



Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations

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ABSTRACT

This work presents investigations on the total removal of chromium from Cr(VI) aqueous solutions by reduction with scrap iron and subsequent precipitation of the resulted cations with NaOH. The process was detrimentally affected by a compactly passivation film occurred at scrap iron surface, mainly composed of Cr(III) and Fe(III). Maximum removal efficiency of the Cr(total) and Fe(total) achieved in the clarifier under circumneutral and alkaline (pH 9.1) conditions was 98.5% and 100%, respectively. The optimum precipitation pH range which resulted from this study is 7.6–8.0. Fe(total) and Cr(total) were almost entirely removed in the clarifier as Fe(III) and Cr(III) species; however, after Cr(VI) breakthrough in column effluent, chromium was partially removed in the clarifier also as Cr(VI), by coprecipitation with cationic species. As long the column effluent was free of Cr(VI), the average Cr(total) removal efficiency of the packed column and clarifier was 10.8% and 78.8%, respectively. Our results clearly indicated that Cr(VI) contaminated wastewater can be successfully treated by combining reduction with scrap iron and chemical precipitation with NaOH.

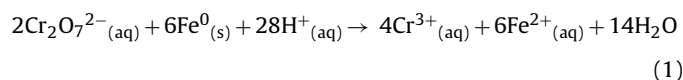
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1. Introduction

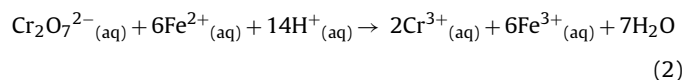
Chromium compounds are used in a wide variety of industrial processes such as: metallurgy, chemical and refractory industries, textile dyeing, tanneries, metal electroplating, wood preserving, and preparation of chromate compounds. Therefore, chromium contamination has been often reported in many industrial sites, due to accidental leakages or improper disposals measures [1–4]. In aquatic environments chromium is present mainly as hexavalent and trivalent species, characterized by markedly different chemical behavior and toxicity [5]. While Cr(VI) exists mainly as highly soluble oxyanions [6], Cr(III) is less soluble and readily precipitates as Cr(OH)₃ [7]. Cr(III) has a low toxicity, being considered an essential nutrient for many organisms [8]. In contrast, Cr(VI) is up to 1000-fold more toxic than Cr(III) [9] and a well-established carcinogen by the inhalation route of exposure [5]. Therefore, Cr(VI) must be removed from wastewaters before their disposal to natural aquatic environments.

During last two decades there has been important interest in finding new materials with high removal efficiency or/and low cost, for the removal of Cr(VI) from contaminated waters [10–23]. Reduction to Cr(III) may be considered a satisfactory solution in

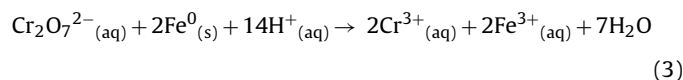
eliminating the toxicity of Cr(VI). Scrap iron is a cheap waste material that has been successfully tested for the removal of Cr(VI) via reduction to Cr(III) according to [24]:



Subsequently, Cr(VI) may be reduced in the solution (homogeneously) by Fe(II):



The two equations can be added together to yield the net reaction for the reduction process:



Gould [25] reported that 1.33 mol of Fe(0) dissolved for each mol of Cr(VI) reduced. Such a high efficiency suggested that hydrogen generated during iron corrosion acts as a reducing agent for the Cr(VI) (see Eq. (4)). Recent theoretical analysis by Noubactep [26,27] supports this view. In fact, contaminants are demonstrated to be removed by adsorption and co-precipitation, while contaminant reduction, when occurs, mainly results from indirect reducing agents (Fe(II) and H₂). In other words, Fe⁰ should be regarded as generator of reducing agents [26].

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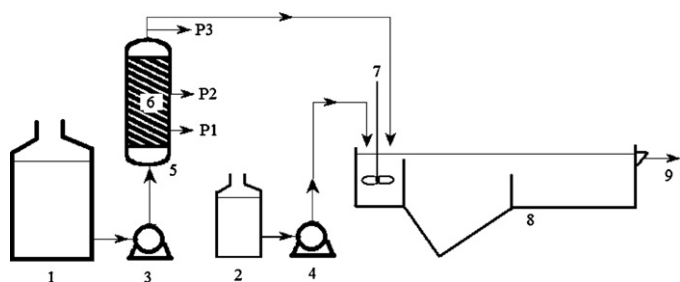


Fig. 1. Experimental setup: 1 – Cr(VI) storage tank; 2 – NaOH storage tank; 3 and 4 – peristaltic pump; 5 – glass column; 6 – scrap iron filling; 7 – overhead stirrer; 8 – horizontal clarifier; and 9 – treated water.

Wastewater treatment systems based only on Cr(VI) reduction at pH < 6.0 cannot remove chromium from the aqueous phase because resulted Cr(III) is still soluble [28]. Since the efficiency of Cr(VI) reduction with Fe(0) is very low under circumneutral conditions, the process must be conducted at acidic pH values (2.5–3.0) [29,30]. Therefore, most of the resulted species (Cr(III), Fe(II), and Fe(III)) will remain dissolved. All these species must be removed from the wastewater in a final step, in order to complete the treatment process.

To the best of our knowledge, no continuous-flow studies concerning both Cr(VI) reduction and removal of resulted chromium and iron species have been reported. As a continuation of our previous work [30–32], the present study describes the treatment of Cr(VI) polluted wastewater in continuous system, by reduction with scrap iron and subsequent precipitation of the resulted cations. This work will present data regarding the mechanism of Cr(VI) reduction inside the column, and of Cr(total) and Fe(total) removal inside the clarifier. Additionally, the optimum pH for the precipitation of cationic species resulted from the reduction process will also be established.

2. Materials and methods

2.1. Scrap iron

Scrap iron spirals (5 mm < spiral diameter < 10 mm; 5 mm < spiral length < 20 mm) used in this study originated from “SPM” metals processing laboratory, at the “Politehnica” University of Timisoara. The scrap iron was washed several times with warm distilled water to assure the complete removal of all impurities, and air dried.

2.2. Background electrolyte

The used background electrolyte was made up of: 50 ppm Ca²⁺; 20 ppm Mg²⁺; 128 ppm Cl⁻; 104 ppm Na⁺; and 293 ppm HCO₃⁻. The mixture was chosen to maintain a constant ionic strength.

2.3. Experimental procedure

A schematic diagram of the treatment system is shown in Fig. 1. A glass column (inner diameter: 2.5 cm, length: 70 cm) equipped with three lateral sampling ports (P₁, P₂, and P₃) positioned at distances from the inlet end corresponding to 22.6%, 56.5%, and 100% from the total filling volume, was employed as Cr(VI) reducing reactor. The column was carefully packed with 360 g scrap iron up to a height of 62 cm. An Ismatec IP08 peristaltic pump was used to feed the Cr(VI) solution from a storage tank to the bottom end of the column. The Cr(VI) concentration (25 mg/L), the feed solution pH (2.5), and the pumping rate (1.6 L/h) were held constant throughout the study. The Cr(VI) concentration value was selected because

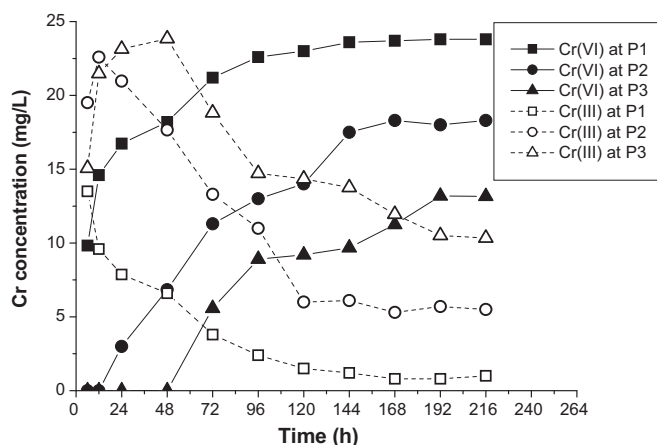


Fig. 2. Cr(VI) and Cr(III) concentration in column pore water vs. time, at P₁, P₂, and P₃ sampling ports.

it is within the range of relevant concentrations for electroplating wastewaters [16], while the pH was selected because it was previously reported as optimum value for Cr(VI) reduction with scrap iron in continuous system [30]. Cationic species resulted from Cr(VI) reduction were removed via precipitation with NaOH solution 5 g/L in a rectangular horizontal-flow clarifier having a working volume of 7 L. The column effluent was directed into the mixing chamber of the clarifier, where it was mixed with the NaOH solution using a Heidolph overhead stirrer, at 50 rpm. The NaOH solution was pumped by a second Ismatec IP08 pump. Samples were collected at regular time intervals from column sampling ports and clarifier effluent for pH, Cr(total), Cr(VI), Cr(III), Fe(total), Fe(II) and Fe(III) analysis.

2.4. Analytical method

Chromium and iron aqueous species were detected by the 1,5-diphenylcarbazide and 1,10-phenanthroline method, respectively [33], using a Jasco V 530 spectrophotometer. The pH of solutions was measured using an Inolab pH-meter, calibrated with pH 4 and 7 standard buffers. All chemicals used were of AR grade. The decanted precipitate was collected from the clarifier as follows: after 48 h (sample N₁), after 96 h (sample N₂), after 144 h (sample N₃), and after 216 h (sample N₄). After the experiment was completed, scrap iron samples were immediately collected along the packed column at distances corresponding to P₁, P₂, and P₃ sampling ports (samples C₁, C₂, and C₃).

Scanning electron microscopy (SEM)–energy dispersive angle X-ray spectrometry (EDAX) was employed to investigate the chemical composition of the scrap iron before (sample C₀) and after the experiments, as well as the composition of the precipitate. 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. For the speciation of chromium and iron species, samples of secondary minerals (mechanically removed from the surface of exhausted scrap iron), and samples of settled precipitate were dissolved using 3 N HNO₃. The as obtained aqueous solutions were then analyzed using the above mentioned spectrophotometric methods.

3. Results and discussion

3.1. Continuous reduction of Cr(VI)

Fig. 2 summarizes the results of Cr(VI) breakthrough. It is shown that, during the first 48 h, Cr(VI) concentration in the column pore

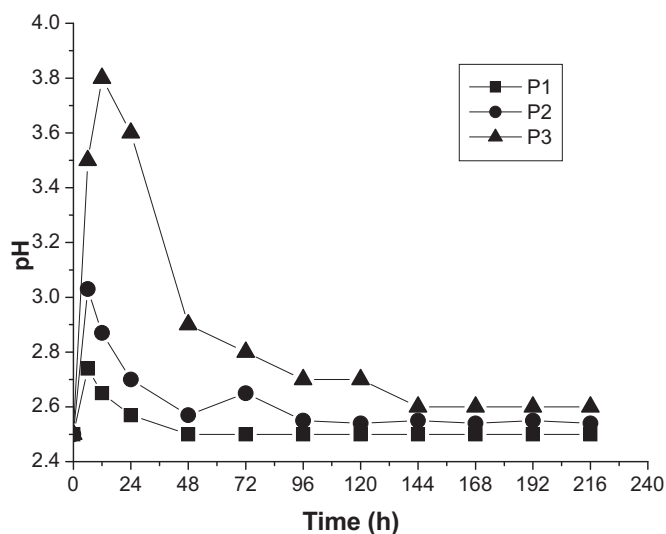


Fig. 3. Column pore water pH, at P₁, P₂, and P₃ sampling ports.

water decreased from the input value to below the detection limit at the front as the Cr(VI) front passes through the column. High concentrations of Cr(VI) were present in the pore water of P₁ from the 6th hour onward. This observation is attributed to two facts: (1) limited extent of Cr(VI) reduction by limited mass of scrap iron available below P₁, and (2) low pH value (<6.0) for which both Cr species are soluble. At P₂, Cr(VI) was totally removed 12 h, while at P₃ total removal of Cr(VI) was observed during the first 48 h.

At all three sampling ports, Cr(VI) concentration continuously increased after its breakthrough, until a steady-state value was observed. The experiment was stopped at this point. The increase of Cr(VI) concentration proceeds in two stages: high increase rates are observed within the first time interval (approximately 24 h after breakthrough), whereas lower increase rates occurred in the second one. The initial rapid increase of Cr(VI) concentration indicates that the most reactive fraction at the surface of scrap iron filling has been rapidly exhausted. Another explanation is the surface passivation due to progressive formation of an oxide-film. The steady-state Cr(VI) concentration indicates that the extent of iron surface passivation had also reached a steady state. At this stage, a dynamic equilibrium between film grow and film destruction is reached and diffusion processes yielding chromium removal are at equilibrium [34]. With increasing the distance from the inlet end of the column, the Cr(VI) steady state concentrations decreased, as follows: 23.8 mg/L, 18.3 mg/L, and 13.2 mg/L at P₁, P₂, and P₃, respectively.

3.1.1. pH evolution in the column

During the first 12 h of the experiment, iron corrosion and Cr(VI) removal were accompanied by an increase in the pore water pH at all sampling ports (Fig. 3). The increase was more significant at P₃ and less important at P₁. Subsequently, the pH dropped until it reached a steady-state value of approximately 2.6, 2.55, and 2.5, at P₃, P₂, and P₁, respectively. Iron corrosion and Cr(VI) reduction, accompanied by the formation of Cr/Fe hydroxides, are the main processes responsible for the observed pH change. The first two processes involve consumption of protons (H⁺), while the formation of Cr/Fe hydroxides occurs via consumption of hydroxide ions (HO⁻). Prior to the formation of the oxide-film, quantitative Cr(VI) reduction could be expected. The observed pH-decrease was presumably determined by the continuous passivation of scrap iron surface, thereby leading to a higher rate of precipitation than of reduction.

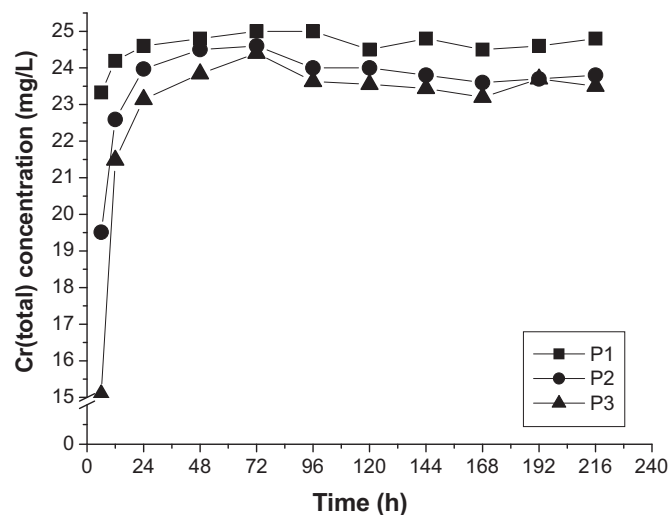


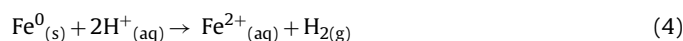
Fig. 4. Cr(total) concentration in column pore water vs. time, at P₁, P₂, and P₃ sampling ports.

3.1.2. Cr speciation in the column

Fig. 2 has already shown that, between P₁ and P₂, Cr(III) concentration along the column increased during the entire experiment. This observation may be attributed to an increase in Cr(VI) reduction efficiency as the Cr(VI) front passes from P₁ to P₂, reaching scrap iron surfaces less affected by passivation. Between P₂ and P₃, Cr(III) concentration decreased during the first 24 h, and continuously increased thereafter until the end of experiment. The initial decrease may be explained by an increase in P₃ effluent pH up to 3.8 (Fig. 3), which probably favored the retaining of some Cr(III) inside the top half of the scrap iron filling. Subsequently, the pH at P₃ continuously decreased until it reached a steady-state value of approximately 2.6, leading thus to the increase of Cr(III) solubility in pore water. Cr(total) concentrations at P₁, P₂, and P₃, as a function of elapsed time, are presented in Fig. 4. The results show that as the Cr(VI) front passes from P₁ to P₃, Cr(total) concentration along the column continuously decreased during the entire experiment, more noticeable at the beginning of the experiment and almost insignificant thereafter. At all three sampling ports, Cr(total) concentration was always less than 25 mg/L, which suggests that chromium was partially retained inside the column during the reduction process.

3.1.3. Fe speciation in the column

Aqueous Fe(II) concentrations inside the column increased as the Cr(VI) front passes from P₁ to P₃, as shown in Fig. 5. Since Fe(II) occurs in column pore water as a result of iron corrosion and heterogeneous Cr(VI) reduction, the increase of Fe(II) concentration along the column suggests an increase in iron corrosion which is sustained by the presence of a strong oxidizing agent: Cr(VI). Accordingly, Fe(II) concentrations were much higher than it should theoretically be according to the stoichiometry of Eq. (1). This observation is supported by the seminal work of Gould [25] and purchase further experimental data supporting the role of Fe(0) as a generator of reducing agents [26,27,35]. In fact, regardless from the presence of any oxidizing species, protons (H⁺) accept electrons released by Fe(0). This is the primary source of soluble Fe(II), according to Eq. (4) [35]:



H₂ bubbles were visualized inside the column at iron–solution interface, especially at the beginning of the experiment. At all three sampling points, Fe(II) concentration continuously decreased in

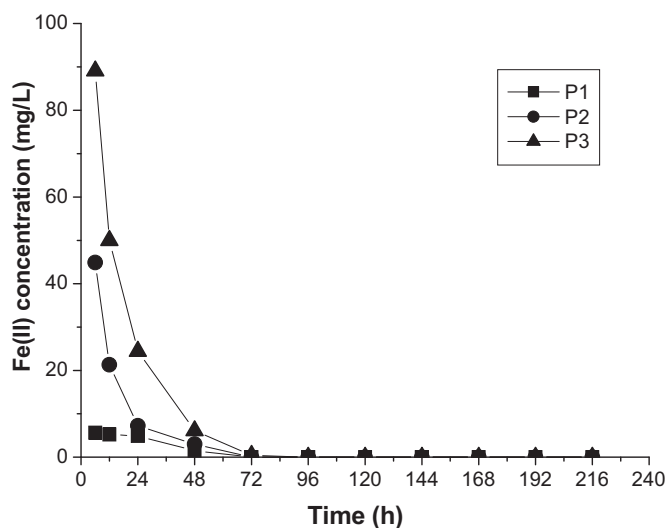


Fig. 5. Fe(II) concentration in column pore water vs. time, at P₁, P₂, and P₃ sampling ports.

time until, after 72 h, Fe(II) could not be identified any more in the column pore water. The rapid decrease of Fe(II) concentration is the result of scrap iron surface passivation, which decreases the rate of reactions (1) and (4). However, this rapid decrease of Fe(II) may also suggest that Fe(II) is one important reducing agent for Cr(VI) (Eq. (2)) as previously reported [26,32]. The disappearance of Fe(II) from the column pore water after 72 h indicates that, starting from this point, all Fe(II) resulted from reactions (1) and (4) was either oxidized to Fe(III), or precipitated. Monitoring of the Fe(III) concentration in P₁, P₂, and P₃ pore water showed a similar behavior of this parameter with the one observed for Cr(III): between P₁ and P₂ Fe(III) concentrations increased during the entire experiment, while between P₂ and P₃ Fe(III) concentrations decreased over the first 36 h, and continuously increased thereafter until the end of experiment (Fig. 6).

3.1.4. Cr removal

Since the ionic radii of Cr³⁺ and Fe³⁺ are close (0.63 and 0.64 Å, respectively) [36], and Fe(OH)₃ and Cr(OH)₃ have similar low solubility products ($K_{sp} = 1.1 \times 10^{-36}$ and 5.4×10^{-31} , respectively), the explanations given for Cr(III) behavior inside the column may be applied also for Fe(III). Fe(III) concentrations in column pore water were also much greater than they should theoretically be if all Fe(II) would have been generated only by Eq. (1), confirming thus once again the occurrence of reaction (4) inside the column. Total iron concentrations at P₁, P₂, and P₃, as a function of elapsed time, are presented in Fig. 7. As the Cr(VI) front passes from P₁ to P₃, Fe(total) concentration along the column continuously increased during the entire experiment, due to an increase in Cr(VI) reduction efficiency as the solution reaches scrap iron surfaces less affected by passivation. Nevertheless, Fe(total) concentration continuously decreased in time at all three sampling points until the end of the experiment, due to scrap iron passivation. The decrease of Fe concentration is certainly due to precipitation, which is always accompanied by co-precipitation of foreign species (here Cr) [26]. Accordingly, whether Cr(VI) is reduced or not, Cr concentration will decrease along the column. In other words, a fraction of Cr will remain in the column and the fraction passing through should be precipitated (here by NaOH).

For the studied wastewater treatment technology, it is important to know the dependence of aqueous chromium and iron species concentration in column effluent (at P₃) as a function of elapsed time. From Fig. 2 it is apparent that Cr(VI) breakthrough

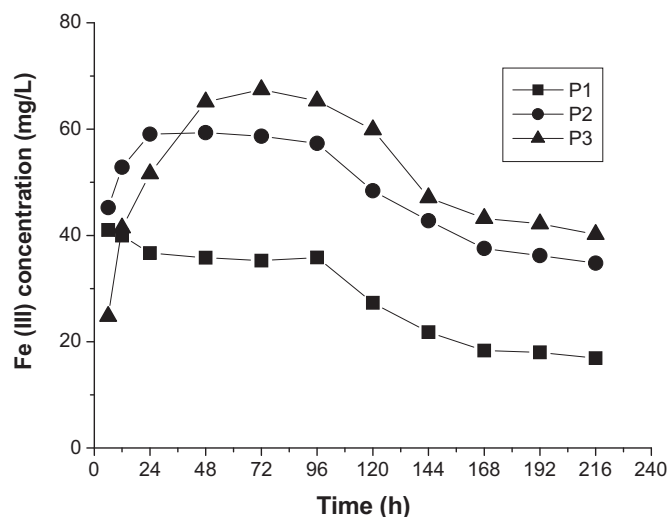


Fig. 6. Fe(III) concentration in column pore water vs. time, at P₁, P₂, and P₃ sampling ports.

in column effluent occurred immediately after Cr(III) concentration reached its maximum value. Similarly, the maximum peak of Fe(III) concentration at P₃ seems also to predict Cr(VI) breakthrough in column effluent, as may be observed from Figs. 2 and 6. The increase of Cr(VI) and Cr(total) concentration, coupled with the decrease of Cr(III) and Fe(total) concentration, noticed after Cr(VI) breakthrough, can be ascribed to passivation of scrap iron surface, process that blocks the access of Cr(VI) to the iron surface and leads to a decrease in Cr(VI) reduction rate. In spite of the low pH, the passivation process was still possible due to formation of secondary solid species on the scrap iron surface, as reported by several previous studies conducted under acidic conditions [28,37–40].

3.1.5. Solid phase characterization

Scrap iron passivation was visually distinguishable through the walls of the column, and the brownish color of the coatings migrated during the experiment from the inlet to the outlet end of the column. EDAX analysis supports this observation, indicating that, while fresh scrap iron contained 81.45% Fe, 15.56% O, and small amounts of Al, Si, and Mn (Fig. 8 and Table 1), after the reaction with Cr(VI) S and Cr were also detected, and the concentration

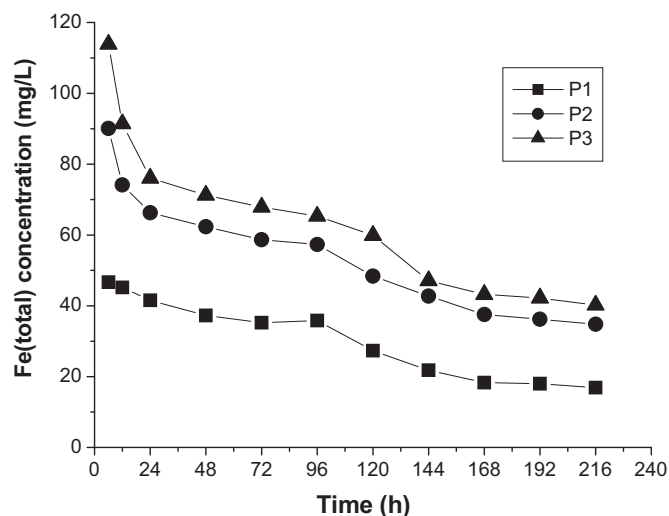


Fig. 7. Fe(total) concentration in column pore water vs. time, at P₁, P₂, and P₃ sampling ports.

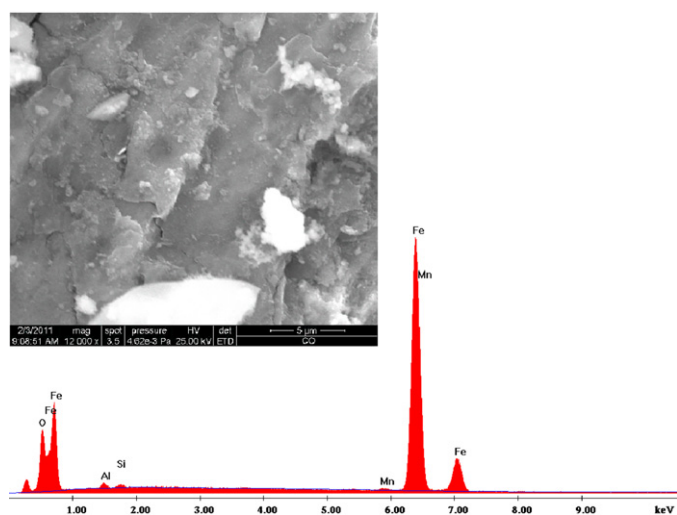


Fig. 8. EDAX pattern and SEM micrograph of un-reacted scrap iron.

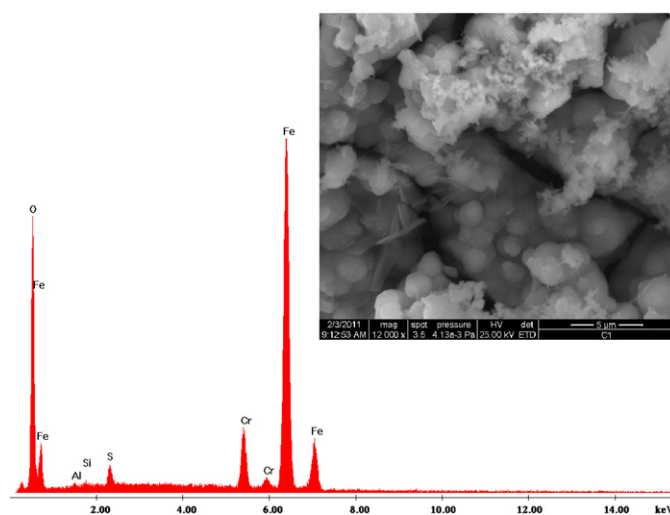


Fig. 9. EDAX pattern and SEM micrograph of exhausted scrap iron.

Table 1

Element composition (wt%) of decanted precipitate and scrap iron surface as measured by SEM–EDAX.

Element	Sample							
	N ₁	N ₂	N ₃	N ₄	C ₀	C ₁	C ₂	C ₃
O	54.74	54.46	43.42	37.14	15.56	31.08	32.36	38.11
Cr	7.21	8.51	14.71	15.74	NA	6.23	5.94	1.24
Fe	22.98	26.18	37.96	42.53	81.45	60.41	59.80	58.95
Si	2.60	2.25	1.78	2.01	0.73	0.34	0.66	0.56
Al	0.53	0.47	NA	0.58	1.52	0.42	NA	NA
S	0.53	0.73	1.09	0.68	NA	1.51	1.24	1.13
Ca	5.07	3.63	1.05	1.31	NA	NA	NA	NA
Mg	5.23	2.44	NA	NA	NA	NA	NA	NA
Na	1.11	0.54	NA	NA	NA	NA	NA	NA
Mn	NA	NA	NA	NA	0.74	NA	NA	NA

NA: not available.

of oxygen increased up to 38.11% (Fig. 9 and Table 1). Chromium and iron concentration at the scrap iron surface decreased with increasing the distance from the inlet end of the column, as presented in Table 1; thus, the top half of the scrap iron filling was less affected by the passivation process. Speciation analysis of the secondary mineral phases revealed the existence of chromium mainly as Cr(III) (Table 2). However, low concentrations of Cr(VI) were also detected, probably as a result of Cr(VI) adsorption. The increase of Cr(VI) concentrations along the column may be ascribed to changes in scrap iron surface reactivity during the experiment. These results are in agreement with similar literature reports who also showed the existence of Cr(VI) at the surface of exhausted ZVI, in concentrations accounting up to 20% of the Cr(total) [41–43]. The predominant iron species was Fe(III), consistent with a previous study reporting a mixture of 90% Fe(III) and 10% Fe(II) at the

Table 2

Chromium and iron speciation in exhausted scrap iron coatings and decanted precipitate.

Sample	wt% from Cr(total)		wt% from Fe(total)	
	Cr(VI)	Cr(III)	Fe(III)	Fe(II)
N ₁	0	100	99.62	0.38
N ₂	4.25	95.75	100	0
N ₃	11.71	88.29	100	0
N ₄	7.94	92.06	100	0
C ₁	2.53	97.47	89.67	10.33
C ₂	2.98	97.02	94.28	5.72
C ₃	3.19	96.81	95.87	4.13

surface of spent ZVI [44]. From the substantial increase in oxygen concentration and the occurrence of chromium on the surface of the exhausted scrap iron, it can be deduced that there are not only iron, but also chromium oxides/hydroxides formed onto the scrap iron surface as a result of Cr(VI) reduction. SEM micrographs of the scrap iron also confirm the occurrence of secondary mineral phases; while the un-reacted scrap iron was only partially covered by iron oxides (Fig. 8), the exhausted scrap iron was completely covered by secondary phases (Fig. 9). Three types of precipitates were discerned in the micrograph of the exhausted scrap iron. The predominant morphology seems to be as botryoidal clusters, covering the entire scrap iron surface. Euhedral tabular crystalline structures, occurred as thin plates oriented to the surface, are placed between botryoidal phases. Finally, some amorphous structures were also noticed, partially covering the botryoidal clusters. The observed botryoidal morphologies are consistent with the results of a very recent study, carried out at pH values as low as 4, showing that they were composed of FeCr₂O₄ [45]. The euhedral structures and amorphous forms are also in good agreement with previous results, in which they were reported to be iron and chromium (oxy)hydroxides [18,36,41]. Thus, the results of SEM, EDAX, and chemical speciation were coincident one another, revealing the formation at the spent scrap iron surface of iron and chromium secondary phases, mainly as Cr(III) and Fe(III) species.

3.2. Continuous precipitation of the resulted Cr and Fe species

Our previous batch study [46] carried out using aqueous solutions with pH 2.5, and Cr(III), Fe(II), and Fe(III) concentrations of 50 mg/L, 75 mg/L, and 50 mg/L, respectively, indicated the 500 mg/L value as optimum NaOH dose for cations removal. However, since the first analysis of the column effluent revealed Cr(total) and Fe(total) concentrations lower than the above mentioned, the precipitation process was initialized, starting from the 6th hour onward, with a 400 mg/L NaOH dose. Six hours later, the pH of the clarifier effluent increased up to 9.1, as presented in Fig. 10. Because this pH was considered to alkaline, from the 12th hour onward the NaOH dose was set to 300 mg/L. As a result, the clarifier's effluent pH subsequently decreased to 7.4 and therefore this dose was maintained until the end of experiment. After another 48 h with relatively constant pH, despite the unchanged NaOH dose, the pH of clarifier effluent slowly increased up to 7.9 at the end of experiment, as a result of decreasing Cr(III) and Fe(total) concentrations in column effluent.

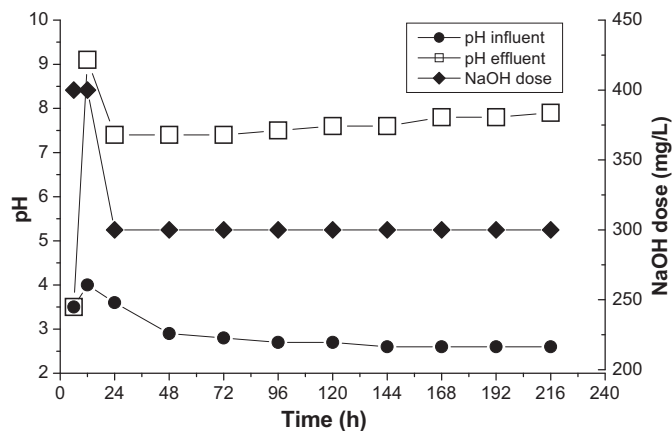


Fig. 10. Variation of clarifier effluent pH, as a function of NaOH dose.

3.2.1. Fe removal

From Fig. 11 it can be observed that, after the precipitation was started, Fe(II) removal efficiency noticeably increased from 2.5% to 100% and remained at this value as long Fe(II) was present in the clarifier influent. A similar removal efficiency increase, from 3.1% to 100%, was observed also for Fe(III) after the initialization of the precipitation process. Subsequently, Fe(III) removal efficiency decreased to 95.3%, as a result of pH decrease from 9.1 to 7.4. From the 48th hour onward, Fe(III) removal efficiency slowly increased back, up to 98% at the end of experiment, due to pH increase inside the clarifier. Since the solubility of $\text{Fe}(\text{OH})_2$ is much higher than that of $\text{Fe}(\text{OH})_3$ ($K_{\text{SP}} = 1.6 \times 10^{-14}$ vs. 1.1×10^{-36}), the 100% removal efficiency of Fe(II) was mainly determined by the oxidation of Fe(II) to Fe(III) in the mixing chamber of the clarifier, process kinetically favored over the pH range of 5–8 [47]. This conclusion was confirmed by the very low Fe(II) concentration in the precipitate decanted during the first 48 h of the experiment (sample N₁, Table 2). Thus, we can reasonable estimate that, inside the clarifier, Fe(total) was almost entirely removed as Fe(III) species.

3.2.2. Cr removal

The evolution of chromium species removal efficiency vs. NaOH dose is presented in Fig. 12. After the initialization of the precipitation process, Cr(total) removal efficiency markedly increased from 3.2% to 100%. A slight decrease in Cr(total) removal efficiency, up to 94.2%, was noticed afterwards, caused by the pH decrease

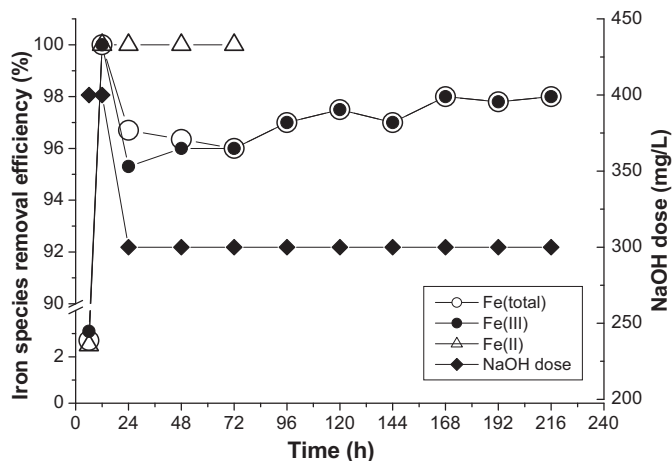


Fig. 11. Fe species removal efficiency in clarifier, as a function of elapsed time and NaOH dose.

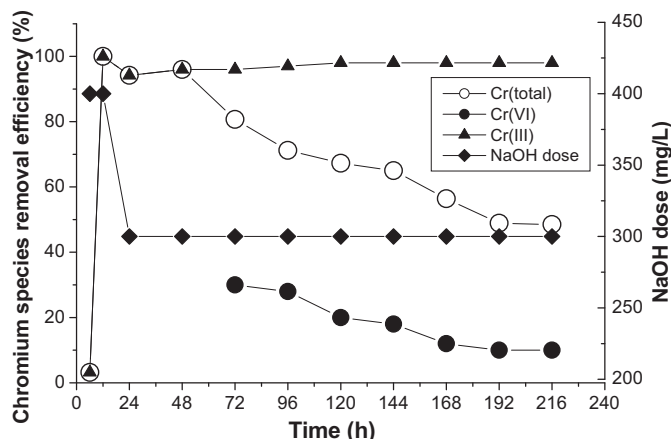
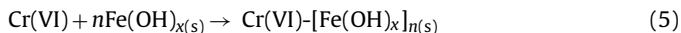


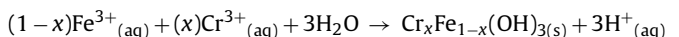
Fig. 12. Cr species removal efficiency in clarifier, as a function of elapsed time and NaOH dose.

from 9.1 to 7.4. However, it is important to point out that, during the first 48 h, Cr(total) in clarifier influent consisted only in Cr(III), which explains the high removal efficiency of Cr(total). After Cr(VI) breakthrough in column effluent, Cr(total) removal efficiency dropped significantly, up to 48.5% at the end of experiment. This decrease can be attributed to the fact that, after Cr(VI) breakthrough, Cr(total) was comprised from both Cr(III) and Cr(VI); moreover, from the 48th hour onward, Cr(VI) concentration in clarifier influent continuously increased, while Cr(III) concentration continuously decreased. Despite the fact that Cr(VI) exists under circumneutral conditions as highly soluble chromate oxyanions, it was, however, partially removed from the clarifier influent, by coprecipitation with Cr(III) and Fe(III). For example, Cr(VI) may be entrapped in the structure of growing iron hydroxides [48–50]:



Cr(VI) removal efficiency was significantly lower than Cr(III) removal efficiency, and continuously decreased in time until the end of experiment; this decrease was probably determined by the decrease in time of the volume of settled precipitate. On the contrary, Cr(III) removal efficiency recorded after 48 h slowly increased up to 98.5% at the end of experiment, as a result of pH increase. Chemical speciation of the decanted precipitate supports these observations, as presented in Table 2. The precipitate collected during the first 48 h was free of Cr(VI), because the clarifier influent did also not contain Cr(VI) over the same period. Nevertheless, Cr(VI) was still detected in the precipitate, but only after its breakthrough in column effluent. Cr(VI) concentration in precipitate increased up to 11.71% after 144 h, and decreased thereafter during the final 72 h of the experiment. The initial increase of Cr(VI) concentration in precipitate can be attributed to the increase of Cr(VI) and decrease of Cr(III) and Fe(III) concentrations in clarifier influent. But, from the 144th hour onward, Cr(VI) concentration in clarifier influent slowly reached to a steady state value; in the same time, the amount of Cr(III)–Fe(III) precipitate settled in the clarifier was much lower than at the beginning of the experiment. Thus, the mass of Cr(VI) removed by coprecipitation during the final 72 h of the experiment was also much lower, determining the decrease of Cr(VI) concentration in the decanted precipitate.

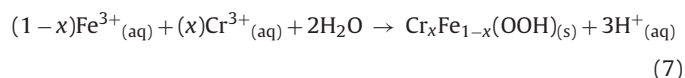
Previous studies have shown that dissolved Fe(III) and Cr(III) readily co-precipitate as mixed Fe(III)–Cr(III) (oxy)hydroxides, at pH values greater than 4 [51,52], according to [13]:



(6)

Table 3
Chromium and iron mass balance.

	Column			Clarifier		
	In	Out	Retained	In	Out	Retained
$C_{Cr(VI)}$ (mg/L)	25	0	–	0	0	–
$C_{Cr(III)}$ (mg/L)	0	22.3	–	22.3	2.6	–
$C_{Cr(total)}$ (mg/L)	25	22.3	–	22.3	2.6	–
$C_{Fe(II)}$ (mg/L)	0	26.5	–	26.5	10.8	–
$C_{Fe(III)}$ (mg/L)	0	53.7	–	53.7	4.9	–
$C_{Fe(total)}$ (mg/L)	0	80.2	–	80.2	15.7	–
$M_{Cr(VI)}$ (mg)	1920	0	6.2	0	0	0
$M_{Cr(III)}$ (mg)	0	1712.6	201.2	1712.6	199.6	1513
$M_{Cr(total)}$ (mg)	1920	1712.6	207.4	1712.6	199.6	1513
$M_{Fe(II)}$ (mg)	0	2035.2	330.4	2035.2	829.4	1205.8
$M_{Fe(III)}$ (mg)	0	4124.1	5103.4	4124.1	376.3	3747.8
$M_{Fe(total)}$ (mg)	0	6159.3	5433.8	6159.3	1205.7	4953.6
$M_{(scrap\ iron)_i}$ (mg)	360000					
$M_{(scrap\ iron)_f}$ (mg)	348406.9					



EDAX analysis of the settled precipitate (Table 1) indicates that while chromium and iron concentrations increased, oxygen concentration decreased with increasing the elapsed experimental time. Therefore, the degree of precipitates hydration also decreased in time, which could suggest that at the beginning of experiment $Cr_xFe_{1-x}(OH)_3$ was the predominant form in precipitate, while at the end of experiment the precipitate consisted mainly from $Cr_xFe_{1-x}(OOH)$.

3.3. Chromium and iron mass balance

Because the proposed wastewater treatment process is efficient as long Cr(VI) is totally reduced, the mass balance was calculated only up to the moment of Cr(VI) breakthrough in column effluent; the mathematical equations are presented in the supplementary material. The results of first 48 h mass balance, presented in Table 3, indicate an average removal efficiency of 88.3% for Cr(total), and 80.4% for Fe(total). These moderate values were caused by the fact that, before starting the precipitation process, Cr(total) and Fe(total) removal efficiencies were only 3.2% and 2.5%, respectively. However, after the initialization of the precipitation process, the removal efficiencies markedly increased, reaching up to 96.7% under circumneutral conditions. This means that Cr(total) and Fe(total) concentrations in clarifier effluent were as low as 0.8 mg/L and 2.5 mg/L, respectively. As long the column effluent was free of Cr(VI), the average Cr(total) removal efficiency of the packed column and clarifier was 10.8% and 78.8%, respectively; the remaining 10.4% was found in the clarifier effluent, as dissolved Cr(III). The mass balance also shows that, until the moment of Cr(VI) breakthrough, only 3.2% from the initial mass of metallic scrap iron was consumed. Since Cr(VI) breakthrough however occurred, despite the significant mass of unreacted scrap iron, it proves once more that Cr(VI) reduction was significantly retarded by the build-up of a passivating layer on the scrap iron surface. The scrap iron reduction capacity and the total treatment capacity of the wastewater treatment process, calculated up to the moment of Cr(VI) breakthrough, were 5.3 mg Cr(VI)/g scrap iron and 0.2 L/g scrap iron, respectively. This is consistent with the value of 19.2 mg Cr(VI)/g scrap iron, previously reported by a study carried out under same pH conditions, but at a Cr(VI) concentration of only 10 mg/L [30].

4. Conclusions

Long-term column experiment performed in this work confirmed the possibility of Cr(VI) conversion to Cr(III) by using scrap iron. Although 96.8% from the initial metallic scrap iron still remained unreacted in the column, Cr(VI) breakthrough occurred after 48 h, due to a compactly Cr–Fe composed passivation film formed on the scrap iron. Cr(VI) breakthrough seems to be predicted by the maximum peak of Fe(III) and Cr(III) concentrations in column effluent. The precipitation of Cr–Fe secondary minerals was more intense at the bottom half of the column, while the top half was less affected. Cr(III) and Fe(III) were the main chromium and iron species detected at the surface of spent scrap iron; however, low concentrations of Cr(VI) and Fe(II) were also identified. After the initialization of the precipitation process, total chromium and iron removal was achieved in the clarifier at pH 9.1, while under circumneutral conditions removal efficiencies as high as 98.5% were observed. The high removal efficiency of Fe(II), in contrast with $Fe(OH)_2$ relative high solubility, was the result of Fe(II) oxidation to Fe(III), kinetically favored over the pH range of 5–8. Although Cr(VI) is highly soluble, it was however partially removed from the clarifier influent by coprecipitation with Cr(III) and Fe(III). This indicates that high Cr(total) removal efficiencies could be attained in the clarifier even after Cr(VI) breakthrough in column effluent, but only for a short period of time. The optimum precipitation pH range (7.6–8.0) was achieved with a 300 mg/L NaOH dose. The experimental results from this study clearly indicate that chromium can be totally removed from Cr(VI) contaminated wastewater by a treatment process combining reduction with scrap iron and chemical precipitation with NaOH. However, in order to assure total reduction of Cr(VI) for a longer period of time, after Cr(VI) breakthrough the scrap iron filling must be re-activated for further reuse. Alternatively, the use of several columns in series should be tested. In this effort, admixing inert materials (e.g. sand, pumice) to Fe(0) in reactive zones could be an efficient tool to save iron costs [53] while possibly increasing sustainability [54].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.09.002.

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