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## Use of activated carbon as a reactive support to produce highly active-regenerable Fe-based reduction system for environmental remediation

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### ABSTRACT

Composites based on iron supported on high surface area activated carbon were prepared and characterized with <sup>57</sup>Fe Mössbauer spectroscopy, X-ray diffraction, saturation magnetization measurements and temperature-programmed reduction. Upon thermal treatment, the supported iron oxides react with carbon to yield reduced chemical species, i.e. Fe<sub>3</sub>O<sub>4</sub> and Fe(0). This so produced composite was found to be highly efficient in two environmental applications: (i) degradation of textile dye and (ii) reduction of Cr(VI) in aqueous medium. Sequential reuses evidenced a progressive chemical deactivation of the composites due to a corresponding oxidation of the reactive species. Even after being virtually deactivated, the initial chemical reducing ability of the composites can be regenerated by heating at 800 °C under N<sub>2</sub> atmosphere, and then reused for several consecutive times.

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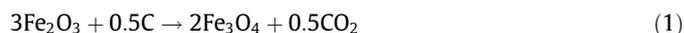
### 1. Introduction

Metallic iron has been extensively used in several environmental remediation processes, such as the reduction of organochlorated (Wang et al., 2009), nitroaromatic (Barreto-Rodrigues et al., 2009), dyes (Costa et al., 2010), pesticides (Ghauch, 2008), nitrate/nitrite (Li et al., 2010), Cr(VI) (Sharma et al., 2008), Hg(II) (Kluczka, 2009) and in the Fenton reaction (Moura et al., 2006). Although Fe(0) is a widely available, low cost and relatively bio-safe reducing agent, several aspects, such as low reduction rates, deactivation of the iron by surface passivation, can be overcome and be suitably prepared for applications in environmental remediation.

A simple strategy to increase the chemical reduction efficiency is to diminish the Fe(0) particle size (Cundy et al., 2008), as in large metallic particles the reducing sites tend to become unavailable due to their passivation by secondary mineral coatings, formed due to Fe(0) oxidation on the surface (Jeen et al., 2008).

An alternative way to produce Fe(0) with small particle sizes (20–100 nm) would be to produce them by chemically reducing ferric precursors on a carbon matrix. Utilization of carbonaceous materials as catalyst supports is well documented (Rodríguez-Reinoso, 1998). Recently, Dantas et al. (2006) and Zazo et al. (2006) prepared Fe<sub>2</sub>O<sub>3</sub>/AC (activated carbon) composites to cata-

lyze the degradation of pollutants in water. These composites, however, contain only Fe(III) species, which are less active than Fe(II) towards Fenton-like reactions. Alternatively, Magalhães et al. (2009) have prepared composites by thermal treatment of synthetic hematite (40 wt.%) in tar. Upon thermal treatment the hematite reacts with tar-carbon to produce reduced iron forms. The corresponding composites are found to be highly active for promoting Cr(VI) reduction and degradation of contaminants, such as textile dyes, as the iron species do occur chemically in their more reduced forms, often as Fe<sub>3</sub>O<sub>4</sub> and Fe(0). These species, active for Cr(VI) reduction reactions, can be prepared by thermal treatment under N<sub>2</sub> atmosphere, as follows:



We have recently observed that composites Fe(0)/Fe<sub>3</sub>O<sub>4</sub> are much more efficient reductant than is Fe(0) only (Coelho et al., 2008).

In this work, AC was used as a reactive support to produce highly reactive iron phases, i.e. Fe(0) and Fe<sub>3</sub>O<sub>4</sub>, for two environmental applications: (i) the reduction of Cr(VI) in aqueous medium and (ii) chemical degradation of a textile dye through a combined reduction/Fenton process. These Fe/AC composites show some innovative aspects: (i) the high surface area carbon supports significantly higher loads of Fe-bearing chemical species, dispersed as very small particles, enhancing further the composite reactivity.

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These composites have been early investigated as magnetic adsorbents in our laboratories (Oliveira et al., 2002); (ii) after deactivation, the oxidized iron in the composite can be regenerated by a thermal treatment. In this treatment, Fe(III) species react with carbon to produce new amounts of Fe(0) and Fe<sub>3</sub>O<sub>4</sub>, which are the active species.

Hereon, we report our results on the preparation, characterization and use of Fe/AC composites for the reduction of Cr(VI) in aqueous medium and the degradation of a textile dye by a combined reduction/Fenton process.

Chromium(VI) compounds are contaminants of special concern due to carcinogenic and mutagenic activities (Callao and Gómes, 2006). Chromium(VI) in the environment comes most from industrial activities, e.g. in electroplating, leather tanning, pulp production, ore and petroleum refining processes (Park et al., 2008), and from the high mobility of their oxyanions, e.g. CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> in water (Park et al., 2008). From their side, textile dye wastewaters are also very important pollutants for leading to xenobiotic compounds. The non-biodegradability of these dyes limits any effective biological treatment; an alternative physicochemical processes is necessary to allow safely manage or discard these wastewaters.

## 2. Material and methods

### 2.1. Composites preparation

Composites containing 28 wt.% Fe on microporous AC (Aldrich 865 m<sup>2</sup> g<sup>-1</sup>) were prepared by impregnation of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, followed by drying at 80 °C for 2 h and then heating them up to 400 °C for 1 h at 20 °C min<sup>-1</sup> under N<sub>2</sub> flow (50 mL min<sup>-1</sup>). Composites treated at 400 °C were also heated at 600, 700 and 800 °C for additional 1 h in the same conditions.

### 2.2. Characterization

Total Fe contents in the composites were measured by an atomic absorption spectrometer (AAS) Carls Zeiss Jena. Powder XRD patterns were obtained in a Rigaku model Geigerflex equipment, using Co K $\alpha$  radiation and taking scans from 20 to 95° (2 $\theta$ ) at a rate of 4° min<sup>-1</sup>. Silicon was used as external standard.

Mössbauer spectra were collected in a constant acceleration transmission mode with a 50 mCi Co<sup>57</sup>/Rh source. Mössbauer isomer shifts are quoted relatively to  $\alpha$ -Fe. The experimental resonance lines were fitted to Lorentzian functions with the least-square fitting statistical procedure of the NORMOSTM-90 computer program.

Temperature-programmed reduction (TPR) experiments were performed with a CHEMBET 3000 equipment, using 20 mg sample under 25 mL min<sup>-1</sup> H<sub>2</sub> (5%)/N<sub>2</sub> with heating rate of 10 °C min<sup>-1</sup>. Saturation magnetization measurements were performed in a portable magnetometer with magnetic field of 0.3 T calibrated with Ni metal.

### 2.3. Catalytic tests

The catalytic activity of the composites heated at 400, 600, 700 and 800 °C was evaluated basing on two reactions: (i) H<sub>2</sub>O<sub>2</sub> decomposition to O<sub>2</sub> and (ii) oxidation of model contaminant Drimaren Red (DR) with H<sub>2</sub>O<sub>2</sub>, in aqueous medium.

H<sub>2</sub>O<sub>2</sub> decomposition was carried out with addition of 3.5 mL of 30% H<sub>2</sub>O<sub>2</sub> into 6.5 mL of distilled water and 30 mg catalyst by measuring the formation of gaseous O<sub>2</sub> in a volumetric glass system. The experiments were carried out at 26 °C and pH 6.

The experiments with the DR were carried out with 10 mL solution (100 mg L<sup>-1</sup>) mixed with 30 mg of composite or pure AC. The

absorbance was monitored at 510 nm for 180 min. After this time, H<sub>2</sub>O<sub>2</sub> (0.3 M) was added at pH 6.0 and the absorbance monitored for additional 180 min. The Fe contents in solution after the reactions were determined by AAS.

### 2.4. Cr(VI) reduction reaction

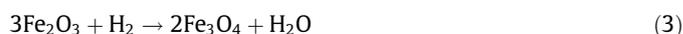
The experiments of Cr(VI) reduction were performed using 50 mL Cr solution (50 mg L<sup>-1</sup>) and 60 mg of composite under magnetic stirring at 28 ± 2 °C. The initial pH was adjusted to predetermined values by adding small quantities of 1:1 HCl or NaOH solutions. Total Cr and Fe contents in solutions before and after reactions were determined by AAS. Chromate desorption, using 0.1 M KH<sub>2</sub>PO<sub>4</sub> to compete for adsorption sites was used to assure that Cr(VI) was reduced in these system rather than merely adsorbed onto the composite (Zayed and Terry, 2003). The phosphate solution was in contact with the composite for 2 h after the reduction reaction. Then, the composite was magnetically removed from the reaction medium and the solution was acidified with HCl for analyses by AAS. The deactivation reaction was performed in five cycles using 50 mg L<sup>-1</sup> Cr and a solid/solution ratio of 4 g L<sup>-1</sup>. Their pH values were kept between 5 and 7 during the reactions by adding small quantities of 1:1 HCl solution. After deactivation, the composite was heated up to 800 °C for 1 h at 20 °C min<sup>-1</sup> under N<sub>2</sub> flow (50 mL min<sup>-1</sup>). Then, the reduction reactions were performed again with the regenerated composite.

## 3. Results and discussion

### 3.1. Characterization of the composites

To investigate the reduction of the iron oxides by carbon support, the Fe/AC composites were thermally treated at 400, 600, 700 and 800 °C under N<sub>2</sub> atmosphere for additional 1 h. Fe content was 28 ± 1 wt.% in all composites, as determined by AAS.

The TPR profiles for Fe/AC composites are shown in Supplementary material (SM), Fig. SM-1. It is observed an intense peak centered at 404 °C, for the sample Fe28% (400), which is interpreted as being due to the step involving reduction of hematite to magnetite (Eq. (3)). This peak practically disappears for samples Fe28% (600), Fe28% (700) and Fe28% (800), suggesting that hematite was converted to other more reduced species, putatively Fe<sub>3</sub>O<sub>4</sub> but also FeO and/or Fe(0) in the sequential chain of reactions with carbon.



The peak at 577 °C corresponds to the reduction of magnetite to wüstite (FeO) (Eq. (4)). It is interesting to observe that this peak disappears for the sample Fe28% (800), indicating that the iron in this composite was most drastically reduced by carbon to produce metallic iron.



A broad shoulder centered at 670 °C is due to the transition of wüstite to metallic iron (Eq. (5)). In all samples it can observe these shoulders, except in the composites heated at 800 °C, suggesting that this sample is basically constituted by Fe(0).



The XRD patterns (Fig. 1) for the sample Fe28% (400) showed reflections at 30.7° 2 $\theta$  corresponding to carbon (JCPDS File No. 1-640), hematite ( $a = 5.0347(2)$  Å and  $c = 13.7523(8)$  Å) and magnetite ( $a = 8.3856(5)$  Å). The average particle sizes estimated with the Scherrer equation (Patterson, 1939) were 28 and 33 nm for this

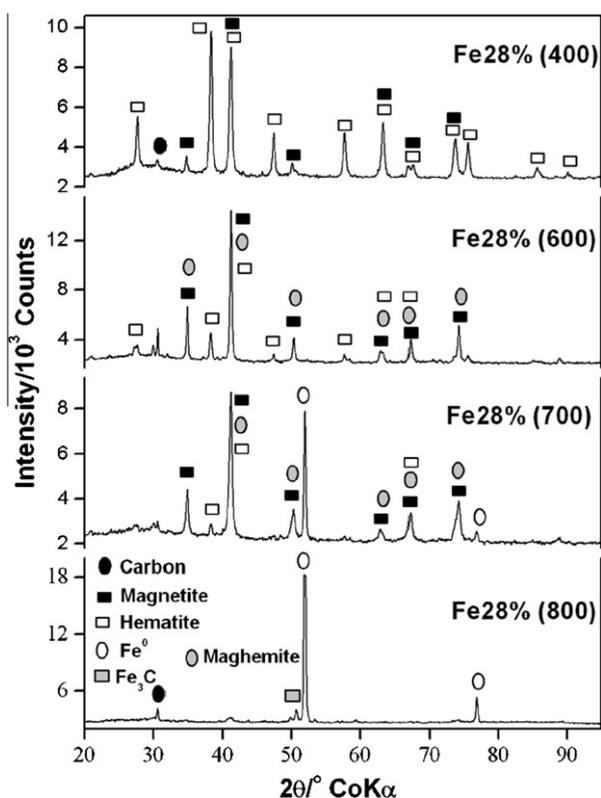


Fig. 1. Powder XRD patterns for composites heated at different temperatures.

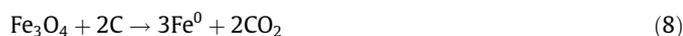
hematite and magnetite, respectively. Reflections of ferric nitrate were not observed in the diffraction pattern, suggesting that it was completely converted to produce iron oxides.

298 K Mössbauer spectrum (Fig. 2) revealed that sample Fe28% (400) does contain hematite (relative area, RA = 69%, Table SM-1), magnetite (20%) and a superparamagnetic Fe<sup>3+</sup> doublet (11%), which corresponds to disperse hematite in the material.

The XRD peaks for hematite (Fig. 1) strongly decreased after treatment at 600 °C with simultaneous increase of the characteristic reflections for the spinel structure, which could be magnetite ( $a = 8.388(1) \text{ \AA}$ ) and/or maghemite ( $a = 8.3431(3) \text{ \AA}$ ). Mössbauer analysis of this sample (Fig. 2) revealed the formation of large amounts of maghemite (RA = 63%). In less proportion it was observed resonance lines related to magnetite (7%), hematite (21%) and superparamagnetic Fe<sup>3+</sup> (9%). Maghemite in this sample was likely formed *via* the oxidation of magnetite. Therefore, it is proposed that magnetite is first formed (Eq. (6)), being then progressively oxidized to maghemite (Eq. (7)) when exposed to air at room temperature. This oxidation is well known to take place rapidly, especially for small particle size magnetite (Moura et al., 2005, 2006).



The XRD pattern (Fig. 1) for the sample Fe28% (700) shows a strong reflection at  $51.7^\circ 2\theta$ , which is characteristic of metallic iron, indicating that magnetite was indeed further reduced to Fe(0), according to the following equation:



The corresponding area of the Mössbauer spectrum (Fig. 2) may be decomposed in 25% due to Fe(0), 21% to magnetite, 42% to maghemite, 5% to hematite and 7% assignable to superparamag-

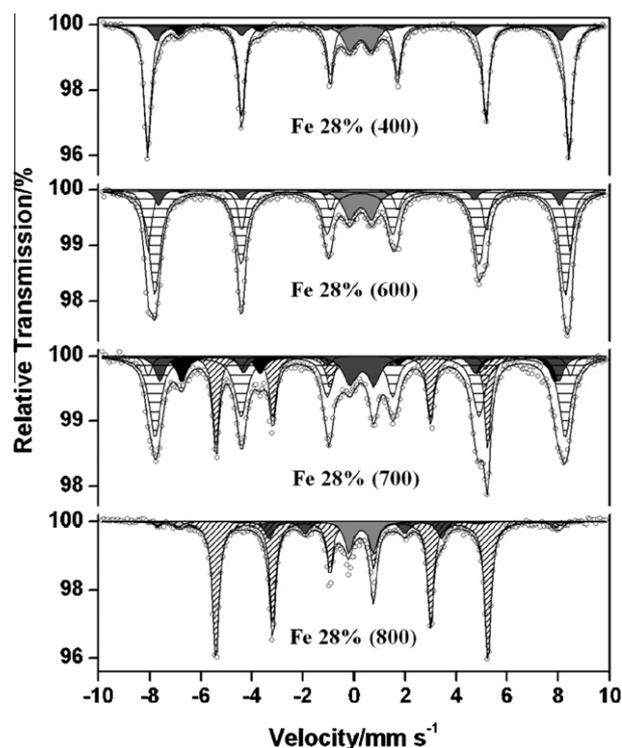


Fig. 2. 298 K Mössbauer spectra for composites heated at different temperatures.

netic Fe<sup>3+</sup> species. On the other hand, the XRD pattern for the sample Fe28% (800) shows reflections due to carbon and Fe(0) and a reflection, at  $50.8^\circ 2\theta$ , corresponding to Fe<sub>3</sub>C. Calculations by Scherrer equation showed Fe(0) particles with average crystallite size of 50 nm. Mössbauer revealed the formation of approximately 11% of iron carbide, suggesting the following process:



The corresponding Mössbauer spectrum (Fig. 2) still shows lines related to metallic iron (relative subspectral area, RA = 72%), magnetite (7%), superparamagnetic Fe<sup>3+</sup> (7%) and disperse metallic iron (3%) on the carbon.

As a result of the formation of magnetic phases, namely maghemite, magnetite (Fe28% (400) and Fe28% (600) samples) and, especially Fe(0) in the samples Fe28% (700) and Fe28% (800), there is a strong increase of the saturation magnetization  $\sigma$  for the composites:  $\sigma = 6, 26, 35$  and  $70 \text{ J T}^{-1} \text{ kg}^{-1}$ , respectively.

Considering the total iron chemical analysis and the Mössbauer RA, it was possible to estimate the proportion of iron phases in the composites. It can be clearly observed the decreasing amount of hematite and the appearing of other products due to reduction process with carbon (Fig. SM-2). The reduction process was more efficient when the composite was heated at higher temperatures, i.e. 700 and 800 °C, following the proportion of formed Fe(0) and Fe<sub>3</sub>C.

### 3.2. H<sub>2</sub>O<sub>2</sub> decomposition

The composites and pure AC treated at 400, 600, 700 and 800 °C were used to promote the hydrogen peroxide decomposition.



The H<sub>2</sub>O<sub>2</sub> decomposition is a versatile probe reaction to investigate the activity of heterogeneous systems towards the Fenton reaction. The obtained results for H<sub>2</sub>O<sub>2</sub> decomposition are shown

in Fig. 3. It can be observed a linear behavior of  $\text{H}_2\text{O}_2$  decomposition suggesting that the reaction can be approximated to a pseudo zeroth order dependence on the  $\text{H}_2\text{O}_2$  concentration. The  $\text{H}_2\text{O}_2$  without catalyst decomposes very slowly with rate constant of  $0.13 \text{ mM min}^{-1}$ . AC treated at 400, 600, 700 and  $800^\circ\text{C}$  showed rate constant of 0.66, 0.68, 1.1 and  $1.2 \text{ mM min}^{-1}$ , respectively.

The mechanism of  $\text{H}_2\text{O}_2$  decomposition with AC is based on the Haber–Weiss mechanism for Fenton reaction (Kimura and Miyamoto, 1994): the AC transfers electrons to the  $\text{H}_2\text{O}_2$  molecule to produce hydroxyl radicals:



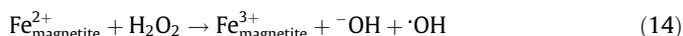
The  $\cdot\text{OH}$  radicals can then react with another  $\text{H}_2\text{O}_2$  molecule to produce  $\cdot\text{OOH}$ :



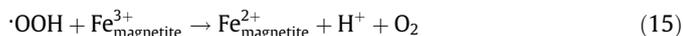
Finally, the  $\cdot\text{OOH}$  transfers one electron to  $\text{AC}^+$  species to produce  $\text{O}_2$  molecule and to regenerate the carbon surface.



The rate constants for composites were higher than the rate constants for AC, suggesting that iron phases are more active to  $\text{H}_2\text{O}_2$  than pure carbon. The rate constants for Fe28% (400), Fe28% (600), Fe28% (700) and Fe28% (800) were 3.2, 2.5, 3.7 and  $2.4 \text{ mM min}^{-1}$ , respectively. The activity of these composites is directly related to  $\text{Fe}^{2+}$  on the magnetite structure. Thus, a simplified mechanism of  $\text{H}_2\text{O}_2$  decomposition can be proposed. In this mechanism, the  $\text{Fe}^{2+}$  ions can donate an electron to  $\text{H}_2\text{O}_2$  molecule to produce  $\cdot\text{OH}$ :



The  $\cdot\text{OH}$  radicals can then react with another  $\text{H}_2\text{O}_2$  molecule to produce  $\cdot\text{OOH}$  (Eq. (12)). Posteriorly, the  $\cdot\text{OOH}$  radicals transfer one electron to  $\text{Fe}^{3+}$  on the magnetite structure to regenerate the  $\text{Fe}^{2+}$  species and to produce  $\text{O}_2$ :



Thus, both AC and magnetite do activate the  $\text{H}_2\text{O}_2$  molecule and produce  $\cdot\text{OH}$ , which can further promote the oxidation of contaminants.

### 3.3. DR degradation

The chemical activity of these composites was also investigated relatively to DR degradation. The experiments were carried out in

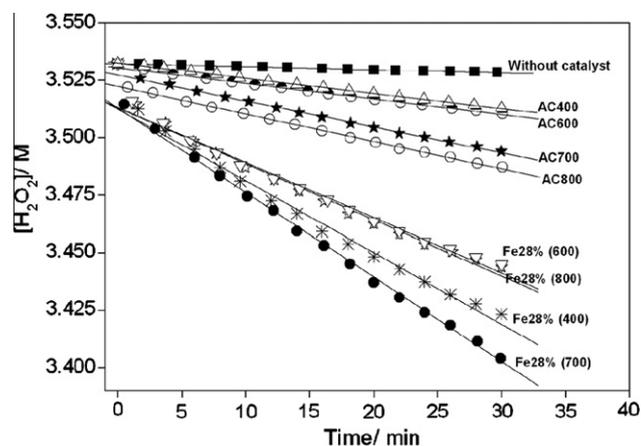


Fig. 3.  $\text{H}_2\text{O}_2$  decomposition in presence of pure AC and composites treated at different temperatures.

two stages: (i) adsorption and reduction of DR (the first 180 min) and (ii) oxidation via a heterogeneous Fenton reaction (Fig. 4).

It was observed that pure AC adsorbs only ca. 10% of the dye after 180 min. On the other hand, in presence of the samples Fe28% treated at different temperatures, especially  $800^\circ\text{C}$ , strong discoloration is observed in the first 180 min. This discoloration is mainly due to the chemical reduction of DR by  $\text{Fe}(0)$ , for being a more efficient reductant comparatively to magnetite.

A further discoloration is observed by adding  $\text{H}_2\text{O}_2$  after 180 min of the beginning of the reaction with the composite Fe28% treated at 600, 700 and  $800^\circ\text{C}$ . This discoloration is probably due to an oxidation step through the Fenton reaction. Previous works have shown that magnetite and  $\text{Fe}(0)/\text{Fe}_3\text{O}_4$  composites are highly active for the oxidation of organics with  $\text{H}_2\text{O}_2$  in water (Moura et al., 2005, 2006). In addition to this activity, carbon in the presence of  $\text{H}_2\text{O}_2$  produces hydroxyl radicals, which enhance the catalytic action of the whole system.

The composite Fe28% (800) tends to be slowly deactivated after consecutive reactions with the dye. However, its virtually complete reactivation can be achieved by thermal-treating the composite at  $800^\circ\text{C}$  in  $\text{N}_2$  atmosphere.

To investigate the possibility that homogeneous reactions involving leached Fe from the composites into the aqueous media may occur, the aqueous phases were analyzed by AAS. Fe contents were found to be below the  $0.08 \text{ mg L}^{-1}$  and this result can be taken to exclude any possibility of side-reactions due to dissolved iron species. Moreover, the leached Fe, as it was monitored by measuring the oxidation of DR solution in a batch experiment, had a removal capacity of 2%. This confirms that the oxidation reaction takes place dominantly via a heterogeneous mechanism.

### 3.4. Cr(VI) reduction reaction

The reaction of Cr(VI) in aqueous medium showed that pure AC decreased 5% of the initial Cr(VI); and commercial  $\text{Fe}(0)$ , which is usually used for this purpose, removed only 11% of Cr(VI) after 3 h. On the other hand, the composites Fe28% (400), Fe28% (600), Fe28% (700) and Fe28% (800) were able to removed 17%, 37%, 75% and 92% respectively, after 3 h.

Our results for chromate adsorption–desorption experiments suggest that  $\text{Fe}(0)$  in the composite is the most active phase for the reduction of Cr(VI). Also, the Cr(VI) reduction efficiency strongly depends on the amount of Fe in the composite as lower

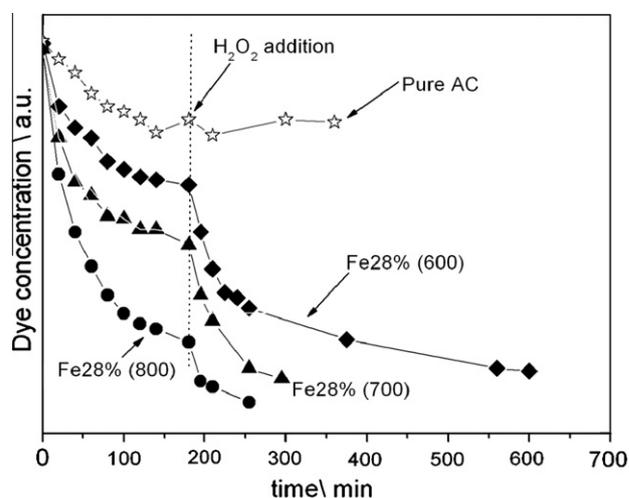


Fig. 4. DR discoloration using pure AC and composites treated at different temperatures.

iron contents, i.e. 4, 7 and 14 wt.% treated at 800 °C showed lower Cr(VI) reduction, namely 10%, 15% and 22%, respectively.

Fe28% (800) was used consecutively for three times without any significant loss of efficiency. From the fourth reaction a deactivation occurs, reaching ca. 15% Cr reduction after sixth reuse (Fig. 5, inset). This deactivation is likely related to oxidation of the Fe(0) by the successive reactions with  $\text{CrO}_4^{2-}$ . In fact, Mössbauer spectrum (Fig. 6) showed a strong  $\text{Fe}^{3+}$  doublet (RA = 36%) related to oxidized iron oxides phases and an increase in the magnetite content from 7% (before reaction) to 30% (after reaction). On the other hand, the Fe(0) content strongly decreases from 74% (before reaction) to 27% (after reaction).

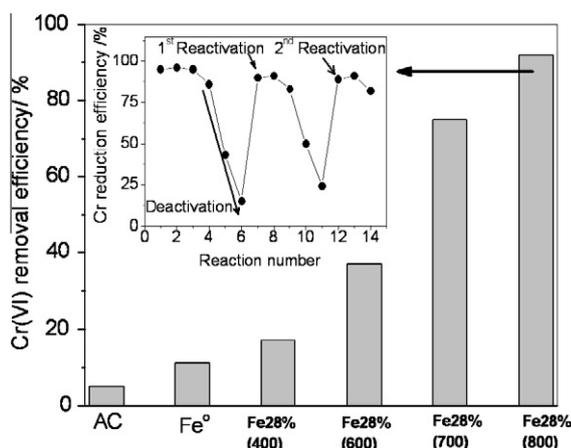


Fig. 5. Cr(VI) removal efficiency using pure AC, commercial Fe<sup>0</sup> and composites treated at different temperatures.

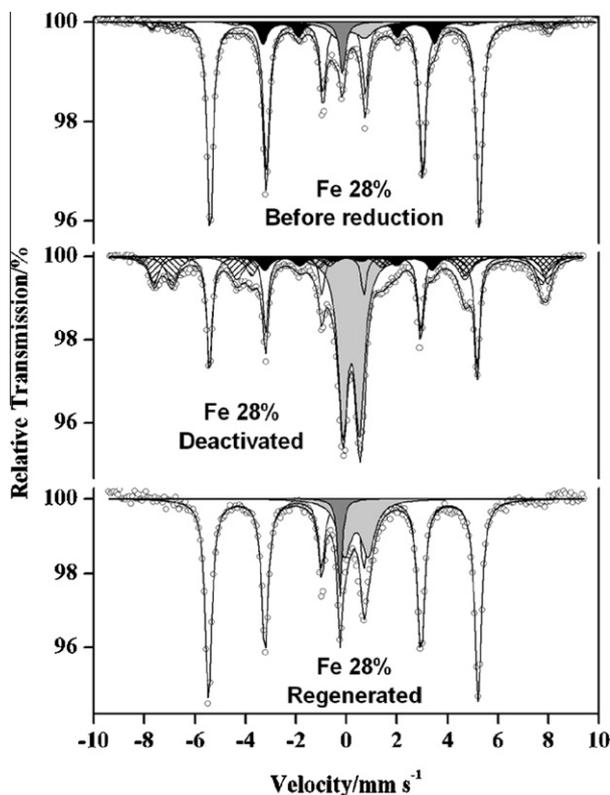
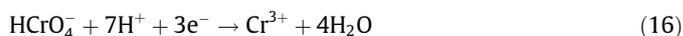


Fig. 6. 298 K Mössbauer spectra for the composite Fe28% (800) before reaction, after deactivation and after reactivation.

To investigate the regeneration of the reducing activity it was carried out a treatment of the composite at 800 °C under N<sub>2</sub> atmosphere, to favor carbon to react with oxidized iron forms, so to produce Fe(0). Mössbauer spectrum (Fig. 6) showed that after treatment, the Fe(0) was indeed massively regenerated. This means that oxidized species, i.e. magnetite and Fe<sup>3+</sup>, were reduced by reaction with carbon to produce back Fe(0) (RA = 81%). After this thermal treatment, the Cr reduction efficiency was completely restored for three more consecutive reactions, before being again deactivated. Similar result was observed by the time of a second reactivation cycle (Fig. 6, inset).

The kinetics of the Cr(VI) reduction was investigated by using the most active composite Fe28% treated at 800 °C and the results are shown in Fig. SM-3. It can be observed a rapid decrease in the Cr(VI) concentration during the first hours of reaction. However, after ca. 20 h reaction the reduction of Cr(VI) completely stops. The solution pH also strongly increases in the first 2 h of reaction reaching a value of 9. The reduction of  $\text{CrO}_4^{2-}$  consumes H<sup>+</sup> raising the pH as suggested by the simplified equations:



It is interesting to observe that after the reaction ceased, if the pH is adjusted down from 9 to ca. 6, the chemical activity on Cr(VI) reduction is restored. This result indicates that pH strongly affects the composite activity and the reaction kinetics.

#### 4. Conclusions

This novel and chemically very reactive system, acting at a time as reducer or oxidizer, depending on the reacting medium or on the substrate, can be independently accomplished with a single composite, which is prepared by thermal treatment of hematite supported on AC. Even after its chemical deactivation, the active Fe-reduced species of the composite can be regenerated by direct thermal re-treatment. This is a singular condition, as the carbon in the composites functions both as reactive support in iron-rich phases and as a catalyst promoter on the  $\cdot\text{OH}$  generation, a H<sub>2</sub>O<sub>2</sub>-containing medium. From the technological viewpoint, this novel reduction/oxidation system is very promising and represents an important insight on the development of new inexpensive and chemically efficient materials to environmental remediation processes.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.07.056.

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