Universitat Politecnica de Catalunya, Chemical Engineering Fabregat, Azael; University of Rovira i Virgili, Chemical Engineering Font, J.; University of Rovira i Virgili, Chemical Engineering
Keywords:	Phenol, Activated carbon, Zero valent iron, Catalytic wet peroxide oxidation

Catalytic wet peroxide oxidation of phenol using nanoscale zero-valent iron supported on activated carbon

S.A. Messele[1], C. Bengoa[1], F. Stüber[1], A. Fortuny[2], A. Fabregat[1] and J. Font[*,1]

[1] Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalunya, Spain

[2] Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, EUPVG, Av. Víctor Balaguer, s/n, 08800 Vilanova i la Geltrú, Catalunya, Spain

(*) corresponding author: jose.font@urv.cat, Tel: 34977559646, Fax: 34977559621

Dr. Selamawit Ashagre MESSELE, *Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalunya, Spain.* Tel: 34977559618, E-mail: selamawit.ashagre@urv.cat

Dr. Christhophe BENGOA, *Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalunya, Spain.* Tel: 34977558619, E-mail: christophe.bengoa@urv.cat

Dr. Frank STUBER, *Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalunya, Spain.* Tel: 34977559671, E-mail: frankerich.stuber@urv.cat

Dr. Agustin FORTUNY, *Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, EUPVG, Av. Víctor Balaguer, s/n, 08800 Vilanova i la Geltrú, Catalunya, Spain.* Tel: 34977559646, E-mail: agustin.fortuny@upc.es

Dr. Azael. FABREGAT, *Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalunya, Spain.* Tel: 34977559646, E-mail:afabrega@urv.cat

Dr. Josep FONT, *Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalunya, Spain* Tel: 34977559646, E-mail: jose.font@urv.cat

Abstract

The main objective of the work is to prepare catalysts based on nanoscale zero-valent iron supported on activated carbon (nZVI/AC) and to test their activity for catalytic wet peroxide oxidation (CWPO) of phenol. The catalysts were characterized by XRD, SEM, ICP and N_2 adsorption-desorption and their performance evaluated in terms of phenol and TOC removal. The effect of the initial phenol concentration and initial pH on the oxidation process was investigated. Possible leaching of iron from the catalyst into the aqueous solution was also examined. The experimental results indicate that the catalytic activity towards phenol degradation was found to be enhanced by nano scale zero-valent iron supported on activated carbon catalysts (nZVI/AC) compared to that of Fe/AC. In the range 150-1000 mg/L, phenol conversion above 90% can be reached using these catalysts after only 15 min of reaction and using the stoichiometric hydrogen peroxide for complete mineralization. The leaching observed is less than 4% of the total initial iron in the catalyst even after 120 min of reaction. It was also observed that the stability or reutilization of the catalyst is fairly good.

Keywords: Phenol; Activated carbon; Zero-valent iron; Catalytic wet peroxide oxidation

1 Introduction

The treatment of refractory organic compounds such as phenol and its derivatives from industrial wastewater is of interest due to their biotoxic properties [1]. Phenol is often taken as model compound for wastewater treatment examination, because it appears as starting or intermediate compound in many chemical, petrochemical and pharmaceutical process industries and also it is formed in the oxidation pathway of higher-molecular-weight aromatic hydrocarbons [2, 3].

Various methods are widely studied for the removal of phenol such as biological treatment, extraction, and wet oxidation [4-7]. However, advanced oxidation processes (AOPs) such as Fenton, photo-Fenton, ozone oxidation, and photo-catalytic oxidation are successfully used for wastewaters containing high concentration of more toxic pollutants [8-11]. AOPs generate hydroxyl radical, a strong oxidant, which can completely degrade the pollutants and non-selectively mineralize into harmless products. Among these, the interest in the use of Fenton system for the removal of phenolic compounds in water is increasing because this method avoids the use of costly reactors, it can be done at room temperature and atmospheric pressure, H_2O_2 decomposition leads to harmless products, and it is easy to manage [12-17]. However, its application to the treatment of real wastewater has been limited mainly due to the narrow operational pH range, the disposal of iron-containing waste sludge, which needs subsequent separation steps, and most importantly the loss of reagent activity resulting in high operational expenses. On the premise of reducing the operation cost, an alternative solution is proposed, which is based on the use of a heterogeneous catalyst consisting of home-made nano zero-valent iron particles supported on activated carbon (nZVI/AC).

Activated carbon is being used since decades ago as an excellent adsorbent and supporting material due to its unique properties in mechanical strength and porous structure [18, 19]. On the other hand, several studies have demonstrated that zero-valent iron (ZVI) has been able to effectively oxidize various organic and inorganic pollutants in the presence of oxygen [20, 21]. Thus, a modified Fenton process, which utilizes ZVI, has been explored as a potential technique to degrade different pollutants in wastewater [22, 23]. ZVI acts as a heterogeneous catalyst for the degradation of phenol in aqueous solution by effectively decomposing hydrogen peroxide and generating hydroxyl radical, which reacts at high rate with phenol and its intermediates [24]. For example, the degradation of organic compounds using ultrasound combined with the ZVI/H_2O_2 system under acidic conditions was studied by Bremner [25, 26], but in the above cases the degradation was always examined using high excess of hydrogen peroxide. In this alternative, the oxidation of the metallic iron generates *in situ* ferrous iron giving rise to an effective Fenton-type reaction. The main advantage of this process is the faster recycling of ferric iron at the iron surface to give ferrous iron which is one of the Fenton reagents [26]. Furthermore, the use of zero-valent iron/granular activated carbon (Fe^0/GAC) in the presence of ultrasound was also proven to give good results in the degradation of dyes [27].

Taking into consideration the aforementioned disadvantages of classical Fenton system and the advantage of using ZVI as a catalyst and AC as a good adsorbent, a strategy is proposed to synthesize heterogeneous nZVI/AC catalysts and investigate their performance on the CWPO of phenol aqueous solutions. The effect of the initial phenol concentration and pH over the oxidation process has been investigated. The possible leaching of iron from the catalyst into the aqueous solution and its homogeneous contribution has also been examined. Finally, the catalyst stability (regeneration and reusability) after reaction was also addressed.

2 Experimental

2.1. Materials

All chemicals were used without further purification. Phenol was an analytical standard purchased from Panreac (99% purity). Hydrogen peroxide (H_2O_2 30%wt), iron nitrate nonahydrate (98% purity), sulphuric acid (98% purity), sodium hydroxide (98% purity) were purchased from Sigma-Aldrich. The activated carbon (particle size 1.5 mm) was purchased from Merck. Deionised water was used to prepare all the aqueous solutions.

2.2. Catalyst preparation

The Fe/AC catalysts were prepared by incipient wetness impregnation with an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$. Prior to use, the commercial activated carbon was ground and sieved with US standard sieve to obtain 25-50 mesh (0.3-0.7 mm) uniform particles and washed with deionised water in order to remove residuals or fines adsorbed on the surface. Finally, it was dried in an oven at 105 ºC for 15 h. This sample was hereafter labelled as AC. The amount of ferrous nitrate needed for 9% wt of iron in the final catalyst was dissolved in the minimum amount of deionised water and added drop wise on the support (AC). After impregnation, the slurry was left for 2 h at room temperature, dried overnight at 105 ºC and these dried slurry was then divided into two portions and submitted to heat treatment under two different conditions in order to have catalysts having different iron state. In the first one, the AC was heat treated under a nitrogen flow at 400 ºC for 4 h. After this step, the Fe is in the form of Fe_2O_3 (see section 3.1, XRD results) and the catalyst was labelled as Fe/AC. In the second route, it was heat treated under a nitrogen flow at 400 ºC for 1 h, and then reduced at 400 ºC under a hydrogen flow for 3 h [28,29]. In this case the Fe is in the ZVI form (see section 3.1, XRD results) and this catalyst was labeled as nZVI/AC.

2.3. Characterization techniques

Specific surface area and pore volume of the catalysts were determined by N_2 adsorption/desorption at 77 K, using a Micromeritics ASAP 2000 surface analyser. The samples were outgassed overnight at 523 K prior to the adsorption analysis. The Fe content of the catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-OES) after microwave-assisted digestion of samples. X-ray diffraction (XRD) analysis using a Siemens model of D5000 diffractometer with Cu Kα (λ = 1.406 A) radiation was employed to determine the crystal structure and crystallinity of the catalyst (AC composite). The surface morphology was investigated by scanning electron microscopy (SEM) using a Philips model XL 30 apparatus operated at an acceleration voltage of 20 kV.

2.4. Adsorption and catalytic activity tests

All adsorption/oxidation assays were carried out in a magnetically stirred jacketed batch reactor. The reactor was filled with 100 mL of phenol solution of initial concentration 150 mg/L. The reaction temperature was set to 30 ºC and maintained constant by circulating water from a thermostatic bath through the jacket. The pH of the solution was adjusted to pH 3.0 with sulphuric acid when required. Once the temperature reached 30 ºC, the theoretical stoichiometric amount of H_2O_2 based on complete phenol mineralization (750 mg/L, 0.25 mL) and 100 mg of catalyst were added simultaneously to start the reaction. Phenol adsorption assays were carried out in the same conditions without H_2O_2 addition.

During the reaction, liquid samples of 1 mL were periodically withdrawn. Then each sample was filtered with a syringe nylon filter of 0.45 µm (Teknokroma, ref.TR-200101) and placed in a glass vial (Agilent) for immediate analysis. Some experiments were conducted three times to check the reproducibility of the results and the experimental error was within ±3%.

2.5. Analytical Methods

The concentration of phenol was quantified by means of a High Performance Liquid Chromatograph (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and a C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). The analyses were performed with a mobile phase (flow rate 1 mL/min) of a 40/60% mixture of methanol and ultrapure water (Milli-Q water). The pH of the water was adjusted at 1.41 with sulphuric acid (H_2SO_4). The detection was performed by UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL of sample.

The Total Organic Carbon (TOC) was measured in a TC Multi Analyzer 2100 N/C equipment (Analytic Jena) with a non-diffractive IR detector. Fe leached from the catalyst to the reaction media was determined by using Atomic Absorption Spectroscopy (AAS) at 249 nm.

The main parameters used to compare the results in the discussion section are the removal of phenol (X_{PhOH}) and TOC (X_{TOC}) which are respectively defined as:

$$X_{PhOH}(\%) = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \qquad (1)$$

where $[PhOH]_0$ is the initial concentration and $[PhOH]_t$ is the concentration at time t, and

$$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \qquad (2)$$

where TOC_0 is the initial concentration and TOC_t is the concentration at time t.

3 Results and discussion

3.1 Catalyst characterisation

Table 1 lists the properties, i.e., surface area (S_{BET}), mesoporous surface area (S_{meso}), pore volume (V_{micro}) and Fe content of the original AC, Fe/AC and nZVI/AC catalysts. Surface area of Fe/AC catalyst was reduced from 1055 to 962 m^2/g and total pore volume was reduced from 0.640 to 0.538 cm^3/g compared to the original AC. In the case of ZVI/AC, surface area was reduced from 1055 to 978 m^2/g and total pore volume was reduced from 0.640 to 0.544 cm^3/g. Similar results were also reported by Li and co-workers concerning the effect of nZVI loadings on the pore volume and surface area of their resulting resin-based hybrid [30]. In general, slightly decrease in surface area and total pore volume for both catalysts was observed with respect to the original AC. This indicates that the pores were partially blocked by the active iron species, irrespective of being oxidised or reduced. From the ICP-OES analysis, slight variations (<10%) are noticed between the expected and the determined iron content of the sample, which means that most of the soluble iron was incorporated onto the support and validates the catalyst synthesis procedure.

Microimages of the synthesized Fe/AC, nZVI/AC and the original AC are shown in Fig. 1. As it can be seen, the original AC is highly porous and smooth, whereas, the supported Fe particles in the pores of AC are needle shaped. In turn, the supported ZVI particles in the pores of AC are clusters of aggregates of round-shaped particles and, their particle size being approximately 80-190 nm in diameter. Fig. 1b (nZVI/AC) shows that most of the nZVI particles were loaded into the pores and cracks rather than onto the outer surface as observed elsewhere [31]. This interestingly helps to allow the repeated use of the catalyst without loss of the iron particles as commented later.

The XRD analysis of AC, Fe/AC and nZVI/AC is shown in Fig. 2. The zero valence state and crystalline structure of nZVI were confirmed by X-ray diffraction analysis for the sample nZVI/AC. For sample Fe/AC, the iron was in the form of Fe^{II} or Fe^{III} oxides.

3.2 *Catalytic activity*

3.2.1 *Preliminary adsorption and oxidation tests*

In first place, the potential catalytic performance of the iron containing carbon materials was demonstrated. Thus, tests using original activated carbon (AC), iron oxide loaded AC (Fe/AC) and the nZVI supported AC (nZVI/AC) were performed to check out their activity for phenol oxidation due to their iron state. The results are also contrasted against adsorption, i.e., without addition of hydrogen peroxide. The adsorption/oxidation tests were carried out using an initial concentration of phenol of 150 mg/L, 1 g/L of catalyst, 750 mg/L of H_2O_2, pH of 3.0, and 30 ºC.

Fig. 3a illustrates the results for the phenol removal by adsorption (without H_2O_2) and oxidation using the different adsorbents/catalysts. The adsorption tests show that the original AC possesses a slightly higher adsorption capacity than that of the AC-supported samples, which is aligned with its somewhat greater surface area. In turn, the adsorption capacity for both the supported samples is nearly the same, in accordance with their similar textural properties.

However, the results from phenol removal by peroxidation show that the AC-supported Fe or nZVI catalysts are capable of effectively decomposing phenol. It must be noted that AC alone does not shown relevant catalytic activity by itself in the tested conditions as the phenol disappearance profiles using virgin AC as a catalyst both in the absence and the presence of H_2O_2 are slightly different within 120 min, giving a final value of 65% and 73% of phenol removal, respectively. The slightly higher phenol disappearance in presence of H_2O_2, could be related to occurrence of natural iron content in small amounts (Table 1). Anyway, this indicates that oxidation of phenol is insignificant and phenol removal takes place mainly by adsorption in both cases. On the contrary, the AC containing supported Fe or nZVI enhances the initial rate, so after 60 min of reaction, the phenol removal is 83% for Fe/AC and already 99% for nZVI/AC.

Similar results were obtained for the oxidation of phenolic contaminants using Fe loaded mesoporous SBA-15 [32].

It is worth that the nZVI/AC catalyst allows higher phenol removal (>90%) than that of Fe/AC (41%) after 15 min of reaction, and probably it is because of the iron oxidation state as shown in the XRD spectra (Fig. 2). The iron state in the Fe/AC catalyst is in the form of Fe_2O_3 and Fe_3O_4, whereas in the case of nZVI/AC catalysts, the iron is in the zero valent state, which has an advantage for Fenton chemistry. According to Segura et al [33,34], the oxidation of ZVI at acidic conditions generates in situ Fe^{2+}, Eq (3), which in turn promotes the generation of hydroxyl radicals (Eq. (4)) [35]. The generated $^{\cdot}OH$ radicals are capable of oxidizing a wide range of organics in wastewater. The main advantage of this alternative (using ZVI as a source of Fenton reagent) is a faster recycling of ferric iron into ferrous species at the metallic iron surface through the reaction shown in Eq (5), so that they are more readily available throughout the reaction time.

$$\mathrm{ZVI} + 2H^{+} \longrightarrow Fe^{2+} + H_2 \tag{3}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + {}^{\cdot}OH \tag{4}$$

$$2Fe^{3+} + \mathrm{ZVI} \longrightarrow 3Fe^{2+} \tag{5}$$

Removal of TOC is presented in Fig 3b. The results illustrate that original AC, both in the absence and the presence of H_2O_2, provided the highest TOC removal after 120 min of reaction, above 64% compared to the AC-supported catalysts in respective of adsorption and oxidation tests. Moreover, the TOC removal by adsorption for the AC-supported catalysts is relatively lower than that of the original AC but quite similar among them. Whereas, the TOC removal by oxidation for the first 15 min of reaction with the AC-supported catalysts is much better than that of the original AC but through time the TOC removal is not increasing as expected. This is related to the behaviour of AC as a very efficient adsorbent for phenol but not so good for some of its partial oxidation products during the oxidation of phenol. Thus, adsorbed phenol retains all its TOC content, so phenol removal by adsorption and TOC removal values are almost identical, within the experimental error, even coming from different measures. However, it must be noted that for AC in the absence of iron the TOC is not actually destroyed but only adsorbed onto the AC. On the contrary, when phenol is actually degraded by the hydrogen peroxide, the intermediate products are partially released back to the solution, apparently increasing the TOC content. In any case, the TOC removal by oxidation for nZVI/AC is better compared to Fe/AC catalysts, which leads to a conclusion that using nZVI/AC as catalyst enhances a deeper oxidation of phenol [36].

Some small contribution of homogeneous reaction may take place in the case of the AC-supported catalysts due to iron leaching. In order to know the total iron content in solution, samples were analysed by AAS at three reaction times (30, 60 and 120 min) for both adsorption and oxidation tests using Fe/AC and nZVI/AC catalysts. The obtained iron leached values for both catalysts are presented in Table 2. The results show that the iron leaching during phenol adsorption tests is quite similar for both Fe/AC and nZVI/AC catalysts, giving less than 1% after 30 min, less than 1.5% after 60 min and below 2.5% after 120 min. Nevertheless, it is important to highlight that iron leaching from both catalysts during the phenol oxidation tests is slightly higher than that of adsorption tests; especially at longer time of reaction. This is because of the decrease of solution pH due to the intermediates formation, so more acidic pH favours iron leaching according to [37]. For instance, iron leaching from the nZVI/AC catalyst after 120 min of reaction is slightly higher than that of Fe/AC, which are 3.12% and 2.80% respectively, but the iron leaching at shorter time (30 min) of reaction is quite similar for both catalysts. Therefore, the enhancement of the initial reaction rates of the nZVI/AC catalyst can not be related with the amount of iron leached. However, in terms of stability, in all the cases, the leaching of active phase (Fe) is insignificant as it is below 4%. Overall, the leaching is reasonable as only less than 4% of the total initial iron in the catalyst is lost, even after 120 min of reaction.

3.2.2 Effect of initial phenol concentration

The effect of the initial phenol concentration was investigated in the range of 150–1000 mg/L at pH 3.0 and 30 ºC with the addition of 100 mg of nZVI/AC and the stoichiometric ratio of H_2O_2. Fig. 4a shows the phenol conversion evolution as a function of reaction time for the four initial phenol concentrations studied.

All the curves revealed a similar trend. As expected, the higher the phenol initial concentration, the greater the time required for total phenol conversion. Anyway, above 90% phenol removal was still obtained within 15 min reaction with an initial phenol concentration of 1000 mg/L. After 10 min, the phenol conversion obtained was 91%, 88%, 86% and 83%, respectively for 150, 250, 500 and 1000 mg/L.

As it can be seen in Fig. 4b, the TOC conversion of the experiments for the four initial phenol concentrations were 55% for 150 mg/L, 51% for 250 mg/L, 37% for 500 mg/L and 35% for 1000 mg/L after 2 h of reaction. These values indicate that mineralization also correlate with the initial phenol concentration and deeper oxidation mainly took place for the lower phenol concentration. As in the previous cases, some iron leaching was observed during the reaction. Maximum of 5% iron leaching is observed for the greatest concentration of phenol (1000 mg/L). For higher concentration of phenol the leaching is relatively high, this is probably related to the amount of peroxide used. i.e., the actual concentration of hydrogen peroxide is dependent on the concentration of phenol as we used a stoichiometric ratio for the same amount of catalyst.

3.2.3 Effect of initial pH

It is well known that the optimum pH for homogeneous Fenton process is around 3.0 [15, 38]. At higher pH, the precipitation of the insoluble iron hydroxides takes place and the rate of of H_2O_2 decomposition decreased. This is the major limitation of the wet peroxide oxidation process because it needs previous acidification of the initial solution and later subsequent separation of the precipitated iron. Nowadays, the design of heterogeneous catalysts working in a wide range of pH is a big challenge. In order to investigate the influence of pH on the present process, the experiments were conducted at three pH values. First, H_2SO_4 was added to the phenol solution to adjust the initial initial pH value to 3.0. Second, NaOH was added to adjust the initial pH to 7.0. And finally, without any adjustment, naturally occurring pH of phenol (5.6) solution was left. Moreover, the effect of pH on the catalyst stability was also examined.

The increase of the pH evidently slows down the reaction rate. Fig. 5a shows that the phenol removal for pH 3.0 is almost complete within 60 min of reaction, but for pH

5.6 and 7.0, the phenol removal drops up to 67% and 59%, respectively, after 120 min of reaction. On the other hand, the extent of Fe leaching decreases when the pH increases (Table 3). It is clear that the iron lost is higher for lower pH and this fact favors working at a higher pH values, in order to achieve long term stability. Nevertheless, the iron lost at shorter time of reaction is relatively comparable for all initial pH runs. For instance, after 30 min of reaction, the leached iron was 1.31%, 1.25% and 1.19% for the initial pH of 3.0, 5.6 and 7.0, respectively. Therefore, the leached iron can not be responsible for the higher activity of this catalyst, but rather the initial solution pH affects the initial reaction rates.

3.3 Stability and recycling of nZVI/AC catalyst

It is important to evaluate the stability of the catalyst for heterogeneous catalytic system. For this purpose, consecutive runs were performed with the same catalyst. After each run, the used catalyst was filtered and washed with distilled deionised water. The sample was then dried at 105 ºC for 15 h, and then the CWPO of phenol was repeated with initial phenol concentration of 150 mg/L in the presence of the recycled catalyst and 750 mg/L of hydrogen peroxide at pH 3.0 and 30 ºC.

Table 4 summarizes the evolution of phenol removal, TOC removal and leached iron (%) upon reaction time with the recycled catalysts for the three consecutive runs. Even though measurable activity decay is observed, phenol conversion decreases only from 100% to 93% in three runs after 120 min of reaction each. Considering shorter time, the catalyst is still able to yield about 90% phenol conversion at 60 min in the third run. Similar trend was also observed by Melero [39], after testing a Fe_2O_3/SBA-15 catalyst for the CWPO of phenolic aqueous solutions, they came up with the conclusion that the presence of residual organic compounds adsorbed on to the catalyst had a negative effect on its reusability. Moreover, it must be considered that there was some loss of used catalyst during the filtration process for subsequent recycling. As it can be observed, this catalyst showed a fairly good activity, allowing a TOC reduction of 53% after the third run. Furthermore, for the consecutive runs, the iron leaching is significantly reduced, around 1.8% of iron was found after 120 min of reaction after the third run, but the phenol conversion achieved remains remarkably unaltered.

In spite of this good stability, XRD characterization of the used catalysts was performed in order to know if ZVI survives or not. The XRD spectra in Fig. 6 illustrate that the ZVI still appears after the three consecutive runs, though the intensity is a bit lower than that of the fresh catalyst. Moreover, for the used catalysts there is some Fe_2O_3 form of iron, which is already expected after the first run, because some of the iron has undergone oxidation at some extent during the reaction.

3.4 Homogeneous contribution

The active species leached from the catalyst may contribute to the phenol degradation through a homogeneous Fenton path. For this reason, an additional test was carried out to assess this possibility. A heterogeneous catalytic run was performed under typical conditions (30 ºC, 750 mg/L of H_2O_2, 100 mg of nZVI/AC and pH 3.0) for 30 and 120 min of reaction. The resultant solution was filtered to remove the catalyst and the clean liquid was collected, where 1.13 mg/L (1.25%) of leached iron specious was detected after 30 min of reaction and 2.80 mg/L (3.12%) of leached iron specious after 120 min of reaction. Then, phenol and hydrogen peroxide were further added to set again initial concentration of both in the filtered solution and a new reaction started to determine the homogeneous contribution.

The result (not shown) reveals that the phenol conversion for 1.13 mg/L of iron specious in homogeneous test was 41% after 120 min of reaction while for heterogeneous system the phenol conversion was completed just after 60 min of reaction. This clearly indicates that, the phenol conversion progress of this homogeneous test is much slower than that of the heterogeneous reaction. On the other hand, for the homogeneous test having 2.80 mg/L of iron specious in the filtered solution, phenol conversion was found to reach 71% after 120 min. This could be due to overestimation of the homogeneous contribution as we used the filtered solution after 120 min of the heterogeneous reaction. Therefore, according to these results, the overall activity of the catalyst is mainly due to heterogeneous phenomena and the contribution of the leached iron must be taken as secondary.

4 Conclusions

In this study, nZVI/AC catalysts have been prepared and tested for CWPO of phenol in batch system. The SEM analyses indicated that nZVI were mostly found as clusters of aggregates of round-shaped particles and were loaded into the pores and cracks rather than onto outer surface. This interestingly allows the repeated use of the catalyst without noticeable loss of iron.

The heterogeneous catalyst performance in the adsorption and subsequent degradation of phenol has been examined. The catalytic activity towards phenol degradation was found to be enhanced by nano scale zero-valent iron supported on activated carbon catalysts. Phenol conversion above 90% can be reached using this catalyst after only 15 min of reaction using the stoichiometric hydrogen peroxide for phenol concentrations in the range 150-1000 mg/L.

The recycling and consecutive reutilization of catalyst gave final phenol removal nearly the same obtained with the fresh catalyst although at later time. In all the cases, the iron concentration leached into the solution was less than 5% and appears to be mostly independent of the reaction conditions. The leaching observed is not excessive as it means less than 5% of the total initial iron in the catalyst even after 120 min of reaction.

Acknowledgements

Financial support for this research was provided by the Spanish Ministerio de Educación y Ciencia and FEDER, projects CTM2008-03338 and CTM2011-23069. The Spanish Ministerio de Ciencia e Innovación is also thanked for providing a doctoral scholarship (Programme FPI, BES-2009-017016) to carry out this research work. The author's research group is recognised by the Comissionat per a Universitats i Recerca del DIUE de la Generalitat de Catalunya (2009SGR865) and supported by the Universitat Rovira i Virgili (2010PFR-URV-B2-41).

5 References

[1] Y.I. Matatov-Meytal, M. Sheintuch, Catalytic abatement of water pollutants, Ind. Eng. Chem. Res. 37 (1998) 309–326.

[2] A. Fortuny, C. Bengoa, J. Font, F. Castells, A. Fabregat, Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, Catal. Today 53 (1999) 107–114.

[3] A. Santos, P. Yustos, A. Quintanilla, S. Rodríguez, F. García-Ochoa, Route of the catalytic oxidation of phenol in aqueous phase, Appl. Catal. B: Environ. 39 (2002) 97–113.

[4] M. Pera-Titus, V García-Molina, M.A. Baños, J Giménez, S Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

[5] H. H. P. Fang, D. W. Liang, T. Zhang, and Y. Liu, Anaerobic treatment of phenol in wastewater under thermophilic condition, Water Res. 40 (2006) 427–434.

[6] W. Kujawski, A. Warszawski, W. Ratajczak, T. Porebski, W. Capała, and I. Ostrowska, Removal of phenol from wastewater by different separation techniques, Desalination 163 (2004) 287–296.

[7] A. Santos, P. Yustos, S. Gomis, G. Ruiz, and F. Garcia-Ochoa, Reaction network and kinetic modeling of wet oxidation of phenol catalyzed by activated carbon, Chem. Eng. Sci. 61 (2006) 2457–2467.

[8] M. Pérez, F. Torrades, J. A. García-Hortal, X. Domènech, and J. Peral, Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, Appl. Catal. B: Environ. 36 (2002) 63–74.

[9] M. G. Joshi and R. L. Shambaugh, The kinetics of ozone-phenol reaction in aqueous solutions, Water Res. 16 (1982) 933–938.

[10] A. M. Amat, A. Arques, F. López, and M. A. Miranda, Solar photo-catalysis to remove paper mill wastewater pollutants, Solar Energy, 79 (2005) 393–401.

[11] G. Busca, S. Berardinelli, C. Resini, and L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288.

[12] C. W. Jones, Applications of hydrogen peroxide and derivates, Royal Society of Chemistry: London, (1999) pp. 264.

[13] N. Azbar, T. Yonar, K. Kestioglu, Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere 55 (2004) 35–43.

[14] S. Esplugas, J. Giménez, S. Contreras, E.Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[15] J.J. Pignatello, E.E. Oliveros, A. Mackay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Critical Rev. Environ. Sci. Technol. 36 (2006) 1–84.

[16] S. Caudo, G. Centi, C. Genovese, and S. Perathoner, Copper and iron-pillared clay catalysts for the WHPCO of model and real wastewater streams from olive oil milling production, Appl. Catal. B: Environ. 70 (2007) 437–446.

[17] S. Perathoner and G. Centi, Wet hydrogen peroxide catalytic oxidation (WHPCO) of organic waste in agro-food and industrial streams, Top. Catal. 33 (2005) 207–224.

[18] E. Ahumada, H. Lizama, F. Orellana, C. Suárez, A. Huidobro, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, Catalytic oxidation of Fe(II) by activated carbon in the presence of oxygen: Effect of the surface oxidation degree on the catalytic activity, Carbon 40 (2002) 2827–2834.

[19] F. Rodríguez-Reinoso, The role of carbon materials in heterogeneous catalysis, Carbon 36 (3) 1998, 159–175.

[20] S. H. Joo, A.J. Feitz, D.L. Sedlak, D. Waite, Quantification of the oxidizing capacity of nanoparticulate zero-valent iron, Environ. Sci. Technol. 39 (2005) 1263–1268.

[21] I.A. Katsoyiannis, T. Ruettimann, S.J. Hug, pH dependence of Fenton reagent generation and As(III) oxidation and removal by corrosion of zero valent iron in aerated water, Environ. Sci. Technol. 42 (2008) 7424–7430.

[22] M. Kallel, C. Belaid, T. Mechichi, M. Ksibi, B. Elleuch, Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron, Chem. Eng. J. 150 (2009) 391–395.

[23] H. Sun, G. Zhou, S. Liu, H. Ang, M. Tadé, S. Wang, Nano-Fe0 encapsulated in Microcarbon spheres: Synthesis, Characterization, and Environmental Applications ACS-Appl. Mater. Interfaces, 4 (2012) 6235−6241.

[24] T. Zhou, Y. Li, J. Ji, F. Wong, X. Lu, Oxidation of 4-chlorophenol in a heterogeneous zero valent iron/H_2O_2 Fenton-like system: kinetic, pathway and effect factors, Sep. Purif. Technol., 62 (2008) 551–558.

[25] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing, Chem. Eng. J. 152 (2009) 498–502.

[26] D.H. Bremner, A.E. Burgess, D. Houllemare, K.C. Namkung, Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, Appl. Catal. B: Environ. 63 (2006) 15–19.

[27] H. Liu, G. Li, J. Qu, H. Liu, Degradation of azo dye Acid Orange 7 in water by Fe0/granular activated carbon system in the presence of ultrasound, J. Hazard. Mater. 144 (2007) 180–186.

[28] B.T. Meshesha, R.J. Chimentào, F. Medina, J.E. Sueiras, Y. Cesteros, P. Salagre, F. Figueras, Catalytic hydrodechlorination of 1,2,4-trichlorobenzene over Pd/Mg(Al)O catalysts, Appl. Catal. B: Environ. 87 (2009) 70–77.

[29] A. Pineau, N. Kanari, I. Gaballah, Kinetics of reduction of iron oxides by H_2 part I: Low temperature reduction of hematite, Thermochim. Acta, 447 (2006) 89–100.

[30] A. Li, C. Tai, Z. Zhao, Y. Wang, Q. Zhang, G. Jiang, J. Hu, Debromination of decabrominated diphenyl ether by resin-bound iron nanoparticles, Environ. Sci.Technol. 41 (2007) 6841–6846.

[31] H. Zhu, Y. Jia, X. Wu, Removal of arsenic from water by supported nano zero-valent iron on activated carbon, J. Hazard. Mater. 172 (2009) 1591–1596.

[32] P. Shukla, S. Wang, H. Sun, H. Ang, M. Tadé, Adsorption and heterogeneous advanced oxidation of phenolic contaminants using Fe loaded mesoporous SBA-15 and H_2O_2, Chem. Eng. J., 164 (2010) 255-260.

[33] Y. Segura, F. Martínez, J.A. Melero, R. Molina, R. Chand, D.H. Bremner, Enhancement of the advanced Fenton process (Fe0/H_2O_2) by ultrasound for the mineralization of phenol, Appl. Catal. B: Environ. 113–114 (2012) 100–106.

[34] Y. Segura, F. Martínez, J.A. Melero, Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron, Appl. Catal. B: Environ. 136–137 (2013) 64–69.

[35] C. Walling, Fenton´s reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.

[36] A. Eftaxias, J. Font, A. Fortuny, A. Fabregat, F. Stüber, Catalytic wet air oxidation of phenol over active carbon catalyst: Global kinetic modelling using simulated annealing, Appl Catal B: Environ. 67 (2006) 12–23.

[37] A. Rey, M. Faraldos, J.A. Casas, J.A. Zazo, A. Bahamonde, J.J. Rodríguez, Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: Influence of iron precursor and activated carbon surface, Appl. Catal. B: Environ. 86 (2009) 69–77.

[38] A. Santos, E. Barroso, F. Garcia-Ochoa, Overall rate of aqueous-phase catalytic oxidation of phenol: pH and catalyst loading influences, Catal. Today 48 (1999) 109–117.

[39] J.A. Melero, G. Calleja, F. Martínez, R. Molina, M.I. Pariente, Nanocomposite Fe_2O_3/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions, Chem. Eng. J. 131 (2007) 245–256.

FIGURE CAPTIONS

Fig. 1. SEM images of the AC, Fe/AC and nZVI/AC (a) ×500 (b) ×20000

Fig. 2. X-ray diffraction analysis of (a) AC, (b) Fe/AC and (c) nZVI/AC

Fig. 3. (a) Phenol and (b) TOC removal for different catalysts. (30 ºC, initial pH = 3.0, 150 mg/L of phenol, 1 g/L of catalyst, 750 mg/L of H_2O_2, 120 min). Open and full symbols represent results by adsorption and oxidation respectively.

Fig. 4. (a) Phenol removal versus time and (b) TOC removal and Leached Fe (%) after 120 min of reaction for different initial concentrations of phenol. (1 g/L of nZVI/AC-9%-H, 30 ºC, pH 3.0, stoichiometric ratio of H_2O_2, and 120 min).

Fig. 5. Phenol removal versus time for different initial solution pH of phenol. (150 mg/L of phenol, 1 g/L of nZVI/AC, 30 ºC, 750 mg/L of H_2O_2, 120 min).

Fig. 6. X-ray diffraction analysis of a) nZVI/AC (fresh catalyst), b) After 1st run c) After 2nd run and d) After 3rd run

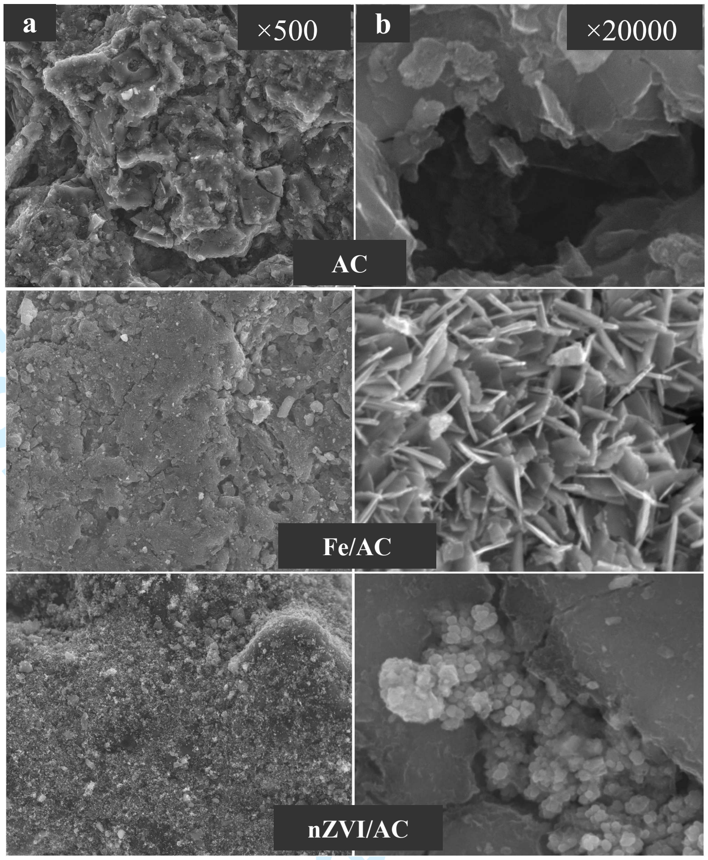

Fig. 1

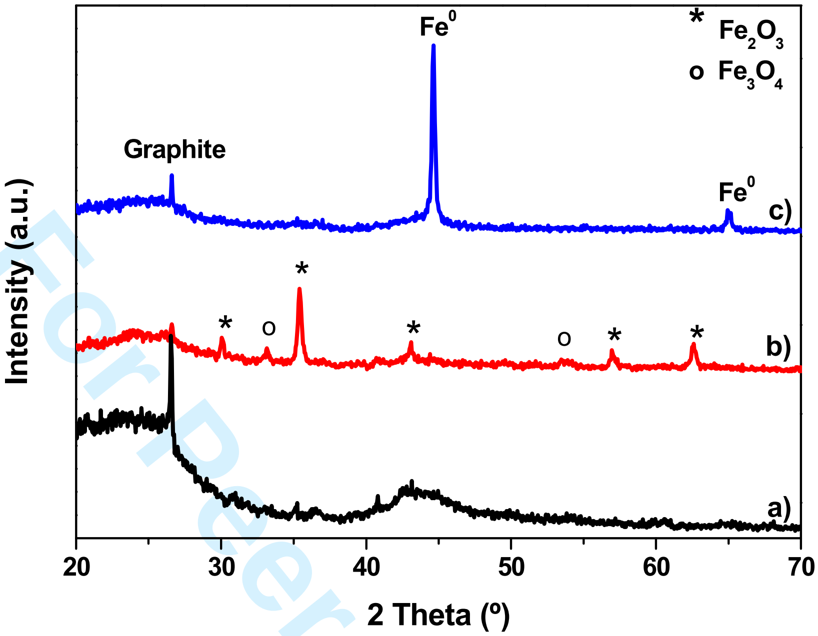
Fe^0
* Fe_2O_3
o Fe_3O_4
Graphite
Fe^0
c)
b)
a)
Intensity (a.u.)
20
30
40
50
60
70
2 Theta (º)

Fig. 2

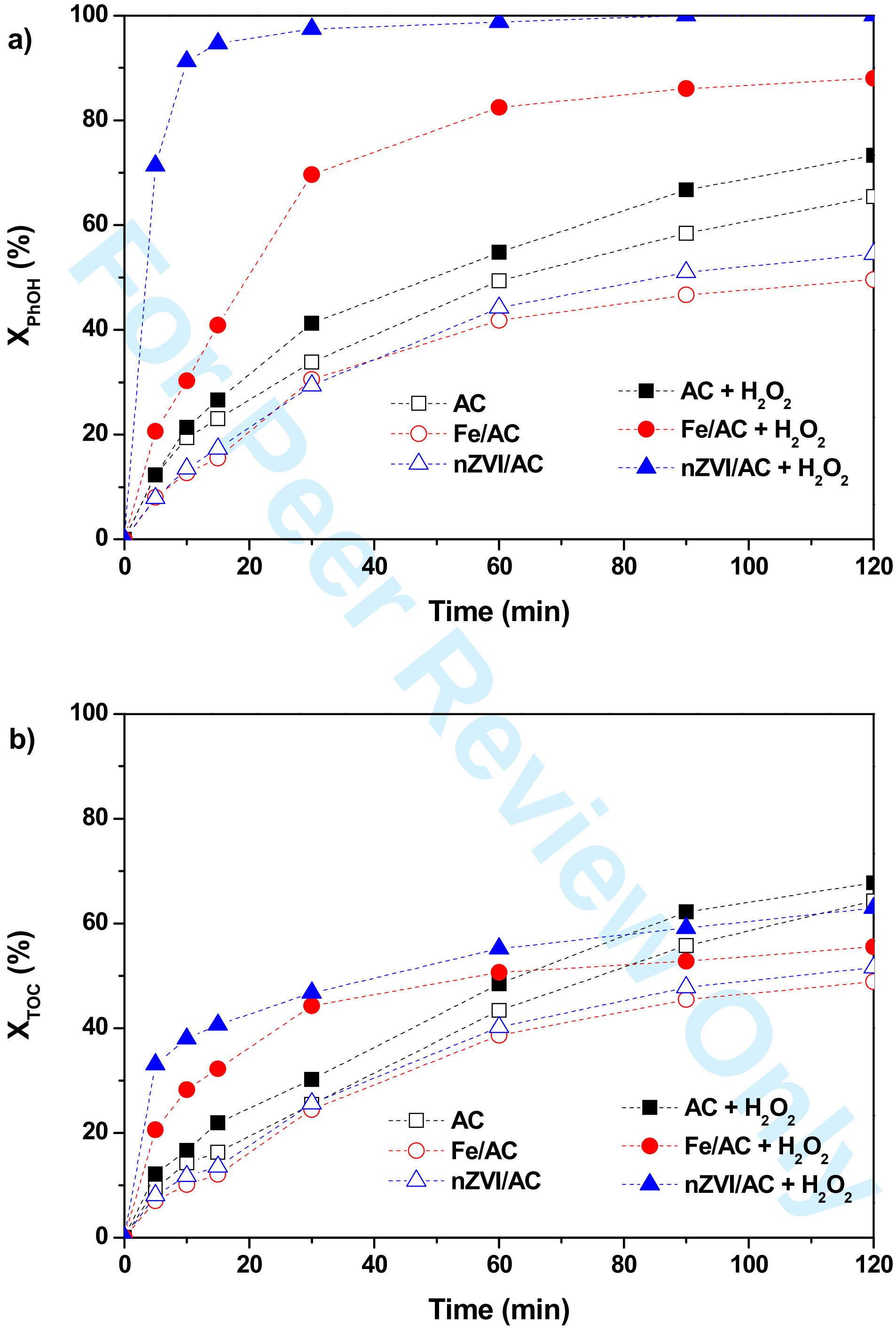
a)
X_{PhOH} (%)
0
20
40
60
80
100
0
20
40
60
80
100
120
Time (min)
AC
Fe/AC
nZVI/AC
AC + H_2O_2
Fe/AC + H_2O_2
nZVI/AC + H_2O_2
b)
X_{TOC} (%)
0
20
40
60
80
100
0
20
40
60
80
100
120
Time (min)
AC
Fe/AC
nZVI/AC
AC + H_2O_2
Fe/AC + H_2O_2
nZVI/AC + H_2O_2

Fig. 3

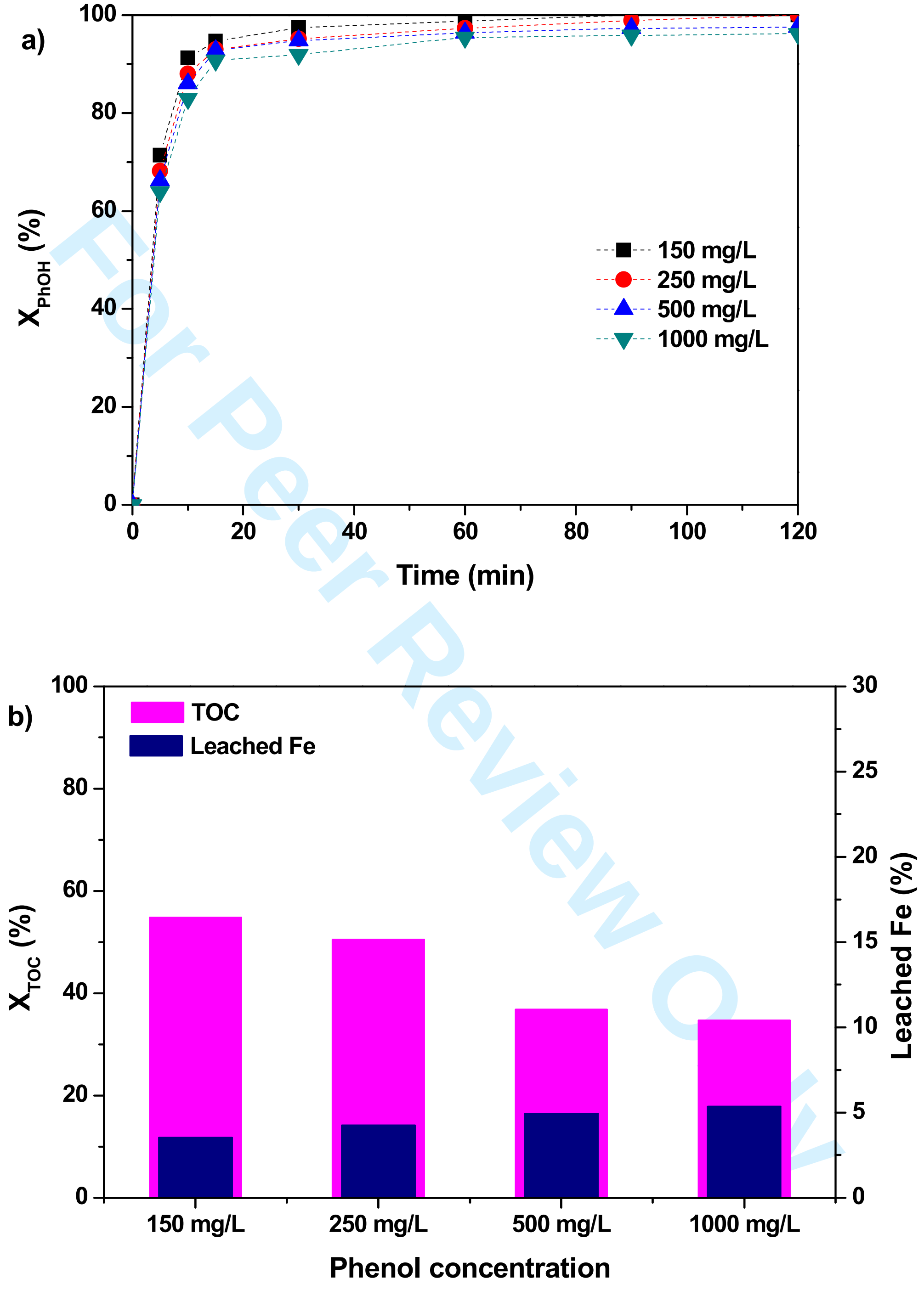
a)
X_{PhOH} (%)
0
20
40
60
80
100
Time (min)
0
20
40
60
80
100
120
150 mg/L
250 mg/L
500 mg/L
1000 mg/L
b)
X_{TOC} (%)
Leached Fe (%)
TOC
Leached Fe
0
20
40
60
80
100
0
5
10
15
20
25
30
150 mg/L
250 mg/L
500 mg/L
1000 mg/L
Phenol concentration

Fig. 4

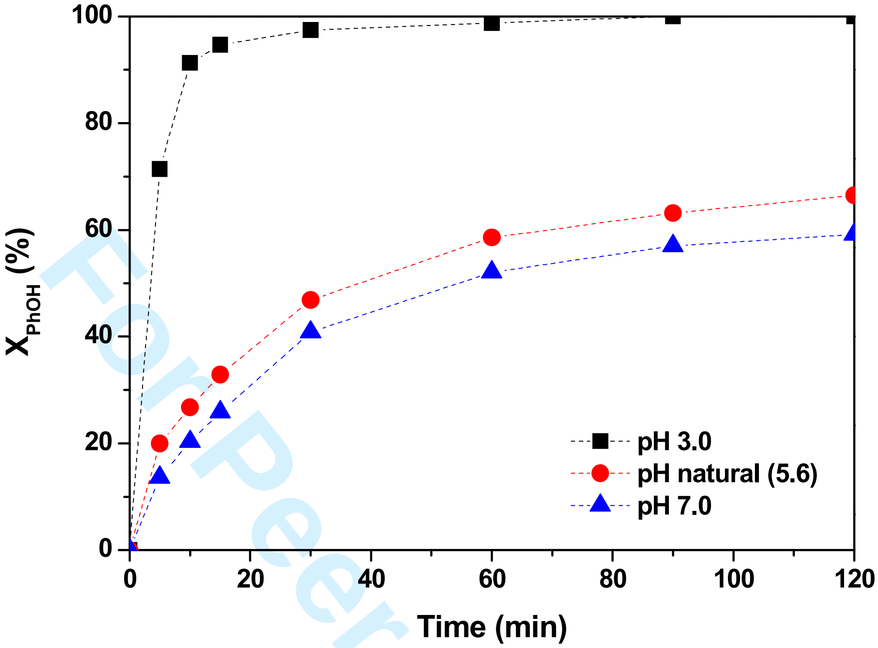
100
80
60
40
20
0
X_{PhOH} (%)
0
20
40
60
80
100
120
Time (min)
pH 3.0
pH natural (5.6)
pH 7.0

Fig. 5

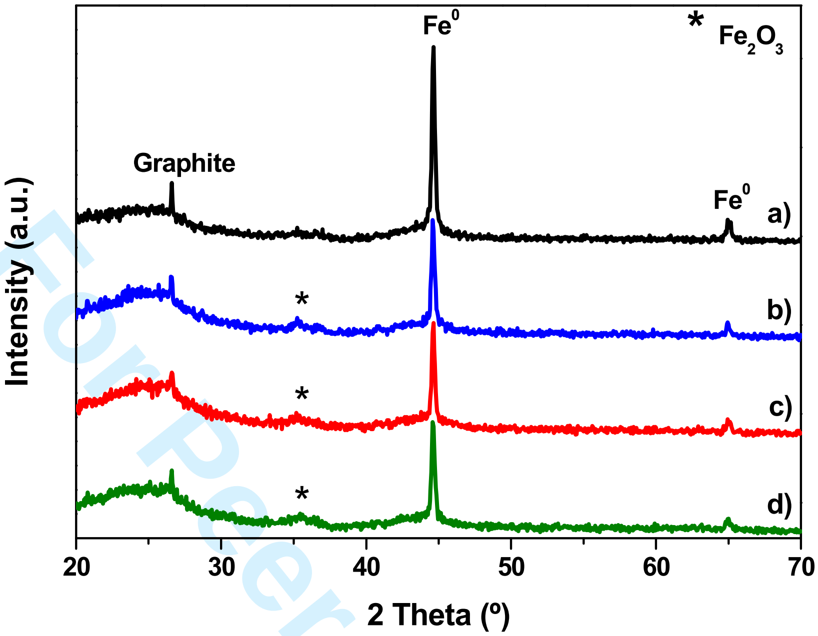
Fe^0
* Fe_2O_3
Graphite
Fe^0
a)
b)
c)
d)
*
*
*
Intensity (a.u.)
20
30
40
50
60
70
2 Theta (º)

Fig. 6

Table 1. Properties of the support and the supported catalysts.

Catalyst	**S_{BET} (m^2/g)**	**S_{meso} (m^2/g)**	**V_{micro} (cm^3/g)**	**Fe load (wt %)**
AC	1055	200	0.640	0.31
Fe/AC	962	212	0.538	8.17
nZVI/AC	978	198	0.544	8.20

Table 2. Leached iron after 30, 60 and 120 min of adsorption/oxidation tests for Fe/AC and ZVI/AC catalysis. (150 mg/L of phenol, 1 mg/L of catalyst, 30 ºC, 750 mg/L of H_2O_2).

Samples	**Leached iron (%)**					
	In adsorption tests			**In oxidation tests**		
	30 min	60 min	120 min	30 min	60 min	120 min
Fe/AC	0.75	1.51	2.32	1.31	1.50	2.81
nZVI/AC	0.83	1.42	2.54	1.25	2.05	3.12

Table 3. Effect of initial pH on Fe leaching from the catalyst after 30, 60 and 120 min of reaction (150 mg/L of phenol, 1 mg/L of nZVI/AC, 30 ºC, 750 mg/L of H_2O_2).

Initial solution pH	**Reaction time (min)**	**Leached Fe (%)**
3.0	30	1.25
	60	2.05
	120	3.12
5.6	30	1.25
	60	1.46
	120	1.99
7.0	30	1.19
	60	1.23
	120	1.38

Table 4. Catalytic behaviour of the catalyst after 30, 60 and 120 min of reaction for the three consecutive runs (30 ºC, initial pH 3.0, 150 mg/L of initial phenol concentration, 100 mg of nZVI/AC, 750 mg/L of H_2O_2).

Run	**Time (min)**	**X_{PhOH} (%)**	**X_{TOC} (%)**	**Leached Fe (%)**
1	30	97.4	46.7	1.25
	60	98.8	55.2	2.05
	120	100	62.9	3.12
2	30	89.3	37.2	0.50
	60	92.9	48.1	0.92
	120	96.4	56.6	1.74
3	30	84.4	32.4	0.83
	60	89.7	44.0	1.16
	120	93.3	53.3	1.77