

# Hexavalent chromium reduction with scrap iron in continuous-flow system Part 1: Effect of feed solution pH

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## Abstract

The reduction of hexavalent chromium by scrap iron was investigated in continuous system, using long-term column experiments, for aqueous Cr(VI) solutions having low buffering capacities, 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. The highest reduction capacity was determined to be 19.2 mg Cr(VI)/g scrap iron, at pH 2.50, and decreased with increasing the initial pH of Cr(VI) solution. A considerable decrease in scrap iron reduction capacity (25%) was also observed at pH 2.00, as compared to pH 2.50, due to the increased contribution of H<sup>+</sup> ions to the corrosion of scrap iron, which leads to a rapid decrease in time of the scrap iron volume. Over the pH range of 2.50–7.30, hexavalent chromium concentration increases slowly in time after its breakthrough in column effluent, until a steady-state concentration was observed; similarly, over the same pH range, the amount of solubilized Cr(III) in treated column effluent decreases in time, until a steady-state concentration was observed. The steady-state concentration in column effluent decreased for Cr(VI) and increased for Cr(III) with decreasing the initial pH of Cr(VI) solution. No steady-state Cr(VI) or Cr(III) concentrations in column effluent were observed at pH 2.00. Over the entire studied pH range, the amount of Fe(total) in treated solution increases as the initial pH of column influent is decreased; the results show also a continuously decrease in time of Fe(total) concentration, for a constant initial pH, due to a decrease in time of iron corrosion rate. Cr(III) concentration in column effluent also continuously decreased in time, for a constant initial pH, over the pH range of 2.50–7.30. This represents an advantage, because the amount of precipitant agent used to remove Fe(total) and Cr(III) from the column effluent will also decrease in time. The optimum pH for Cr(VI) reduction with scrap iron in continuous-flow system was established at the value of 2.50.

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## 1. Introduction

Chromium is an important metal, which is used in a variety of industrial applications (e.g. textile dyeing, tanneries, metallurgy, metal electroplating, wood preserving, preparation of chromate compounds); hence, large quantities of chromium have been discharged into the environment due to accidental releases or inadequate precautionary measures [1,2]. Although chromium oxidation states range from (–IV) to (+VI) [3], only the (+III) and (+VI) states are stable in the natural environment

[4]. The chemical and toxicological behaviors of chromium depend on its oxidation state. Under environmentally relevant pH values, hexavalent chromium exists as oxyanions of chromate (pH > 6.5) and bichromate (pH < 6.5) [5]. Because it has a high solubility in water and it is only weakly sorbed onto inorganic surfaces, Cr(VI) has a significant mobility in the environment [6]. Chromium(III), on the other hand, has a lower solubility in water and readily precipitates as Cr(OH)<sub>3</sub> [7] or as mixed Fe(III)–Cr(III) (oxy)hydroxides [8,9] under alkaline or even slightly acidic conditions. Hexavalent chromium is toxic to most living organisms [5,10–12] and a known human carcinogen by the inhalation route of exposure [13,14]. Although trivalent chromium is considered an essential nutrient for the human body [15] and the toxicity of trivalent chromium is 500–1000 times

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less to a living cell than hexavalent chromium [16], exposure to excessive doses of Cr(III) for long periods of time may also cause some adverse health effects [17–19]. Thus, removal of chromium, and especially of Cr(VI), is an essential pollution abatement process that should be applied to all industrial effluents that contain this contaminant, prior to discharge them in to the natural water bodies.

Chemical reduction to Cr(III) (followed by precipitation), adsorption, ion exchange and membrane separation processes are the most used techniques for the decontamination of wastewaters polluted with Cr(VI) compounds. However, for developing countries, all these methods can be prohibitively expensive. Waste materials recycling can become a crucial component for those communities in their efforts to prevent the pollution associated with industrial applications. Therefore, in recent years, attention has been focused on the use of low-cost and locally abundant waste materials that can substitute traditional adsorbents or reducing agents, for the abatement of hexavalent chromium pollution. Materials such as soya cake [20], hazelnut shell [21], maple sawdust [22], coal ash [23], blast furnace sludge [24], have been tried as adsorbents. Previous reports have also described the use of different non-conventional reducing agents like magnetite [25–27], siderite [28], mackinawite [29,30], pyrite [31], hematite, biotite [32], copper smelter slag [33].

Zero-valence-state metals, such as metallic iron, can also serve as electron donors for reducing redox reactive metals to valence states that are less water soluble [34,35]. Although in last years there has been great interest in using zerovalent iron for in situ reduction of hexavalent chromium from contaminated groundwater [8,9,36–40], from our knowledge, there are only a few references in the literature concerning the use of scrap iron for the reduction of Cr(VI) in above-ground treatment systems. The galvanic reduction of hexavalent chromium with scrap iron using a divided parallel plate cell was investigated by Abdo and Sedahmed [41]; the advantage of this technique is that the reduced chromium salt is free of iron impurities and electrical energy is produced from the galvanic cell as by-product. The kinetics of Cr(VI) reduction in a fixed bed of scrap iron bearings was studied by El-Shazly et al. [42]; the activation energy of the reaction was found to be low (4.51 kcal/mol) which shows that the reaction is diffusion controlled. Ozer et al. [43] studied the reduction of Cr(VI) by steel wool in continuous system; although the results showed that the process depended to a large extent on acid concentration, no optimum pH value was proposed. Our previous batch studies [44,45] have also shown that scrap iron can be a potentially useful reducing material for treating hexavalent chromium contaminated wastewaters, especially at low pH values. However, it was difficult to assess long-term performance of hexavalent chromium reduction by scrap iron using only short-term batch experiments. Therefore, as a continuation of our previous work, the present work examines the use of scrap iron for the continuous reduction of hexavalent chromium in flow-through columns. The main purpose of this paper is to establish the optimum pH for the reduction of hexavalent chromium with scrap iron in continuous-flow system. Additionally, we present data regarding the pH influence on

chromium and iron species concentration in column effluent and on scrap iron reduction capacity.

## 2. Materials and methods

### 2.1. Materials

In our previous studies [44,45] four different types of scrap iron resulted from the mechanic processing of steel were characterized and tested for Cr(VI) reduction: large spiral fibers, small spiral fibers, iron shavings and fine iron powder; the optimum shape for batch reduction experiments was found to be as iron shavings that pass through 2.5 mm screen; therefore, all column experiments conducted in this study were also performed by using iron shavings.

Hexavalent chromium stock solutions (1 g/l) were prepared by dissolving 2.829 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.  $H_2SO_4$  was used for adjusting pH of the feed solution. All chemicals used were of AR grade.

### 2.2. Methods

The laboratory apparatus used for the flow-through experiments is presented in Fig. 1. Reduction experiments were conducted by using a glass column (inner diameter: 2.00 cm; height: 12.00 cm) with a porous plate at the bottom. The column was packed with 30 g scrap iron up to a 6.00 cm height (scrap iron volume:  $18.84\text{ cm}^3$ ) and 10 mg Cr(VI)/l aqueous solution with low buffering capacity was passed through the column, from the bottom to the top, by using a Unipan peristaltic pump. This concentration was selected because it is within the range of relevant concentrations for electroplating wastewaters [46]. To remove traces of chromium and iron, the column was soaked in HCl 35% and washed with distilled deionised water before each experiment.

The hydraulic contact time in the column was 2.60 min (pumping rate of 0.3 l/h). Column effluent samples were withdrawn at regular time intervals (as a manner of shortened intervals in the beginning of experiments) and pH, Cr(total),

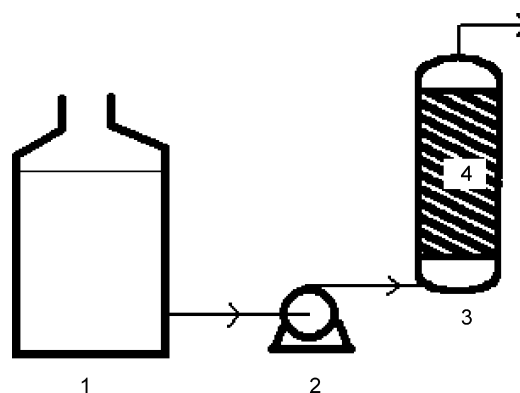


Fig. 1. Experimental setup: (1) storage tank; (2) peristaltic pump; (3) glass column; (4) scrap iron filling.

Cr(VI), Cr(III), Fe(total), Fe(II) and Fe(III) concentration were determined. All experiments were performed at room temperature (24 °C), in a background electrolyte mixture (50 ppm Ca<sup>2+</sup>; 20 ppm Mg<sup>2+</sup>; 128 ppm Cl<sup>-</sup>; 104 ppm Na<sup>+</sup>; 293 ppm HCO<sub>3</sub><sup>-</sup>) to maintain a constant ionic strength. The effect of feed solution pH on the reduction of hexavalent chromium with scrap iron in continuous system was studied over the pH range of 2.00–7.30.

The analysis of hexavalent chromium in solution was carried out by the diphenylcarbazide colorimetric method [47]. The purple color was fully developed after 15 min and the sample solutions were transferred to a Jasco V 530 spectrophotometer; the absorbance of the color was measured at 540 nm in a 1 cm long glass cell. The total chromium concentration was determined by oxidizing any trivalent chromium with potassium permanganate [47], followed by analysis as hexavalent chromium. Trivalent chromium was determined from the difference between total and hexavalent chromium. Fe(II) concentrations in the samples were determined by the 1,10-phenanthroline method [47]; the absorbance of the reddish orange color was measured at 510 nm using the same spectrophotometer. Total Fe was determined by reduction of any Fe(III) to Fe(II) with hydroxylamine hydrochloride and subsequent analysis as Fe(II) [47]. Trivalent iron was determined from the difference between total and bivalent iron. The pH of solutions was measured using an Inolab pH-meter.

### 3. Results and discussion

#### 3.1. pH 7.30

Aqueous chromium species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 2. The results show that at the beginning of the column experiment, during the first 3 h, Cr(VI) was completely reduced. Cr(III) concentration in column effluent, after 1 h, was only 2.0 mg/l, and slowly decreased in time during the experiment. After 168 h, a steady-state Cr(III) concentration of approximately 0.9 mg/l was observed. This low concentration in column effluent can be explained by the precipitation of the most part of the Cr(III) on the scrap iron surface, probably as mixed Fe(III)–Cr(III) (oxy)hydroxides, process that occurs at pH greater than 4 [48].

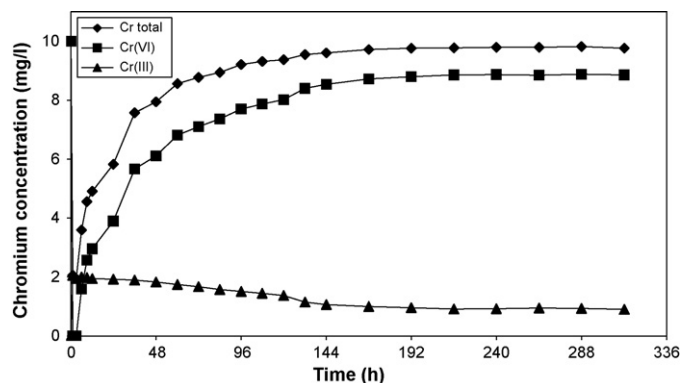


Fig. 2. Chromium species concentration in column effluent vs. time, at feed solution pH 7.30.

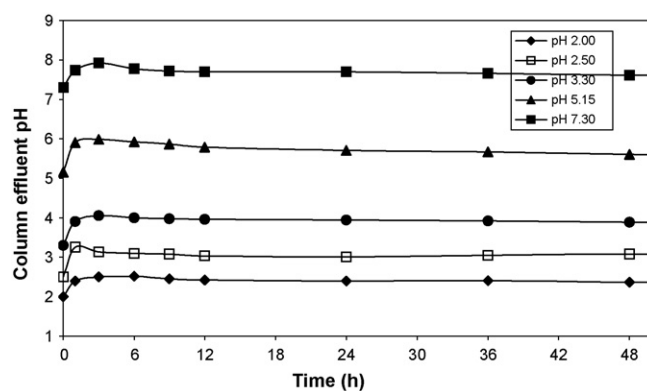
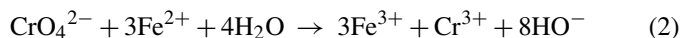


Fig. 3. pH in column effluent vs. time, at different initial pH. (Only data for first 48 h is presented.)

According to Sato [49], the metal hydroxides produced due to metallic corrosion in aqueous solutions will further be transformed in a condensed phase of metal oxide layer. Hexavalent chromium breakthrough in column effluent occurs after 6 h and its concentration increases slowly in time. The increase of Cr(VI) concentration and the decrease of Cr(III) concentration are most likely due to co-precipitation of mixed Fe(III)–Cr(III) (oxy)hydroxides, which may block the access of Cr(VI) to the iron surface and leads to a decrease in Cr(VI) reduction rate. After 168 h, a steady-state Cr(VI) concentration of approximately 8.8 mg/l was observed. Starting from a similar observation, Melitas [34] suggest that the steady-state concentration of Cr(VI) 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 oxide layer.

During the first 3 h, hexavalent chromium reduction was accompanied by an increase in the pH up to 7.92, as shown in Fig. 3. Afterwards, the pH in column effluent continuously decreased until it reached a steady-state value of approximately 7.4. While iron corrosion and reduction of Cr(VI) by scrap iron are responsible for the observed pH-increase, iron surface passivation (which cause a decrease in iron corrosion and Cr(VI) reduction rates) is responsible for the subsequent pH-decrease. Iron species in column effluent were not identified for the entire experiment duration (312 h). This means that all Fe(II) formed due to reduction of hexavalent chromium with zerovalent iron, according to Eq. (1), was oxidized to Fe(III), according to Eq. (2), and subsequently all Fe(III) precipitated inside the column:



The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 0.3 mg Cr(VI)/g scrap iron.

#### 3.2. pH 5.15

Aqueous chromium species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 4. The

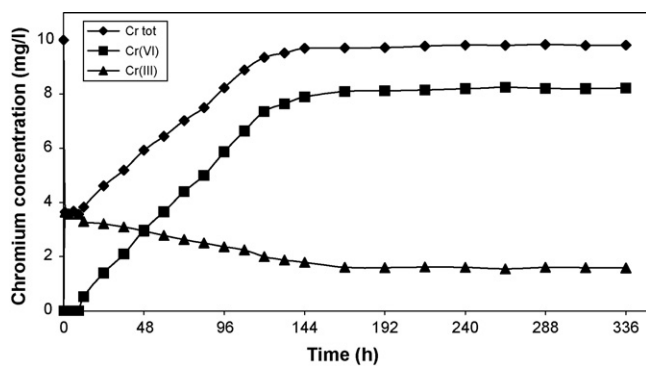


Fig. 4. Chromium species concentration in column effluent vs. time, at feed solution pH 5.15.

results show that, although Cr(VI) was completely reduced during the first 9 h of the column experiment, Cr(III) concentration in column effluent, after 1 h, was only 3.6 mg/l. Cr(III) concentration continuously decreased in time during the experiment until, after 168 h, a steady-state concentration of approximately 1.6 mg/l was observed. Responsible for this low concentration was the precipitation of Cr(III) inside the column. Hexavalent chromium breakthrough in column effluent occurs after 12 h. Its concentration increases slowly in time until, after 240 h, a steady-state Cr(VI) concentration of approximately 8.2 mg/l was observed. Hexavalent chromium reduction was accompanied by an increase in the pH up to 5.98 during the first 3 h. Subsequently the pH continuously decreases, until it reached a steady-state value of approximately 5.2, as presented in Fig. 3. The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 0.9 mg Cr(VI)/g scrap iron.

Aqueous iron species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 5. The results show a continuously decrease of Fe(total) concentration, most likely due to a decrease in time of iron corrosion rate. Fe(II) concentration also continuously decreased in time, faster than Fe(total) and Fe(III), until, after 132 h, Fe(II) could not be identified any more in the column effluent. The rapid decrease of Fe(II) concentration is caused by the decrease in time of hexavalent chromium reduction rate (Eq. (3)), but also by the increased contribution of Fe(II) to the Cr(VI) reduction, according

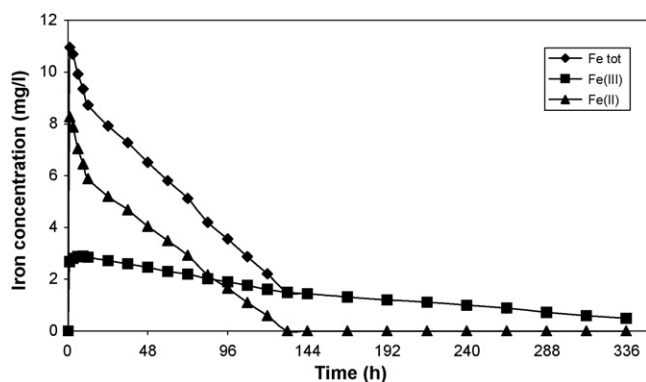


Fig. 5. Iron species concentration in column effluent vs. time, at feed solution pH 5.15.

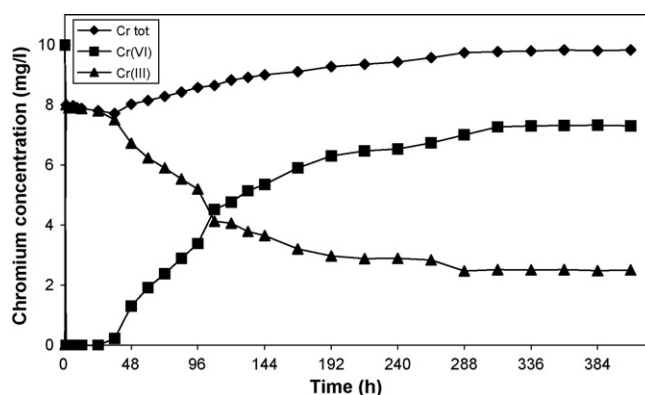
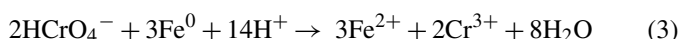


Fig. 6. Chromium species concentration in column effluent vs. time, at feed solution pH 3.30.

to Eq. (4):



Fe(III) concentration in column effluent slowly increased during the first 9 h, also due to the increased contribution of Eq. (4) to the Cr(VI) reduction.

### 3.3. pH 3.30

Aqueous chromium species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 6. The results show that, although Cr(VI) was completely reduced during the first 24 h of the column experiment, Cr(III) concentration in column effluent, after 1 h, was 8 mg/l. This indicates that Cr(III) retaining inside the column appears to happen even at pH values smaller than 4, probably by co-precipitation or adsorption. Cr(III) concentration continuously decreased in time during the experiment until, after 288 h, a steady-state concentration of approximately 2.5 mg/l was observed. Hexavalent chromium breakthrough in column effluent occurs after 36 h and its concentration increases slowly in time. After 312 h, a steady-state Cr(VI) concentration of approximately 7.3 mg/l was observed. Hexavalent chromium reduction was accompanied by an increase in the pH up to 4.0 during the first 3 h. Subsequently, the pH continuously decreases until it reached a steady-state value of approximately 3.6, as presented in Fig. 3. The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 2.4 mg Cr(VI)/g scrap iron.

Aqueous iron species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 7. The results show a continuously decrease of Fe(total) concentration, most likely due to a decrease in time of iron corrosion rate. Fe(II) concentration also continuously decreased in time, faster than Fe(total) and Fe(III), until, after 264 h, Fe(II) could not be identified any more in the column effluent. Only Fe(III) concentration in column effluent slowly increased during the first 36 h. The explanations for the decrease of Fe(II) and increase of Fe(III) concentrations are identical with those given at Section 3.2.

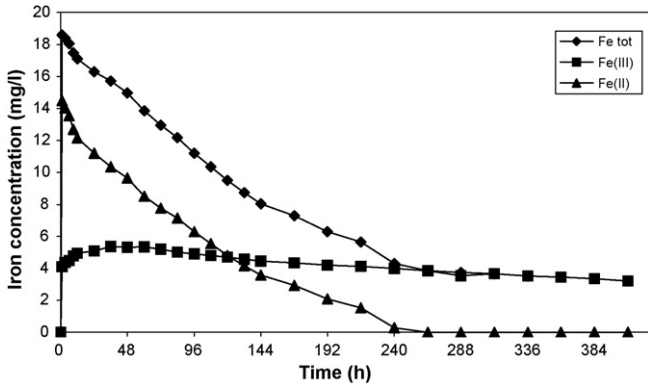


Fig. 7. Iron species concentration in column effluent vs. time, at feed solution pH 3.30.

3.4. pH 2.50

Aqueous chromium species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 8. The results show that, although Cr(VI) was completely reduced during the first 192 h of the column experiment, Cr(III) concentration in column effluent, after 1 h, was 9.4 mg/l. Cr(III) continuously decreased in time during the experiment until, after 408 h, a steady-state concentration of approximately 5.3 mg/l was observed. Therefore, even at  $pH \approx 3$  a very small part of Cr(III) has been retained inside the column, probably by adsorption. 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. Hexavalent chromium reduction was accompanied by an increase in the pH up to 3.26 during the first hour and by a continuously decrease in the pH afterwards, until it reached a steady-state value of approximately 2.6, as presented in Fig. 3. The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 19.2 mg Cr(VI)/g scrap iron.

Aqueous iron species concentrations in column effluent, as a function of elapsed time, presented in Fig. 9, are close with those obtained for pH 5.15 and 3.30. The results show that Fe(total) and Fe(II) concentrations continuously decreased until the end

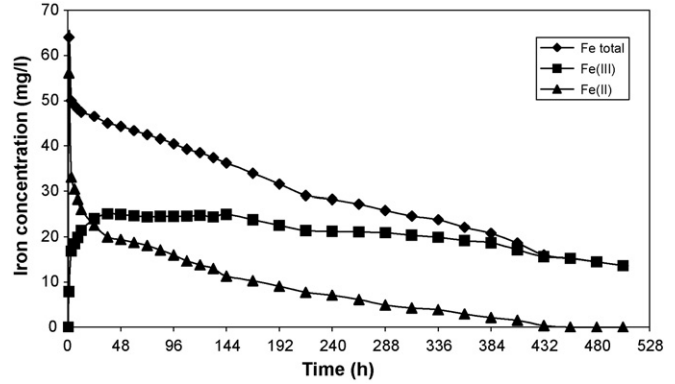


Fig. 9. Iron species concentration in column effluent vs. time, at feed solution pH 2.50.

of experiment. Only Fe(III) concentration slowly increased in column effluent during the first 48 h. The explanations for the decrease of Fe(II) and increase of Fe(III) concentrations are the same with those given for pH 5.15 and 3.30.

3.5. pH 2.00

Two important phenomena were observed inside the column during the experiment conducted under this strong acidic conditions: the occurrence of a gas ( $H_2$ ) at iron-solution interface and the rapid decrease in time of the scrap iron volume (Fig. 10). This indicates that at  $pH \leq 2$  reduction of  $H^+$  appears to be the dominant reaction contributing to scrap iron corrosion, according to Eq. (5):



Aqueous chromium species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 11. The results show that Cr(VI) was completely reduced during the first 144 h of the column experiment. Hexavalent chromium breakthrough in column effluent occurs after 168 h and its concentration increases very fast in time until, after 240 h, equals the value of Cr(VI) in column influent (10 mg/l). No steady-state Cr(VI) concentration in column effluent was observed at pH 2.00.

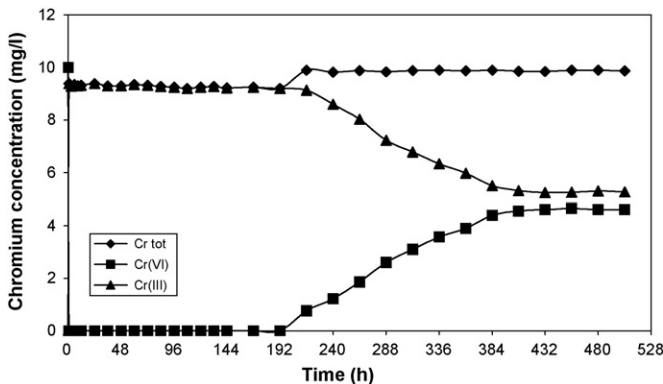


Fig. 8. Chromium species concentration in column effluent vs. time, at feed solution pH 2.50.

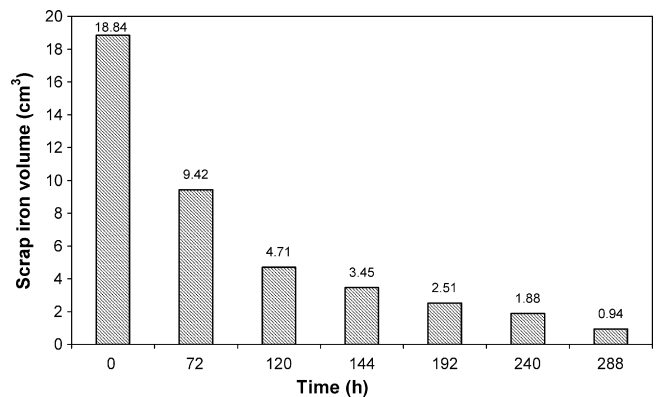


Fig. 10. Scrap iron volume in column vs. time, at feed solution pH 2.00.

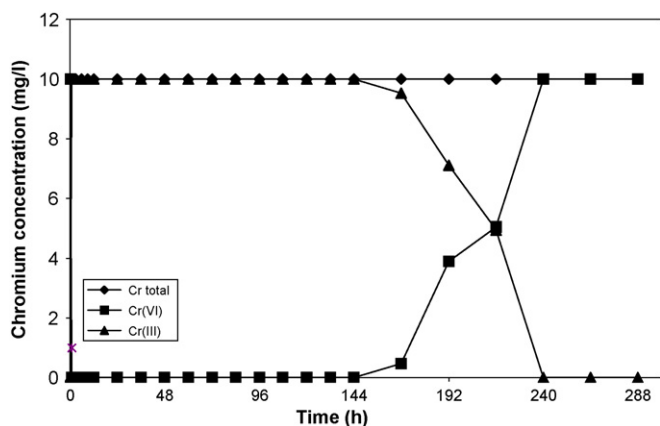


Fig. 11. Chromium species concentration in column effluent vs. time, at feed solution pH 2.00.

Cr(III) concentration in column effluent was constant and equal with the initial Cr(VI) concentration (10 mg/l) until the breakthrough of hexavalent chromium in column effluent. After Cr(VI) breakthrough, Cr(III) concentration decreases very fast in time, until, after 48 h, it could not be identified any more in the column effluent. No Cr(III) retaining inside the column and no steady-state Cr(III) concentration in column effluent was observed at pH 2.00. Hexavalent chromium reduction was accompanied by an increase in the pH up to 2.52 during the first 6 h. Afterwards, the pH continuously decreased, until it reached a steady-state value of approximately 2.05, as presented in Fig. 3. The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 14.4 mg Cr(VI)/g scrap iron.

Aqueous iron species concentrations in column effluent, as a function of elapsed time, are presented in Fig. 12. The results show a very rapid decrease of Fe(total) and Fe(II) concentrations, due to a fast decrease in time of the scrap iron mass. Only Fe(III) concentration in column effluent slowly increased during the first 36 h, due to the increased contribution of Eq. (4) to the Cr(VI) reduction.

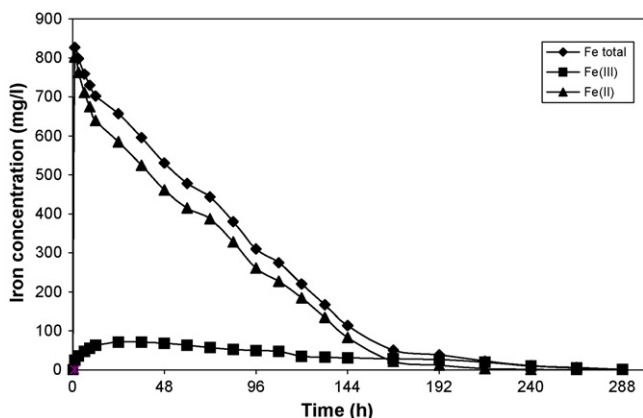


Fig. 12. Iron species concentration in column effluent vs. time, at feed solution pH 2.00.

Table 1  
Chromium mass balance

	7.30	5.15	3.30	2.50	2.00
pH	7.30	5.15	3.30	2.50	2.00
$T$ (h)	3.0	9.0	24.0	192.0	144.0
$Q$ (l/h)	0.3	0.3	0.3	0.3	0.3
$C_{Cr(VI)in}$ (mg/l)	10.0	10.0	10.0	10.0	10.0
$C_{Cr(III)out}$ (mg/l)	2.0	4.6	7.9	9.3	10.0
Cr(VI) <sub>in</sub> (mg)	9.0	27.0	72.0	576.0	432.0
Cr(III) <sub>out</sub> (mg)	1.8	12.4	56.9	535.7	432.0
Cr(III) <sub>col</sub> (mg)	7.2	14.6	15.1	40.3	0
Cr(III) <sub>col</sub> /Cr(VI) <sub>red</sub> (mg/mg)	0.8	0.5	0.2	0.07	0

### 3.6. Chromium mass balance

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

$$Cr(VI)_{in} = Cr(VI)_{red} = Cr(III)_{col} + Cr(III)_{out} \quad (6)$$

$$Cr(III)_{col} = Cr(VI)_{in} - Cr(III)_{out} \quad (7)$$

$$Cr(III)_{col} = QT(C_{Cr(VI)in} - C_{Cr(III)out}) \quad (8)$$

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

The results, presented in Table 1 show that the average Cr(III) concentration in column effluent increased with decreasing initial pH of Cr(VI) solution. This means that the amount of reduced Cr(VI) increased with decreasing pH values. Another conclusion that should result from the analysis of chromium mass balance is the one regarding the pH influence on the amount of Cr(III) retained inside of column. If in Table 1 we look at  $Cr(III)_{col}$ , it seems that, over the pH range of 2.50–7.30, the amount of Cr(III) retained increases with decreasing initial pH. But, this is a rather incorrect conclusion, because the real reason for the increase of  $Cr(III)_{col}$  is the increase of column experiment duration with decreasing initial pH; the lower the pH, the greater the column experiment duration and, therefore, the greater the  $Cr(III)_{col}$ . To find the correct answer to this problem, we believe that the influence of pH should be studied on the ratio  $Cr(III)_{col}/Cr(VI)_{red}$ . In this case, it is obvious that the amount of Cr(III) retained for each mg of reduced Cr(VI) decreases with decreasing initial pH, as shown in Table 1.

## 4. Conclusions

Results obtained using long-term column experiments, under oxidic conditions, indicate that complete reduction of Cr(VI) in water solutions is possible using scrap iron as reducing agent. The mobile and toxic chromate is converted to the less toxic and insoluble chromic ion which, at pH greater than 3, presu-

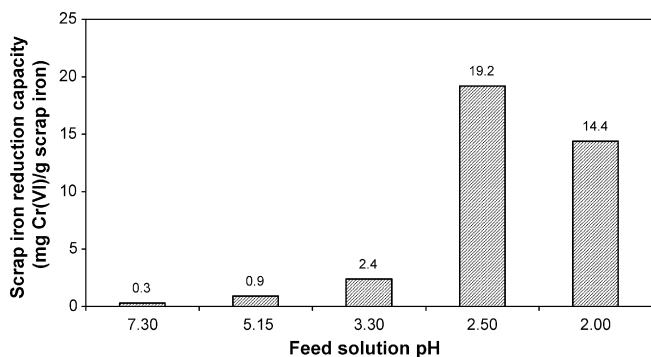


Fig. 13. Scrap iron reduction capacity at different initial feed solution pH values.

ably forms an insoluble mixed Cr–Fe (oxy)hydroxide phase, via corrosion of the elemental Fe.

The reduction capacity of scrap iron is directly dependent on the concentration of hydrogen ions in initial Cr(VI) solution. The amount of reduced Cr(VI) increased with decreasing pH values up to 2.50, suggesting an acid catalyzed behavior. The highest reduction capacity of scrap iron was determined to be 19.2 mg Cr(VI)/g scrap iron, at pH 2.50, and decreased with increasing the initial pH of Cr(VI) solution (Fig. 13). A considerable decrease in scrap iron reduction capacity (25%) was also observed at pH 2.00, as compared to pH 2.50 (Fig. 13), due to the increased contribution of  $H^+$  ions to the corrosion of scrap iron, which leads to a rapid decrease in time of the scrap iron mass. Therefore, while at  $pH > 2$  Cr(VI) is the dominant electron acceptor, at  $pH \leq 2$   $H^+$  appears to be the dominant electron acceptor contributing to scrap iron corrosion.

Over the pH range of 2.50–7.30, after the breakthrough of hexavalent chromium in column effluent, its concentration increases slowly in time until a steady-state concentration was observed; the steady-state Cr(VI) concentration in column effluent decreased with decreasing the initial pH of Cr(VI) solution up to 2.50, as presented in Fig. 14. Similarly, over the same pH range, it was observed that the amount of solubilized Cr(III) in the treated column effluent decreases in time, until a steady-state concentration of was observed. The steady-state Cr(III) concentration in column effluent increased with decreasing the

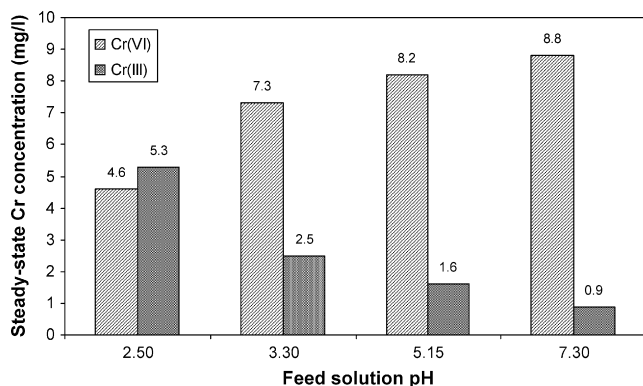


Fig. 14. Steady-state Cr concentration in column effluent, at different initial feed solution pH values.

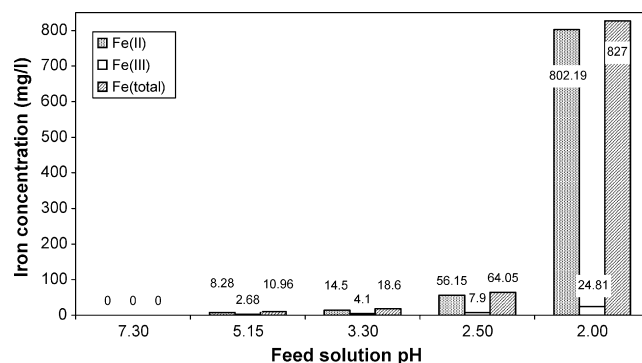


Fig. 15. Iron species concentration in column effluent, after 1 h, at different initial feed solution pH values.

initial pH of Cr(VI) solution up to 2.50 (Fig. 14). No steady-state Cr(VI) or Cr(III) concentration in column effluent was observed at pH 2.00.

Over the entire studied pH range, the amount of solubilized iron (Fe(total)) in the treated solution increases as the initial pH of column influent is decreased (Fig. 15). 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. The results show a continuously decrease in time of Fe(total) concentration in column effluent, for a constant initial pH, due to a decrease in time of iron corrosion rate. Cr(III) concentration in column effluent also continuously decreased in time, for a constant initial pH, over the pH range of 2.50–7.30. This represents an advantage, because the amount of precipitant agent used to remove Fe(total) and Cr(III) from the column effluent will also decrease in time.

The experimental results from the column experiments indicate that scrap iron seems to be a suitable material for reduction of Cr(VI) in the aqueous wastes. The changes in column effluent pH and concentrations of Fe(II) and Fe(III) indicate that the reduction of Cr(VI) occurred both at iron-solution interface and in solution. Because the reduction capacity increases with the decrease of pH, this process may be readily used in the treatment of wastewaters with high  $H^+$  concentration (i.e. electroplating wastewater). The optimum pH for Cr(VI) reduction with scrap iron in continuous-flow system was established at the value of 2.50. In addition, the influence of other factors (initial Cr(VI) concentration, shape of scrap iron, rate of feed solution, etc.) that must be considered in the development of the long-term column Cr(VI) reduction process, will be investigated by us with separate studies.

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