# Potential of modified iron-rich foundry waste for environmental applications: Fenton reaction and Cr(VI) reduction

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## ARTICLE INFO

## ABSTRACT

A magnetic fraction (15%) from a waste of foundry sand (WFS), composed of sand, carbon, bentonite clay and iron (10%) was modified by thermal treatment at 400, 600 and 800 °C under inert atmosphere. Mössbauer analyses showed that the thermal treatment increased the amount of $Fe_3O_4$ from 25 to 55% by reduction of $Fe_2O_3$ and highly dispersed $Fe^{3+}$ by the carbon present in the waste. The $Fe_3O_4$ caused a significant increase on the activity of two important reactions with application in environmental remediation: the Fenton oxidation of indigo carmine dye with $H_2O_2$ and the reduction of Cr(VI) to Cr(III). The magnetic fraction of WFS was also mixed with hematite ($Fe_2O_3$) and thermally treated at 400, 600 and 800 °C. This treatment produced large amounts of surface $Fe_3O_4$ and increased substantially the rate of Fenton reaction as well as Cr(VI) reduction. This reactivity combined with the presence of carbon (an adsorbent for organic contaminants), bentonite clay (an adsorbent for metallic contaminants) and the granulometry/packing/hydrodynamic features make WFS a promising material for use in reactive permeable barriers.

## 1. Introduction

Waste foundry sand (WFS) is produced in large amounts in different parts of the world. Although this waste represents a significant problem for the foundry industry, only few studies have been carried out to address its reuse potential. For example, WFS has been investigated as aggregate in asphalt mix, in concrete production and in agriculture [1–3]. Also some applications for environmental remediation have been studied such as adsorbent for organic contaminants, e.g. trichloroethylene and metals, e.g. $Zn^{+2}$ [4,5].

Permeable reactive barriers (PRB) have been investigated to treat groundwater contamination for the last 20 years. PRB should combine a reactive material with appropriate physical/hydrodynamic properties to allow contaminant removal and fluid transportation. Several reactive materials have been investigated [6,7] for application in PRB. Zero-valent iron, an available and innocuous low cost reactive agent, has been extensively studied for the reduction of different contaminants, specially chromium(VI) species [8–11].

In this context, waste sands from the iron foundry industry (WFS) show several interesting features for application in PRB, e.g.

(i) composition based on harmless materials, e.g. silica sand, clay binder, carbon and residual iron particles; (ii) only Brazilian industries generate, per year, ca. 2 millions t of this waste and (iii) WFS contains sands with specific size, as required by PBRs composition.

In this work, a new approach is used to convert the iron rich magnetic fraction of WFS into a versatile material suitable for different environmental applications. In this approach, the magnetic iron rich fraction of the WFS is thermally treated and the carbon present in the waste reduces the different iron species to form active reducing iron phases (Eq. (1)).

$$Fe_2O_3/C(\text{waste sand}) \xrightarrow{N_2} Fe_3O_4 \xrightarrow{N_2} FeO \xrightarrow{N_2} Fe^0) \tag{1}$$
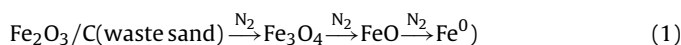
Two different environmental applications for the reduced WFS have been investigated, i.e. the heterogeneous Fenton reaction and the reduction of Cr(VI).

The classical Fenton reagent (a mixture of $Fe^{2+}$ and $H_2O_2$) is one of the most active systems for the oxidation of organics in water. This reactivity is due to the in situ generation of highly oxidative species, i.e. hydroxyl radicals, according to Eq. (2):

$$Fe^{2+}_{(aq)} + H_2O_2 \rightarrow Fe^{3+}_{(aq)} + OH^- + {}^\bullet OH \tag{2}$$
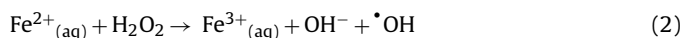
The development of an active heterogeneous system to promote the Fenton chemistry is of considerable interest since it could offer some advantages over the classical homogeneous Fenton reaction, such as no sludge formation, operation at near neutral pH and the possibility to recycle the iron promoter.

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In previous works, we have demonstrated that the combination of $Fe^0$ and $Fe_3O_4$ powder mixed by simply grinding accelerates the rate of the Fenton reaction [12–14]. This effect was discussed in terms of a thermodynamically favorable electron transfer from $Fe^0$ to $Fe^{3+}$ to produce $Fe^{2+}$ active for Fenton reaction [15].

Some works in the literature have suggested the use of $H_2O_2$ in PRB in a Fenton like reaction [16].

Iron reduced phases, e.g. $Fe^0$ and $Fe_3O_4$, are also involved in reduction of very hazardous Cr(VI) to Cr(III). Chromium is widely used in industrial processes, such as metal electroplating, leather tanning and metal surfaces coatings. Nevertheless, inefficient wastewater treatment or accidents, may result in contamination of groundwater with chromium (VI) [8]. In the present study we have investigated the use of $Fe^0$ and $Fe_3O_4$, produced by the reduction of WFS, for Cr(VI) reduction in aqueous phase.

## 2. Experimental

The waste of foundry sand (TEKSID, Brazil) was separated magnetically and only the magnetic fraction (15 wt% of the raw waste) was used in this work. The controlled reaction under inert atmosphere ($N_2$, 99.99%, 80 mL min$^{-1}$) was carried out by heating at 10 °C min$^{-1}$ up to 400, 600 or 800 °C for 1 h (these materials were named hereon as W400, W600 and W800, respectively). The magnetic fraction of WFS was also mixed with 20% of synthetic hematite, $Fe_2O_3$, manually ground for 2 min and with subsequent treated at 400, 600 and 800 °C (WHt400, WHt600 and WHt800) as described before. All prepared materials were cooled in inert atmosphere ($N_2$, 99.99%, 80 mL min$^{-1}$) until room temperature.

The transmission Mössbauer spectroscopy experiments were carried out in a CMTE spectrometer model MA250 with a $^{57}$Co/Rh source at room temperature using $\alpha$-$Fe^0$ as reference. Magnetization measurements were carried out in a portable magnetometer with a magnetic field of 0.3 T calibrated with Ni metal [17]. Scanning electron microscopy (SEM) analyses were carried out in a Jeol JKA 8900RL.

The adsorption tests were performed with 10 mL solution of methylene blue dye at the concentration of 50 mg L$^{-1}$ and 100 mg of adsorbent and monitored by UV/vis measurements.

The hydrogen peroxide (synth) decomposition was carried out with 7 mL of a 2,7 mol L$^{-1}$ solution of $H_2O_2$ at pH 5.5 ± 0.2 (natural pH of the $H_2O_2$ solution) with 30 mg catalyst (WFS) measuring the formation of $O_2$ in a volumetric glass system. The oxidation of the indigo carmine dye (IC) 3.5 mL at the concentration of 50 mg L$^{-1}$ was carried out with $H_2O_2$ (0.3 M) at pH 6.0 ± 0.2 (natural pH of the dye/$H_2O_2$ solution) with 15 mg of catalyst (WFS) and monitored by UV/vis measurements.

Cr(VI) reduction was performed using a 10 mL solution of 50 mg L$^{-1}$ Cr (initial pH ca. 6.5) with 200 mg of WFS catalyst at 28 ± 2 °C. During the reaction aliquots of 0.1 mL were collected (catalyst was separated magnetically) and the Cr(VI) complexed with 1,5-diphenylcarbazide (5 g L$^{-1}$ in acetone) at pH 1 ($H_2SO_4$). The concentration of the red complex formed was determined spectrophotometrically at 542 nm. Commercial $Fe^0$ powder (synth) at pH 6.5 was used to compare with the activity of the WFS catalysts.

## 3. Results and discussion

### 3.1. Magnetic fraction of waste foundry sand

In the foundry process silica (sand), coal and bentonite clay are mixed to produce the green sand which is used to mold the molten metal (Fig. 1). After the casting process the green sand used becomes a waste, WFS. The WFS can be separated by a simple magnetic process into two fractions, i.e. an iron rich magnetic waste of

**Table 1**
BET surface area of the raw materials and the magnetic WFS.

| Material | BET surface area/m$^2$ g$^{-1}$ |
|---|---|
| Silica sand | 0.1 |
| Coal | 50 |
| Bentonite clay | 35 |
| MWFS | 0.8 |

foundry sand (MWFS) corresponding to approximately 15 wt%, and a non-magnetic fraction (85 wt%). Magnetization measurements showed values of 12 J T$^{-1}$ kg$^{-1}$ for the magnetic fraction of WFS.

The SEM images for the raw materials, the green sand and the WFS are shown in Fig. 2.

It can be observed that particle size ranges from 100 to 800 μm for silica (Fig. 2(a)) and coal (Fig. 2(b)), whereas bentonite particles (Fig. 2(c)) are much smaller and less regular. Green sand (Fig. 2(d)), a mechanical mixture of silica (90 wt%), coal (1–4 wt%) and bentonite (6–9 wt%), showed very similar morphology with silica and coal. The magnetic WFS (Fig. 2(e)) showed similar morphology with green sand. These results suggest that the magnetic particles introduced during the casting process are small and likely incorporated on the WFS particles. An important point to observe in WFS for PRB application is the particle size. Previous works suggest that the particle size of sand used in PRB is between 150 and 2000 μm [18–20]. Therefore, WFS with particle size of ca. 200 μm seems suitable for PRB applications.

Coal and bentonite show relatively high surface areas in contrast to the low surface area of silica (Table 1). The mixture of these components with high silica content exhibits small surface area.

### 3.2. Thermal treatment of the WFS under $N_2$ atmosphere

Mössbauer analysis of the WFS (Fig. 3, hyperfine parameters are given in Supplementary Material) showed the presence of different iron phases, i.e. highly dispersed $Fe^{3+}$ (poorly crystallized iron phases and $Fe^{3+}$ species dispersed on the material surface) $\alpha$-$Fe_2O_3$, $Fe_3Si_8O_{22}(OH)_2$, $Fe_3O_4$ and $Fe^0$ with spectral areas of 20, 14, 14, 26, 26%, respectively.

In order to increase the amount of reduced Fe phases, i.e. $Fe_3O_4$ and $Fe^0$, the magnetic fraction was thermally treated under a nitrogen atmosphere to promote the reaction of $Fe^{3+}$ species with carbon. Previous works showed that between 400 and 600 °C carbon can react with oxidized iron phases, $Fe^{3+}$ and $Fe_2O_3$, to produce $Fe_3O_4$ [21,22]. At temperatures near 800 °C metallic iron is formed. Moreover, metallic iron can react with $Fe_2O_3$ to generate $Fe_3O_4$ [23,24]. Based on these results, reduction temperatures of 400, 600, and 800 °C were selected to produce reduced iron phases from WFS.

The Fe phase compositions obtained from the relative Mössbauer spectral areas are shown in Fig. 4.

After treatment at 400 °C (W400) an increase of $Fe_3O_4$ from 26 to 42% with a decrease on $Fe_2O_3$ and $Fe^{3+}$ can be observed. These results clearly indicate that the oxidized Fe phases are reduced to magnetite. As the $Fe^0$ phase shows only a small decrease in relative area, the reduction of the $Fe_2O_3$ and $Fe^{3+}$ phases is likely due to the presence of carbon in the sample (Eq. (3)).

$$C + 6Fe_2O_3 \text{ (or } Fe^{3+}) \rightarrow 4Fe_3O_4 + CO_2 \qquad (3)$$
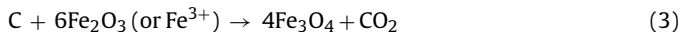
Upon treatment at 600 °C the $Fe_3O_4$ content further increased to 56% with a significant decrease on $Fe^0$ and only a small decrease on $Fe_2O_3$ and $Fe^{3+}$. These results suggest that at 600 °C the main reaction taking place is: (Eq. (4))

$$Fe^0 + 4Fe_2O_3 \text{ (or } Fe^{3+}) \rightarrow 3Fe_3O_4 \qquad (4)$$
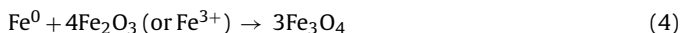
After treatment at 800 °C, $Fe_2O_3$ completely disappears with the production of low amount of $Fe_3O_4$ but with a higher $Fe^{3+}$
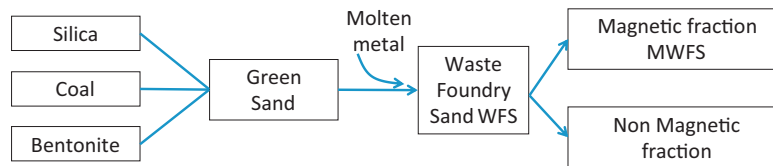
**Fig. 1.** Raw materials and products during the casting process.

concentration. According to previous work [25] this result is typical for $Fe^0$ small particles formed at 800 °C from $Fe_2O_3$ that are oxidized to $Fe^{3+}$ when exposed to air at room temperature.

For all samples, Mössbauer suggested the presence of a Fe silicate phase $Fe_3Si_8O_{22}(OH)_2$, likely formed by the reaction of silica with Fe at high temperatures [26]. No significant change on the surface area and texture was observed for the WFS after thermal treatment even at temperatures as high as 800 °C.

### 3.3. Thermal treatment of MWFS mixed with hematite under $N_2$ atmosphere

Another approach to increase the concentration of reduced Fe phases in the material is to mix the magnetic WFS with hematite followed by thermal treatment. The added $Fe_2O_3$ will react with carbon in the WFS to produce $Fe_3O_4$ and $Fe^0$. Moreover, raw $Fe_2O_3$ is a low cost material and can be found in nature and even in wastes
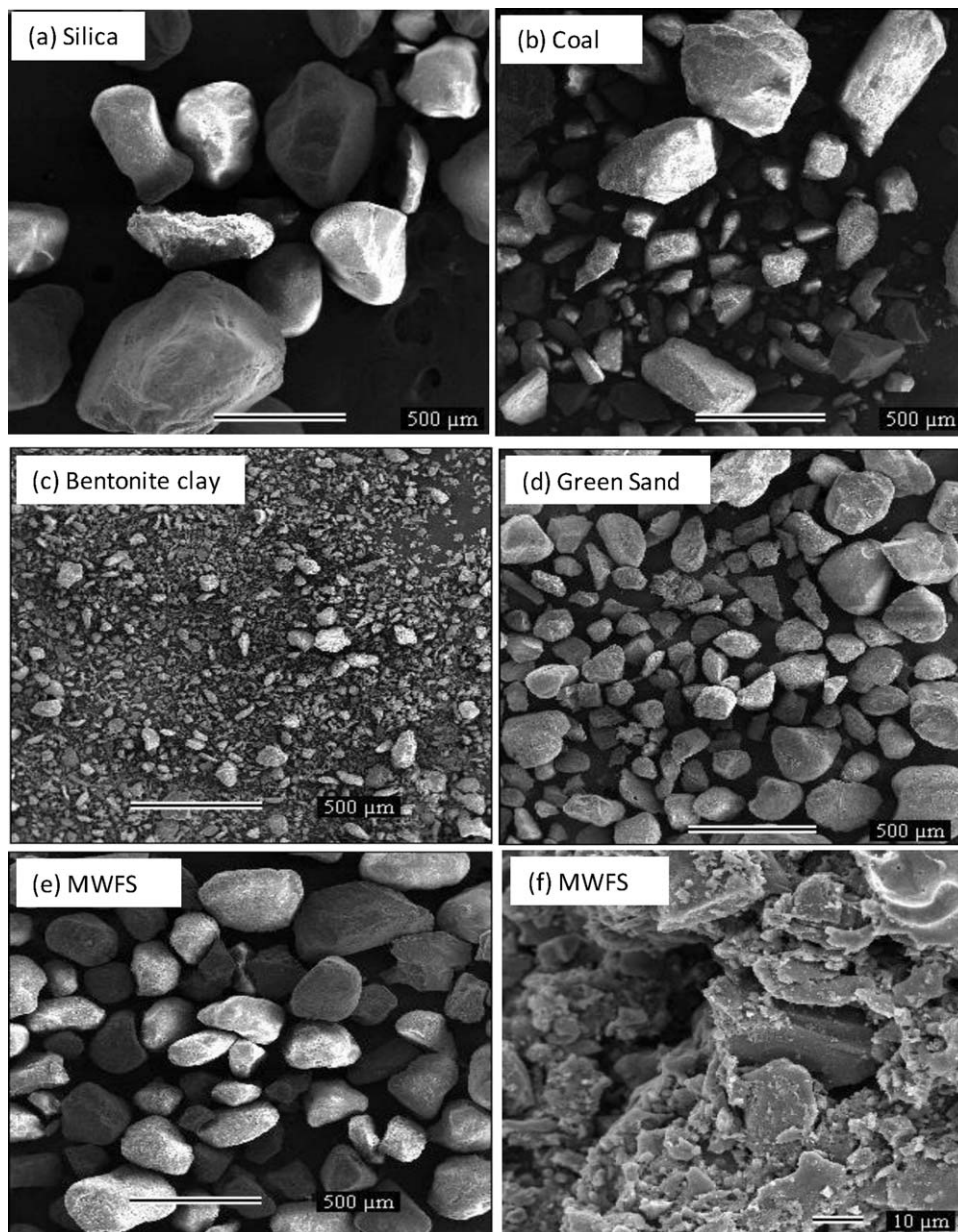


**Fig. 2.** SEM images for silica (a), coal (b), bentonite clay (c), green sand (d), and magnetic fraction of WFS ((e) and (f)).
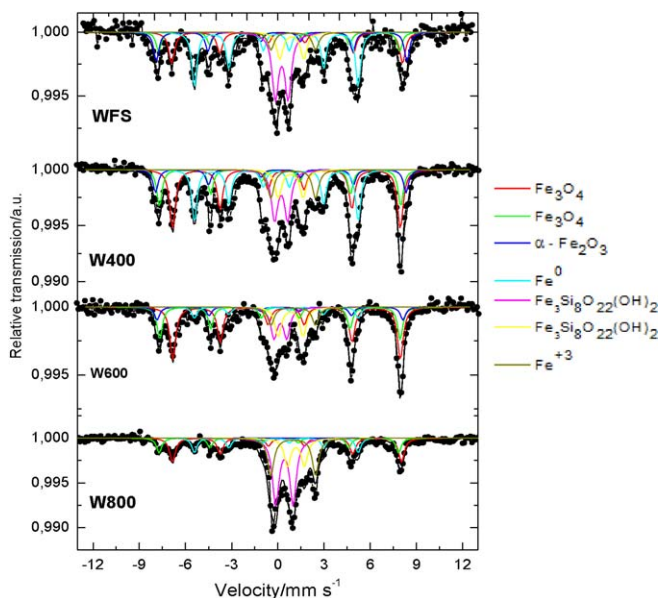
**Fig. 3.** Mössbauer spectra of WFS before and after treatment at 400, 600 and 800 °C under $N_2$.



**Fig. 5.** Distribution of iron phases in WFS with addition of $Fe_2O_3$, before and after thermal treatment, determined by Mössbauer spectroscopy.

of different industries. The XRD of the $Fe_2O_3$ used in this work and all Mössbauer spectra and hyperfine parameters are shown in Supplementary Material.

The mixture of 20% $Fe_2O_3$ with magnetic WFS was manually ground and treated at 400 °C under $N_2$. Mössbauer analysis of this sample showed the presence of large amount of non reacted $Fe_2O_3$, 76%, with ca. 20% of $Fe_3O_4$ (Fig. 5). At 600 °C, $Fe_2O_3$ decreased to 47% whereas $Fe_3O_4$ increased to 36%. Upon treatment at 800 °C $Fe_3O_4$ was the major component (76% w/w). This result suggests that $Fe_2O_3$ is reduced by the carbon present in the magnetic WFS according to Eq. (3).

### 3.4. Peroxide decomposition in the presence of the treated WFS

The thermally treated WFSs were used to promote hydrogen peroxide decomposition to water and oxygen. The hydrogen peroxide decomposition is a versatile probe reaction and can be used to investigate the activity of heterogeneous systems towards
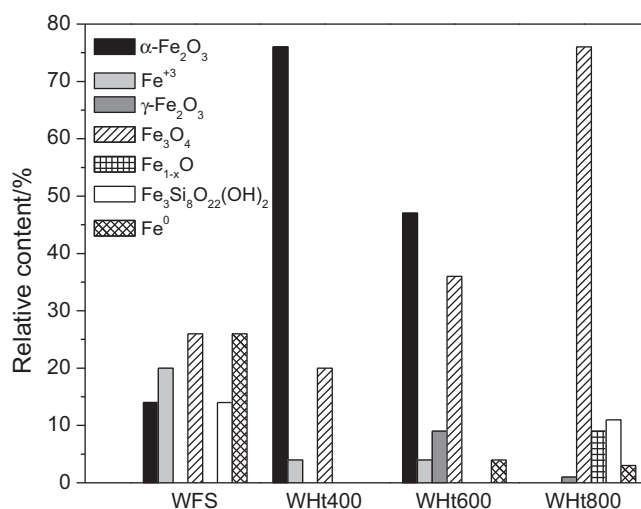
Fenton chemistry. The obtained results for peroxide decomposition in the presence of the reduced materials are shown in Fig. 6.

WFS showed no activity for peroxide decomposition. After treatment at 400 °C the $H_2O_2$ decomposition activity of WFS increased. No significant difference was observed in the peroxide decomposition when the WFS was treated at higher temperatures, i.e. 600 and 800 °C. On the other hand, the mixture WFS/$Fe_2O_3$ treated at 600 and especially at 800 °C showed a remarkable increase in reactivity towards $H_2O_2$. This increase in reactivity is likely related to the production of higher concentrations of the active $Fe_3O_4$ phase. Previous works showed that the decomposition activity is favored by the presence of two iron phases: magnetite and metallic iron [13,23,27].

### 3.5. Oxidation of the indigo carmine dye

The oxidation reactions were carried out using the indigo carmine dye (IC) and $H_2O_2$. The IC dye shows several interesting features as a probe molecule for oxidation reactions, such as: (i) high solubility in water, (ii) oxidation can be monitored simply by spectrophotometric measurements, (iii) is not adsorbed by MWFS, since bentonite clay is a cation exchanger, (iv) simulates the
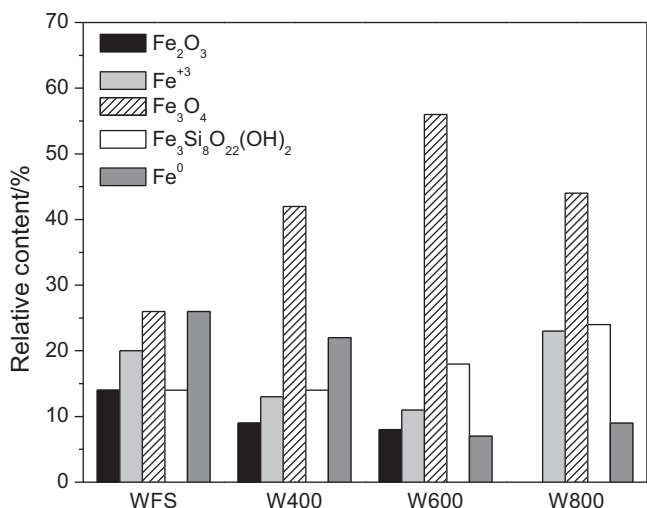


**Fig. 4.** Distribution of iron phases in WFS before and after thermal treatment, determined by Mössbauer spectroscopy.
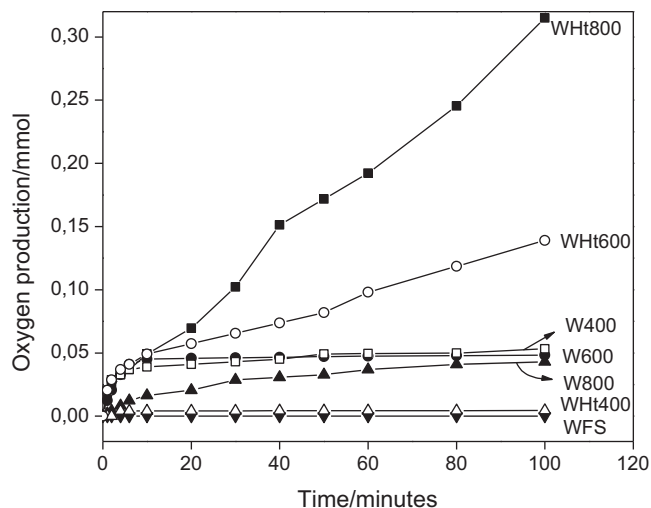


**Fig. 6.** Peroxide decomposition in the presence of thermally treated MFWS (7 mL, [$H_2O_2$] = 2.7 mol $L^{-1}$, 30 mg.
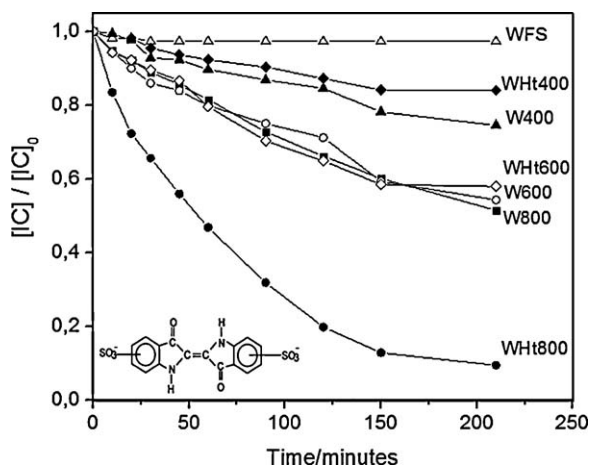
**Fig. 7.** Discoloration of indigo carmine ($50\,mg\,L^{-1}$, $3.5\,mL$) in the presence of treated WFS ($3.5\,mL$, $[H_2O_2]=0.3\,mol\,L^{-1}$, pH $=6.0\pm0.2$, $15\,mg$).



**Fig. 9.** Chromate (Cr(VI)) reduction in the presence of WFS before and after treatment ($10\,mL$, $[Cr(VI)]=50\,mg\,L^{-1}$, pH $=6.5\pm0.2$, $200\,mg$).

behavior of textile dyes which are an important class of contaminants and (v) is not easily reduced by pure iron metal [14].

The oxidation of the IC dye was monitored by its discoloration which is related to the first oxidation steps to produce non-colored intermediates. TOC (Total Organic Carbon) measurements were also carried out to obtain information on the mineralization process (Eq. (5)):

$$Dye + H_2O_2 \rightarrow non\text{-}colored\,intermediates \rightarrow CO_2/H_2O \qquad (5)$$

The discoloration of IC solutions with $H_2O_2$ in the presence of the different WFS materials is shown in Fig. 7.

WFS does not promote the IC discoloration with $H_2O_2$. When the WFS is treated at $400\,°C$ but especially at 600 and $800\,°C$, a high increase in discoloration activity is observed. This increase in activity is likely related to the increase of the $Fe_3O_4$ concentration in the treated WFS. On the other hand, the mixture WFS/$Fe_2O_3$ treated at $800\,°C$ shows a remarkable increase in the discoloration activity.

Plot of $\ln C_t/C_0$ (where $C_t$ is the concentration at time $t$ and $C_0$ is the concentration at time zero) versus time produced fairly straight lines, suggesting that the discoloration process under reaction conditions can be approximated to a first order dependence on the dye concentration $V_{discol} = k_{discol}\cdot[dye]^{\sim 1}$. From these plots $k_{discol}$ values were calculated (Fig. 8). Fig. 8 also shows the degree of TOC obtained with WFS treated at different temperatures.

The two parameters, i.e. $k_{discol}$ and TOC removal, have very similar behavior, showing maximum values for the sample MFHt800.
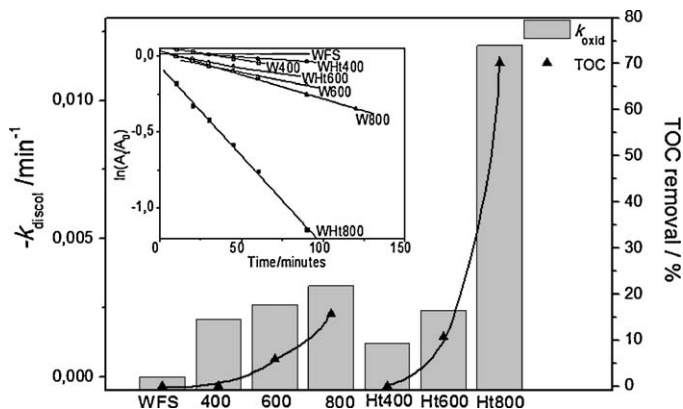


**Fig. 8.** Discoloration rates and TOC removal (detail: $A_t/A_0$ versus time for the discoloration of indigo carmine).
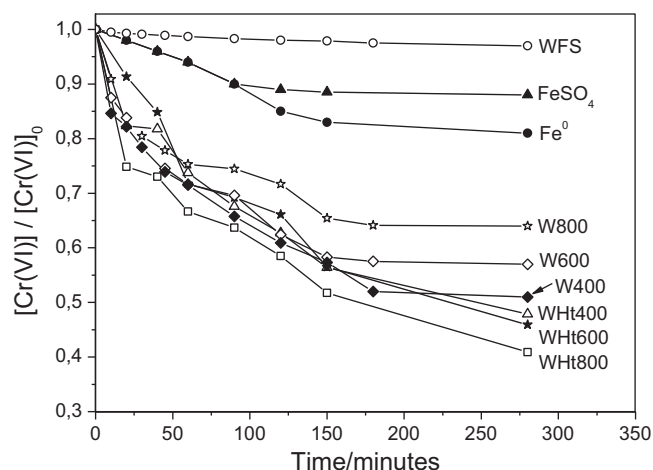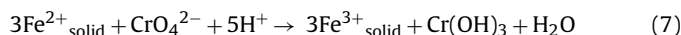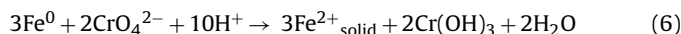
The effect of thermal treatment on the reactivity of WFS towards Fenton chemistry can be discussed in terms of the iron species present and their availability for surface reactions. Although the non-treated WFS showed considerable concentration of reduced phases, such as $Fe_3O_4$ and $Fe^0$, it was not active for the discoloration of IC. This result indicates that iron phases in WFS are likely coated by a layer of non active oxidized Fe species, i.e. $Fe^{3+}$ and $Fe_2O_3$. Once WFS is treated, surface $Fe_3O_4$ and $Fe^0$ active phases are exposed and/or formed. This activation may occur due to: (i) the reaction of coal with hematite or $Fe^{3+}$, forming $Fe_3O_4$ (Eq. (3)) and (ii) the reaction of hematite with metallic iron, producing $Fe_3O_4$ (Eq. (4)). The addition of hematite and the reduction at $800\,°C$ produced a composite of $Fe^0/Fe_3O_4$ which increased discoloration of IC and TOC removal. Previous works showed that the simple mixture of $Fe^0$ metal and $Fe_3O_4$ oxide by mechanical alloying increased significantly the rate of Fenton reaction [12,13,23,28]. The reaction mechanism for these $Fe^0/Fe_3O_4$ alloyed mixtures has been discussed in terms of a facile electron transfer from $Fe^0$ to the reaction medium via $Fe_3O_4$ to form $HO^\bullet$ radicals by the Haber–Weiss reaction.

### 3.6. Cr(VI) reduction by treated WFS

Thermally treated WFS materials were also used for the reduction of chromate in aqueous medium. The obtained results are shown in Fig. 9.

The non treated WFS did not show any activity for Cr(VI) reduction, likely due to the non exposure of the reduced Fe phases, $Fe_3O_4$ and $Fe^0$. Among the materials obtained by thermal treatment of WFS, the system obtained at $400\,°C$ (W400) showed the best result, reducing ca. 40% of Cr(VI) to Cr(III). This result is probably related to the high content of metallic iron (20%), combined with the large amount of $Fe_3O_4$ present (42%). Both $Fe^0$ and $Fe^{2+}$ present in magnetite can reduce Cr(VI) according to the simplified reactions (Eqs. (6) and (7)):

$$3Fe^0 + 2CrO_4{}^{2-} + 10H^+ \rightarrow 3Fe^{2+}{}_{solid} + 2Cr(OH)_3 + 2H_2O \qquad (6)$$

$$3Fe^{2+}{}_{solid} + CrO_4{}^{2-} + 5H^+ \rightarrow 3Fe^{3+}{}_{solid} + Cr(OH)_3 + H_2O \qquad (7)$$

Previous works [12–15] showed that at near neutral pH the contribution of soluble Fe species to Cr reduction is negligible.

Although the WFS treated at $600\,°C$ shows a higher amount of $Fe_3O_4$, the low content of metallic iron might affect the reaction. Treatment at $800\,°C$ produced a less active system likely due to the formation of high amounts of $Fe^{3+}$ surface species.

The materials based on the treated WFS/Fe$_2$O$_3$ mixtures showed higher activity for the reduction of Cr(VI). After treatment at 400, 600 and 800 °C, the mixture WFS/Fe$_2$O$_3$ showed increased reduction activity, probably due to the increase of the Fe$_3$O$_4$ phase which reaches 80% at 800 °C. Preliminary studies showed that under the reaction conditions employed, the system WFS/Fe$_2$O$_3$ treated at 800 °C (WHt800) can be reused two more times without any noticeable decrease in reactivity in terms of Cr(VI) reduction; a drop of reactivity is seen afterwards.

Reactions using an equivalent amount of commercial Fe$^0$ powder showed low Cr(VI) reduction activity compared to the WFS systems. This is likely due to the high dispersion of Fe reducing species in the WFS. This Cr(III) species precipitate as oxy/hydroxide and an important aspect of the WFS based system is the presence of bentonite which is a powerful cation adsorbent and can remove Cr(III) species avoiding further contamination [29]. Several adsorption tests with cationic species are shown in Supplementary Material.

## 4. Conclusions

The waste of foundry sand can be modified by two simple processes, i.e. thermal treatment or by mixing with Fe$_2$O$_3$ and thermal treatment up to 800 °C to produce very reactive materials for different environmental applications. Especially the WFS/Fe$_2$O$_3$ system treated at 800 °C shows very high activity for the oxidation of the indigo carmine dye with H$_2$O$_2$ and for the reduction of Cr(VI) to Cr(III). This reactivity is discussed in terms of the formation of the reduced Fe$_3$O$_4$ phase combined with Fe$^0$.

Moreover, foundry waste sand shows several interesting features for application in permeable reactive barriers: (i) it is non hazardous waste produced in big quantities (ii) it shows a very regular granulometry compatible with permeable reactive barriers which allows good hydrodynamic characteristics, (iii) the carbon particles can adsorb different organic and inorganic contaminants and (iv) the bentonite clay can adsorb different cationic contaminants by an exchange mechanism. We are currently carrying out experiments in columns to simulate the hydrodynamics of PRB to access the real potential of modified WFS for leachate decontamination.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.08.002.

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