Hexavalent chromium reduction with scrap iron. The effect of Cr(VI) initial concentration

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Abstract: - The reduction of hexavalent chromium by scrap iron was investigated in continuous system, using long-term column experiments, over the Cr(VI) concentration range of 5 – 40 mg/L. The results showed that initial Cr(VI) concentration significantly affects the scrap iron reduction efficiency. The greater the Cr(VI) concentration, the lower the time period when Cr(VI) was totally reduced. The mechanism of Cr(VI) reduction also seems to be directly dependent on the Cr(VI) concentration. While at low Cr(VI) concentrations heterogeneous reduction was the dominant Cr(VI) reduction process, at high Cr(VI) concentrations homogeneous reduction appears to be the main reaction contributing to Cr(VI) reduction. In conclusion, Cr(VI) concentration is an important factor that must be considered in the development of a long-term column Cr(VI) reduction process.

Key-Words: - hexavalent chromium; heavy metals; reduction; scrap iron; wastewater treatment.

1 Introduction
Metals are problematic environmental contaminants because, unlike most organic contaminants, they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain [1]. While some of these metals are necessary in small amounts for the normal development of the biological life [2], most of them become toxic at high concentrations [3]. Chromium is an important metal used in a variety of industrial applications, such as wood preserving, preparation of chromate compounds, textile dying, tanneries, iron and steel production, electroplating etc. [4]. The most stable oxidation states of chromium in natural environments are the +III and +VI, and each of them has very different biological and toxicological properties [5]. Under environmentally relevant pH values, Cr(VI) exists mainly as relatively soluble and mobile HCrO$_4$/$Cr_2$O$_7^{2-}$ or CrO$_4^{2-}$ oxyanions [6]. On the contrary, Cr(III) has a lower solubility and mobility in water because readily precipitates as Cr(OH)$_3$ [7] or as mixed Fe(III)-Cr(III) (oxy)hydroxides [8]. Cr(VI) compounds are well known for their toxic, mutagenic, teratogenic, and carcinogenic effects [5]. On the contrary, Cr(III) is much less toxic than Cr(VI) [5], being also an essential nutrient for the human body [2]. In recent years, attention has been focused on the use of various low-cost materials that can substitute traditional reducing agents for the abatement of Cr(VI) pollution. Scrap iron is an industrial waste that can become a cheaper alternative to other Cr(VI) reducing agents. The reduction of Cr(VI) to Cr(III) with zero-valent iron may proceed heterogeneously according to [9]:

$$2Cr_2O_7^{2-}(aq) + 6Fe^0(s) + 28H^{+}(aq) \rightarrow 4Cr^{3+}(aq) + 6Fe^{2+}(aq) + 14H_2O \quad (1)$$

Subsequently, Cr(VI) may be reduced in the solution (homogeneously) by Fe(II) [9]:

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O \quad (2)$$

Thus, the net reaction for the reduction process is:

$$Cr_2O_7^{2-}(aq) + 2Fe^0(s) + 14H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + 2Fe^{3+}(aq) + 7H_2O \quad (3)$$

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With two previous studies we have investigated the effect of pH [10] and of scrap iron shape and size [11] on the Cr(VI) reduction continuous system. As a continuation of our work, the present study has the purpose to establish the effect of Cr(VI) concentration on the reduction of Cr(VI) with scrap iron in continuous system. This work will present data regarding the influence of Cr(VI) concentration on column effluent pH and on chromium and iron species concentration in column effluent. The mechanism of Cr(VI) reduction, as a function of Cr(VI) concentration, will also be discussed.

2 Problem Formulation

All column experiments performed in this study 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. Cr(VI) stock solution (10 g/L) was prepared by dissolving 28.29 g K₂Cr₂O₇ in 1000 mL of distilled deionized 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 [12]. Concentrated H₂SO₄ was used for adjusting pH of the feed solution at 2.5; this value was selected because it was found, in our previous work [10], 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, packed with 30 g scrap iron. 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 and volume (30g/18.84 cm³), the 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 and pH, Cr(total), Cr(VI), Cr(III), Fe(total), Fe(II) and Fe(III) concentration were determined. All experiments were performed at room temperature (24°C), in a background electrolyte mixture (50 ppm Ca²⁺; 20 ppm Mg²⁺; 128 ppm Cl⁻; 104 ppm Na⁺; 293 ppm HCO₃⁻) to maintain a constant ionic strength. Cr(VI) was detected by the 1,5-diphenylcarbazide colorimetric method, at 540 nm [13]. The total chromium concentration was determined by oxidizing any Cr(III) with KMnO₄, followed by analysis as Cr(VI) [13]. Cr(III) was determined from the difference in concentrations between the total and hexavalent chromium. Ferrous ions were analyzed colorimetrically, at 510 nm, according to the 1,10-phenanthroline method [13]. Total iron was determined by reduction of any Fe(III) to Fe(II) with hydroxylamine hydrochloride and subsequent analysis as Fe(II) [13]. Fe(III) was determined by subtracting Fe(II) concentration from total iron concentration. A Jasco V 530 spectrophotometer was used for measuring the absorbance of chromium and iron colored complexes. The pH of solutions was measured using an Inolab pH-meter. An Inspect S scanning electron microscope (SEM) (FEI, Holland) was used to investigate the morphology of the scrap iron before and after the experiments.

3 Problem Solution

3.1. Cr(VI) concentration in column effluent

Hexavalent chromium concentrations in column effluent, as a function of elapsed time and initial Cr(VI) concentration, are presented in Fig. 1. The results show that, during the first hours of the column experiment, Cr(VI) was completely reduced. The greater the Cr(VI) concentration, the lower the time period when Cr(VI) was totally reduced. After Cr(VI) breakthrough, its concentration in column effluent continuously increases, until a steady-state concentration, lower than the initial Cr(VI) concentration, was observed. The ratio steady-state Cr(VI) concentration : initial Cr(VI) concentration increased with increasing the initial Cr(VI) concentration, from 0.38 at 5 mg/L, to 0.91 at 40 mg/L. This indicates that the efficiency of the reduction process decreased with increasing Cr(VI) concentration. The breakthrough of Cr(VI) followed by the increase of its concentration can be ascribed to the passivation of scrap iron surface with chromium and iron simple or mixed (oxy)hydroxides. The build-up of a passivating layer blocks the access of Cr(VI) to the iron surface and leads to a decrease in Cr(VI) reduction rate. This supposition was confirmed by the SEM analysis, as can be seen from Figs. 2 and 3. The results are consistent with previous studies which have reported the existence at Fe(0) surface of mixed or simple Cr and Fe oxides, even if the Cr(VI) reduction was performed under highly acidic conditions (pH 1-3) [14-16]. During the reduction process, the column effluent pH increased at the beginning of the
experiment, and continuously decreased afterwards until a steady-state value of about 2.6 was reached (Fig. 4). The pH increase may indicate that during the first hours of the experiment the dominant process seems to be Cr(VI) reduction, which involves consumption of protons. The precipitation of Cr and Fe solid species, which involves consumption of hydroxyl ions, appears to be the dominant reaction inside the column, responsible for the subsequent pH-decrease.

![Fig. 1. Cr(VI) concentration in column effluent vs. time, at different feed solution concentrations](image1)

Fig. 1. Cr(VI) concentration in column effluent vs. time, at different feed solution concentrations

![Fig. 2. SEM micrograph of fresh scrap iron](image2)

Fig. 2. SEM micrograph of fresh scrap iron

![Fig. 3. SEM micrograph of spent scrap iron](image3)

Fig. 3. SEM micrograph of spent scrap iron

![Fig. 4. Column effluent pH vs. time, at different feed solution concentrations](image4)

Fig. 4. Column effluent pH vs. time, at different feed solution concentrations

3.2. Cr(III) concentration in column effluent

Trivalent chromium concentrations in column effluent, as a function of elapsed time and initial Cr(VI) concentration, are presented in Fig. 5. The results show that, over the entire Cr(VI) concentration range, a steady-state Cr(III) concentration was observed at the beginning of the experiment. The higher the initial Cr(VI) concentration, the shorter the initial steady-state Cr(III) value. After Cr(VI) breakthrough, Cr(III) concentration in column started to decrease until a second steady state value was recorded; the highest the initial Cr(VI) concentration, the fastest the Cr(III) concentration decrease. However, it is important to point out that even at the very beginning of the experiment (at t = 1 h), Cr(III) concentration was lower than the initial Cr(VI) concentration. This confirms the fact that chromium was partially retained inside the column, either by coprecipitation as Cr(III)-Fe(III) solid species, or by adsorption as Cr(VI), as previously reported [17-19].

![Fig. 5. Cr(III) concentration in column effluent vs. time, at different feed solution concentrations](image5)

Fig. 5. Cr(III) concentration in column effluent vs. time, at different feed solution concentrations
Just like the increase of Cr(VI) concentration, the decrease of Cr(III) concentration was determined by the same phenomenon: the passivation of the scrap iron surface, indicating that with increasing initial Cr(VI) concentration the rate of scrap iron surface passivation also increases.

3.3. Cr(total) concentration in column effluent
Total chromium concentrations in column effluent, as a function of elapsed time and initial Cr(VI) concentration, are shown in Fig. 6. From this figure, two steady-state Cr(total) concentrations in column effluent are apparent. The first steady-state concentration was noticed at the beginning of the column experiment, and its duration increased with decreasing initial Cr(VI) concentration. After Cr(VI) breakthrough, Cr(total) concentration in column effluent increased until a second steady-state concentration was reached; the lower the initial Cr(VI) concentration, the lower the increase of Cr(total) concentration. Thus, it can be concluded that, shortly after Cr(VI) breakthrough, a quasi-equilibrium has been reached between the decreasing concentration of Cr(III) and the increasing concentration of Cr(VI).

3.4. Fe(II) concentration in column effluent
Aqueous ferrous iron concentrations in column effluent, as a function of elapsed time and initial Cr(VI) concentration, are given in Fig. 7. It can be seen that higher initial Fe(II) concentration were observed for higher initial Cr(VI) concentrations, and that Fe(II) concentrations continuously decreased until the end of experiment; the highest the initial Cr(VI) concentration, the fastest the decrease of Fe(II) concentration. Moreover, ferrous iron even disappeared from the column effluent for Cr(VI) concentrations of 10, 20, and 40 mg/L. The decrease of Fe(II) concentration was caused by the decrease in time of scrap iron corrosion rate, but possibly also by the increased contribution of Fe(II) to the Cr(VI) reduction. Thus, with increasing initial Cr(VI) concentration, the intensity of the heterogeneous reduction process also increases, as results from the highest initial Fe(II) concentration at 40 mg Cr(VI)/L. However, this high reduction intensity occurs only for a short time, because the intensity of scrap iron passivation also increases with increasing initial Cr(VI) concentration, as demonstrated by the most rapid decrease of Fe(II) concentration, which was observed at 40 mg Cr(VI)/L.

3.5. Fe(III) concentration in column effluent
Fig. 8 presents the variation of ferric iron concentrations in column effluent, as a function of elapsed time and initial Cr(VI) concentration. Over the initial Cr(VI) concentration range of 5-20 mg/L, Fe(III) concentration in column effluent increased during the first hours of the experiment until a maximum concentration was observed. Subsequently, Fe(III) concentration in column effluent slowly decreased until the end of the experiment. The initial increase of Fe(III) concentration was probably determined by a faster rate of Cr(VI) reduction compared to that of Fe(III) precipitation. Afterwards, the rate of Cr(VI) reduction decreases in time, due to passivation of the scrap iron surface, leading to a decrease of Fe(III) concentration in column effluent. However, at 40 mg Cr(VI)/L, Fe(III) concentration in column effluent continuously decreased from the very beginning of the experiment, indicating that at such
high Cr(VI) concentration the scrap iron passivation process was rapid and significant even at initial experimental times.

Fig. 8. Fe(III) concentration in column effluent vs. time, at different feed solution concentrations

3.6. Fe(total) concentration in column effluent
Total iron concentrations in column effluent, as a function of elapsed time and initial Cr(VI) concentration, are presented in Fig. 9. It can be observed that Fe(total) concentrations continuously decreased in time, as a result of scrap iron surface passivation, process that leads to the decrease of both heterogeneous and homogenous Cr(VI) reduction rates. The initial Fe(total) concentration (at \( t = 1 \) h) had its lowest value at 10 mg Cr(VI)/L, and increased with increasing Cr(VI) concentration over 10 mg/L, but also with decreasing Cr(VI) concentration below 10 mg/L. The greater initial Fe(total) concentration observed at 5 mg Cr(VI)/L, in comparison with that at 10 mg (CrVI)/L, can be ascribed to a reduced contribution of Eq. (2) to Eq. (3). Basically, at Cr(VI) concentrations lower than 10 mg/L, the reduction process is almost entirely the result of direct electron transfer from Fe(0) to Cr(VI) (heterogeneous reduction). Thus, most of the Fe(total) will remain in column effluent as Fe(II) and, since Fe(II) has a higher solubility than Fe(III), a higher mass of Fe(total) will remain dissolved in the column effluent. Although at 10 mg Cr(VI)/L Eq. (1) generates more Fe(II) than at 5 mg Cr(VI)/L, due to increased contribution of Eq. (2) to Eq. (3), greater amounts of Fe(II) are converted to the less soluble specie Fe(III), which will subsequently precipitate. Therefore, this is the explanation for the greater initial Fe(total) concentration observed at 5 mg Cr(VI)/L than at 10 mg Cr(VI)/L. By further increasing Cr(VI) concentration over 10 mg/L, the initial value of Fe(total) concentration increases as a result of increasing Fe(II) and Fe(III) concentrations generated by Eqs. (1) and (2). Therefore, it can be presumed that at low Cr(VI) concentrations heterogeneous reduction was the dominant Cr(VI) reduction process, while at high Cr(VI) concentrations homogeneous reduction appears to be the main reaction contributing to Cr(VI) reduction.

Fig. 9. Fe(total) concentration in column effluent vs. time, at different feed solution concentrations

4 Conclusion
The present work evaluates the effect of Cr(VI) concentration on the continuous reduction of Cr(VI) with scrap iron. During the first hours of the column experiment, Cr(VI) was completely reduced. The greater the Cr(VI) concentration, the lower the time period when Cr(VI) was totally reduced. After Cr(VI) breakthrough, its concentration in column effluent continuously increased, until a steady-state concentration, lower than the initial Cr(VI) concentration, was observed. Shortly after Cr(VI) breakthrough, a quasi-equilibrium has been reached between the decreasing concentration of Cr(III) and the increasing concentration of Cr(VI), leading to a steady-state concentration of Cr(total). In spite of the low pH, chromium was, however, partially retained inside the column. Cr(VI) reduction was accompanied by a pH increase at the beginning of the column experiment, up to a maximum value of approximately 3.1-3.2; thereafter, the pH continuously decreased, until a steady-state value was observed, close to the initial pH. The contribution of homogeneous and heterogeneous chemical processes to Cr(VI) reduction was found to be strongly influenced by the initial Cr(VI) concentration. While at low Cr(VI) concentrations heterogeneous reduction was the dominant Cr(VI) reduction process, at high Cr(VI) concentrations homogeneous reduction appears to be the main reaction contributing to Cr(VI) reduction. Long-term column experiments performed in this work
confirms that scrap iron is a suitable material for the complete reduction of Cr(VI) in aqueous solutions. However, the results of this study clearly indicate that Cr(VI) concentration significantly influenced the efficiency of the reduction process, as well as the concentration and speciation of chromium and iron in column effluent.

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