



Hexavalent chromium reduction with scrap iron in continuous-flow system. Part 2: Effect of scrap iron shape and size

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ABSTRACT

Hexavalent chromium reduction with scrap iron has the advantage that two wastes are treated simultaneously. The reduction of hexavalent chromium by scrap iron was investigated in continuous system, using as reducing agent the following scrap iron shapes and sizes: (1) spiral fibers, (2) shavings, and (3) powder. The shape and size of scrap iron were found to have a significant influence on chromium and iron species concentration in column effluent, on column effluent pH and on Cr(VI) reduction mechanism. While for large scrap iron particles (spiral fibers) homogeneous reduction is the dominant Cr(VI) reduction process, for small scrap iron particles (powder) heterogeneous reduction appears to be the dominant reaction contributing to Cr(VI) reduction. All three shapes and sizes investigated in this work have both advantages and disadvantages. If found in sufficient quantities, scrap iron powder seem to be the optimum shape and size for the continuous reduction of Cr(VI), due to the following advantages: (1) the greatest reduction capacity, (2) the most important pH increase in column effluent (up to 6.3), (3) no chromium was detected in the column effluent during the first 60 h of the experiment, and (4) the lowest steady-state Cr(VI) concentration observed in column effluent (3.7 mg/L). But, despite of a lower reduction capacity in comparison with powder particles, spiral fibers and shavings have the advantage to result in large quantities from the mechanic processing of steel.

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1. Introduction

Environmental pollution has been accepted for a long time as an undesired consequence of civilization and industrialization. For decades, large quantities of various pollutants have been discharged into the environment, due to inadequate precautionary measures or accidental leakages. Unlike most organic pollutants, metals environmental contaminants are particularly problematic because they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain [1]. Although at low doses some heavy metals are essential micronutrients for plants and animals, being responsible for biochemical, immunological and physiological activities [2–6], in higher doses they can detrimentally affect the health of most living organisms [7–12].

Chromium is an extremely important metal and finds a wide variety of uses in industries such as: metallurgy, chemical and refractory industries, textile dyeing, tanneries, metal electroplating, wood preserving, preparation of chromate compounds. Chromium oxidation states range from (–IV) to (+VI) [13], but only (+III) and

(+VI) states are usually encountered in the environment, depending on the local redox conditions [14,15]. Cr(VI) compounds exhibit a high mobility in the environment and have been shown to exert toxic effects in most living organisms [8,16–19]. In addition, Cr(VI) is a well-established human carcinogen by the inhalation route of exposure [20–23] and a possible human carcinogen by the oral route of exposure [24,25]. On the contrary, Cr(III) has a lower mobility in the environment [26] and is up to 1000 times less toxic to a living cell than Cr(VI) [16,24]. Moreover, Cr(III) is considered to be an essential nutrient for humans and animals [5,19]. Thus, the removal of Cr(VI) from industrial aqueous effluents polluted with this contaminant is an important step in the pollution control of surface water bodies and groundwater. Removal of hexavalent chromium has been investigated by using adsorption [27–30], reduction to Cr(III) followed by precipitation [31–34], biological [35–39] and membrane [40–44] separation processes. Chemical reduction to Cr(III) followed by precipitation is the most used technique for the decontamination of Cr(VI) polluted wastewaters. The major drawback of this treatment method is the high cost of chemicals used for the reduction and precipitation purposes. Therefore, in last years, there has been great interest in using low-cost waste materials that can substitute traditional reducing agents. Recycling of waste materials has both environmental benefits (preventing the pollution associated with producing virgin materials, reduc-

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ing odors and congestion associated with the transportation of disposable wastes, decreasing the amount of landfilled materials) and socio-economic benefits (savings in material and energy costs, increase of products competitiveness in the international marketplace and generating employment for collection and recycling activities). Although scrap iron can be a potentially useful reducing material for treating Cr(VI) contaminated wastewaters, to the authors knowledge there are only a few references in the literature concerning the use of this waste material for the reduction of Cr(VI) to Cr(III) [45–51], comparing with the numerous papers that studied the Cr(VI) removal by adsorption on waste materials [52]. The kinetics of Cr(VI) reduction with iron waste was evaluated in two batch studies [45,46] and in one flow-trough study [47]. The galvanic reduction of Cr(VI) with scrap iron [48] was found to have the advantage that the reduced chromium salt is free of iron impurities and that electrical energy is produced as by-product. The reduction of Cr(VI) by steel wool was studied under continuous conditions [49]; unfortunately, in this study, the Cr(VI) feed solution was saturated with air, which makes the experimental results difficult to compare with other studies. A more recent paper reported the continuous reduction of hexavalent chromium with cast iron waste, under very strong acidic conditions, and obtained the minimum hydraulic retention time (HRT) at different pHs [50]. In our previous study [51] we investigated the effect of H^+ concentration on the Cr(VI) reduction by scrap iron, in continuous system, over the pH range of 2.00–7.30. The results showed that the initial pH of Cr(VI) solution significantly affects the reduction capacity of scrap iron, and the optimum pH was established at the value of 2.50. However, none of the above cited studies has had the aim to precisely establish the effect of scrap iron shape and size on Cr(VI) reduction. Therefore, as a continuation of our previous work [51], the present study has the purpose to establish the influence of scrap iron shape and size on the continuous reduction of hexavalent chromium in flow-through columns. All experiments were conducted at short HRT values, needed for a potentially use of this method in full-scale above-ground wastewater treatment systems. This work will present data regarding the influence of scrap iron shape and size on chromium and iron species concentration in column effluent, on column effluent pH, and on scrap iron reduction capacity. The mechanism of Cr(VI) reduction, as a function of scrap iron shape and size, will also be discussed.

2. Materials and methods

The scrap iron applied in this research originated from “SPM” metals processing laboratory, at the “Politehnica” University of Timisoara. Three different shapes and sizes of scrap iron were used for Cr(VI) reduction: (1) spiral fibers (5 mm < spiral diameter < 10 mm; 5 mm < spiral length < 20 mm), (2) iron shavings that pass through 2.5 mm and remain on 1.25 mm screen, and (3) iron powder that pass through 1.25 mm screen, as presented in Fig. 1. Hexavalent chromium stock solutions (10 g/L) were prepared by dissolving 28.29 g $K_2Cr_2O_7$ in 1000 mL of distilled deionised water; feed solutions of the desired initial Cr(VI) concentration (10 mg/L) were prepared by diluting the stock solution. Concentrated H_2SO_4 was used for adjusting pH of the feed solution. All chemicals used were of AR grade.

Reduction experiments were conducted by using a glass column (inner diameter: 2.0 cm; height: 12.0 cm) with a porous plate at the bottom, packed with scrap iron up to a 6.0 cm height. The initial Cr(VI) concentration (10 mg/L), the scrap iron volume (18.84 cm³), the feed solution pH (2.5) and the pumping rate (0.3 L/h) were held constant throughout the study. The Cr(VI) feed solution was passed through the column, from the bottom to the top, by using a Ismatec IP08 peristaltic pump. A description of the experimental



Fig. 1. Scrap iron used for Cr(VI) reduction: (1) powder; (2) shavings; (3) spiral fibers.

setup was presented in our previous work [51]. The 10 mg Cr(VI)/L concentration was selected because it's within the range of relevant concentrations for both electroplating [53] and metal cleaning [54] facilities wastewaters. The pH 2.5 was selected because it was found, in our previous work [51], to be the optimum pH for reduction of Cr(VI) with scrap iron in continuous system. Although the filling volume and the pumping rate were held constant throughout the study, the filling mass, the filling pore volume and the HRT were different for each type of scrap iron (due to differences in shape and size) as presented in Table 1. To remove traces of chromium and iron, the column was soaked in HCl 35% and washed with distilled deionised water up to neutral pH before each experiment. Column effluent samples were withdrawn at regular time intervals and pH, Cr(total), Cr(VI), Cr(III), Fe(total), Fe(II) and Fe(III) concentration were determined. Each sample was measured in duplicate and relative error was less than 2%. All experiments were performed at room temperature (24 °C), in a background electrolyte mixture (50 ppm Ca^{2+} ; 20 ppm Mg^{2+} ; 128 ppm Cl^- ; 104 ppm Na^+ ; 293 ppm HCO_3^-) to maintain a constant ionic strength.

Hexavalent chromium was detected by the 1,5-diphenylcarbazide colorimetric method [55]. In acidic solutions, Cr(VI) forms a purple complex in the presence of 1,5-diphenylcarbazide; the concentration of Cr(VI) was calculated from the absorbance of the purple complex at 540 nm, using a Jasco V 530 spectrophotometer. The total chromium concentration was determined by oxidizing any trivalent chromium with potassium permanganate [55], followed by analysis as hexavalent chromium. Trivalent chromium was determined from the difference in concentrations between the total and hexavalent chromium. Ferrous ions were analyzed colorimetrically, at 510 nm, by measuring the absorbance of the reddish-orange colored complexes formed with 1,10-phenanthroline, using the same spectrophotometer. Total Fe was determined by reduction of any

Table 1
Experimental conditions.

	Scrap iron		
	Spiral fibers	Shavings	Powder
Column filling volume (cm ³)	18.84	18.84	18.84
Pumping rate (L/h)	0.30	0.30	0.30
Column filling mass (g)	19.50	30.00	40.00
Pore volume of the filling (cm ³)	17.10	13.00	8.00
Hydraulic retention time (min)	3.42	2.60	1.60

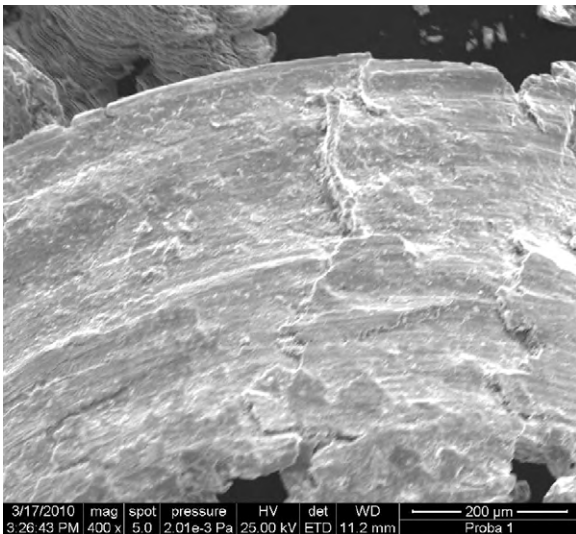


Fig. 2. SEM micrograph of un-reacted scrap iron.

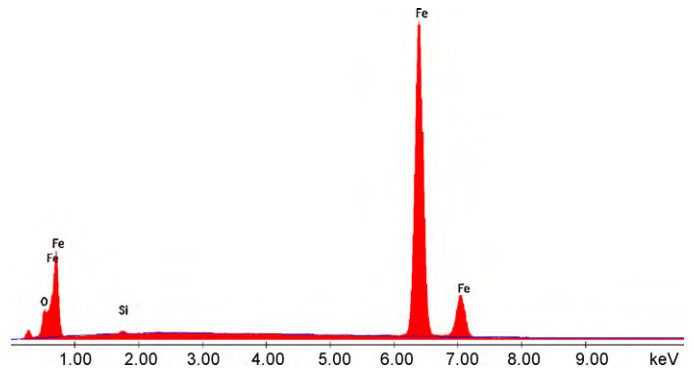


Fig. 4. EDAX pattern of un-reacted scrap iron.

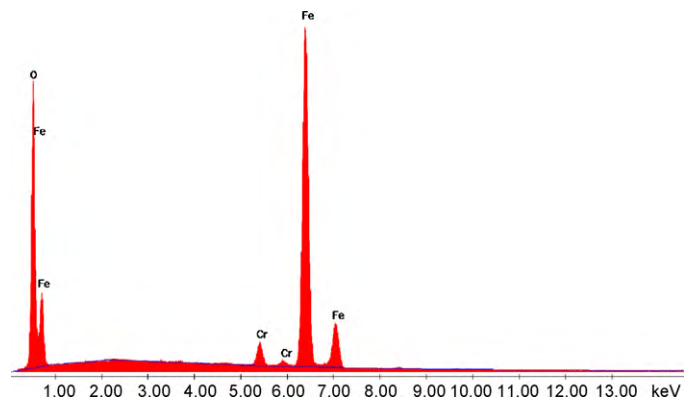


Fig. 5. EDAX pattern of exhausted scrap iron.

Fe(III) to Fe(II) with hydroxylamine hydrochloride and subsequent analysis as Fe(II) [55]. Trivalent iron was determined by subtracting Fe(II) concentration from total iron concentration. The pH of solutions was measured using an Inolab pH-meter.

X-ray diffraction (XRD) and scanning electron microscopy (SEM)-energy dispersive angle X-ray spectrometry (EDAX) were employed to investigate the chemical composition and surface morphology of the scrap iron before and after the experiments, and the results are shown in Figs. 2–7. The SEM-EDAX analysis was performed on an Inspect S scanning electron microscope (FEI, Holland) coupled with a GENESIS XM 2i energy dispersive angle X-ray spectrometer, to obtain the atom composition. The XRD measurements were performed at 40 kV and 30 mA on a X'Pert PRO MPD Diffractometer (FEI, Holland) equipped with Cu anode X-ray tube and PixCEL detector (Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$). As presented in Figs. 2, 4 and 6, the un-reacted scrap iron was composed of Fe(0) and was covered by oxides such as Fe₂O₃ and iron-silica oxides. This in accord with other studies which previously have reported the presence at Fe(0) surface of different iron oxides [56–60] or of mixed iron-silica oxides [60].

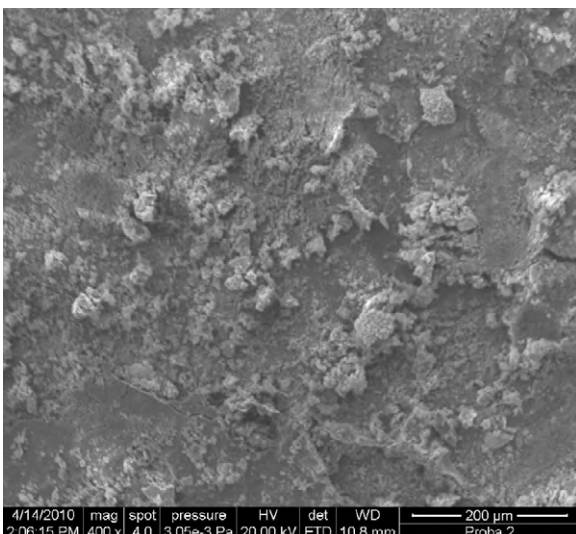


Fig. 3. SEM micrograph of exhausted scrap iron.

3. Results and discussion

3.1. Continuous reduction of Cr(VI) by spiral fibers scrap iron

Aqueous chromium species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 8. The results show that, during the first 120 h of the column experiment, Cr(VI) was completely reduced. Over the same period of time, total chromium consisted only in Cr(III) and its concentration was less than 10 mg/L. The difference in concentration, up to 10 mg/L, leads to the conclusion that Cr(III) was partial retained inside the column. Hexavalent chromium breakthrough in col-

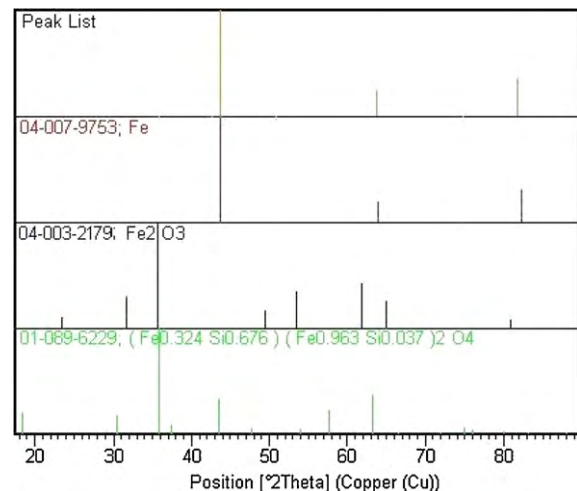


Fig. 6. XRD pattern of un-reacted scrap iron.

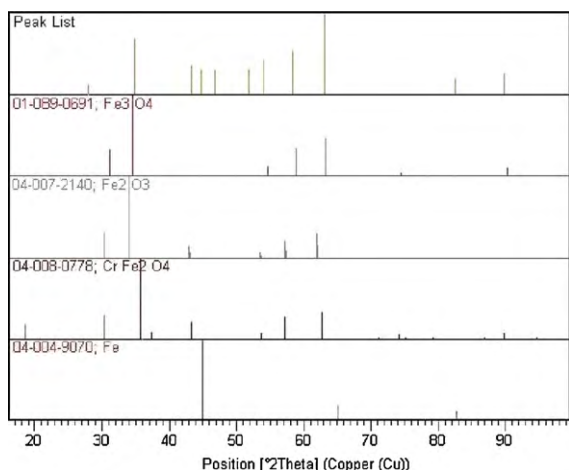
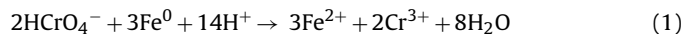
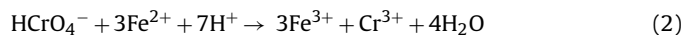


Fig. 7. XRD pattern of exhausted scrap iron.

umn effluent occurs after 132 h and its concentration increases slowly in time thereafter, until a steady-state concentration of approximately 4.5 mg/L was observed (after 744 h). The steady-state Cr(VI) concentration indicates that the extent of iron surface passivation had also reached a steady state, due to continuous generation of new diffusion pathways and reaction sites arising from crack formation in the hydroxide/oxide layer [61]. During the first 120 h of the experiment, Cr(III) concentration in column effluent increased in time up to 9.4 mg/L. After Cr(VI) breakthrough, Cr(III) concentration in column effluent starts to decrease, until a steady-state concentration of approximately 5.0 mg/L was observed (after 744 h). Aqueous iron species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 9. The results show a continuously decrease in time of both Fe(II) and Fe(total) concentrations. Fe(II) occurs in column effluent mainly as a result of the heterogeneous Cr(VI) reduction on the zerovalent iron surface:



Subsequently, some of the Fe(II) formed according to Eq. (1) reduced Cr(VI) in the solution, homogeneously:



Due to passivation in time of scrap iron surface, the rate of heterogeneously Cr(VI) reduction (Eq. (1)) decrease in time and, therefore, the amount of Fe(II) resulted from this reaction also decreased in time. With less scrap iron surface available for the heterogeneously reduction (due to passivation), Fe(II) will have, in

time, an increased contribution to Cr(VI) reduction, according to Eq. (2). The decrease of Eq. (1) rate and the increase of Eq. (2) rate leads to a continuously decrease in time of Fe(II) concentration, until, after 168 h, Fe(II) could not be identified any more in the column effluent. Fe(III) concentration in column effluent slowly increased during the first 144 h, due to the increased contribution of Eq. (2) to the Cr(VI) reduction. The disappearance of Fe(II) from the column effluent indicates that, starting from this point, all Fe(II) resulted from Eq. (1) was either oxidized to Fe(III), according to Eq. (2), or precipitated, according to Eq. (5). After the disappearance of Fe(II) from the column effluent, the contribution of Eq. (2) to the Cr(VI) reduction starts to decrease and, therefore, the concentration of Fe(III) in column effluent also starts to decrease.

During the first 120 h, hexavalent chromium reduction was accompanied by a slow increase in the pH up to 3.0, as shown in Fig. 10. Afterwards, the pH in column effluent continuously decreased until it reached a steady-state value of approximately 2.6. Heterogeneous and homogeneous reduction of Cr(VI) (Eqs. (1) and (2)), which involves consumption of protons, are responsible for the observed pH increase, while formation of Cr and Fe hydroxides/oxydes, which take place with consumption of hydroxide ions, is responsible for the subsequent pH-decrease.

The increase of Cr(VI) concentration and the decrease of Cr(III) concentration, observed after Cr(VI) breakthrough, as well as the decrease of Fe(II) and Fe(total) concentrations, are most likely due to passivation of scrap iron surface, process that block the access of Cr(VI) to the iron surface and leads to a decrease in Cr(VI) reduction rate. The passivation can be attributed to formation of iron and chromium solid species on the scrap iron surface. The SEM results (Figs. 2 and 3) confirmed that, at the end of column experiment, scrap iron surface was partially covered by a newly formed layer. The increase of oxygen peak in Fig. 5 in comparison with Fig. 4, as well as the absence of hydrogen peaks, indicates the formation at the surface of exhausted scrap iron of an oxide layer. XRD analysis of the exhausted scrap iron (Fig. 7) identified three oxides at the surface of scrap iron at the end of the column experiments: Fe₂O₃, Fe₃O₄ and CrFe₂O₄. The presence of non-porous Fe₂O₃ at the surface of scrap iron should inhibit its reactivity towards oxidizing species [56]. However, Fe₂O₃ can indirectly contribute to the reduction of Cr(VI) by its autoreduction reaction which generates Fe²⁺ ions [56,57]:



Moreover, previous studies indicate that Fe₂O₃ may be converted to a porous layer of magnetite (Fe₃O₄), which will allow

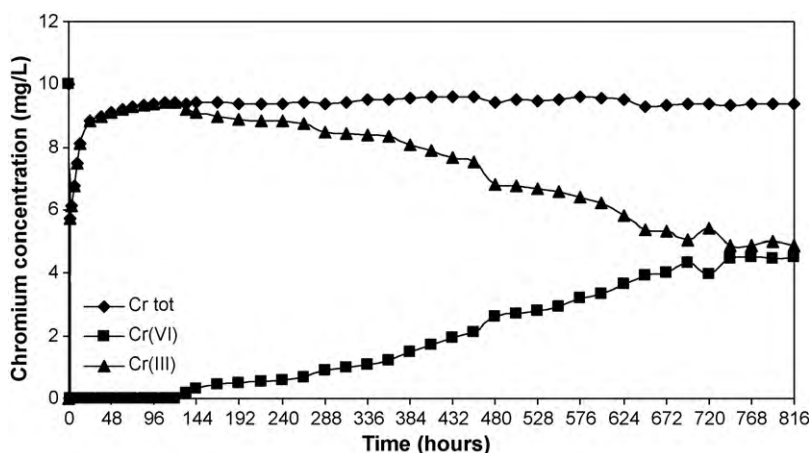


Fig. 8. Chromium species concentration in column effluent vs. time, for the reduction with spiral fibers scrap iron.

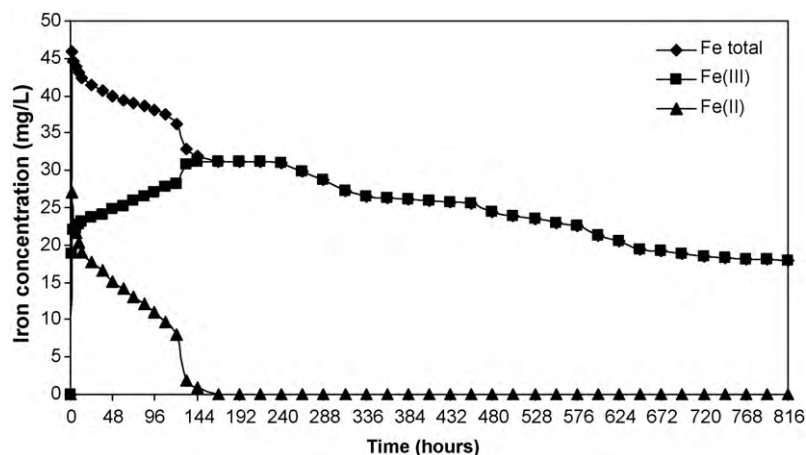
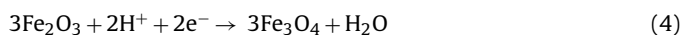


Fig. 9. Iron species concentration in column effluent vs. time, for the reduction with spiral fibers scrap iron.

the electron transfer from Fe(0) to Cr(VI) [56,57]:



Ferrous and ferric hydroxide are possible products of the Cr(VI) reduction with Fe(0); however, ferrous hydroxide is thermodynamically unstable and may also be converted to magnetite (Schikorr reaction) [56]:



Ferric hydroxide may be converted to FeOOH [50] and further to Fe_3O_4 [62] according to:



Since the ionic radii of Cr^{3+} (0.63 Å) and Fe^{3+} (0.64 Å) are close [63] and both cations have the same charge, the substitution of Fe^{3+} by Cr^{3+} into the magnetite structure may lead to the formation of the CrFe_2O_4 phase [64], according to:



The oxides identified at the surface of exhausted scrap iron are consistent with previous studies which have reported, after Cr(VI) reduction at $\text{pH} \leq 2$, the existence at Fe(0) surface of mixed (Cr_2FeO_4) or simple (Fe_3O_4) oxides [50,63]. Other studies also reported the existence on the Fe(0) surface, after Cr(VI) reduction over the pH range of 2–3, of Cr and Fe (oxy)hydroxides, as sub-micrometer particle aggregates and plates [65]. Equilibrium studies

of the Fe(III)/Cr(VI)/ H_2O system revealed the formation, in the pH range between 2.5 and 3.6, of a new distinct iron(III)-chromate mixed precipitate: $\text{FeOHCrO}_4 \cdot 2\text{Fe}(\text{OH})_3$ [66,67]. The spiral fibers scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 18.46 mg Cr(VI)/g scrap iron.

3.2. Continuous reduction of Cr(VI) by scrap iron shavings

Monitoring of the effluent pH during the column experiment showed a similar behavior of this parameter with the one observed for spiral fibers: an increase in the solution pH, up to 3.3, during the first hour, followed by a slowly and continuously decrease thereafter, until it reached a steady-state value of approximately 2.6 (Fig. 10), due to same reasons as those mentioned in Section 3.1. Aqueous chromium species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 11. The results show that, during the first 192 h of the column experiment, Cr(VI) was completely reduced. Over the same period of time, total chromium consisted only in Cr(III), and its concentration was less than 10 mg/L. The difference in concentrations between initial Cr(VI) in column influent and total chromium in column effluent confirmed the observation from Section 3.1, that, even at $\text{pH} \approx 3$, a small part of the resulted Cr(III) has been retained inside the column. Hexavalent chromium breakthrough in column effluent occurs after 216 h and its concentration increases slowly in time until, after 408 h, a steady-state concentration of approximately 4.6 mg/L was observed. Cr(III) concentration in column effluent increased very rapidly within the first 24 h of the

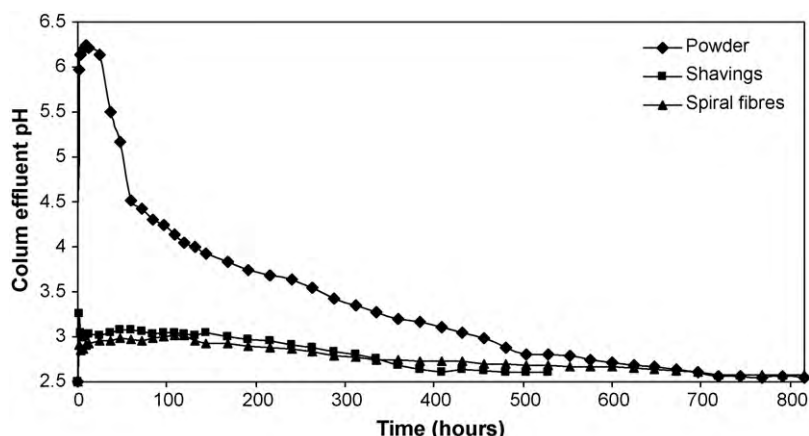


Fig. 10. Column effluent pH vs. time, for different scrap iron types.

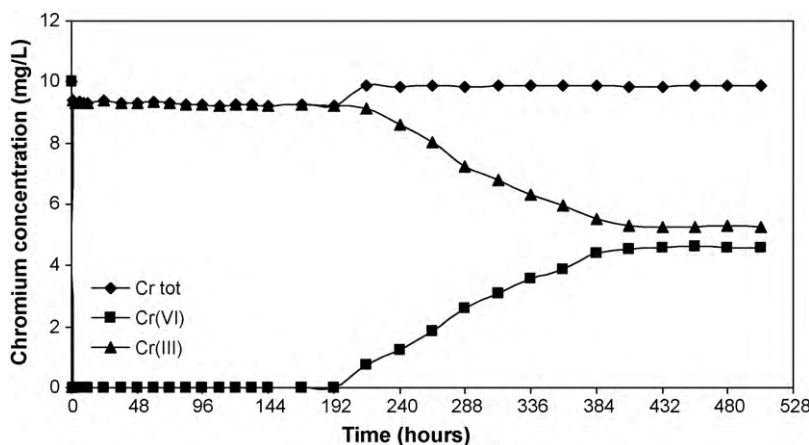


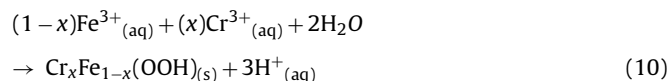
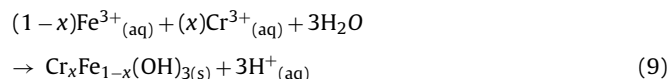
Fig. 11. Chromium species concentration in column effluent vs. time, for the reduction with scrap iron shavings.

experiment, up to 9.4 mg/L, and slowly decreased thereafter until the moment of Cr(VI) breakthrough. Subsequently, the decrease of Cr(III) concentration was more rapid, until, after 408 h, a steady-state concentration of approximately 5.3 mg/L was observed. In Fig. 12 are presented the aqueous iron species concentrations in column effluent, as a function of elapsed time. It can be seen that, while Fe(total) and Fe(II) concentrations continuously decreased throughout the column experiment, Fe(III) concentration rapidly increased in column effluent during the first 48 h, and slowly decreased thereafter. After 432 h, Fe(II) could not be identified any more in the column effluent and, from this moment, Fe(total) consisted only in Fe(III). The SEM-EDAX and XRD analysis of the exhausted scrap iron shavings showed similar results with those obtained for spiral fibers (data not shown); therefore the explanations for the behavior of chromium and iron species concentrations in column effluent, and for the scrap iron surface passivation are identically with those given in Section 3.1. The reduction capacity of scrap iron shavings, calculated up to the moment of Cr(VI) breakthrough, was 19.20 mg Cr(VI)/g scrap iron.

3.3. Continuous reduction of Cr(VI) by scrap iron powder

The characteristics of Cr(VI) reduction in the column packed with scrap iron powder are presented in Fig. 13. From this figure it can be seen that, during the first 60 h of the experiment, Cr(VI) was completely reduced and, subsequently, the resulted Cr(III) was

totally retained inside the column. During this period of time, the retaining of Cr(III) may also be attributed to its precipitation inside the column as mixed Fe(III)-Cr(III) (oxy)hydroxides, process that occurs at pH values greater than 4 [68], according to [46]:



where x vary from 0 to 1.

This process is possible because during the first 60 h of the experiment hexavalent chromium reduction was accompanied by a sharp increase in the pH up to 6.3, as shown in Fig. 10. However, these species were not identified at the surface of scrap iron at the end of the experiment; in fact, the SEM-EDAX and XRD analysis of scrap iron powder showed similar results with those obtained when spiral fibers and shavings were used (data not shown); the absence of mixed Fe(III)-Cr(III) (oxy)hydroxides could be due to the fact that the pH inside the column was greater than 4 just for the first 100 h of the experiment (Fig. 10); during the next 700 h the column effluent had a pH <4, which continuously decreased until the end of the experiment, up to 2.6. This low pH value could determine the dissolution of the mixed Fe(III)-Cr(III) (oxy)hydroxides presumably formed. Obviously, the precipitation of chromium and iron species conducted to the passivation of the

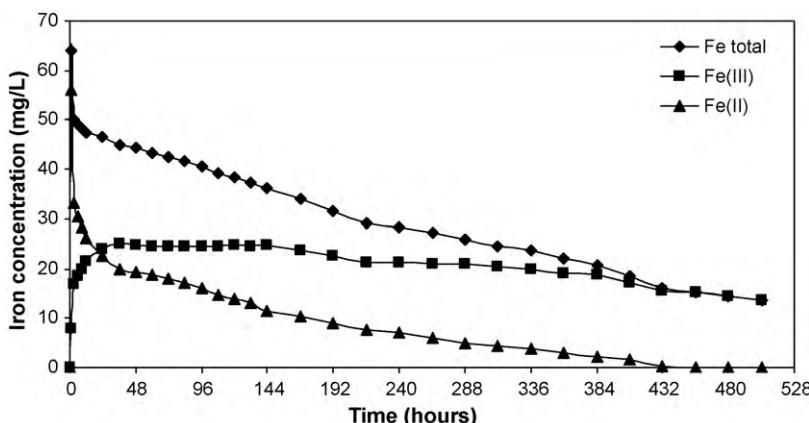


Fig. 12. Iron species concentration in column effluent vs. time, for the reduction with scrap iron shavings.

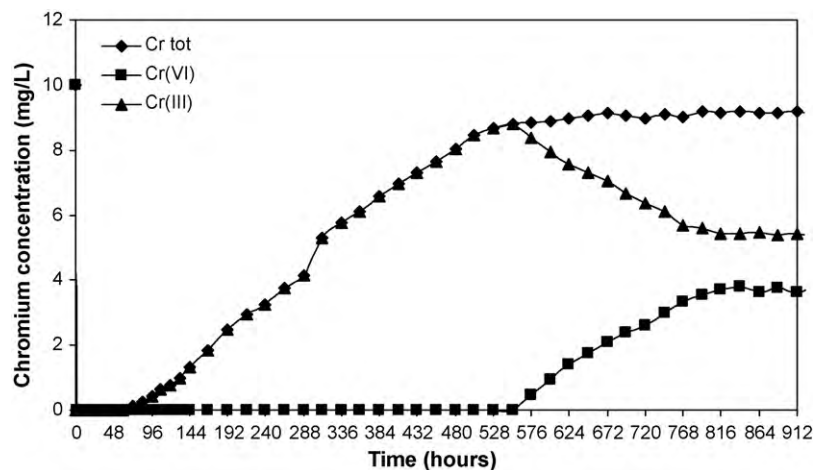


Fig. 13. Chromium species concentration in column effluent vs. time, for the reduction with scrap iron powder.

scrap iron surface, which subsequently affected the concentration of Cr and Fe species in column effluent throughout the experiment. Hexavalent chromium breakthrough in column effluent occurs after 576 h and its concentration increases slowly in time until, after 816 h, a steady-state concentration of approximately 3.7 mg/L was observed. Cr(III) breakthrough in column effluent occurs after 72 h and its concentration continuously increases in time, up to 8.8 mg/L, until the moment of Cr(VI) breakthrough. Afterwards, Cr(III) concentration in column effluent starts to decrease, until a steady-state concentration of approximately 5.3 mg/L was observed (after 816 h). Iron species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 14. From this figure it can be seen that, during the first 312 h of the experiment, no Fe(III) was detected in column effluent. This means that, in this case, Fe(0) had the main contribution to Cr(VI) reduction; however, even if a small part of the resulted Fe(II) has been involved in the homogeneously reduction of Cr(VI), all resulted Fe(III) subsequently precipitated inside the column. The results also show a continuous decrease in time of Fe(total) and Fe(II) concentrations, due to passivation in time of scrap iron surface. After Fe(III) breakthrough, its concentration rapidly increased up to the moment of Fe(II) disappearance from the column effluent. Thereafter, Fe(III) was the only component of Fe(total) and its concentration slowly decreased in time until the end of column experiment. The reduction capacity of scrap iron powder, calculated up to the moment of Cr(VI) breakthrough, was 41.40 mg Cr(VI)/g scrap iron.

3.4. Chromium mass balance

Chromium mass balance for the column experiments, up to the moment of Cr(VI) breakthrough, can be calculated as follows:

$$C_{Cr(VI)_{in}} = C_{Cr(VI)_{red}} = C_{Cr(III)_{col}} + C_{Cr(III)_{out}} \quad (11)$$

$$C_{Cr(III)_{col}} = C_{Cr(VI)_{in}} - C_{Cr(III)_{out}} \quad (12)$$

$$C_{Cr(III)_{col}} = QT(C_{Cr(VI)_{in}} - C_{Cr(III)_{out}}) \quad (13)$$

where $C_{Cr(VI)_{in}}$ (mg) is the amount of Cr(VI) entered in the column with the influent, $C_{Cr(VI)_{red}}$ (mg) is the amount of Cr(VI) reduced to Cr(III) inside of column, $C_{Cr(III)_{col}}$ (mg) is the amount of Cr(III) retained inside of column, $C_{Cr(III)_{out}}$ (mg) is the amount of Cr(III) that left the column with the effluent, $C_{Cr(VI)_{in}}$ (mg/L) is the inlet Cr(VI) concentration, $C_{Cr(III)_{out}}$ (mg/L) is the average trivalent chromium concentration in column effluent, Q (L/h) is the volumetric inflow rate, and T (h) is the column experiment duration up to the moment of Cr(VI) breakthrough.

The results of chromium mass balance, presented in Table 2, show that the greatest amount of Cr(III) was retained inside the column when scrap iron powder was used as reducing reagent. But, this finding could be influenced by the increase of column experiment duration with decreasing scrap iron size. Therefore, in order to disregard this influence, the effect of scrap iron shape and size on $C_{Cr(III)_{col}}$ was also studied by comparing the ratio $C_{Cr(III)_{col}}/C_{Cr(VI)_{red}}$ for the three different scrap iron types. The comparison of this

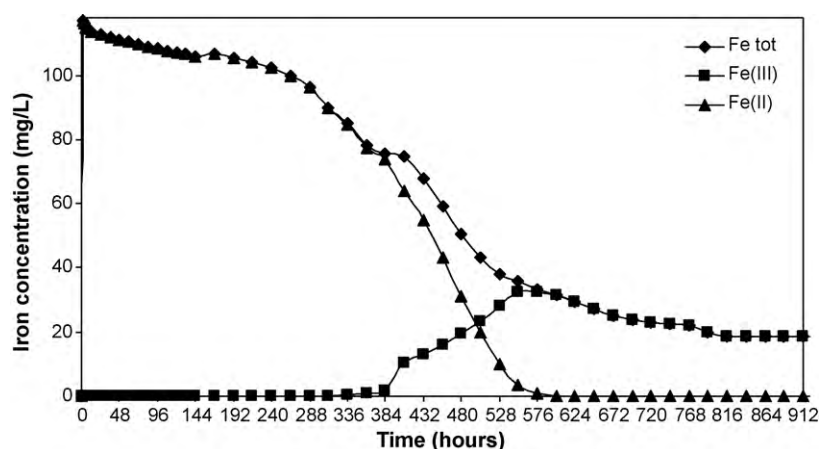


Fig. 14. Iron species concentration in column effluent vs. time, for the reduction with scrap iron powder.

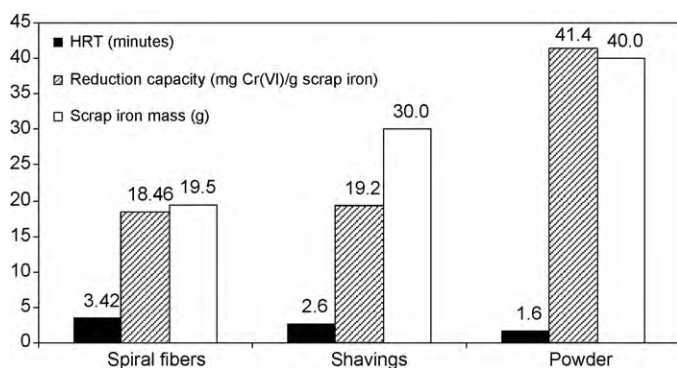
Table 2
Chromium mass balance.

	Scrap iron		
	Spiral fibers	Shavings	Powder
T (h)	120.0	192.0	552.0
Q (L/h)	0.3	0.3	0.3
$C_{Cr(VI)in}$ (mg/L)	10.0	10.0	10.0
$C_{Cr(III)out}$ (mg/L)	8.4	9.3	3.1
$Cr(VI)_{in}$ (mg)	360.0	576.0	1656.0
$Cr(III)_{out}$ (mg)	302.4	535.7	513.4
$Cr(III)_{col}$ (mg)	57.6	40.3	1142.6
$Cr(III)_{col}/Cr(VI)_{red}$ (mg/mg)	0.16	0.07	0.7
Reduction capacity (mg Cr(VI)/g scrap iron)	18.46	19.20	41.40

parameter confirmed the initial conclusion and showed that the amount of Cr(III) retained inside the column for each mg of reduced Cr(VI) followed the order: powder > spiral fibers > shavings.

Another conclusion that results from the analysis of chromium mass balance is the one regarding the shape and size influence on scrap iron reduction capacity. For the same filling volume and pumping rate, the reduction capacity of scrap iron increased with decreasing scrap iron size, as presented in Fig. 15. It must be noticed that, although there was an important increase in scrap iron mass (53.8%) when spiral fibers were replaced by shavings, the reduction capacity of scrap iron increased only with 4%. The almost similar reduction capacity of spiral fibers and shavings, despite the lower mass of spiral fibers, is due to a 31.5% greater HRT observed for spiral fibers filling. This led to an increased contribution of Fe(II) to the Cr(VI) reduction, which compensated almost totally the reduced surface of spiral fibers (due to the reduced mass) available for the heterogeneously Cr(VI) reduction. The increased rate of homogeneously Cr(VI) reduction, observed for spiral fibers in comparison with shavings, is proven by Figs. 9 and 12. From the comparison of the two figures it can be seen that Fe(II) disappeared much faster from the column effluent when spiral fibers scrap iron were used as column filling, due to the increased rate of Fe(II) oxidation, according to Eq. (2). The comparable reduction capacity observed for spiral fibers and shavings leads to the conclusion that the intensity of the overall Cr(VI) reduction process, for the two scrap iron shapes, should also be similar. This conclusion is confirmed by the fact that the pH curves (Fig. 10) of the two scrap iron types are almost identical, which means that, in both cases, a similar equilibrium has been reached, during the column experiment, between the H^+ consuming and the HO^- consuming redox processes.

When shape and size of scrap iron were further lowered, by using scrap iron powder instead of shavings, the reduction capacity increased with 115.62%, as shown in Fig. 15, although the mass of

**Fig. 15.** Reduction capacity, HRT and scrap iron mass, as a function of scrap iron type.

scrap iron increased with only 33.33% and the HRT decreased with 38.46%. The significant increase of the reduction capacity is due to the increased surface area of scrap iron powder, which led to an increased contribution of Fe(0) to the Cr(VI) reduction. Therefore, heterogeneous reduction (Eq. (1)) appears to be the dominant reaction contributing to Cr(VI) reduction with scrap iron powder. This conclusion is confirmed by the comparison between Figs. 12 and 14. From Fig. 12 it can be seen that both Fe(II) and Fe(III) are present in column effluent, from the beginning of the experiment. This means that, when scrap iron shavings are used, homogeneous reduction (Eq. (2)) still has an important contribution to Cr(VI) reduction, leading to the occurrence, from the beginning of the experiment, of Fe(III) ions in column effluent. On the contrary, when scrap iron powder was used, no Fe(III) was detected in column effluent during the first 312 h of the experiment, as can be seen from Fig. 14. This means that, in this case, heterogeneous reduction (Eq. (1)) has had the main contribution to Cr(VI) reduction. However, it is also possible that a small part from the resulted Fe(II) could be involved in the homogeneously reduction of Cr(VI) (Eq. (2)) but, in this case, all resulted Fe(III) subsequently precipitated inside the column.

4. Conclusions

The present work evaluates the use of three scrap iron shapes and sizes (spiral fibers, shavings, powder) as reducing agent for the reduction of Cr(VI) from aqueous solutions. Cr(VI) reduction with scrap iron has the advantage that two wastes are treated simultaneously. Results obtained in long-term column experiments indicate that all three scrap iron types investigated in this work are suitable for the complete reduction of Cr(VI) in aqueous solutions. However, the shape and size of scrap iron were found to significantly influence chromium and iron species concentration in column effluent, column effluent pH, and scrap iron reduction capacity. The amount of Fe(total) in the treated solution increases as the scrap iron size is decreased. This is, unfortunately, an disadvantage, because the dissolved iron in the column effluent is a contaminant that must be removed, together with Cr(III), in a final treatment step. However, the results also show that, for a given scrap iron shape and size, Fe(total) concentration in column effluent continuously decreased in time, due to a decrease in time of iron corrosion rate. This represents an advantage, because the amount of precipitant agent used to remove Fe(total) from the column effluent will also decrease in time. For all three scrap iron shapes investigated in this study, hexavalent chromium reduction was accompanied by an increase in the pH during the first hours of the column experiment, up to a maximum value; the greater the scrap iron size, the lower the maximum pH value. Thereafter, the pH continuously decreased, until a steady-state value was observed, near to the initial pH. The pH increase represents an advantage, because less precipitant reagent must be used to remove Fe(total) and Cr(III) from the column effluent. The contribution of homogeneous and heterogeneous chemical processes to Cr(VI) reduction was found to be strongly influenced by the scrap iron shape and size. While for large scrap iron particles (spiral fibers) homogeneous reduction is the dominant Cr(VI) reduction process, for small scrap iron particles (powder) heterogeneous reduction appears to be the dominant reaction contributing to Cr(VI) reduction. The establishing of an optimum scrap iron shape and size has been a difficult task, because all three shapes and sizes investigated in this work have both advantages and disadvantages. Powder particles seem to be the optimum shape and size of scrap iron, because they have some significant advantages: (1) the greatest reduction capacity, (2) the most important pH increase in column effluent (up to 6.3), (3) no Cr(III) was detected in the column effluent during the first 60 h of the experiment, and (4) the lowest steady-state Cr(VI) concentration observed in column efflu-

ent (3.7 mg/L). But, in the same time, the use of scrap iron powder was accompanied by the highest Fe (total) concentration in column effluent; moreover, powder particles are difficult to extract from a mixture of different scrap iron shapes and sizes. On the contrary, spiral fibers and shavings are the most often scrap iron shapes that results from the mechanic processing of steel, and the concentration of Fe (total) in column effluent was lower when they were used for Cr(VI) reduction; however, they still have the disadvantage of a lower reduction capacity in comparison with powder particles.

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