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

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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 of phenol. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), ICP, and N_2 adsorption–desorption, and their performance was 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 toward phenol degradation was found to be enhanced by nZVI/AC catalysts compared to that of Fe/AC. In the range 150–1,000 mg/L, phenol conversion above 90% can be reached using these catalysts after only 15 min of the 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 the reaction. It was also observed that the stability or reutilization of the catalyst was 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 a starting or intermediate compound in many chemical, petrochemical, and pharmaceutical process industries; and also it is formed in the oxidation pathway of high-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 concentrations of more toxic pollutants [8–11]. AOPs

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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 nanoscale zero-valent iron particles supported on activated carbon (nZVI/AC).

Activated carbon is being used since decades as an excellent adsorbent and supporting material due to its unique properties in mechanical strength and its 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 rates 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 Chaknialaet al. [25] and Bremner et al. [26], but in the above cases the degradation was always examined using 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 phenolic 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 the 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), sulfuric acid (98% purity), and sodium hydroxide (98% purity) were purchased from Sigma–Aldrich. The activated carbon (particle size 1.5 mm) was purchased from Merck. Deionized 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 deionized water in order to remove residuals or fines adsorbed on the surface. Finally, it was dried in an oven at 105˚C for 15 h. This sample was hereafter labeled as AC. The amount of ferrous nitrate needed for 9% wt of iron in the final catalyst was dissolved in minimum amount of deionized 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˚C and the 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 states. In the first one, the AC was heat treated under a nitrogen flow at 400˚C for 4 h. After this step, the Fe was in the form of Fe_2O_3 (see Section 3.1, XRD results) and the catalyst was labeled as Fe/AC. In the second route, it was heat treated under a nitrogen flow at 400˚C for 1 h, and then reduced at 400˚C under a hydrogen flow for 3 h [28,29]. In this case, the Fe was 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 analyzer. The samples were out gassed 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 the samples. X-ray diffraction (XRD) analysis using a Siemens model of D5000 diffractometer with Cu Kα ($\lambda = 1.406$ 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 XL30 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˚C 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 sulfuric acid when required. Once the temperature reached 30˚C, 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 nylon syringe 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 chromatography (HPLC, model 1220 Infinity LC, Agilent Technologies) equipped with UV detector and a C18 reverse phase column (Hypersil ODS, 5 μm, 25 × 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 to 1.41 by the addition of sulfuric 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:

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

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

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

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

3. Results and discussion

3.1. Catalyst characterization

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 1,055 to 962 m^2/g and the 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 1,055 to 978 m^2/g and the 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, slight decrease in the surface area and the 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 oxidized or reduced. From the ICP–OES analysis, slight variations (<10%) were 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,

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	1,055	200	0.640	0.31
Fe/AC	962	212	0.538	8.17
nZVI/AC	978	198	0.544	8.20

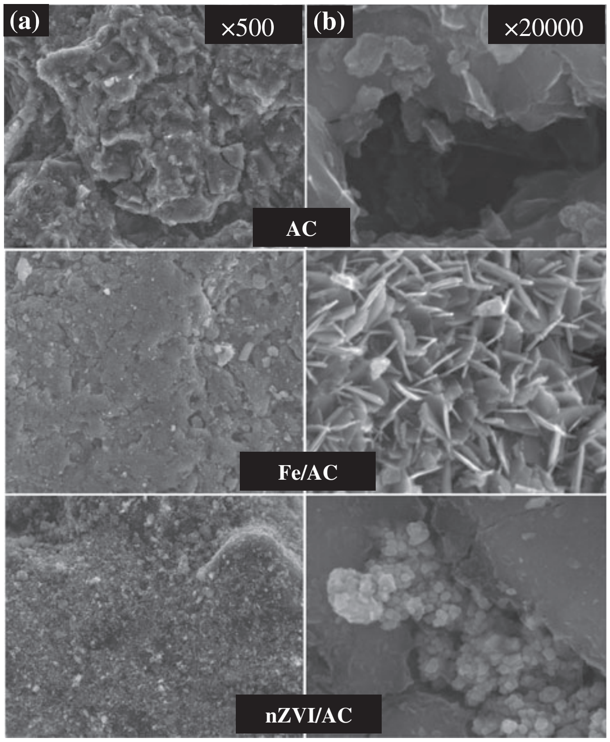

Fig. 1. SEM images of the AC, Fe/AC, and nZVI/AC (a) ×500 (b) ×20,000.

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. 1(b) (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 allowed 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.

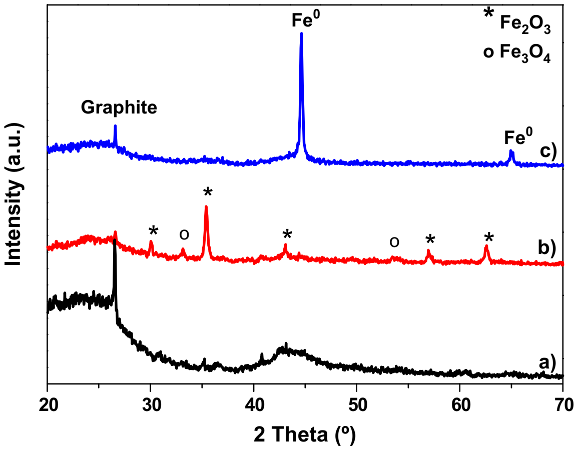

Fig. 2. XRD analysis of (a) AC, (b) Fe/AC, and (c) nZVI/AC.

3.2. Catalytic activity

3.2.1. Preliminary adsorption and oxidation tests

In the 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 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˚C.

Fig. 3(a) 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

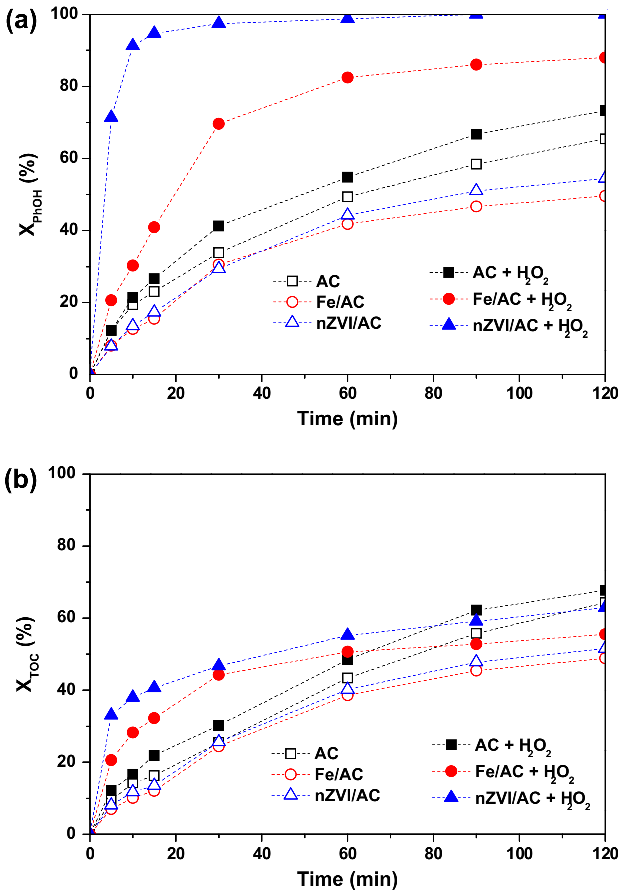

Fig. 3. (a) Phenol and (b) TOC removal for different catalysts (30˚C, initial pH 3.0, 150 mg/L of phenol, 1 g/L of catalyst, 750 mg/L of H_2O_2, for 120 min). Open and full symbols represent results by adsorption and oxidation, respectively.

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 the 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 the cases. On the contrary, the AC containing supported Fe or nZVI enhances the initial rate, so after 60 min of the 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 the 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.

$$\mathrm{ZVI} + 2\mathrm{H}^+ \longrightarrow \mathrm{Fe}^{2+} + \mathrm{H}_2 \tag{3}$$

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \longrightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^- + \cdot\mathrm{OH} \tag{4}$$

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

Removal of TOC is presented in Fig. 3(b). 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 the reaction, above 64% compared to the AC-supported catalysts in respect with 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 the 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 behavior 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 of 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 analyzed 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 the reaction. This is because of the decrease of solution pH due to the intermediates formation, so more acidic pH favors iron leaching according to Rey et al. [37]. For instance, iron leaching from the nZVI/AC catalyst after 120 min of the 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 the reaction is quite similar for both the catalysts. Therefore, the enhancement of the initial reaction rates of the nZVI/AC catalyst cannot 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 the reaction.

3.2.2. Effect of initial phenol concentration

The effect of the initial phenol concentration was investigated in the range of 150–1,000 mg/L at pH 3.0 and 30℃, with the addition of 100 mg of nZVI/AC and the stoichiometric ratio of H_2O_2. Fig. 4(a) shows the phenol conversion evolution as a function of the 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 of the reaction with an initial phenol concentration of 1,000 mg/L. After 10 min, the phenol conversion obtained was 91, 88, 86, and 83%, respectively, for 150, 250, 500, and 1,000 mg/L.

As it can be seen in Fig. 4(b), 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 1,000 mg/L, after 2 h of the reaction. These values indicate that mineralization also correlates 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 (1,000 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 a higher pH, the precipitation of the insoluble iron hydroxides takes place and the rate of H_2O_2 decomposition is 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

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℃, and 750 mg/L of H_2O_2)

	Leached iron (%)					
	In adsorption tests			In oxidation tests		
Samples	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

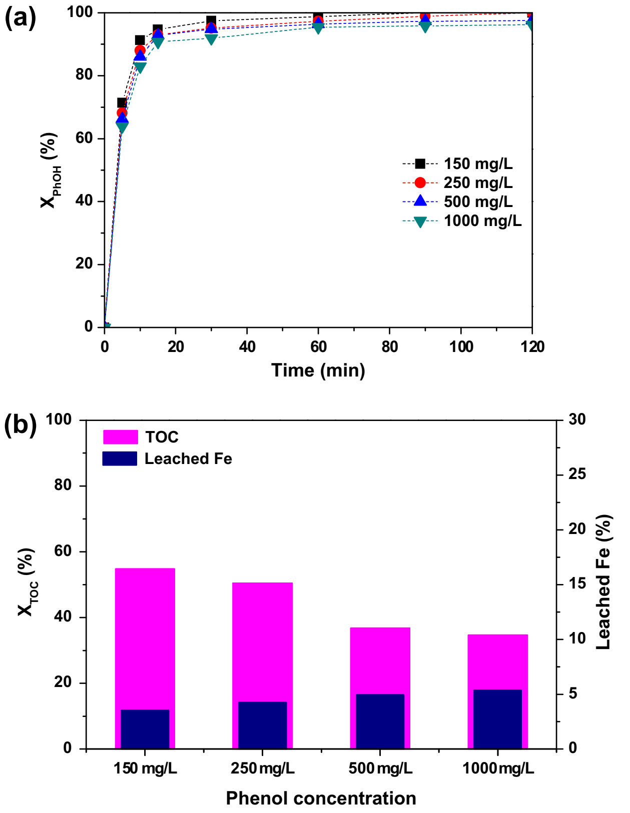

Fig. 4. (a) Phenol removal versus time and (b) TOC removal and Leached Fe (%) after 120 min of reaction for different initial concentrations of phenol (1 g/L of nZVI/AC, 30 ˚C, pH 3.0, stoichiometric ratio of H_2O_2, and 120 min).

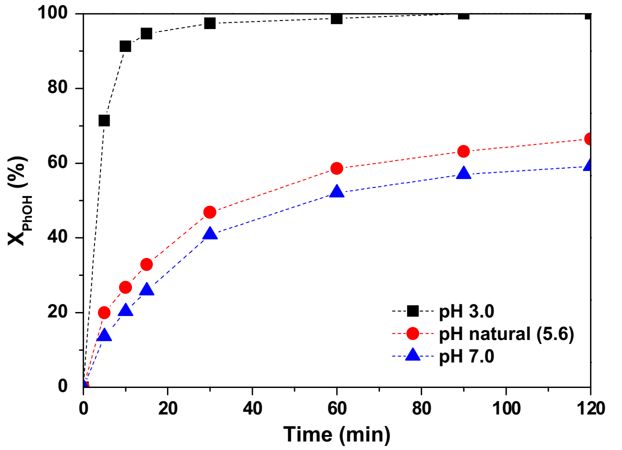

Fig. 5. Phenol removal vs. time for different initial solution pH of phenol (150 mg/L of phenol, 1 g/L of nZVI/AC, 30 ˚C, 750 mg/L of H_2O_2, 120 min).

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 ˚C, and 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

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 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. 5 shows that the phenol removal for pH 3.0 is almost complete within 60 min of the reaction, but for pH 5.6 and 7.0, the phenol removal drops up to 67 and 59%, respectively, after 120 min of the 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 the reaction is relatively comparable for all initial pH runs. For instance, after 30 min of the 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 cannot 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 and deionized water. The sample was then dried at 105 ˚C 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 ˚C.

Table 4 summarizes the evolution of phenol removal, TOC removal, and leached iron (%) upon

Table 4
Catalytic behavior of the catalyst after 30, 60, and 120 min of reaction for the three consecutive runs (30°C, initial pH 3.0, 150 mg/L of initial phenol concentration, 100 mg of nZVI/AC, and 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

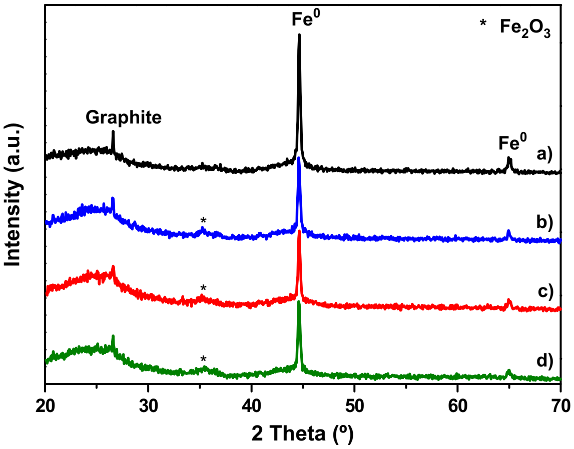

Fig. 6. XRD analysis of (a) nZVI/AC (fresh catalyst), (b) after 1st run (c) after 2nd run, and (d) after 3rd run.

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 the 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 et al. [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 the 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 survived 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°C, 750 mg/L of H_2O_2, 100 mg of nZVI/AC, and pH 3.0) for 30 and 120 min of the 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 species was detected after 30 min of the reaction and 2.80 mg/L (3.12%) of leached iron species after 120 min of the reaction. Then, phenol and hydrogen peroxide were further added to set the initial concentration of both in the filtered solution and a new reaction was started to determine the homogeneous contribution.

The result (not shown) reveals that the phenol conversion for 1.13 mg/L of iron species in homogeneous test was 41% after 120 min of the reaction, while for heterogeneous system the phenol conversion was completed just after 60 min of the 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 species 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 analysis indicated that nZVI was mostly found as clusters of aggregates of round-shaped particles and were loaded into the pores and cracks, rather than onto the outer surface. This interestingly allowed 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 nanoscale ZVI supported on activated carbon catalysts. Phenol conversion above 90% can be reached using this catalyst after only 15 min of the reaction using the stoichiometric hydrogen peroxide for phenol concentrations in the range 150-1,000 mg/L.

The recycling and consecutive reutilization of catalyst gave final phenol removal and nearly the same result was 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 the reaction.

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