

Decontamination of Cr(VI) Polluted Wastewater by use of Low Cost Industrial Wastes

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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 Cr(VI) concentration range of 5 – 40 mg/L. The results showed that the initial Cr(VI) concentration significantly affects the reduction capacity of scrap iron. Maximum reduction capacity of scrap iron was observed at the beginning of the column experiments; the lower the Cr(VI) concentration, the greater the experiment duration with maximum scrap iron reduction capacity. However, due to passivation of active surface, scrap iron reduction capacity continuously decreased in time, especially after Cr(VI) breakthrough. The experimental results showed that highest reduction capacity recorded until Cr(VI) breakthrough was 22.8 mg Cr(VI)/g scrap iron, at $C_1 = 5$ mg/L, and decreased with increasing Cr(VI) concentration. In order to assure total reduction of greater Cr(VI) concentrations for a longer period of time, either the mass of scrap iron filling, or the hydraulic retention time should be increased.

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

I. INTRODUCTION

THE presence of heavy metals in the environment has increased in last decades to levels which threaten the health of both aquatic and terrestrial organisms. Metals environmental contaminants are particularly problematic because, unlike most organic contaminants, they do not undergo degradation. Chromium is a major heavy metal pollutant of aquatic environments which is released mainly from industrial processes (leather tanning, electroplating, textile dyeing, metallurgy, wood preserving etc.) as a result of unsuitable storage, leakages or improper disposal practices [1]. In the environment, chromium is commonly found in two most stable oxidation states, Cr(III) and Cr(VI). The chemical behavior, toxicity and bioavailability of chromium for this two valences is quite different [1,2]. Hexavalent chromium compounds readily penetrate cell membranes via anion transport systems, and, therefore, they are known to be toxic to humans, animals, plants and microorganisms [3]-[8]. Besides the harmful effects to living organisms, Cr(VI) also

accumulate throughout the food chain and may affect human beings [2]. Because of its significant mobility in the subsurface environment, the potential risk of groundwater contamination is high [9]. Trivalent chromium, on the other hand, has a low solubility, being readily immobilized by precipitation under alkaline or even slightly acidic conditions [10]. Because trivalent chromium compounds does not resemble any biological nutrient, they do not have the capacity to cross cell membranes easily; therefore their toxicity is generally considered 500 to 1000 times less to a living cell than hexavalent chromium [3]. Moreover, Cr(III) is a necessary trace element of the human body, that plays an important role in carbohydrates, lipids, proteins and minerals metabolism [11]; however, excessive intake of Cr (III) may also have toxic effects [12]. Hence, it's obvious that Cr(VI) is chromium most dangerous oxidation state for the health of natural ecosystems and also for the human health. Thus, removal of Cr(VI) is an essential pollution abatement process that should be applied to all industrial effluents that contain this contaminant before their discharge to the natural water bodies. At present, there are known several methods for Cr(VI) removal from polluted waters: reduction followed by chemical precipitation, ion exchange, adsorption, membrane separation, electrokinetic remediation, reverse osmosis, bioremediation [13]. Because of the differences between Cr(VI) and Cr(III), the conventional procedure currently used to treat Cr(VI) contaminated waters consist in the reduction of Cr(VI) to Cr(III) followed by precipitation of Cr(III) [14], process that has also the advantage of simplicity. The reducing agents commonly used for Cr(VI) are: ferrous sulfate, sulfur dioxide, sodium sulfite, sodium bisulfite, sodium metabisulfite, sodium thiosulfate [13]. However, in last decades, there has been important interest in using low-cost materials [15]-[18] or even waste materials [19]-[21] that can substitute traditional Cr(VI) reducing agents. Therefore, as a continuation of our previous work [22], the aim of this study was to explore the possibility of reducing Cr(VI) to Cr(III) by use of scrap iron, a cheap and locally available industrial waste, and to investigate the effect of Cr(VI) concentration on scrap iron capacity to reduce Cr(VI) in continuous system

II. MATERIALS AND METHODS

Column experiments were carried out using scrap iron shavings that pass through 2.5 mm and remain on 1.25 mm screen, originated from "SPM" metals processing laboratory, at the "Politehnica" University of Timisoara. Hexavalent chromium stock solution (10 g/L) was prepared by dissolving

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28.29 g $K_2Cr_2O_7$ in 1000 mL of distilled deionised water; feed solutions of the desired initial Cr(VI) concentration (5, 10, 20, and 40 mg/L) were prepared by diluting the stock solution. These concentrations were selected because they are within the range of relevant concentrations for electroplating wastewaters [23]. Concentrated H_2SO_4 was used for adjusting pH of the feed solution at 2.5; this value was selected because it was found, in our previous work [24], to be the optimum pH for reduction of Cr(VI) with scrap iron in continuous system. All chemicals used were of AR grade. 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 and Cr(VI) aqueous solution was passed through the column, from the bottom to the top, by using a Ismatec IP08 peristaltic pump. To remove traces of chromium and iron, the column was soaked in HCl 35% and washed with distilled deionized water before each experiment. The scrap iron mass (30g), feed solution pH (2.5) and the pumping rate (0.3 L/hour) were held constant throughout the study. Column effluent samples were withdrawn at regular time intervals for Cr(VI) concentration analysis. 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 [25]. 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 pH of solutions was measured using an Inolab pH-meter.

III. RESULTS AND DISCUSSION

In this study, the total duration of the column experiment was divided in 24 hours time units; the mass of reduced Cr(VI) ($M_{Cr(VI)}$) and the reduction capacity of scrap iron (RC_{SI}) were calculated, for each time unit, as follows:

$$M_{Cr(VI)} = (C_I - C_E) \cdot 0.3 \cdot 24 \text{ (mg)} \quad (1)$$

$$RC_{SI} = \frac{M_{Cr(VI)}}{M_{SI}} \text{ (mg Cr(VI)/g scrap iron)} \quad (2)$$

where: C_I (mg/L) is the inlet Cr(VI) concentration, C_E (mg/L) is the average Cr(VI) concentration in column effluent during the 24 hour time unit, 0.3 (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 filling (30 g).

The total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) during the column experiment was calculated according to:

$$TM_{Cr(VI)} = \sum_{i=1}^n M_{Cr(VI)}^i \text{ (mg)} \quad (3)$$

where n is the number of time units of the column experiment.

From Eq. (1) it can be seen that, during a 24 hour time unit, the theoretical maximum value of $M_{Cr(VI)}$ (which can be achieved only if $C_E = 0$ mg/L and the volumetric inflow rate and the inlet Cr(VI) concentration are maintained constant) depends on the inlet Cr(VI) concentration, as presented in Table 1.

TABLE I
 THEORETICAL MAXIMUM $M_{Cr(VI)}$ AND RC_{SI} VALUES

C_I	$M_{Cr(VI)}$	RC_{SI}
5	36	1.2
10	72	2.4
20	144	4.8
40	288	9.6

Similarly, from Eq. (2) it can be observed that, during a 24 hour time unit, the theoretical maximum value of RC_{SI} can be achieved only if $M_{Cr(VI)}$ has reached to its maximum value, and the mass of scrap iron filling is maintained constant at the above mentioned value, as shown in Table 1.

Experiments carried out at $C_I = 5$ mg/L have shown that Cr(VI) was not detected in column effluent during the first 19 time units, as can be seen from Fig. 1. Therefore, the theoretical maximum RC_{SI} value (1.2 mg Cr(VI)/g scrap iron) and the theoretical maximum $M_{Cr(VI)}$ value (36 mg) were achieved during the first 456 hours of the experiment, when Cr(VI) was totally reduced. Hexavalent chromium breakthrough in column effluent occurred during the 20th time unit, as a result of scrap iron surface passivation. Despite the low pH, the passivation process could take place due to formation of iron and chromium solid species on the scrap iron surface, as reported by several previous studies conducted under strong acidic conditions (pH = 1.5-3.6) [26]-[30]. The passivating layer may act as electric insulator, occluding the iron surface and inhibiting thus the electron transfer to Cr(VI). After Cr(VI) breakthrough, RC_{SI} and $M_{Cr(VI)}$ continuously decreased in time during the column experiment, more significant at the beginning and less noticeable at the end of the column experiment, as presented in Figs. 1 and 2. Beside decreasing the RC_{SI} and $M_{Cr(VI)}$, the passivation of scrap iron surface also leads to a continuously increase of average Cr(VI) concentration in column effluent, as presented in Fig. 1. However, the value of $TM_{Cr(VI)}$ continuously increased in time up to 1076 mg at the end of experiment, as presented in Fig.3. Nevertheless, an important factor that must be considered in the development of a long-term column Cr(VI) reduction process, is the value of $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough. At $C_I = 5$ mg/L, the $TM_{Cr(VI)}$ recorded up to the 19th time unit, when Cr(VI) was not detected in column effluent, was 666 mg. The column experiment at $C_I = 5$ mg/L was considered completed after 34 time units, when RC_{SI} and $M_{Cr(VI)}$ reached to a steady-state value of approximately 0.74 mg Cr(VI)/g scrap iron and 22 mg, respectively (Figs. 1 and 2). The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 22.8 mg Cr(VI)/g scrap iron.

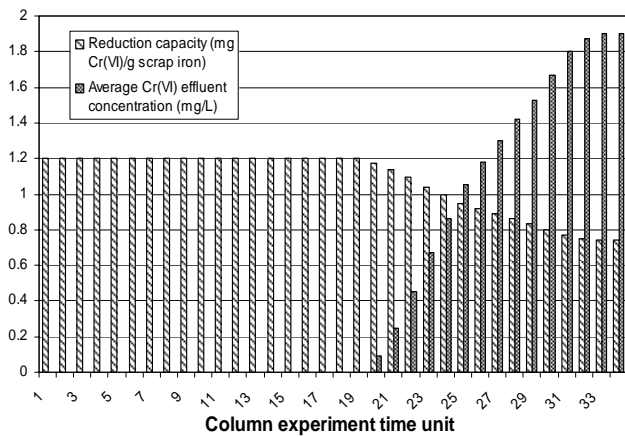


Fig. 1 Scrap iron reduction capacity (RC_{Si}) and average Cr(VI) effluent concentration vs. time, at Cr(VI) inlet concentration = 5 mg/L

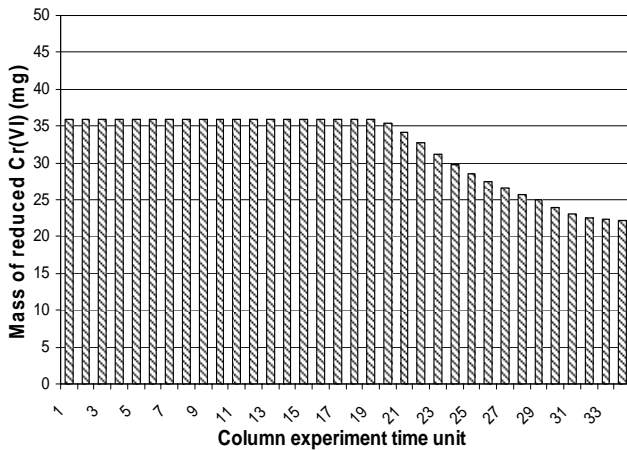


Fig. 2 Mass of reduced Cr(VI) ($M_{Cr(VI)}$) vs. time, at Cr(VI) inlet concentration = 5 mg/L

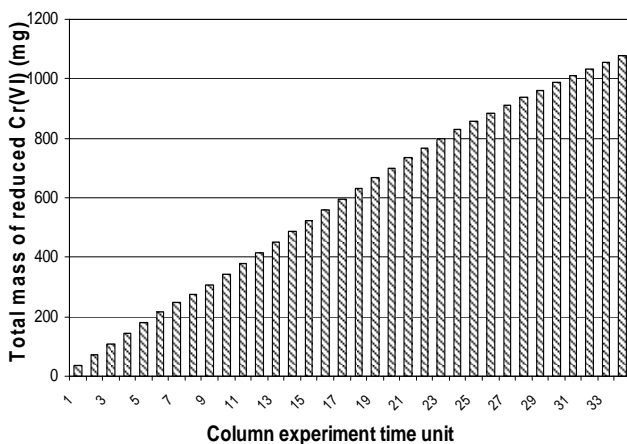


Fig. 3 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at Cr(VI) inlet concentration = 5 mg/L

At $C_i = 10$ mg/L, the column effluent was free of Cr(VI) during the first eight time units of the experiment, as shown in Fig. 4. Therefore, the maximum RC_{Si} value (2.4 mg Cr(VI)/g scrap iron) and maximum $M_{Cr(VI)}$ value (72 mg) were recorded during the first 192 hours of the column experiment, as presented in Figs. 4 and 5. Thereafter, Cr(VI) breakthrough in column effluent occurred as a result of scrap iron surface passivation; this process led to a continuously decrease in time of RC_{Si} and of $M_{Cr(VI)}$ until the end of experiment. The value of $TM_{Cr(VI)}$ continuously increased in time up to 1131 mg at the end of experiment, as presented in Fig. 6. Anyway, the $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough was 576 mg, less than at $C_i = 5$ mg/L. The column experiment at $C_i = 10$ mg/L was considered completed after nineteen time units, when the RC_{Si} and the $M_{Cr(VI)}$ reached to a steady-state value of approximately 1.3 mg Cr(VI)/g scrap iron and 39 mg, respectively (Figs. 4 and 5). The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 19.2 mg Cr(VI)/g scrap iron.

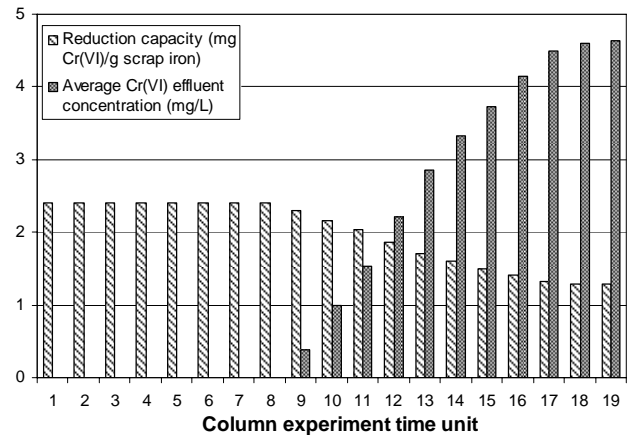


Fig. 4 Scrap iron reduction capacity (RC_{Si}) and average Cr(VI) effluent concentration vs. time, at Cr(VI) inlet concentration = 10 mg/L

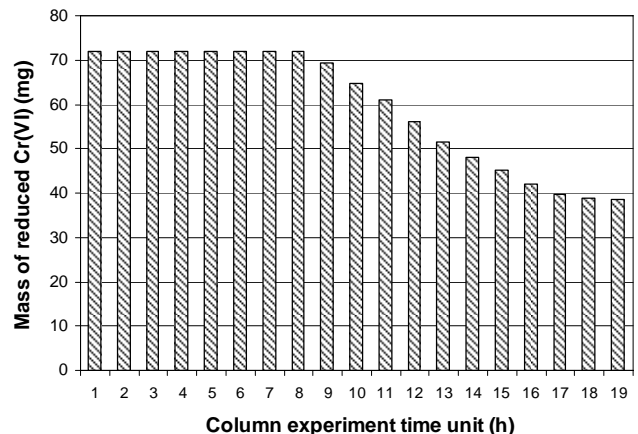


Fig. 5 Mass of reduced Cr(VI) ($M_{Cr(VI)}$) vs. time, at Cr(VI) inlet concentration = 10 mg/L

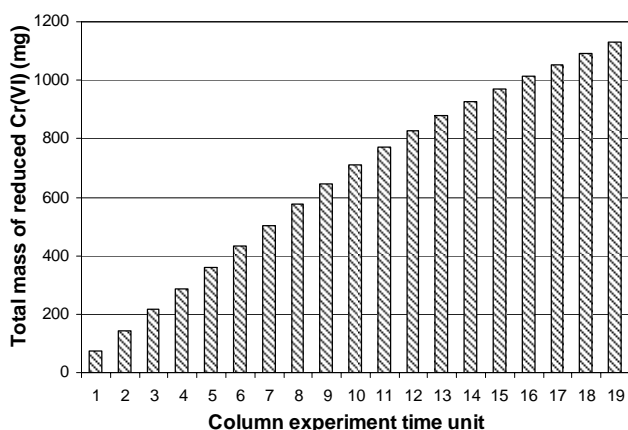


Fig. 6 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at Cr(VI) inlet concentration = 10 mg/L

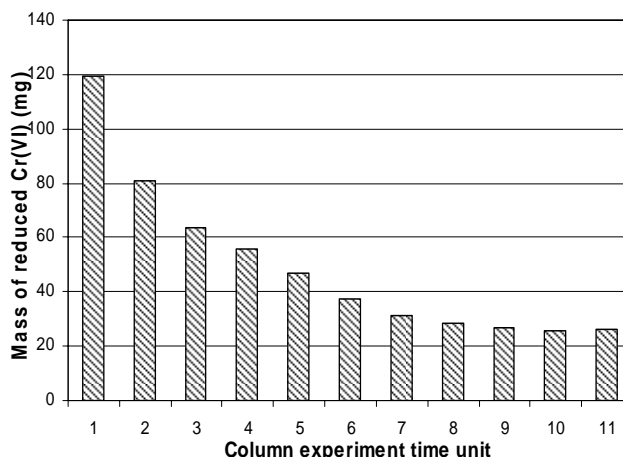


Fig. 8 Mass of reduced Cr(VI) ($M_{Cr(VI)}$) vs. time, at Cr(VI) inlet concentration = 20 mg/L

The experimental results obtained at $C_1 = 20$ mg/L show that Cr(VI) was completely reduced only during the first nine hours of the column experiment (data not shown). As a result, at $C_1 = 20$ mg/L, the theoretical maximum values of RC_{SI} (4.8 mg Cr(VI)/g scrap iron) and $M_{Cr(VI)}$ (144 mg) were not recorded (Figs. 7 and 8), even if at the beginning of the column experiment the scrap iron was still unaffected by passivation. Actually, the highest values observed during the first time unit for RC_{SI} (3.9 mg Cr(VI)/g scrap iron) and $M_{Cr(VI)}$ (119 mg) represented only 81.2 and 82.6 %, respectively, from the theoretical maximum values. As a result, Cr(VI) was detected in the column effluent starting from the first time unit, and its concentration continuously increased in time due to scrap iron surface passivation, as presented in Fig.7. RC_{SI} and $M_{Cr(VI)}$ also continuously decreased in time, more significant at the beginning and almost negligible at the end of the column experiment. Despite scrap iron passivation and $M_{Cr(VI)}$ decrease, the value of $TM_{Cr(VI)}$ continuously increased in time up to 568 mg at the end of experiment, as presented in Fig.9. However, the $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough was only 54 mg, then time lower than at $C_1 = 10$ mg/L.

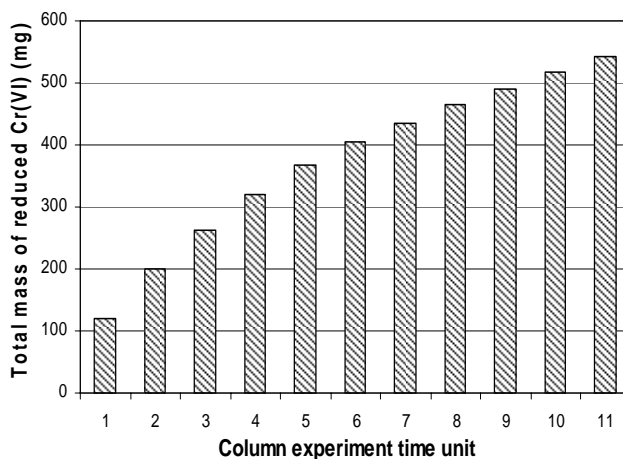


Fig. 9 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at f Cr(VI) inlet concentration = 20 mg/L

The column experiment at $C_1 = 20$ mg/L was considered completed after eleven time units, when RC_{SI} and $M_{Cr(VI)}$ reached to a steady-state value of approximately 0.86 mg Cr(VI)/g scrap iron and 26 mg, respectively (Figs. 7 and 8). The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 1.8 mg Cr(VI)/g scrap iron.

At $C_1 = 40$ mg/L, just like at $C_1 = 20$ mg/L, the theoretical maximum values of RC_{SI} (9.6 mg Cr(VI)/g scrap iron) and $M_{Cr(VI)}$ (288 mg) were not recorded (Figs. 10 and 11), even during the first time unit. In this case, the Cr(VI) reduction efficiency was lower than at $C_1 = 20$ mg/L, total reduction being observed only during first three hours of the column experiment (data not shown). As a result, the highest values observed during the first time unit for RC_{SI} (7.4 mg Cr(VI)/g scrap iron) and $M_{Cr(VI)}$ (223 mg) represented only 70.1 and 77.4 %, respectively, from the theoretical maximum values. Cr(VI) breakthrough occurred thus at $C_1 = 40$ mg/L starting from the first time unit, and its concentration continuously increased in time (due to scrap iron surface passivation), as presented in Fig.10. RC_{SI} and $M_{Cr(VI)}$ also continuously decreased in time, more significant at the beginning and almost negligible at the end of the column experiment. The value of $TM_{Cr(VI)}$

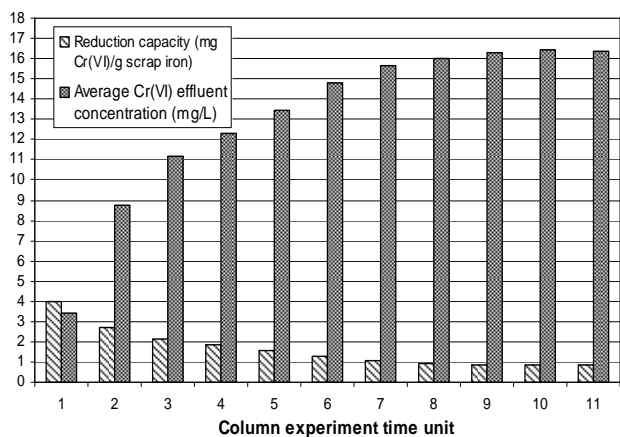


Fig. 7 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, Cr(VI) inlet concentration = 20 mg/L

continuously increased in time up to 694 mg at the end of experiment, as presented in Fig.12. However, the $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough was only 36 mg, less than at than at $C_1 = 20$ mg/L.

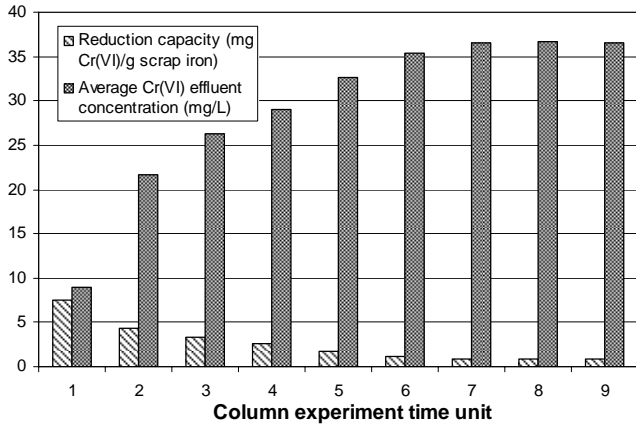


Fig. 10 Scrap iron reduction capacity (RC_{Si}) and average Cr(VI) effluent concentration vs. time, at Cr(VI) inlet concentration = 40 mg/L

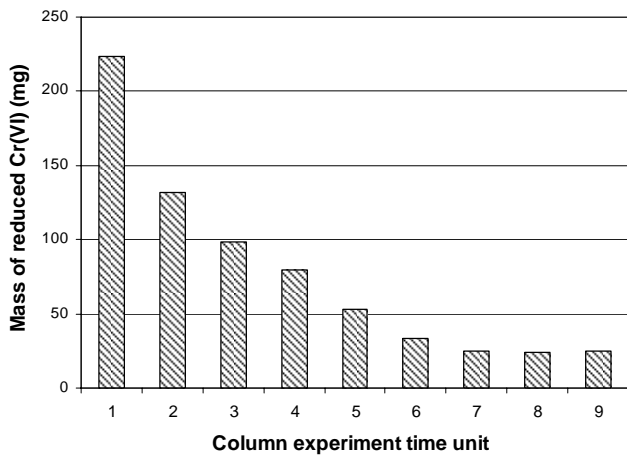


Fig. 11 Mass of reduced Cr(VI) ($M_{Cr(VI)}$) vs. time, at Cr(VI) inlet concentration = 40 mg/L

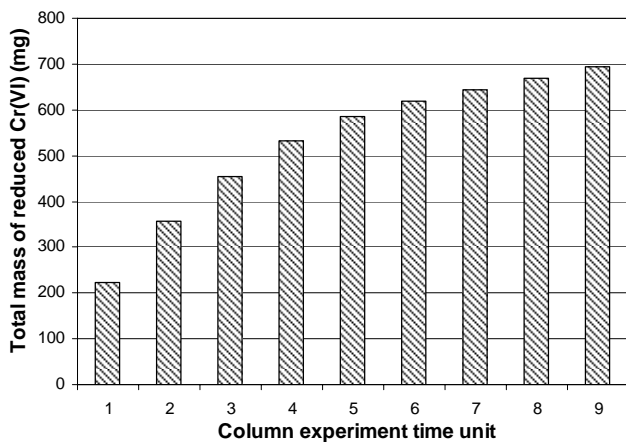


Fig. 12 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at Cr(VI) inlet concentration = 40 mg/L

The column experiment at $C_1 = 40$ mg/L was considered completed after nine time units, when RC_{Si} and $M_{Cr(VI)}$ reached to a steady-state value of approximately 0.82 mg Cr(VI)/g scrap iron and 24 mg, respectively (Figs. 10 and 11). The scrap iron reduction capacity, calculated up to the moment of Cr(VI) breakthrough, was 1.2 mg Cr(VI)/g scrap iron.

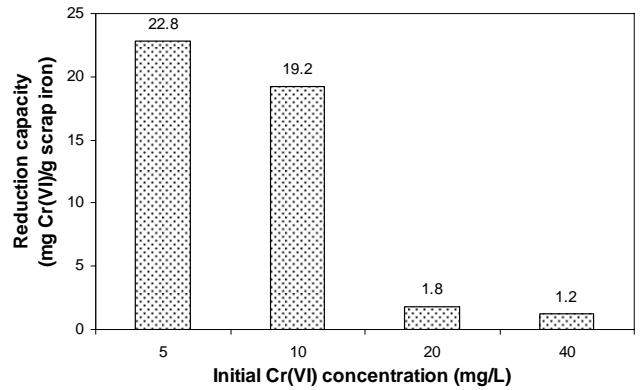


Fig. 13 Scrap iron reduction capacity recorded until Cr(VI) breakthrough, at different initial feed solution concentrations

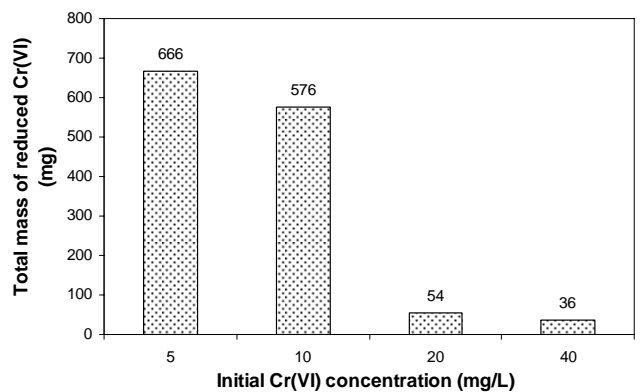


Fig. 14 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) recorded until Cr(VI) breakthrough, at different initial feed solution concentrations

IV. CONCLUSION

Hexavalent chromium is highly toxic to most living organisms and a known human carcinogen by the inhalation route of exposure. Therefore, treatment of Cr(VI) contaminated wastewater is essential before their discharge to the natural water bodies. Cr(VI) 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. This work indicate that reduction capacity of scrap iron is directly dependent on the initial Cr(VI) concentration. Over the concentration range of 5 – 40 mg/L, the theoretical maximum RC_{Si} increased with increasing Cr(VI) concentration (Table 1). However, the theoretical maximum RC_{Si} and $M_{Cr(VI)}$ were recorded only for initial Cr(VI) concentrations of 5 and 10 mg/L, which may suggest that the mass of the scrap iron filling used in this study was not enough for the treatment of

solutions with Cr(VI) concentration greater than 10 mg/L. The total scrap iron reduction capacity and $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough followed the order: 5 mg/L > 10 mg/L > 20 mg/L > 40 mg/L (Figs. 13 and 14). Since better reduction capacities were observed under low Cr(VI) concentration conditions, this wastewater treatment process may be readily used especially in the treatment of diluted wastewaters. However, with increasing Cr(VI) concentration, either the mass of scrap iron used as column filling, or the hydraulic retention time should be increased, in order to assure total reduction of Cr(VI) for a longer period of time.

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