

Removal of Hexavalent Chromium from Wastewater by Use of Scrap Iron

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Abstract—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. Zero-valence-state metals, such as scrap iron, can serve as electron donors for reducing Cr(VI) to Cr(III). The influence of pH on scrap iron capacity to reduce Cr(VI) was investigated in this study. Maximum reduction capacity of scrap iron was observed at the beginning of the column experiments; the lower the pH, the greater the experiment duration with maximum scrap iron reduction capacity. The experimental results showed that highest maximum reduction capacity of scrap iron was 12.5 mg Cr(VI)/g scrap iron, at pH 2.0, and decreased with increasing pH up to 1.9 mg Cr(VI)/g scrap iron at pH = 7.3.

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

I. INTRODUCTION

THE presence of heavy metals in wastewaters has become a serious environmental problem in the last decades.

Metals environmental contaminants are particularly problematic because, unlike most organic contaminants, they do not undergo degradation. However, redox reactive metals often do different degrees of toxicity, depending on the specific metal oxidation state [1]. Chromium is a metal used in various industrial processes (e.g. textile dyeing, tanneries, metallurgy, metal electroplating, and wood preserving); therefore, large quantities of chromium have been discharged into the environment, especially in the past [1]. In the environment, chromium is commonly found in two most stable oxidation states, Cr(III) and Cr(VI), each characterized by different bioavailability, toxicity and chemical behavior [2]. Hexavalent chromium is known to be toxic to humans, animals, plants and microorganisms [3]-[8]. Because of its significant mobility in the subsurface environment, the potential risk of groundwater contamination is high [9]. Trivalent chromium, on the other hand, is less toxic and readily precipitates under alkaline or even slightly acidic conditions [10]. Cr(III) may also have toxic effects [11]-[13],

but its concentration is usually very low due to the low solubility of chromium hydroxide in the pH range of natural waters [10]. Besides the harmful effects to organisms living in water, Cr(VI) also accumulate throughout the food chain and may affect human beings [2]. Hence, Cr(VI) contamination of natural water is considered a major environmental concern. Several methods are available for the decontamination of waters polluted with Cr(VI); these include: reduction followed by chemical precipitation, ion exchange, adsorption, membrane separation, electrokinetic remediation, reverse osmosis, bioremediation [14]. The traditional procedure currently used to remove Cr(VI) is its chemical reduction to Cr(III) followed by precipitation [15]. Commonly used reducing agents are: ferrous sulfate, sulfur dioxide, sodium sulfite, sodium bisulfite sodium metabisulfite, sodium thiosulfate [14]. In last decades, attention has been focused on using zerovalent iron for the in situ reduction of Cr(VI) from contaminated groundwater [16]-[18], but also on the use of low-cost waste materials that can substitute traditional Cr(VI) reducing agents [19]-[24]. Therefore, 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 pH on scrap iron capacity to reduce Cr(VI) in continuous system.

II. MATERIALS AND METHODS

Scrap iron shavings that pass through 2.5 mm and remain on 1.25 mm screen were used as Cr(VI) reducing agent. Hexavalent chromium stock solution (10 g/L) was prepared by dissolving 28.29 g $K_2Cr_2O_7$ in 1000 ml of distilled deionised water; feed solutions of the desired initial Cr(VI) concentration (10 mg/L) were prepared by diluting the stock solution. Concentrated H_2SO_4 was used for adjusting pH of the feed solution. The pH of solutions was measured using an Inolab pH-meter. All chemicals used were of AR grade. The experimental apparatus for the continuous Cr(VI) reduction consisted in: 1) glass column filled with scrap iron, 2) peristaltic pump, and 3) Cr(VI) solution storage tank. The glass column (inner diameter: 2.0 cm; height: 12.0 cm) was packed with scrap iron up to a 6.0 cm height. The effect of feed solution pH on scrap iron reduction capacity was studied in continuous system over the pH range of 2.0 – 7.3. The Cr(VI) feed solution was passed through the column, from the bottom to the top, by using a Ismatec IP08 peristaltic pump. The initial Cr(VI) concentration (10 mg/L), the initial scrap iron mass (30 g) and the pumping rate (0.3 L/hour) were held constant throughout the study. All experiments were performed at room temperature (24°C) in a background

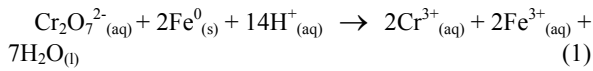
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electrolyte mixture (50 ppm Ca^{2+} ; 20 ppm Mg^{2+} ; 128 ppm Cl^- ; 104 ppm Na^+ ; 293 ppm HCO_3^-) to maintain a constant ionic strength. Before each experiment the column was soaked in HCl 35% and washed with distilled deionised water up to neutral pH to remove traces of chromium and iron. Column effluent samples were withdrawn at regular time intervals for Cr(VI) concentration analysis. Hexavalent chromium was detected by the 1,5-diphenylcarbazide colorimetric method; the absorbance of the purple color was measured at 540 nm in a 1 cm long glass cell using a Jasco V 530 spectrophotometer [25].

III. RESULTS AND DISCUSSION

When metallic iron is immersed in an aqueous solution, electrochemical corrosion will occur; electrons are given up by iron and taken up by Cr(VI) oxidized oxospecies that become reduced according to [26]:



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

$$M_{\text{Cr(VI)}} = (10 - C_E) \cdot 0.3 \cdot 24 \text{ (mg)} \quad (2)$$

$$\text{RC}_{\text{SI}} = \frac{M_{\text{Cr(VI)}}}{M_{\text{SI}}} \text{ (mg Cr(VI)/g scrap iron)} \quad (3)$$

where: 10 (mg/L) is the inlet Cr(VI) concentration, C_E (mg/L) is the average Cr(VI) concentration in column effluent in 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) ($\text{TM}_{\text{Cr(VI)}}$) during the column experiment was calculated according to:

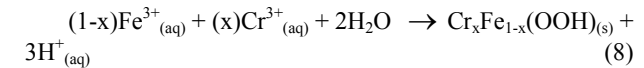
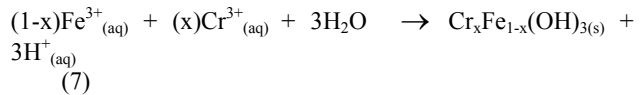
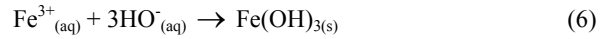
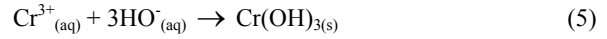
$$\text{TM}_{\text{Cr(VI)}} = \sum_{i=1}^n M_{\text{Cr(VI)}}^i \text{ (mg)} \quad (4)$$

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

From Eq. (2) it can be seen that, during a 24 hour time unit, the maximum possible value of $M_{\text{Cr(VI)}}$ is 72.0 mg, 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 at the above mentioned values. From Eq. (3) it can be seen that, during a 24 hour time unit, the maximum possible value of RC_{SI} is 2.4 mg Cr(VI)/g scrap iron, which can be achieved only if $M_{\text{Cr(VI)}} = 72.0$ mg and the mass of scrap iron filling is maintained constant at the above mentioned value.

At pH = 7.3, the highest value of RC_{SI} (1.9 mg Cr(VI)/g scrap iron) was observed during the first time unit of the

column experiment, as can be seen from Fig. 1, and continuously decreased thereafter until the end of the experiment. The decrease of RC_{SI} was due to scrap iron surface passivation, determined by the precipitation of simple or mixed Fe(III)-Cr(III) precipitates onto scrap iron surface, according to [16], [17], [27]:



where x vary from 0 to 1.

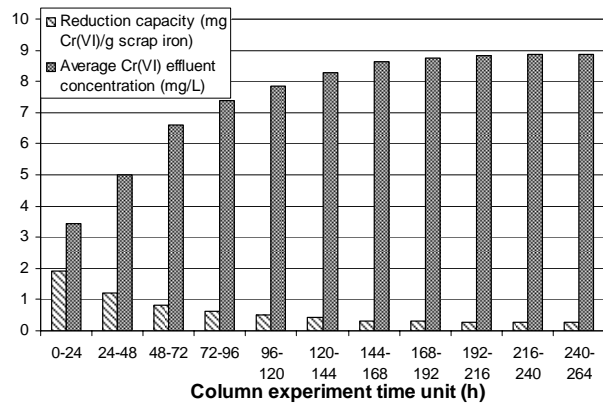


Fig. 1 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at feed solution pH = 7.3

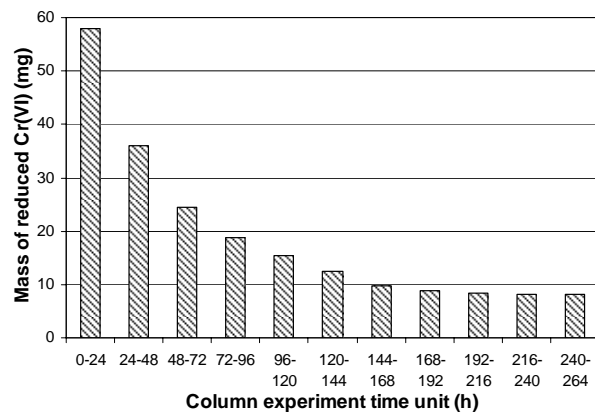


Fig. 2 Mass of reduced Cr(VI) ($M_{\text{Cr(VI)}}$) vs. time, at feed solution pH = 7.3

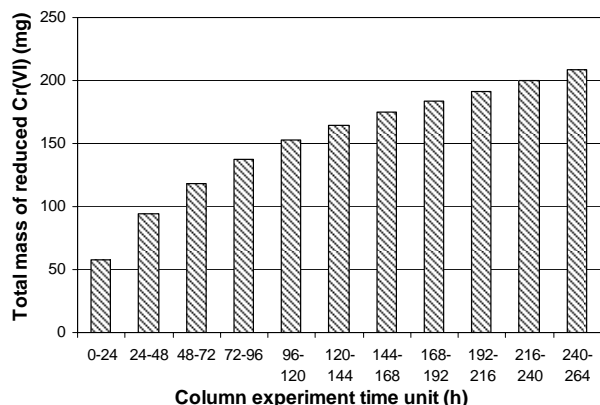


Fig. 3 Total mass of reduced Cr(VI) (TM_{Cr(VI)}) vs. time, at feed solution pH = 7.3

The scrap iron surface passivation 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}, 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. Since Cr(VI) was present in the column effluent from the first time unit, this means that Cr(VI) breakthrough in column effluent occurred during the first 24 hours of the experiment. As a result of the continuously RC_{SI} decrease, the M_{Cr(VI)} also had the highest value (57.9 mg) during the first time unit of the column experiment, and continuously decreased afterwards during the experiment, as presented in Fig. 2. The decrease of M_{Cr(VI)} was 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 208.2 mg at the end of experiment, as presented in Fig. 3. The column experiment at pH = 7.3 was considered completed after nine time units, when RC_{SI} and M_{Cr(VI)} reached to a steady-state value of approximately 0.3 mg Cr(VI)/g scrap iron and 8.2 mg, respectively (Figs. 1 and 2).

At pH = 5.1, the highest value of the RC_{SI} (2.2 mg Cr(VI)/g scrap iron) was observed, just like at pH = 7.3, at the beginning of the column experiment, during the first time unit, as can be observed from Fig. 4; subsequently, RC_{SI} continuously decreased in time until the end of experiment. However, it was noticed that the initial value of the RC_{SI} at pH = 5.1 was greater than the initial RC_{SI} value observed at pH = 7.3. The M_{Cr(VI)} also continuously decreased in time during the column experiment, from an initial value of 66.9 mg, as presented in Fig. 5; however, just like at pH = 7.3, the decrease was more significant at the beginning and almost negligible at the end of the column experiment. The highest values of RC_{SI} and of M_{Cr(VI)}, observed at pH = 5.1 in comparison with pH = 7.3, could be explained by a lower intensity of the scrap iron surface passivation process at pH = 5.1. Just like at pH = 7.3, the value of TM_{Cr(VI)} continuously increased in time up to 312.3 mg at the end of experiment, as presented in Fig. 6. As can be seen from Figs. 3 and 6, the TM_{Cr(VI)} was greater at pH = 5.1 than at pH = 7.3. The hexavalent chromium reduction column experiment at

pH = 5.1 was considered completed after nine time units, when RC_{SI} and M_{Cr(VI)} reached to a steady-state value of approximately 0.4 mg Cr(VI)/g scrap iron and 13.0 mg, respectively (Figs. 4 and 5).

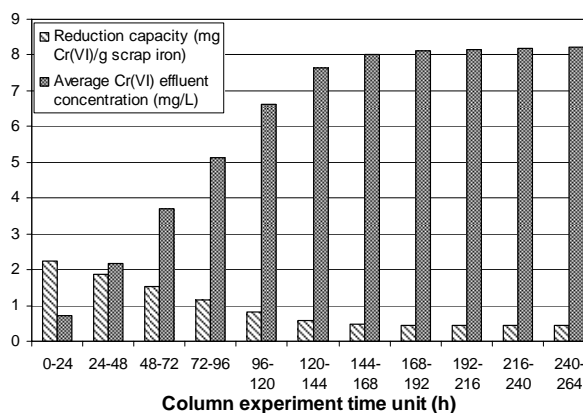


Fig. 4 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at feed solution pH = 5.1

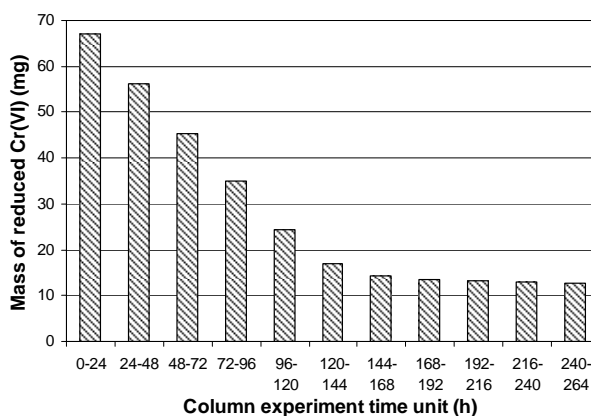


Fig. 5 Mass of reduced Cr(VI) (M_{Cr(VI)}) vs. time, at feed solution pH = 5.1

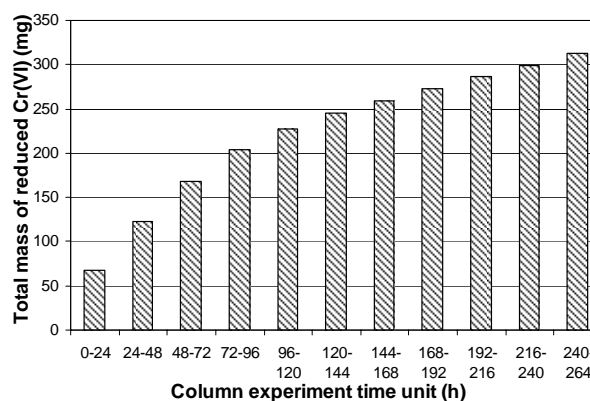


Fig. 6 Total mass of reduced Cr(VI) (TM_{Cr(VI)}) vs. time, at feed solution pH = 5.1

In experiments performed at $\text{pH} = 3.3$ Cr(VI) was not detected in the column effluent during the first time unit of the experiment (Fig. 7). Hence, for the first time in this study, Cr(VI) was totally reduced during the first 24 hours of the experiment. As a result, the maximum RC_{SI} value (2.4 mg $\text{Cr(VI)}/\text{g}$ scrap iron) and the maximum $M_{\text{Cr(VI)}}$ value (72.0 mg) were achieved during the first time unit of the experiment. Thereafter, as a result of scrap iron surface passivation, Cr(VI) breakthrough in column effluent occurred and RC_{SI} and $M_{\text{Cr(VI)}}$ continuously decreased in time during the column experiment, more significant at the beginning and less important at the end of the column experiment (Figs. 7 and 8). The value of $\text{TM}_{\text{Cr(VI)}}$ continuously increased in time up to 544.1 mg at the end of experiment, as presented in Fig.9. At $\text{pH} = 3.3$, the $\text{TM}_{\text{Cr(VI)}}$ was greater than at $\text{pH} = 5.1$ or at $\text{pH} = 7.3$, as can be seen from Figs. 3, 6 and 9. However, an important factor that must be considered in the development of a long-term column Cr(VI) reduction process is the value of $\text{TM}_{\text{Cr(VI)}}$ recorded until the moment of Cr(VI) breakthrough. At $\text{pH} = 3.3$ Cr(VI) breakthrough was for the first time in this study clearly identified as starting from the 2nd time unit of the experiment; therefore, the $\text{TM}_{\text{Cr(VI)}}$ recorded during the 1st time unit, when Cr(VI) was not detected in column effluent, was 72 mg.

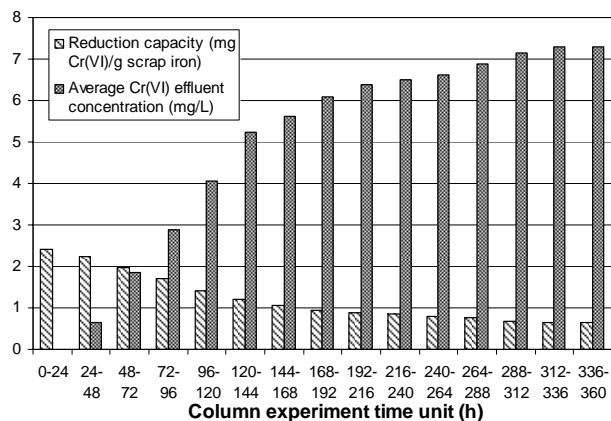


Fig. 7 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at feed solution $\text{pH} = 3.3$

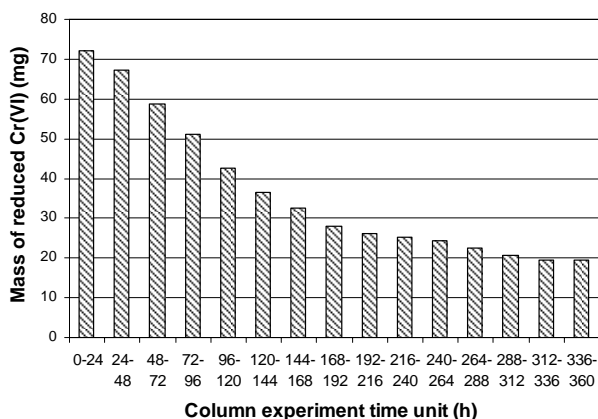


Fig. 8 Mass of reduced Cr(VI) ($M_{\text{Cr(VI)}}$) vs. time, at feed solution $\text{pH} = 3.3$

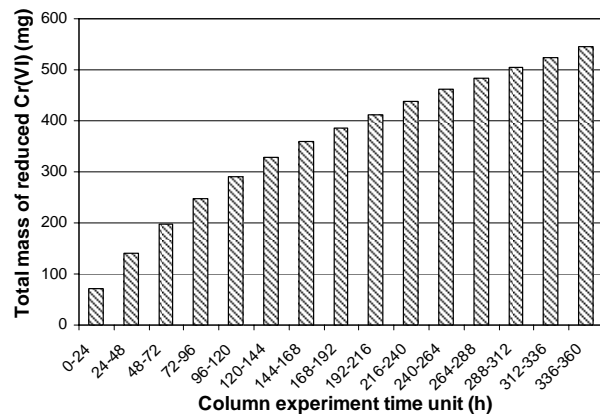


Fig. 9 Total mass of reduced Cr(VI) ($\text{TM}_{\text{Cr(VI)}}$) vs. time, at feed solution $\text{pH} = 3.3$

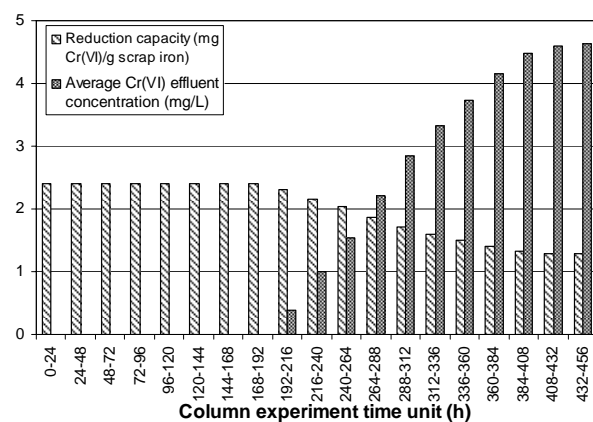


Fig. 10 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at feed solution $\text{pH} = 2.5$

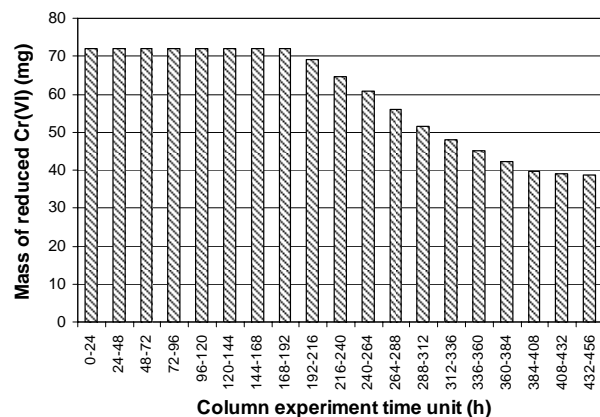


Fig. 11 Mass of reduced Cr(VI) ($M_{\text{Cr(VI)}}$) vs. time, at feed solution $\text{pH} = 2.5$

The column experiment at $\text{pH} = 3.3$ was considered completed after thirteen time units, when RC_{SI} and $M_{\text{Cr(VI)}}$ reached to a steady-state value of approximately 0.6 mg $\text{Cr(VI)}/\text{g}$ scrap iron and 19.5 mg, respectively (Figs. 7 and 8).

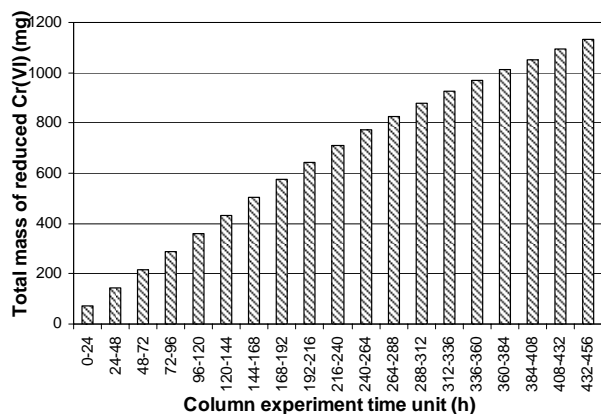


Fig. 12 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at feed solution pH = 2.5

At pH = 2.5 the column effluent was free of Cr(VI) over the first eight time units of the experiment, as seen in Fig. 10. Therefore, the maximum RC_{SI} value (2.4 mg Cr(VI)/g scrap iron) and maximum $M_{Cr(VI)}$ value (72.0 mg) were recorded during the first 192 hours of the column experiment, as presented in Figs. 10 and 11. 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. 12. Anyway, at pH = 2.5, the $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough (576 mg) was much greater than at pH = 3.3 (72 mg), as can be seen from Figs. 9 and 12. The column experiment at pH = 2.5 was considered completed after seventeen 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 38.6 mg, respectively (Figs. 10 and 11).

Experiments conducted at pH = 2.0 revealed that Cr(VI) was completely reduced over the first six time units of the experiment, as presented in Fig. 13. Hence, the maximum $M_{Cr(VI)}$ value (72.0 mg) was recorded during the first six time units of the column experiment, as can be seen from Fig. 14.

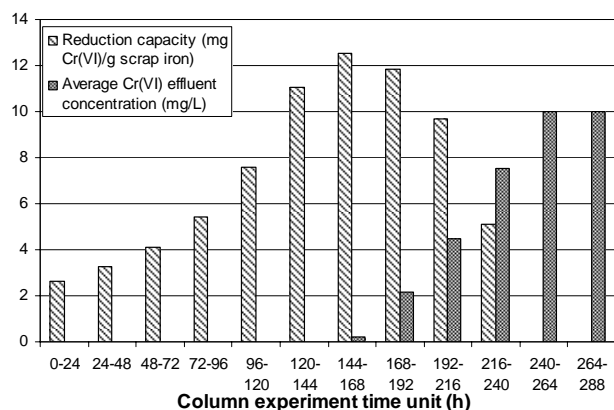


Fig. 13 Scrap iron reduction capacity (RC_{SI}) and average Cr(VI) effluent concentration vs. time, at feed solution pH = 2.0

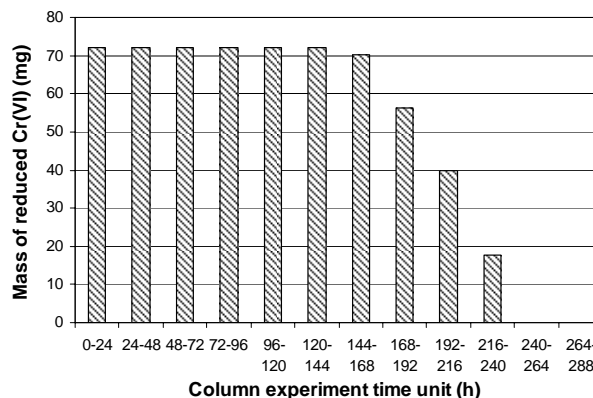


Fig. 14 Mass of reduced Cr(VI) ($M_{Cr(VI)}$) vs. time, at feed solution pH = 2.0

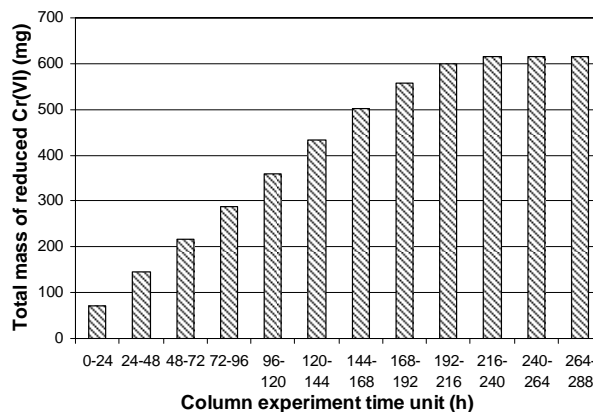


Fig. 15 Total mass of reduced Cr(VI) ($TM_{Cr(VI)}$) vs. time, at feed solution pH = 2.0

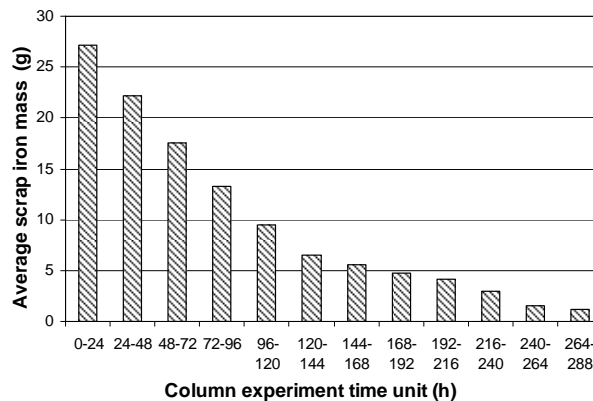


Fig. 16 Average scrap iron filling mass vs. time, at feed solution pH = 2.0

Normally, during the same six time units when $M_{Cr(VI)}$ was maximum and constant, the value of RC_{SI} should also be maximum and constant: 2.4 mg Cr(VI)/g scrap iron. But, two phenomena were observed inside the column during the experiment conducted at pH = 2.0: the occurrence of a gas (H_2) at iron-solution interface, and the decrease in time of the scrap iron filling mass (Fig. 16). This indicates that at pH ≤ 2

reduction of H^+ appears to be the dominant reaction contributing to scrap iron corrosion, according to [26]:



Therefore, at pH = 2.0, the value of RC_{SI} was calculated according to Eq. (3), but, instead of using a constant value (30 g) for the scrap iron filling mass, various filling mass values have been used, according to Fig. 16. As a result, during the first 168 hours, Cr(VI) reduction was accompanied by an increase of the RC_{SI} up to 12.5 mg Cr(VI)/g scrap iron, as shown in Fig. 13. Afterwards, RC_{SI} continuously decreased in time until, after 240 hours, it becomes zero. The $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough at pH = 2.0 (432 mg) was lower than at pH = 2.5 (576 mg), but greater than at pH = 3.3 (72 mg), as can be seen from Figs. 9, 12 and 15. No steady-state values of RC_{SI} and $M_{Cr(VI)}$ were observed at pH 2.0. The column experiment at pH = 2.0 was considered completed after eleven time units, when the concentration of Cr(VI) in column effluent equals the concentration in column influent (Fig. 13).

IV. CONCLUSION

This work indicates that reduction capacity of scrap iron is directly dependent on the pH of Cr(VI) solution. Over the pH range of 2.0 - 7.3 the RC_{SI} increased with decreasing the initial pH of Cr(VI) solution. The highest RC_{SI} was 12.5 mg Cr(VI)/g scrap iron, at pH 2.0, almost seven times greater than at pH 7.3. Despite this fact, the $TM_{Cr(VI)}$ recorded until the moment of Cr(VI) breakthrough followed the order: pH = 2.5 > pH = 2.0 > pH = 3.3. The maximum $TM_{Cr(VI)}$ was achieved at pH = 2.5 and not at pH = 2.0 due to the increased contribution of H^+ ions to the corrosion of scrap iron at pH = 2.0, which led to a considerable decrease in time of the scrap iron mass. Since better reduction capacities were observed under strong acidic conditions, reduction of Cr(VI) by scrap iron may be readily used especially in the treatment of wastewaters with low pH. However, the wastewater pH should not be extremely acidic either, in order to avoid the rapid scrap iron corrosion by H^+ ions.

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