Kinetics of Hexavalent Chromium Removal with Scrap Iron in Continuous-Flow System

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Abstract. The kinetics of hexavalent chromium removal by scrap iron was investigated in continuous system, using acidic (pH 2.5) aqueous Cr(VI) solution with low buffering capacity. Experimental data has been interpreted in terms of zero-order, first-order and second-order integrated kinetic models. Kinetics of Cr(VI) removal process has been found to proceed in two stages, with Cr(VI) removal rates significantly decreasing with increasing the elapsed experimental time. Among the studied kinetic models, the first-order kinetic model was the best fit for the first time interval (first 48 hours), while for the second time interval the process of Cr(VI) removal by scrap iron was best described by a second-order kinetics. The observed deviations of Cr(VI) removal kinetics can be attributed to changes in scrap iron surface reactivity associated with passivation processes.

Keywords: hexavalent chromium, scrap iron, kinetics, heavy metals, wastewater treatment

1. Introduction

The release of heavy metals in the environment due to anthropogenic activities represents a serious threat to human health, living organisms and ecological systems. Although some aquatic ecosystems may naturally contain trace levels of heavy metals, these pollutants have gradually become a major concern worldwide due to increasing anthropogenic activities after the industrial revolution [1]. Metal contaminants are particularly problematic because, unlike most organic contaminants, they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain [2]. In low amounts, various metals are responsible for many immunological, biochemical, and physiological activities of the body as micronutrients. However, most heavy metals can give rise to disordered functions of the immune system, resulting in increased susceptibility to infection, a variety of autoimmune diseases, hypersensitivity reactions, altering the immune response by immunostimulatory or immunosuppressive mechanisms [3, 4]. Chromium is an important metal used in a variety of industrial applications (e.g. wood preserving, metallurgy, textile dying, tanneries, metal electroplating, preparation of chromate compounds etc.). These industries are responsible for the release of chromium compounds into the environment, due to accidental events or inadequate precautionary measures [5]. Chromium exists in natural environments in two main oxidation states, Cr(VI) and Cr(III), that are characterized by different toxicity and chemical behavior [6]. Hexavalent chromium (Cr(VI)) is known to be toxic to humans, animals, plants and microorganisms, and also as a human carcinogen by inhalation route of exposure and, possibly, also by oral route of exposure [7]. Because it has a significant mobility in the subsurface environment, the potential risk of groundwater contamination with Cr(VI) is high [8]. On the other hand, trivalent chromium (Cr(III)) is less toxic [9] and readily (co-)precipitates as $Cr(OH)_3$ [10] or mixed Fe(III)-Cr(III) (oxy)hydroxides [11,12] under alkaline, neutral or even moderate acidic conditions. In small amounts, Cr(III) is an essential micronutrient for lipid, protein and fat metabolism, and acts as a regulator of insulin activity [13,14]. Several treatment technologies have been developed to remove hexavalent chromium from polluted waters. These include reduction to Cr(III) followed by precipitation, sorption, ion exchange, membrane separation, biological remediation, electrochemical remediation. The conventional process currently used to remove hexavalent chromium from contaminated wastewaters consist in its chemical reduction to Cr(III) followed by precipitation. The reducing agents commonly used are ferrous sulfate, sulfur dioxide, sodium sulfite, sodium bisulfite sodium metabisulfite, sodium thiosulfate [7]. In recent years, there has been great interest in using zerovalent iron (Fe(0)) for in situ treatment of contaminated groundwater [15]. Hexavalent chromium removal in $Fe(0)/H_2O$ system is the result of a complex interplay of processes such as adsorption, reduction and (co-)precipitation [16]. The present paper examines the kinetics of hexavalent chromium removal in continuous system, using scrap iron, a cheap and locally available industrial waste, as unconventional reducing agent.

2. Experimental

Scrap iron spiral fibers (5 mm < spiral diameter < 10 mm; 5 mm < spiral length < 20 mm) were used for the removal of hexavalent chromium from synthetic wastewater. The scrap iron was washed with warm distilled water to assure the complete removal of all impurities, and air dried. Hexavalent chromium stock solution (0.48 M) was prepared by dissolving the necessary amount of $K_2Cr_2O_7$ (AR grade) in 1000 mL of distilled deionized

water; feed solution of the desired initial Cr(VI) concentration (0.48 mM) was prepared by diluting the stock solution. Concentrated H_2SO_4 (AR grade) was used for adjusting the feed solution pH at 2.5; this pH value was previously reported as optimum pH for Cr(VI) reduction with scrap iron in continuous system [17]. The experiments were performed at room temperature (24^oC) in a background electrolyte mixture with low buffering capacity (50 ppm Ca^{2+}; 20 ppm Mg^{2+}; 128 ppm Cl^-; 104 ppm Na^+; 293 ppm HCO_3^-), in order to maintain a constant ionic strength. A schematic diagram of the wastewater treatment system involved in this study is shown in Figure 1.
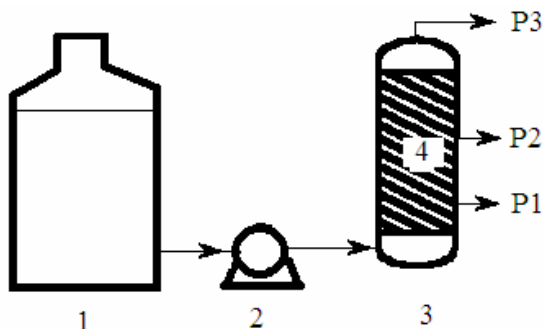

Figure 1. Experimental setup: 1 - Cr(VI) solution storage tank;
2 - Peristaltic pump; 3 - Glass column; 4 - Scrap iron filling;
P_1, P_2 and P_3- sampling ports.

A glass column (inner diameter: 2.5 cm, length: 70 cm) equipped with three sampling ports (P_1, P_2, and P_3) located at distances of 14, 35, and 62 cm, respectively, from the bottom of the scrap iron filling, 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 the storage tank to the bottom end of the column. The initial Cr(VI) concentration (0.48 mM), the feed solution pH (2.5), and the pumping rate (1.6 L/hour) were held constant throughout the study. Samples were collected at regular time intervals from column sampling ports for Cr(VI) analysis. Cr(VI) concentration was measured by the diphenylcarbazide colorimetric method.

The purple color was fully developed after 10 min and the sample solutions were transferred to a Jasco V 530 spectrophotometer; the absorbance of the color was measured at 540 nm in a 1 cm long glass cell [18]. The pH of solution was measured using an Inolab pH-meter.

3. Results and Discussion

The kinetics of Cr(VI) removal was evaluated by the integral method, using zero-order (eq.1), first-order (eq.2), and second-order (eq.3) integrated kinetic models [19]:

$$C_{Cr(VI)} = C_{Cr(VI)}^0 - k \cdot t \qquad (1)$$

$$\ln C_{Cr(VI)} = \ln C_{Cr(VI)}^0 - k \cdot t \qquad (2)$$

$$\frac{1}{C_{Cr(VI)}} = \frac{1}{C_{Cr/VI)}^0} + k \cdot t \qquad (3)$$

where $C_{Cr(VI)}$ is the Cr(VI) concentration at time t (M), $C^0_{Cr(VI)}$ is the initial Cr(VI) concentration (M), k is the removal rate coefficient, and t is the time (minutes).

By plotting $C_{Cr(VI)}$ (zero-order), $\ln C_{Cr(VI)}$ (first-order) and $1/C_{Cr(VI)}$ (second-order) vs. time using the experimental data, a straight line should be obtained; the line equation was calculated by regression analysis. The conformity between experimental data and the kinetic model was expressed by the correlation coefficient R^2; the model that successfully describes the kinetics of the Cr(VI) removal is the one that has the highest R^2 value. Subsequently, the observed rate coefficients were deduced from the slope of the equation with highest R^2. The regression equations and R^2 values for the three integrated kinetic models, calculated at different experimental elapsed times, are presented in table 1.

TABLE 1. Regression equations and R^2 values for the three integrated kinetic models

Elapsed time (h)	Kinetic models		
	Zero-order	First-order	Second-order
12	y = -4.69•10^{-5} x + 3.59•10^{-4} R² = 0.7317	y = -0.757x - 7.2145 R² = 0.9866	y = 210583x - 359369 R² = 0.7326
24	y = -4.7•10^{-5} x + 3.68•10^{-4} R² = 0.7656	y = -0.7495x - 7.0012 R² = 0,9476	y = 210134x - 362940 R² = 0.7243
48	y = -4.8•10^{-5} x + 3.8•10^{-4} R² = 0.8029	y = -0.7454x - 7.0745 R² = 0.9525	y = 210126x - 363555 R² = 0.7237
72	y = -4.6•10^{-5} x + 3.8•10^{-4} R² = 0.7898	y = -0.3365x - 7.6828 R² = 0.9524	y = 4083.9x – 901.66 R² = 0.9729
96	y = -4.06•10^{-5} x + 3.89•10^{-4} R² = 0.7643	y = -0,2133x - 7.7628 R² = 0,8529	y = 1236.7x + 2440.2 R² = 0.91630
120	y = -3.71•10^{-5} x + 4.17•10^{-4} R² = 0.8485	y = -0.1654x - 7.6555 R² = 0.915	y = 699.57x + 2126.8 R² = 0.9890
144	y = -3.51•10^{-5} x + 4.39•10^{-4} R² = 0.8995	y = -0.1419x - 7.5972 R² = 0.9315	y = 503.61x + 2056.1 R² = 0.985
168	y = -3.46•10^{-5} x + 4.5•10^{-4} R² = 0.9207	y = -0.1356x - 7.5694 R² = 0.9446	y = 456.56x + 1999.9 R² = 0.9850

The experimental data indicates that the kinetics of Cr(VI) removal process proceeds in two stages. First-order kinetics was observed within the first time interval (first 48 hours), whereas second-order kinetics appears to describe the second interval, until the end of the experiment. Both first and second-order observed rate coefficients decreased as the experimental elapsed time increased, as shown in figures 2 and 3.
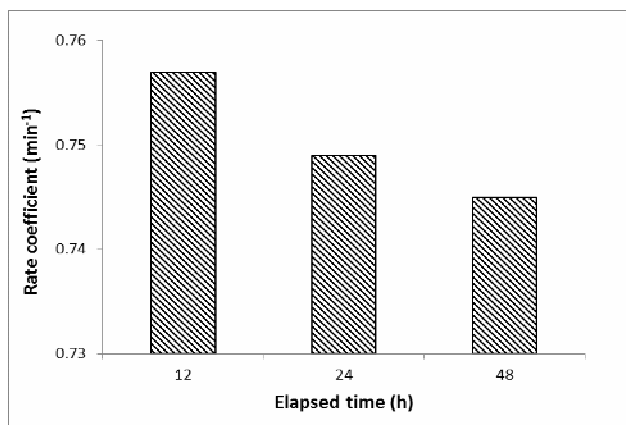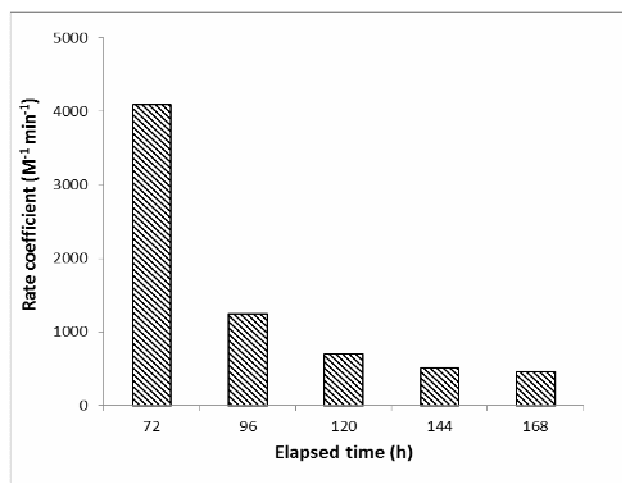

Figure 2. First-order removal rate coefficients vs. experimental elapsed time.

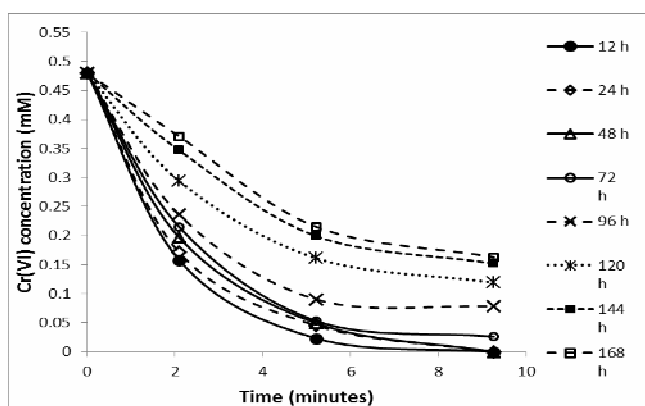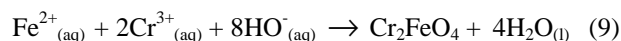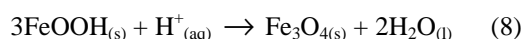Figure 3. Second-order removal rate coefficients vs. experimental elapsed time.
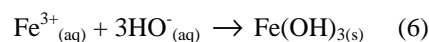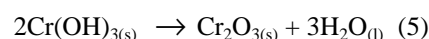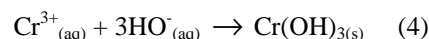

Figure 4. Cr(VI) concentration vs. time at different experimental elapsed times.

The obtained results suggest that the rate of Cr(VI) removal was detrimentally affected by the increase of experimental elapsed time, as presented in figure 4. Both deviation from first-order kinetics and decreasing of observed rate coefficients can be attributed to changes in scrap iron surface reactivity associated with passivation by secondary mineral coatings. The passivation process was visually distinguishable inside the column and the coating front migrated during the experiment from the bottom to the top of the scrap iron filling. This is in accord with previous studies which identified secondary phases such as Fe_3O_4, Cr_2FeO_4, Cr_2O_3 or $FeOOH$ at the surface of metallic iron immersed in strong acidic (pH 1-2) Cr(VI) solutions, formed according to [20,21]:

$$Cr^{3+}_{(aq)} + 3HO^-_{(aq)} \rightarrow Cr(OH)_{3(s)} \quad (4)$$

$$2Cr(OH)_{3(s)} \rightarrow Cr_2O_{3(s)} + 3H_2O_{(l)} \quad (5)$$

$$Fe^{3+}_{(aq)} + 3HO^-_{(aq)} \rightarrow Fe(OH)_{3(s)} \quad (6)$$

$$Fe(OH)_{3(s)} \rightarrow FeOOH_{(s)} + H_2O_{(l)} \quad (7)$$

$$3FeOOH_{(s)} + H^+_{(aq)} \rightarrow Fe_3O_{4(s)} + 2H_2O_{(l)} \quad (8)$$

$$Fe^{2+}_{(aq)} + 2Cr^{3+}_{(aq)} + 8HO^-_{(aq)} \rightarrow Cr_2FeO_4 + 4H_2O_{(l)} \quad (9)$$

4. Conclusions

Hexavalent chromium is a strong toxic and carcinogenic agent and, therefore, pollution abatement processes should be applied to all aqueous effluents containing this contaminant, before discharging them into natural aquatic environments. The present work evaluates the kinetics of Cr(VI) removal using columns packed with scrap iron. The experimental kinetic data, evaluated by the integral method, suggest that the continuous Cr(VI) removal process proceeded in two stages, with first-order kinetics for the first time interval and second-order kinetics for the second time interval. This phenomenon was ascribed to changes in scrap iron surface reactivity associated with passivation processes. The observed rate coefficients were determined for both stages of the Cr(VI) removal process and the results show that the elapsed time strongly affects the rate of Cr(VI) removal, with highest removal rates within the first time interval, and lowest rates at the end of the second one.

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