

Hexavalent Chromium Pollution Abatement by use of Scrap Iron

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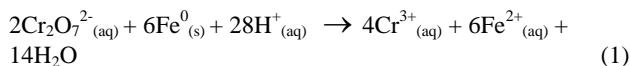
Abstract—In this study, the reduction of Cr(VI) by use of scrap iron, a cheap and locally available industrial waste, was investigated in continuous system. The greater scrap iron efficiency observed for the first two sections of the column filling indicate that most of the reduction process was carried out in the bottom half of the column filling. This was ascribed to a constant decrease of Cr(VI) concentration inside the filling, as the water front passes from the bottom to the top end of the column. While the bottom section of the column filling was heavily passivated with secondary mineral phases, the top section was less affected by the passivation process; therefore the column filling would likely ensure the reduction of Cr(VI) for time periods longer than 216 hours. The experimental results indicate that fixed beds columns packed with scrap iron could be successfully used for the first step of Cr(VI) polluted wastewater treatment. However, the mass of scrap iron filling should be carefully estimated since it significantly affects the Cr(VI) reduction efficiency.

Keywords—hexavalent chromium, heavy metals, scrap iron, reduction capacity, wastewater treatment

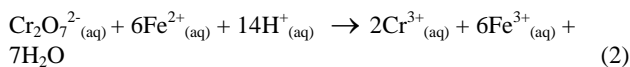
I. INTRODUCTION

ANTHROPOGENIC activities have increased the amount of heavy metals that exist in the environment. The production of heavy metals increased rapidly, especially after the industrial revolution. Therefore, in last decades, the presence of heavy metals in aquatic ecosystems has received a widespread attention due to their potential human health risks and harmful effect to living organisms. Chromium is used in a variety of industrial applications (e.g. wood preserving, preparation of chromate compounds, textile dyeing, tanneries, metallurgy, metal electroplating). As a result, large quantities of chromium have been released into the environment [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 are dependent upon its oxidation state. Because it has a high solubility in water, Cr(VI) has a significant mobility in the environment [5],[6]. On the contrary, Cr(III) has a lower solubility in water and readily precipitates as Cr(OH)₃ [7] or as mixed Fe(III)-Cr(III) (oxy)hydroxides [8],[9] under alkaline or circumneutral conditions. Therefore, Cr(III) has a low mobility in the

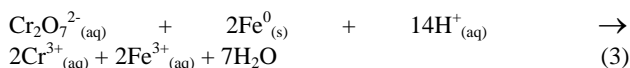
environment. While Cr(III) is considered an essential nutrient for the human body [10], Cr(VI) is toxic to most living organisms [5],[11]–[12], and a known human carcinogen by inhalation route of exposure [13]–[17]. Moreover, recent studies have shown that Cr(VI) is a possible human carcinogen also by oral route of exposure, when ingested with food or water [18]. Thus, it is obvious that removal of chromium, and especially of Cr(VI), is an essential pollution abatement process that should be applied to wastewaters contaminated with this heavy metal, prior to discharging them into the natural water bodies. Chemical reduction to Cr(III) followed by precipitation is the most used technique for the decontamination of wastewaters polluted with Cr(VI) compounds. The reducing agents commonly used are ferrous sulphate, sulphur dioxide and sodium sulphites. The major drawback of this conventional treatment method is the high cost of chemicals used for the reduction purposes. Therefore, in recent years, attention has been focused on the use of various waste materials that can substitute traditional reducing agents. Previous reports have described the use of different non-conventional reducing agents such as: magnetite [19]–[21], siderite [22], mackinawite [23],[24], pyrite [25], hematite, biotite [26], copper smelter slag [27]. Scrap iron is a cheap industrial waste that could be used for the reduction of Cr(VI). Cr(VI) may be removed from solution via direct (heterogeneous) reduction to Cr(III) with scrap iron according to [28]:



Subsequently, Fe(II) resulted in Eq.(1) may also reduce Cr(VI), homogeneously:



Thus, the net reaction for the reduction process is:



Hence, in the present investigation, the ability of scrap iron to reduce Cr(VI) in a packed up-flow column was evaluated. The effect of an important design parameter, bed height (scrap iron mass), on scrap iron reduction capacity and efficiency has been examined in flow-through column experiments.

II. MATERIALS AND METHODS

Hexavalent chromium reduction was performed using scrap

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iron spiral fibers (5 mm < spiral diameter < 10 mm; 5 mm < spiral length < 20 mm) 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. Hexavalent chromium stock solution (25 g/L) was prepared by dissolving the necessary amount of $K_2Cr_2O_7$ in 1000 mL of distilled deionized water; feed solution of the desired initial Cr(VI) concentration (25 mg/L) was prepared by diluting the stock solution. This concentration was selected because it is within the range of relevant concentrations for electroplating wastewaters [29]. Concentrated H_2SO_4 was used for adjusting the feed solution pH at 2.5; this value was selected because it was previously reported as optimum pH for Cr(VI) reduction with scrap iron in continuous system [30]. The 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. All chemicals used were of AR grade. A schematic diagram of the wastewater treatment system involved in this study is shown in Fig. 1.

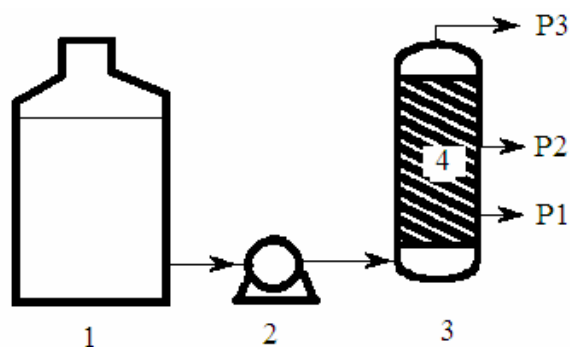


Fig. 1 Experimental setup: 1 - Cr(VI) solution storage tank; 2 - Peristaltic pump; 3 - Glass column; 4 - Scrap iron filling

A glass column (inner diameter: 2.5 cm, length: 70 cm) equipped with three lateral sampling ports (P_1 , P_2 , and P_3) 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, insuring that the filling was homogeneously distributed. 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/hour) were held constant throughout the study. Cr(VI) was detected by the 1,5-diphenylcarbazide colorimetric method [31]; the absorbance of the resulted purple complex was measured at 540 nm using a Jasco V 530 spectrophotometer. The pH of solutions was measured using an Inolab pH-meter calibrated using pH 4 and 7 standard buffers.

III. RESULTS AND DISCUSSION

In this study it was assumed that the scrap iron filling was composed of three sections, as presented in Table 1. The total duration of the experiment (216 hours) was divided in nine time units, each of 24 hours; for each time unit and each filling section the following parameters were determined: The mass of reduced Cr(VI) ($M_{Cr(VI)}$) and the reduction capacity of scrap iron (RC_{SI}) were calculated as follows:

$$M_{Cr(VI)} = (C_I - C_E) \cdot 1.6 \cdot 24 \text{ (mg)} \quad (4)$$

$$RC_{SI} = \frac{M_{Cr(VI)}}{M_{SI}} \text{ (mg Cr(VI)/g scrap iron)} \quad (5)$$

where: C_I (mg/L) is the inlet average Cr(VI) concentration, C_E (mg/L) is the average Cr(VI) concentration at sampling port, 1.6 (L/h) is the volumetric inflow rate, 24 (h) is the duration of one time unit, and M_{SI} (g) is the mass of scrap iron from each column filling section, as presented in Table I. The total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) during the entire column experiment was calculated for each column filling section according to:

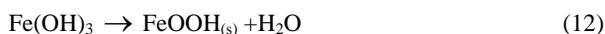
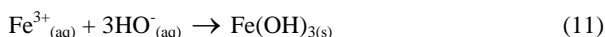
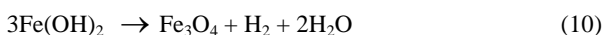
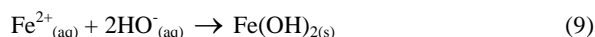
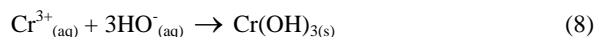
$$TM_{Cr(VI)} = \sum_{i=1}^9 M_{Cr(VI)}^i \text{ (mg)} \quad (6)$$

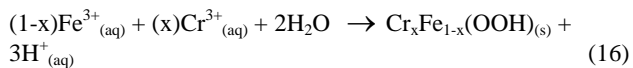
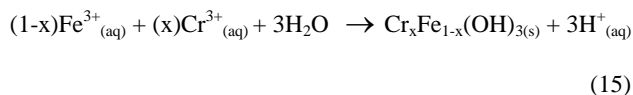
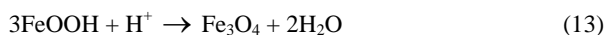
where 9 is the number of time units of the column experiment

The scrap iron efficiency (E) of each filling section was calculated as follows:

$$E = \frac{TM_{Cr(VI)}}{M_{SI}} \text{ (mg Cr(VI)/g scrap iron)} \quad (7)$$

At P_1 , Cr(VI) was detected from the first time unit, as can be seen from Fig. 2; this means that Cr(VI) breakthrough at first sampling port occurred from the very beginning of the experiment, during the first 24 hours. The highest value of RC_{SI} was also observed during the first time unit of the column experiment, and continuously decreased thereafter until the end of the experiment. The decrease of RC_{SI} value was due to passivation of scrap iron surface with simple or mixed Fe-Cr (oxy)hydroxides, formed according to [33]:





where x vary from 0 to 1.

The build-up of a passivating layer on the surface of the scrap iron blocks the transfer of electrons from Fe(0) to Cr(VI) and leads to a decrease in Cr(VI) reduction rate. Beside decreasing the RC_{SI} , scrap iron passivation leads also to the increase of average Cr(VI) concentration, until a steady-state value was attained, as presented in Fig. 2. As a result of the RC_{SI} continuous decrease, the $\text{M}_{\text{Cr(VI)}}$ also decreased, from the first to the last time unit of the column experiment, as shown in Fig. 3. The decrease of $\text{M}_{\text{Cr(VI)}}$ was more significant at the beginning and almost negligible at the end of the column experiment. In spite of scrap iron passivation and $\text{M}_{\text{Cr(VI)}}$ decrease, the value of $\text{TM}_{\text{Cr(VI)}}$ continuously increased in time, up to 1341 mg at the end of experiment, as presented in Fig. 4.

Scrap iron reduction capacity and aqueous Cr(VI) concentrations at second sampling port (P_2), as a function of elapsed time, are presented in Fig. 5. It can be observed that, although Cr(VI) breakthrough occurred, just like at P_1 , during the first time unit, Cr(VI) concentrations are, however, lower than those recorded at P_1 . Similarly, the steady-state Cr(VI) value observed at the end of experiment at P_2 was lower than at P_1 . This may be attributed to the fact that, at the entrance in the P_1 - P_2 section, Cr(VI) concentration was always lower than 25 mg/L.

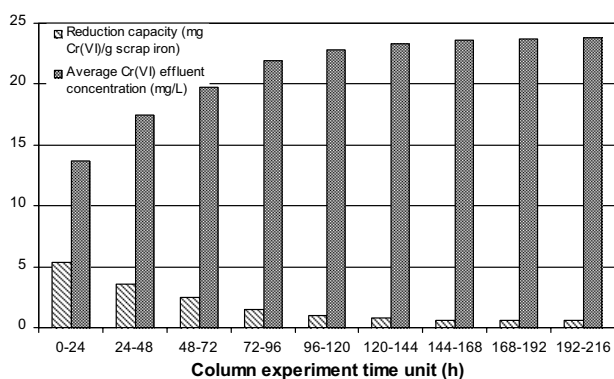


Fig. 2 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at P_1

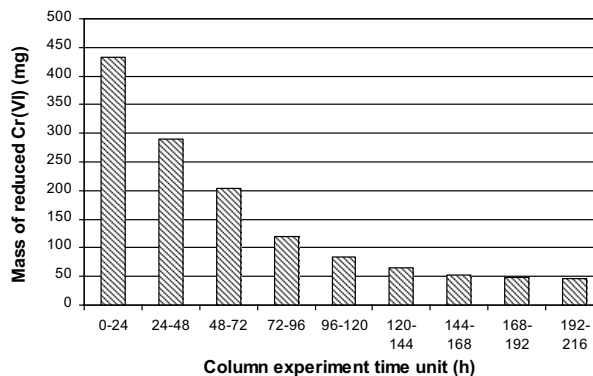


Fig. 3 Mass of reduced Cr(VI) ($\text{M}_{\text{Cr(VI)}}$) vs. time, at P_1

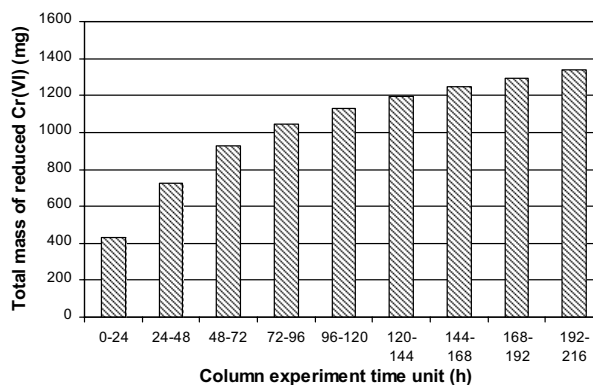


Fig. 4 Total mass of reduced Cr(VI) ($\text{TM}_{\text{Cr(VI)}}$) vs. time, at P_1

Thus, a lower amount of Cr(VI) was reduced between P_1 and P_2 , at least at the beginning of experiment. This also explains the quasi-constant value of the RC_{SI} and $\text{M}_{\text{Cr(VI)}}$ values during the first two time units. However, from the 3rd time unit onward, as a result of increasing Cr(VI) concentration at the entrance in the P_1 - P_2 section, the scrap iron reduction capacity and the mass of reduced Cr(VI) continuously decreased, more significant at the beginning and almost negligible at the end of the column experiment (Figs. 5 and 6). Instead, the value of $\text{TM}_{\text{Cr(VI)}}$ continuously increased in time up to 3070 mg at the end of experiment, as presented in Fig. 7.

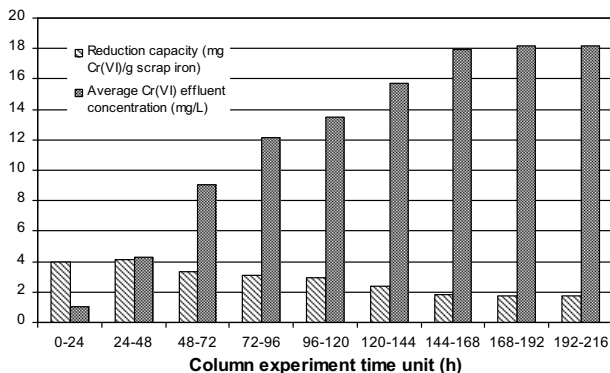
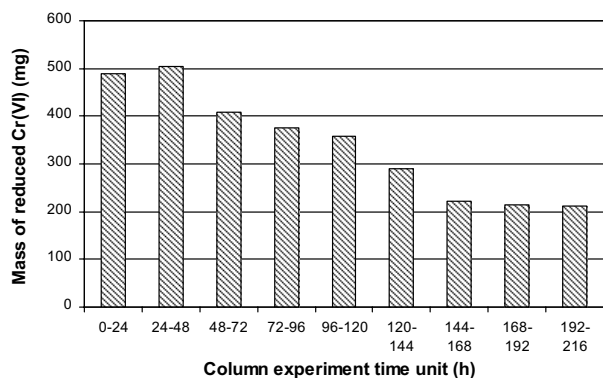
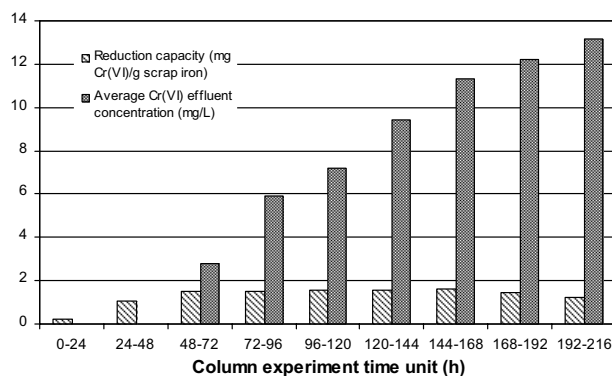
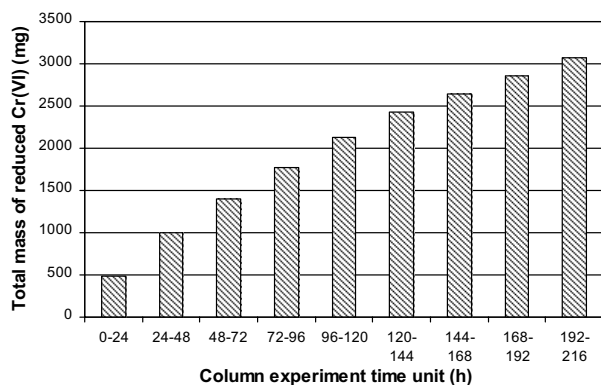
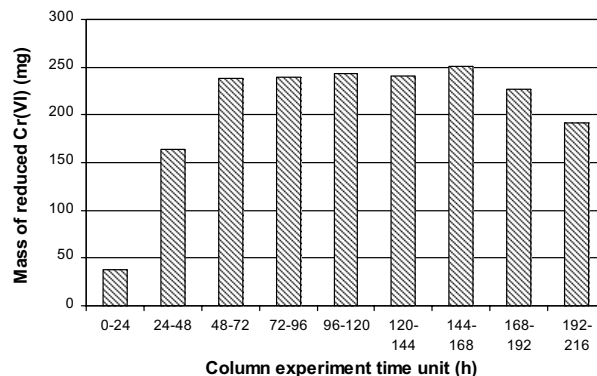
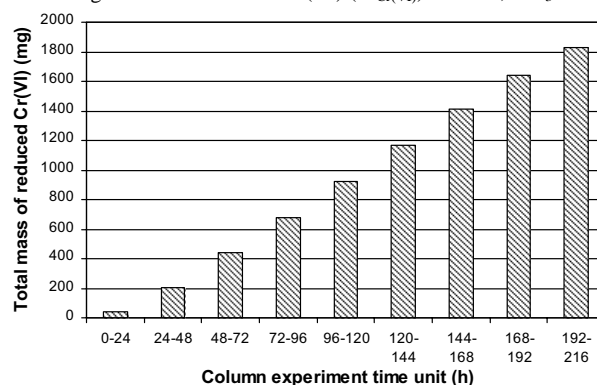


Fig. 5 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at P_2

Fig. 6 Mass of reduced Cr(VI) ($M_{Cr(VI)}$) vs. time, at P₂Fig. 8 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at P₃Fig. 7 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at P₂Fig. 9 Mass of reduced Cr(VI) ($M_{Cr(VI)}$) vs. time, at P₃

Experimental data recorded at P₃ showed that Cr(VI) was not detected in the column effluent during the first two time units of the experiment, as can be seen from Fig. 8. Although Cr(VI) was totally reduced in the P₂-P₃ section during the first 48 hours of the experiment, the RC_{SI} values observed in this time period were lower than those observed at P₁ and P₂. Moreover, RC_{SI} increased during the first two time units, and remained thereafter more or less constant until the end of column experiment, when a slight decrease was observed. A similar trend as for RC_{SI} was noticed also for $M_{Cr(VI)}$, as shown in Fig. 9. This behavior may be ascribed to a constant decrease of Cr(VI) concentration inside the filling as the water front passes from P₁ to P₃. Thus, at the entrance in the P₂-P₃ section, Cr(VI) concentration was lower than at the entrance in the P₁-P₂ section, and much lower than the initial hexavalent chromium concentration (25 mg/L), especially over the first time units of experiment. Thus, a much lower amount of Cr(VI) was reduced by the scrap iron existent in the P₂-P₃ section. However, the value of $TM_{Cr(VI)}$ continuously increased in time up to 1832 mg at the end of experiment, as presented in Fig. 10.

Fig. 10 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at P₃

IV. CONCLUSION

Hexavalent chromium has a significant mobility in the environment, being toxic to most living organisms. Thus, its reduction to Cr(III) can be beneficial because a more mobile and more toxic chromium species is converted to a less mobile and less toxic form. Scrap iron is a cheap industrial waste that may replace commonly used reducing agents. In this experiment, Cr(VI) concentrations were detected at P₁ and P₂ sampling ports from the first time unit onward; this could suggest that the mass of scrap iron existent in the first two sections of the filling was not enough for the total reduction of Cr(VI). This desideratum was however attained, but only after

the Cr(VI) front passes through the last section of the column filling, from P_2 to P_3 . The highest RC_{SI} value (5.1) was observed for the first section of the filling in the first time unit, but it continuously decreased thereafter up to about 0.6 at the end of experiment, due to constantly receiving concentrate (25 mg/L) Cr(VI) solution. A lower RC_{SI} value (about 4) was recorded at the very beginning of the experiment for the second section of the filling; afterwards, RC_{SI} continuously decreased, but less significantly than at first filling section, up to about 1.7 at the end of experiment. Instead, after an increase at the beginning of the experiment, a quasi-constant RC_{SI} value of 1.55 was observed thereafter for the last filling section. This behavior can be ascribed to a constant decrease of Cr(VI) concentration inside the filling as the water front passes from P_1 to P_3 . Scrap iron efficiency followed the order: $P_1 - P_2 > \text{Inlet} - P_1 > P_2 - P_3$, as shown in Table 3. This may suggest that most of the reduction process occurred inside the bottom half of the column filling. Moreover, the order of scrap iron efficiency also may indicate that the first section of the column filling was most affected by the passivation process. Instead, the last section was less affected by this process, and it could presumably assure the reduction of Cr(VI) for time periods longer than 216 hours. This work clearly indicates that Cr(VI) contaminated wastewaters can be successfully detoxified by reducing Cr(VI) to Cr(III) with scrap iron. However, the column should be packed with a adequate mass of scrap iron filling, in order to assure total reduction of Cr(VI) for a longer period of time.

ACKNOWLEDGMENT

The authors gratefully acknowledge the CNCISIS - UEFISCDI for financial support that made this research possible. This research was conducted under PN II IDEI Exploratory Research Project No. 647/19.01.2009 "Innovative technologies for the removal of hexavalent chromium from wastewaters by reuse of scrap iron", CNCISIS code 1031/2008.

TABLE II
SCRAP IRON EFFICIENCY (MG Cr(VI) / G SCRAP IRON)

Column filling section		
1: Inlet - P_1	2: $P_1 - P_2$	3: $P_2 - P_3$
16.5	25.1	11.7

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