

# Kinetics of hexavalent chromium reduction by scrap iron

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## Abstract

The kinetics of Cr(VI) reduction by scrap iron was investigated in batch system, for aqueous solutions having low buffering capacities, as a function of pH (2.10–7.10), temperature (10–40 °C) and Cr(VI) concentration (19.2–576.9 μM). The results obtained using only the experimental data at initial times indicate zero-order kinetics at pH 2.10 and first-order kinetics over the pH range of 2.98–7.10. The reaction order with respect to H<sup>+</sup> concentration, over the pH range of 4.17–7.10 and Cr(VI) concentration range of 19.2–38.4 μM, was found to be 0.31. The effects of pH, Cr(VI) initial concentration and temperature were investigated; the observed Cr(VI) reduction rates increased with decreasing pH, increasing temperature and decreasing initial Cr(VI) concentration. The observed and overall rate coefficients were determined, and a kinetic expression was developed to describe reduction of chromium by scrap iron over the pH range of 4.17–7.10 and Cr(VI) concentration range of 19.2–38.4 μM.

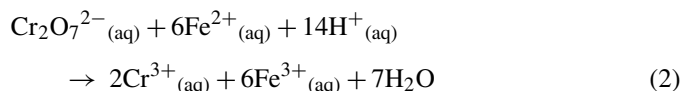
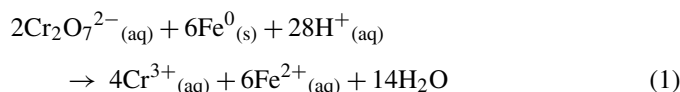
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**Keywords:** Chromium(VI); Toxic metals; Scrap iron; Reduction kinetics; Wastewater treatment

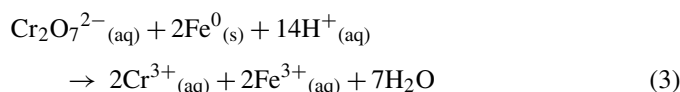
## 1. Introduction

Chromium compounds are used in various industries (e.g. textile dyeing, tanneries, metallurgy, metal electroplating and wood preserving); hence, large quantities of chromium have been discharged into the environment due to improper disposal and leakage [1–3]. Oxidation states of chromium range from –4 to +6 [4], but only the +3 and +6 states are stable under most natural environments. Chromium usually exists in both trivalent and hexavalent forms in aqueous systems, that are characterized by different toxicity and chemical behavior. Chromium(VI) is known to be toxic to humans, animals, plants and microorganisms [5–8]. Because of its significant mobility in the subsurface environment, the potential risk of groundwater contamination is high. Chromium(III), on the other hand, is less toxic and readily precipitates as Cr(OH)<sub>3</sub> [9] or as mixed Fe(III)–Cr(III) (oxy)hydroxides [10,11] under alkaline or even slightly acidic conditions; Cr(III) may also have toxic effects [12,13], but its concentration is usually very low (below water quality standards) due to the low solubility in the pH range of natural waters.

Several methods are available for the decontamination of waters polluted with Cr(VI) compounds. These include: reduction followed by chemical precipitation, adsorption, electrokinetic remediation, membrane separation processes and bioremediation. The conventional process currently used to remove hexavalent chromium is its reduction to Cr(III) by chemical means followed by precipitation [14]. The reducing agents commonly used are ferrous sulphate, sulphur dioxide and sodium sulphites. In recent years, there has been great interest in using zerovalent iron for in situ reduction of redox active metals from contaminated groundwater [11,15–18]. Previous investigators [19] have shown that Cr(VI) may be removed from solution via reduction to Cr(III) according to:

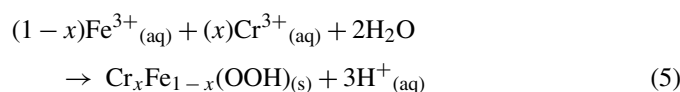
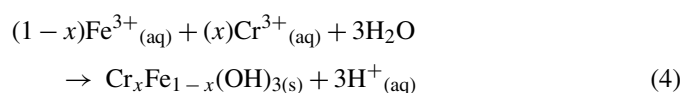


The two equations can be added together to yield Eq. (3), which is the net reaction for the reduction process.



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Chromium may be removed through the precipitation of  $\text{Cr}(\text{OH})_{3(s)}$  or co-precipitation of mixed Fe(III)–Cr(III) hydroxide solid solution [10] or mixed Fe(III)–Cr(III) oxyhydroxide solid solution [11], according to:



where  $x$  vary from 0 to 1.

Rates of chromate removal by zerovalent iron have generally been described by kinetic expression of the form [20,21]:

$$\frac{dC_{\text{Cr(VI)}}}{dt} = -k \cdot C_{\text{Cr(VI)}}^n \cdot C_{\text{H}^+}^m \quad (6)$$

where  $k$  is the reaction rate constant that depends on the iron surface area, solution ionic strength and the mixing rate,  $n$  the reaction order with respect to the aqueous Cr(VI) concentration and  $m$  is the reaction order with respect to the aqueous  $\text{H}^+$  concentration.

The policy framework for managing solid waste today, often-called integrated waste management (IWM), encourages waste prevention and recycling over incineration and landfilling. Recycling of waste materials has environmental benefits (preventing the pollution associated with producing virgin materials, reducing odors and congestion associated with the transportation of disposable wastes and decreasing the amount of landfilled materials) but also socio-economic benefits (savings in material and energy costs, increase of products competitiveness in the international marketplace and generating employment for collection and recycling activities). In recent years, the emphasis has been on urging local communities to take responsibility for the environment. Waste materials recycling must become a crucial component for local communities, especially for poor communities from developing countries, in their efforts to meet the goals of sustainable development: economic development, improved social conditions and environmental protection.

Recycling is particularly significant for metals because, unlike most organic contaminants, metals are persistent and do not readily undergo degradation when disposed into our natural environment. Therefore, recovery and recycling is truly key to the sustainable future of metals. In last decades there has been great interest in metal recycling [22,23], scrap iron being reused in various purposes: production of iron powder [24,25], electrochemical amelioration of acid mine drainage [26], production of reinforcement bars [27] and reducing agent in the galvanic stripping of iron from organic phases [28]. To the authors knowledge, reports about reduction of Cr(VI) with scrap iron are very few, although this waste can become a cheaper alternative to other reducing agents. Galvanic reduction of hexavalent chromium with scrap iron was studied by Abdo and Sedahmed [29] using a divided parallel plate cell. The advantage of this technique is that the reduced chromium salt is free of iron impurities and electrical energy is produced from the galvanic cell as by-product.

Ozer et al. studied the reduction of Cr(VI) by steel wool in continuous system [19]; the results showed that Cr(VI) in aqueous solution can be effectively reduced by steel wool, but the process depended to a large extent on acid concentration.

Aware of the importance of IWM, the authors of this study are involved in researches concerning the recovery of useful substances from waste and their reuse in wastewater treatment [30]. We strongly believe that finding cost effective methods for the reduction of hexavalent chromium from industrial wastewater requires further investigation in the field of industrial or agricultural wastes or by products.

The objective of this study was to explore the kinetics of Cr(VI) reduction by use of a cheap and locally available industrial waste: scrap iron. The effects of pH, Cr(VI) concentration and temperature were investigated.

## 2. Materials and methods

### 2.1. Materials

In our previous study [31], four different types of scrap iron resulted from the mechanic processing of steel were tested for Cr(VI) reduction: large spiral fibers, small spiral fibers, iron shavings and fine iron powder; the optimum shape for batch reduction experiments was found to be as iron shavings that pass through 2.5 mm screen; therefore, all experiments from this study were performed by using iron shavings. The scrap iron, consisted mainly of iron free of chromium, was washed several times with warm water to assure the complete removal of all impurities and air dried in oven at 200 °C; no other treatment was performed on it. Although no chemical or physical characterization was performed, the presence of oxides on iron surface was visible; air-formed oxides on iron surfaces have been previously reported to be relatively thin and nonporous and are composed of an inner layer of magnetite ( $\text{Fe}_3\text{O}_4$ ) coated with an outer layer of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) [32,33].

Hexavalent chromium stock solutions (1000 mg/l) were prepared by dissolving 2.829 g of AR grade  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1000 ml of distilled deionised water; standard solutions of the desired initial Cr(VI) concentration were prepared by diluting the stock solution.

### 2.2. Method

Kinetic batch experiments were performed using a 0.8-l flask open to the atmosphere, containing 300 ml of the standard solution. To remove traces of chromium and iron, the flask was soaked in 0.1N HCl before each experiment. The pH of the standard solutions was adjusted prior to the reduction experiments by small addition of 98%  $\text{H}_2\text{SO}_4$ ; the scrap iron was added in great excess (mass ratio Cr(VI):iron = 1:3333.33) and the flask contents were mixed continuously with a Teflon-coated magnetic stir bar [31]; the mixing rate was held constant (200 rpm) throughout the study [31]. All experiments were performed in a background electrolyte mixture (50 ppm  $\text{Ca}^{2+}$ , 20 ppm  $\text{Mg}^{2+}$ , 128 ppm  $\text{Cl}^-$ , 104 ppm  $\text{Na}^+$  and 293 ppm  $\text{HCO}_3^-$ ) to maintain a constant ionic strength.

Cr(VI) concentration was measured by the diphenylcarbazide colorimetric method, after sample solutions were periodically extracted (as a manner of shortened extraction intervals in the beginning of experiments). Aliquots taken for analysis were filtered immediately for the removal of colloidal particles formed by the precipitation of mixed Cr(III)–Fe(III) oxyhydroxides. The purple color was fully developed after 15 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. Replicate measurements on Cr(VI) samples showed that relative precisions of less than 2% could be routinely obtained. The pH of solutions was measured in samples collected before and after the reaction using an Inolab pH-meter.

### 3. Results and discussion

#### 3.1. Effect of pH

Preliminary experiments indicate that Cr(VI) reduction is very fast in acidic conditions (pH 2.10), but proceeded slowly when pH increase up to 7.10. This is the reason why we could not use the same pair of initial Cr(VI) concentration for the kinetics experiments over the entire studied pH range; the greater the pH, the lower the Cr(VI) concentration, as shown in Table 1. These concentrations were selected because they are within the range of relevant concentrations for electroplating wastewaters [34,35].

The effect of pH on the rate of Cr(VI) reduction was studied at room temperature ( $24 \pm 2^\circ\text{C}$ ), over the pH range of 2.10–7.10, using aqueous solutions with low buffering capacities. From Figs. 1–4, it appears that the Cr(VI) reduction was very fast at pH 2.10 for the two different initial Cr(VI) concentrations, when hexavalent chromium was completely removed within the first 5 min. The reduction process is significantly slower at higher pH values. This is in accord with the stoichiometry of this reaction (Eq. (3)) which requires 7 mol of hydrogen ions for each mol of Cr(VI) and is highly dependent on  $\text{H}^+$  concentration. Control experiments without scrap iron showed no loss of contaminant over the time period of a typical experiment (data not shown).

Table 1  
Cr(VI) concentrations used in kinetic experiments

pH	$C_{\text{Cr(VI)}} (\mu\text{M})$	$C_{\text{Cr(VI)}} (\text{mg/l})$
2.10	192.3	10.00
	576.9	30.00
2.98	192.3	10.00
	576.9	30.00
4.17	19.2	1.00
	38.4	2.00
	192.3	10.00
5.05	19.2	1.00
	38.4	2.00
5.98	19.2	1.00
	38.4	2.00
7.10	19.2	1.00
	38.4	2.00

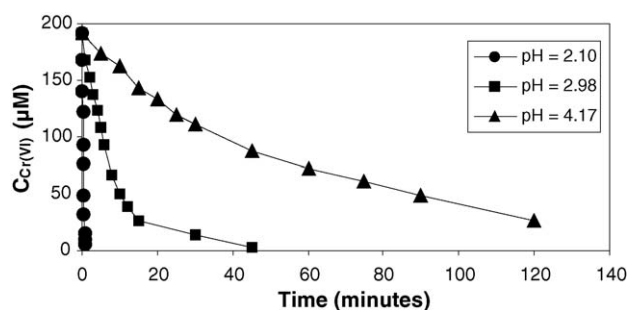


Fig. 1. Cr(VI) concentration vs. time at different initial pH values;  $C_{\text{Cr(VI)}}^0 = 192.3 \mu\text{M}$ ,  $t = 24^\circ\text{C}$ .

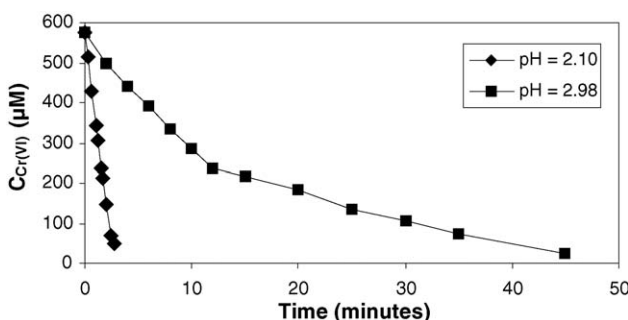


Fig. 2. Cr(VI) concentration vs. time at different initial pH values;  $C_{\text{Cr(VI)}}^0 = 576.9 \mu\text{M}$ ,  $t = 24^\circ\text{C}$ .

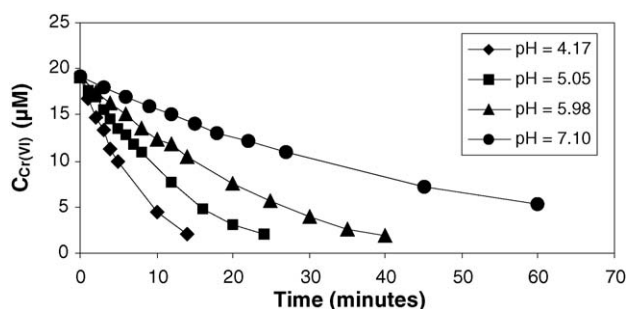


Fig. 3. Cr(VI) concentration vs. time at different initial pH values;  $C_{\text{Cr(VI)}}^0 = 19.2 \mu\text{M}$ ,  $t = 24^\circ\text{C}$ .

From Figs. 1–4 and pH values in the range of 2.98–7.10 two times intervals are apparent. High reduction rates are observed within the first time interval, whereas a strong decrease in the Cr(VI) reduction occurs in the second one. This two

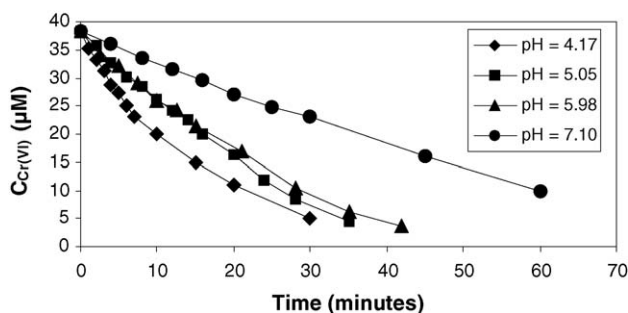


Fig. 4. Cr(VI) concentration vs. time at different initial pH values;  $C_{\text{Cr(VI)}}^0 = 38.4 \mu\text{M}$ ,  $t = 24^\circ\text{C}$ .

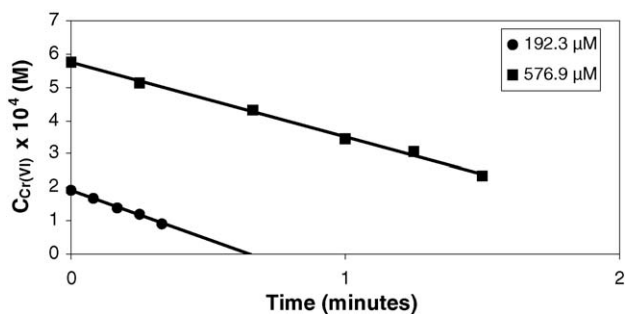


Fig. 5. Cr(VI) concentration vs. time at different initial Cr(VI) concentration;  $t = 24\text{ }^{\circ}\text{C}$ , pH 2.10.

time intervals do not appear at the most acidic pH value (pH 2.10). This behavior, consistent with previous studies [20,36], is most likely due to co-precipitation of mixed Fe(III)–Cr(III) (oxy)hydroxides, which may block the access of Cr(VI) to the iron surface. Starting from the same observation, Ponder et al. [36] suggest that the faster initial reduction of Cr(VI) occurs due to a sorption phase, and the slowing of the rate, at later times, involves a physical mechanism (occlusion of the zerovalent iron) rather than chemical.

Because of our poorly buffered solutions, pH values increased over the course of the reactions; in all batch tests, the final pH increased from the initial value with 2.6–3.0 pH units, which also may cause decreases in the reduction rates with time. Iron corrosion and the reduction of Cr(VI) by scrap iron are probably responsible for the observed pH increase.

### 3.2. Study of reaction order with respect to Cr(VI)

Since the reaction rate decreased slowly in time due to probable co-precipitation of mixed Fe(III)–Cr(III) (oxy)hydroxides on the scrap iron surface at pH greater than 4 [37], but also due to iron surface passivation, the reaction order with respect to Cr(VI) was determined using only the experimental data obtained at initial times, when the reduction efficiency of Cr(VI) did not exceed 40%, at room temperature ( $24 \pm 2\text{ }^{\circ}\text{C}$ ). Experimental kinetic results evaluated by the integral method indicate zero-order kinetics at pH 2.10, and first-order kinetics over the pH range of 2.98–7.10 (Figs. 5–10; Table 2). The same reaction orders with respect to Cr(VI) were obtained when the differential method was used. It was also observed that rates increasingly devi-

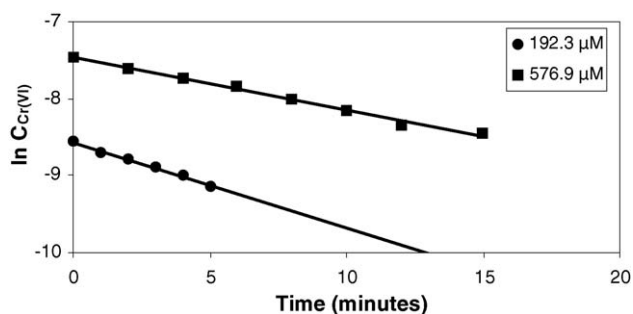


Fig. 6.  $\ln C_{\text{Cr(VI)}}$  vs. time at different initial Cr(VI) concentration;  $t = 24\text{ }^{\circ}\text{C}$ , pH 2.98.

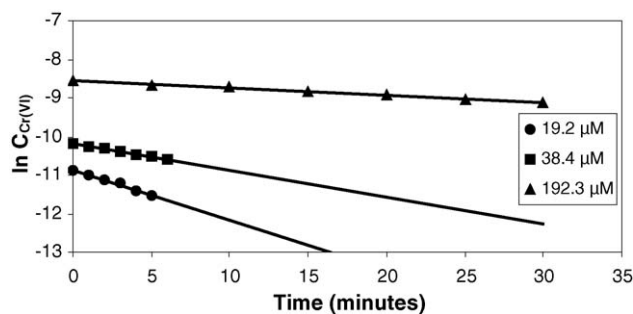


Fig. 7.  $\ln C_{\text{Cr(VI)}}$  vs. time at different initial Cr(VI) concentration;  $t = 24\text{ }^{\circ}\text{C}$ , pH 4.17.

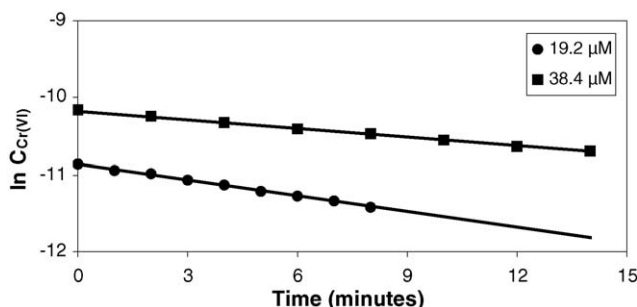


Fig. 8.  $\ln C_{\text{Cr(VI)}}$  vs. time at different initial Cr(VI) concentration;  $t = 24\text{ }^{\circ}\text{C}$ , pH 5.05.

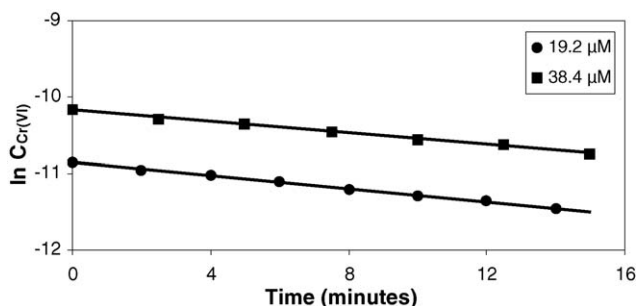


Fig. 9.  $\ln C_{\text{Cr(VI)}}$  vs. time at different initial Cr(VI) concentration;  $t = 24\text{ }^{\circ}\text{C}$ , pH 5.98.

ated from the first-order kinetics with increasing elapsed time, which can be attributed to changes in scrap iron surface reactivity, associated with passivation by absorbed Fe(III)–Cr(III) (oxy)hydroxides. This results are consistent with previous batch studies, which have reported both zero-order [38] and first-order

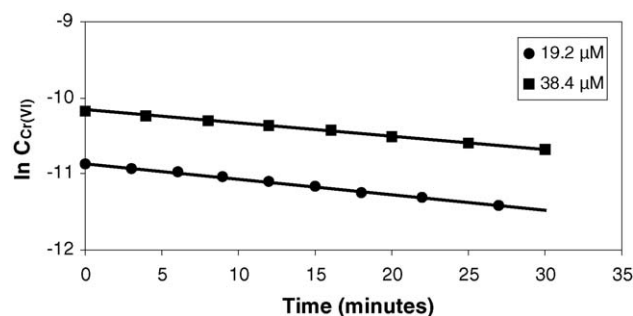


Fig. 10.  $\ln C_{\text{Cr(VI)}}$  vs. time at different initial Cr(VI) concentration;  $t = 24\text{ }^{\circ}\text{C}$ , pH 7.10.

Table 2  
Regression equations and  $R^2$  values for experimental data

Figure	Concentration ( $\mu\text{M}$ )	Regression equation	$R^2$
Fig. 5	192.3	$y = -2.9301 \times 10^{-4}x + 1.9182 \times 10^{-4}$	0.9965
	576.9	$y = -2.2301 \times 10^{-4}x + 57.456 \times 10^{-5}$	0.9976
Fig. 6	192.3	$y = -0.1115x - 8.5643$	0.9968
	576.9	$y = -0.0686x - 7.4584$	0.9915
Fig. 7	19.2	$y = -0.1295x - 10.8600$	0.9962
	38.4	$y = -0.0692x - 10.1730$	0.9982
	192.3	$y = -0.0185x - 8.5575$	0.9960
Fig. 8	19.2	$y = -0.0685x - 10.8640$	0.9983
	38.4	$y = -0.0380x - 10.1700$	0.9991
Fig. 9	19.2	$y = -0.0421x - 10.8650$	0.9967
	38.4	$y = -0.0375x - 10.1740$	0.9957
Fig. 10	19.2	$y = -0.0209x - 10.8580$	0.9979
	38.4	$y = -0.0173x - 10.1640$	0.9982
Fig. 11	19.2	$y = -0.3266x + 0.5801$	0.9914
	38.4	$y = -0.3090x + 0.3164$	0.9426

[20,36] kinetics, with respect to the aqueous Cr(VI) concentration. Melitas and Farrell [39] suggest that the zero-order removal kinetics of Cr(VI) by iron media can be explained by anodic control of iron corrosion and the concomitant anodic control of Cr(VI) reduction.

Zero-order (at pH 2.10) and first-order (at pH 2.98–7.10) observed rate coefficients, determined from initial rates, decreased as the pH increased, as shown in Table 3.

### 3.3. Study of reaction order with respect to $\text{H}^+$

The observed rate coefficient can be expressed as:

$$k_{\text{obs}} = k \cdot C_{\text{H}^+}^m \quad (7)$$

$$\log k_{\text{obs}} = \log k - m \cdot \text{pH} \quad (8)$$

where  $k$  is the overall reaction rate constant and  $m$  is the reaction order with respect to the aqueous  $\text{H}^+$  concentration. By plotting  $\log k_{\text{obs}}$  against pH, using experimental data over the pH range of 4.17–7.10 (first-order kinetics with respect to chromate concentration), results in two straight lines (Fig. 11); the slope of these lines (Table 2), calculated by regression analysis, result in reaction order with respect to  $\text{H}^+$  of 0.30 for  $C_{\text{Cr(VI)}}^0 = 38.4 \mu\text{M}$

Table 3  
Zero-order (pH 2.10) and first-order (pH 2.98–7.10)  $k_{\text{obs}}$  values measured for reduction of Cr(VI) by scrap iron

pH	$k_{\text{obs}}$			
	$C_{\text{Cr(VI)}} = 19.2 \mu\text{M}$	$C_{\text{Cr(VI)}} = 38.4 \mu\text{M}$	$C_{\text{Cr(VI)}} = 192.3 \mu\text{M}$	$C_{\text{Cr(VI)}} = 576.9 \mu\text{M}$
2.10	–	–	$3.1190 \times 10^{-4}$	$2.2586 \times 10^{-4}$
2.98	–	–	0.1078	0.0763
4.17	0.1647	0.1132	0.0336	–
5.05	0.0799	0.0450	–	–
5.98	0.0480	0.0388	–	–
7.10	0.0172	0.0120	–	–

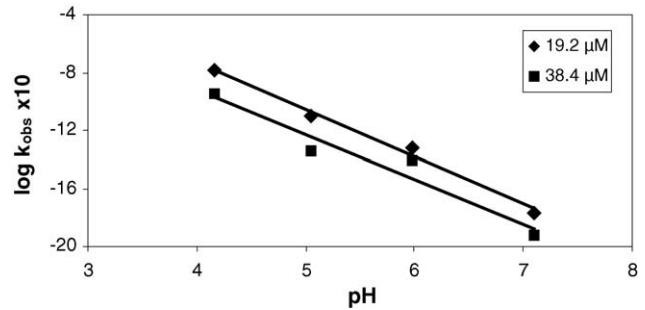


Fig. 11. Effect of pH on first-order rate coefficients at different initial Cr(VI) concentration and  $t = 24 \text{ }^\circ\text{C}$ .

Table 4

First-order overall kinetic constants values measured for reduction of Cr(VI) by scrap iron over the pH range of 4.17–7.10 and Cr(VI) concentration range of 19.2–38.4  $\mu\text{M}$

$C_{\text{Cr(VI)}} (\mu\text{M})$	$k (\text{min}^{-1})$
19.2	3.8027
38.4	2.0725

and 0.32 for  $C_{\text{Cr(VI)}}^0 = 19.2 \mu\text{M}$ ; the average reaction order with respect to  $\text{H}^+$ , over the pH range of 4.17–7.10 and Cr(VI) concentration range of 19.2–38.4  $\mu\text{M}$  can be considered to be 0.31. In a previous study, Gould [21] reported for the reduction of Cr(VI) by an iron wire a reaction order of 0.5, at initial removal rates. Soluble chromate removal by scrap iron over the pH range of 4.17–7.10 can be described by a kinetic expression of the form:

$$V = -\frac{dC_{\text{Cr(VI)}}}{dt} = k \cdot C_{\text{Cr(VI)}} \cdot C_{\text{H}^+}^{0.31} \quad (9)$$

where the overall kinetic constants ( $k$ ) over the pH range of 19.2–38.4  $\mu\text{M}$ , calculated from the intercept of lines in Fig. 11, are presented in Table 4.

### 3.4. Temperature effect

The effect of temperature on the reduction of Cr(VI) by scrap iron was examined at pH 4.17 and  $C_{\text{Cr(VI)}}^0 = 192.3 \mu\text{M}$ , for temperature values ranging from 10 to 40  $^\circ\text{C}$ , using a temperature controlled water bath. The results, presented in Fig. 12, show an important dependence of the rate on temperature and an apparent energy of activation of 24.08 kJ/mol. In the same time, it can be

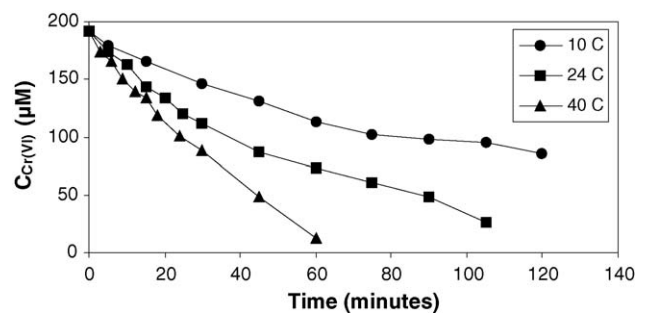


Fig. 12. Cr(VI) concentration vs. time at different temperatures; pH 4.17,  $C_{\text{Cr(VI)}}^0 = 192.3 \mu\text{M}$ .

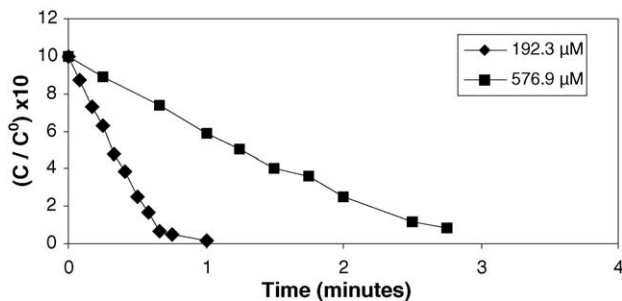


Fig. 13. Cr(VI) concentration vs. time at different initial Cr(VI) concentrations; pH 2.10,  $t = 24^\circ\text{C}$ .

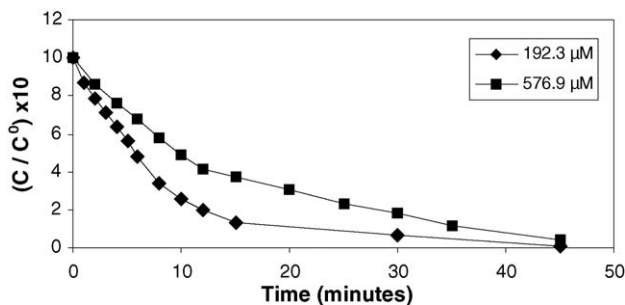


Fig. 14. Cr(VI) concentration vs. time at different initial Cr(VI) concentrations; pH 2.98,  $t = 24^\circ\text{C}$ .

noticed that the favorable effect of temperature on the reduction rate decreased with increasing temperature.

### 3.5. Initial Cr(VI) concentration effect

Aqueous chromate concentrations in the batch reactors at room temperature ( $24 \pm 2^\circ\text{C}$ ) as a function of elapsed time, with differing initial Cr(VI) concentrations, are shown in Figs. 13–18. The results show that for initial concentrations between 19.2 and 576.9  $\mu\text{M}$ , the observed reduction rates decreased with increasing chromate concentration. This conclusion is confirmed by the decreasing of  $k_{\text{obs}}$  values (Table 3) and  $k$  values (Table 4) with increasing chromate concentration. In a previous study, the decreasing of Cr(VI) removal rates with increasing concentration was explained by lower rates of iron corrosion and increasing iron surface passivation at higher chromate concentrations [38].

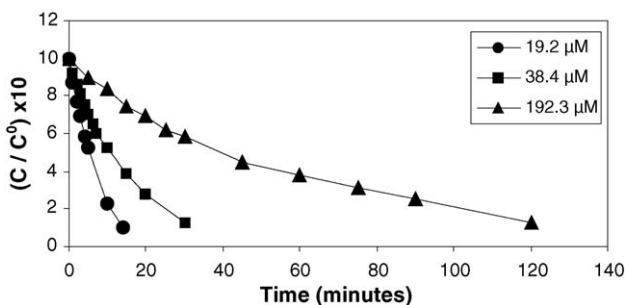


Fig. 15. Cr(VI) concentration vs. time at different initial Cr(VI) concentrations; pH 4.17,  $t = 24^\circ\text{C}$ .

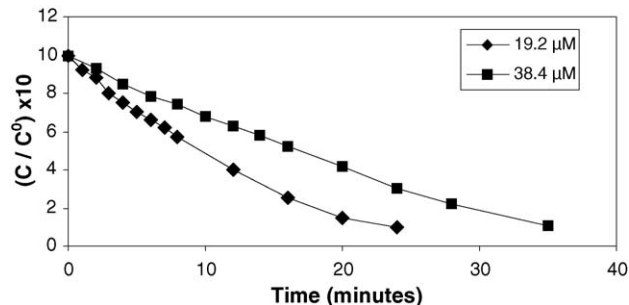


Fig. 16. Cr(VI) concentration vs. time at different initial Cr(VI) concentrations; pH 5.05,  $t = 24^\circ\text{C}$ .

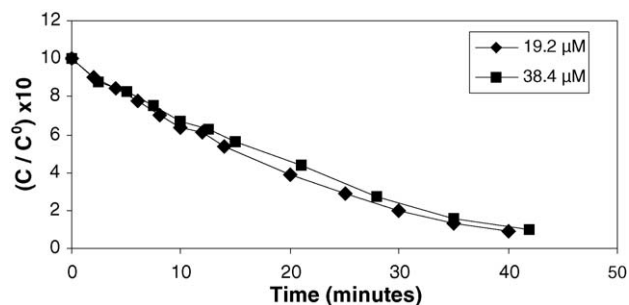


Fig. 17. Cr(VI) concentration vs. time at different initial Cr(VI) concentrations; pH 5.98,  $t = 24^\circ\text{C}$ .

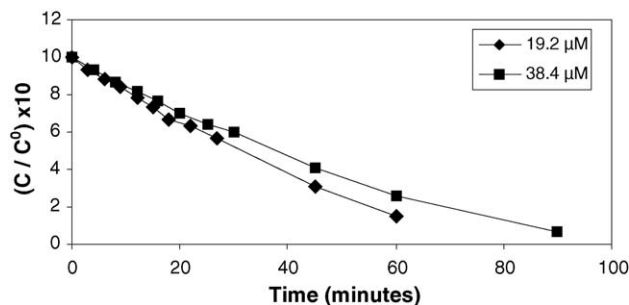


Fig. 18. Cr(VI) concentration vs. time at different initial Cr(VI) concentrations; pH 7.10,  $t = 24^\circ\text{C}$ .

## 4. Conclusions

Chromium(VI) is toxic and needs to be detoxified; 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. Results obtained under oxic conditions show that pH significantly affects the rate of Cr(VI) reduction by scrap iron, with more rapid reduction occurring at lower pH values. The reaction rate decreased slowly in time due to iron surface passivation and probable co-precipitation of mixed Fe(III)–Cr(III) (oxy)hydroxides on the scrap iron surface. Because of the low degree of buffering in our solutions, the pH increased due to the protons consumed by the redox reaction, which also may cause decreases in the reduction rates with time.

Experimental kinetic results evaluated by both integral and differential methods indicate zero-order kinetics at pH 2.10, and first-order kinetics over the pH range of 2.98–7.10, with respect to Cr(VI) concentration; the reaction order with respect to  $\text{H}^+$

was found to be 0.31. The observed and overall rate coefficients were determined, and a kinetic expression was developed to describe reduction of chromium by scrap iron over the pH range of 4.17–7.10 and Cr(VI) concentration range of 19.2–38.4  $\mu\text{M}$ .

The experimental results from the batch experiments indicate that scrap iron can be successfully used for the reduction of Cr(VI) in aqueous solution. Because the reduction efficiency increases with the decrease of pH, this process may be readily used in the treatment of wastewaters with high  $\text{H}^+$  concentrations (i.e. electroplating wastewater). However, it is difficult to assess long-term performance of Cr(VI) reduction by scrap iron using only short-term batch experiments. Batch tests conducted in this study are characterized by very low ratios of scrap iron to Cr(VI) solution and, in the same time, by a large iron surface area with respect to the amount of Cr(VI); moreover, the vigorous mixing of scrap iron particles employed in batch experiments results in particle–particle collisions that may damage the metal surface which will increase the rate of iron corrosion, as previously reported [40]. Hence, during this kind of experiments, only a small fraction of the reductive capacity of the scrap iron was used. Therefore, in order to design long-term above-ground treatment systems, an understanding of the steady state Cr(VI) reduction kinetics is needed. Aware of this concept, we currently investigate, with a separate study, the steady state removal rates by long-term column experiments.

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