จลนพลศาสตร์ของการกัดกร่อนโลหะเหล็กและการรีดักชันโครเมียม (VI)

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บทคัดย่อ

การกัดกร่อนของโลหะเหล็กในน้ำที่พีเอช 2 ถูกควบคุมโดยขั้นตอนของการเคลื่อนที่ของสาร ผลิตภัณฑ์ที่เกิดจากปฏิกิริยารีดอกซ์ผ่านชั้นฟิล์มของน้ำจากผิวของเหล็กไปยังสารละลายซึ่งสามารถแสดงได้ด้วยสมการ

$$\frac{d[Fe^{2+}]}{dt} = 5.9 \times [Area] \times t^{-\frac{1}{2}}$$

โดยที่ "$d[Fe^{2+}]/dt$" มีหน่วยเป็น มก.ล$^{-1}$.นาที$^{-1}$ "[Area]" คือความเข้มข้นของพื้นที่ผิวของโลหะเหล็กมีหน่วยเป็น ม^{2}.ล$^{-1}$ "t" คือเวลามีหน่วยเป็นนาที และค่าคงที่ของอัตราปฏิกิริยามีหน่วยเป็น มก.ม$^{-2}$.นาที$^{-0.5}$ ผลการศึกษากับน้ำเสียโครเมียม (VI) พบว่าโลหะเหล็กทำปฏิกิริยารีดอกซ์กับโครเมียม (VI) เร็วกว่าที่ทำปฏิกิริยากับโมเลกุลของน้ำมาก โดยเป็นปฏิกิริยาอันดับหนึ่งในแง่ของความเข้มข้นโครเมียมและพื้นที่ผิวของโลหะเหล็กหรือเป็นปฏิกิริยาอันดับสองโดยรวม ซึ่งสามารถแสดงด้วยสมการ

$$\frac{d[Cr(VI)]}{dt} = -0.0018 \times [Area] \times [Cr(VI)]$$

โดยที่ "$d[Cr(VI)]/dt$" มีหน่วยเป็น มก.ล$^{-1}$.นาที$^{-1}$ "[Cr(VI)]" มีหน่วยเป็น มก.ล$^{-1}$ และค่าคงที่ของอัตราปฏิกิริยามีหน่วยเป็น ล.ม$^{-2}$.นาที$^{-1}$ จากการทดสอบด้วย Goodness of Fit Test พบว่าสมการจลนพลศาสตร์ทั้งสองสามารถอธิบายพฤติกรรมของข้อมูลที่ได้เป็นอย่างดี ที่ความเชื่อมั่นร้อยละ 95

คำสำคัญ : เหล็กประจุศูนย์ / โครเมียม (VI) / การกัดกร่อน / รีดักชัน / ปฏิกิริยารีดอกซ์

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Kinetics for Metallic Iron Corrosion and Hexavalent Chromium Reduction

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Abstract

Corrosion kinetics of Fe^0 in aqueous at pH 2 is controlled by the transport step of products from redox reaction through a liquid film layer from iron surface to bulk solution which can be represented by the following equation:

$$\frac{d[Fe^{2+}]}{dt} = 5.9 \times [Area] \times t^{-\frac{1}{2}}$$

where "$d[Fe^{2+}]/dt$" is in $mg.l^{-1}.min^{-1}$, "[Area]" is surface area concentration of Fe^0 in $m^2.l^{-1}$, "t" is time in min, and the rate constant in $mg.m^{-2}.min^{-0.5}$. The redox reaction of Fe^0 with Cr(VI) is more rapid than that with water and is the first order with respect to Cr(VI) and Fe^0 surface area concentrations; hence, the second order overall as follows:

$$\frac{d[Cr(VI)]}{dt} = -0.0018 \times [Area] \times [Cr(VI)]$$

where "d[Cr(VI)]/dt" is in $mg.l^{-1}min^{-1}$, "[Cr(VI)]" is in $mg.l^{-1}$, and the rate constant in $l.m^{-2}.min^{-1}$. The results from Goodness of Fit Test show that there is no significant lack of fit at 95% confidence for both rate equations obtained in this study.

Keywords : Zero-valent Iron / Hexavalent Chromium / Corrosion / Reduction / Redox Reaction

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1. Introduction

Metallic iron or Fe^0 has been recently used in many research studies in both water and wastewater treatments. With its highly reductive potential, Fe^0 is one of the promising reductants which can remove many contaminants either organics or inorganics. Several chlorinated organic substances, including hexachlorobenzene [1], trichloroethene [2], carbon tetrachloride [3], were dechlorinated effectively by Fe^0. Likewise, many researchers also successfully removed inorganic pollutants in water using the reductive Fe^0 such as nitrate [4], hexavalent uranium [5, 6], divalent lead [7], and hexavalent chromium ($Cr(VI)$) [4, 7-10]. Reduction of wastewater from hexavalent-chrome-plating batch is one of the potential applications of Fe^0 in environmental engineering practice. However, results from preliminary survey of chrome-plating industry in Thailand reveal that most of the chrome wastewaters have pH around 2 whereas most Fe^0 research works up-to-date with $Cr(VI)$ reduction were performed at pH higher than 2.7. In field practice, it will be more convenient and economic if the chrome wastewater can be reductively treated at its initial pH prior to increasing to alkaline range for $Cr(III)$ precipitation. Moreover, it is necessary to understand thoroughly in the aquatic chemistry of Fe^0 at this low pH since the reductive potential of Fe^0 is low enough to reduce water which is the solvent under highly acidic condition. Therefore, competition in redox reaction between $Cr(VI)$ and water molecules may possibly occur unavoidably. It is the objective of this study to investigate intensively into the kinetics of iron corrosion in water as well as the $Cr(VI)$ reduction by Fe^0 at pH 2 which will form a solid platform for a better understanding in the redox mechanisms of treatment process using Fe^0 as well as for the engineering application.

2. Materials and methods

All experiments were carried out in a 2-liter glass reactor with 1.5 liters of effective volume. Mixing was provided by a stainless turbine agitating at 120 rpm. A steady flow of nitrogen gas was provided to the system through diffusers before and throughout the experiments to minimize the partial pressure of hydrogen and oxygen gases in aqueous phase which prevents ferrous ion, Fe^{2+}, from further oxidizing to ferric ion, Fe^{3+}. Fe^0 was purchased from Aldrich which has a particle size and average specific surface area of 10 µm and 0.90±1.1 m^2/g [4], respectively. The initial concentration of $Cr(VI)$ in the chromium reduction experiments of 10 mg/l was prepared from analytical-grade K_2CrO_4 and was adjusted to pH 2 by 3 N $HClO_4$ which is considerably inert regarding on redox reaction. The reactor was placed in a water bath to control the temperature at 25°C. The pH was maintained consistently at 2 throughout the experiment by a pH controller using 3 N $HClO_4$. The amount of acid being added during each sampling time was also recorded. At predetermined time, a sample was taken from the reactor by a 25 ml syringe and immediately filtered through a GF/C to remove iron particles. The filtrate was then analyzed for ferrous and total chromium concentrations by using Inductive Couple Plasma (Jobin Yvon Emission 124). Remaining $Cr(VI)$ was analyzed by the diphenylcabazide colorimetric method [11].

In model optimization, the unknown parameter(s) was determined by using Solver add-in on Microsoft Excel XP software. The optimal parameter(s) which yielded the best of fit of the model to the observed data was determined by using the method of non-linear least squares regression which minimizing the error of sum of squares or the residual sum of squares (ESS) over all the observations:

$$\mathrm{EES} = \sum_{i=1}^{n} \left\{ M_{obs,i} - M_{pred,i} \right\}^2 \quad \mathbf{(1)}$$

where "$M_{obs,i}$" and "$M_{pred,i}$" are the values observed and predicted by the model, respectively, at corresponding time "i".

3. Results and discussion

3.1 Determination of corrosion kinetics

The time-related Fe^{2+} concentrations of all experiments including duplicates are shown in Fig. 1 (the solid lines represented the best fit which will be discussed later). From theoretical point of view, the reduction and oxidation reactions occur when Fe^0 is in contact with water are as follows:

Oxidation-half reaction: $Fe^0(s) \rightarrow Fe^{2+} + 2e^-$ $E^0 = +0.44$ volt **(2)**

Reduction-half reaction: $2H^+ + 2e^- \rightarrow H_2(g)$ $E^0 = 0.00$ volt **(3)**

Overall redox reaction: $Fe^0(s) + 2H^+ \rightarrow Fe^{2+} + H_2(g)$ $E^0 = +0.44$ volt **(4)**

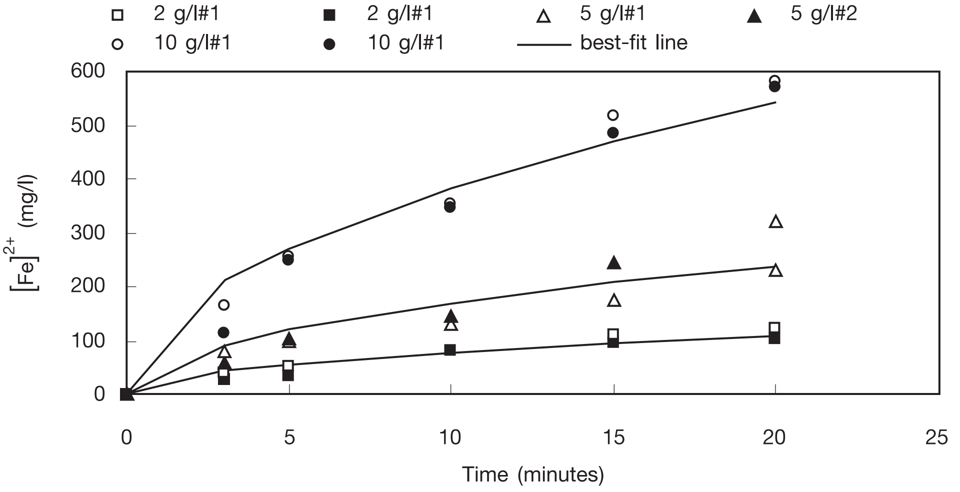

Fig. 1 Concentrations of ferrous ion versus time and best-fit line.

This overall stoichiometric equation is different from that proposed by Gould [8] in which the final species of iron was Fe^{3+}. This study created an anaerobic environment in the mixture by purging with nitrogen gas; hence, preventing further oxidization of Fe^{2+} to Fe^{3+} as indicated by no Fe^{3+} being detected in the solution. Hence, the reduction of $Cr(VI)$ would be expected to proceed through Eq. (4). Since all experiments were controlled at pH 2 and purged with nitrogen gas, the hydroxide ion should be unchanged while the accumulated partial pressure of hydrogen gas should be negligible. As a result, only Fe^0, water molecules, and Fe^{2+} controlled the reaction rate. The molecules of water were enormous (55.4 M at 25°C) as compared to the other two speciess; thus, were considered as a constant and included in the rate constant term. The amount of acid being added to maintain the pH of the solution agreed very well with the measured Fe^{2+}, i.e., approximately 2 moles of $HClO_4$ was added per 1 mole of Fe^{2+} formed. In addition, since the solution is maintained at pH 2, the Fe^{2+} is the major ferrous iron species and the formation of hydrolysis complexes can be neglected.

As it is a heterogeneity system between solid and liquid phases, the surface of the iron powder becomes an important factor that controlling the redox phenomenon particularly on the reaction rate. Modifying from the dissolution mechanisms proposed by Morel and Hering [12] as the reaction similarly takes place on the active size on the surface of the Fe^0, five steps possibly involving in the Fe^0 corrosion are: a) hydrogen ion (H^+) is adsorbed onto the surface of Fe^0 and is attached to an active size; b) H^+ reduction and Fe^0 oxidation happen; c) Fe^{2+} desorbed from the surface, which then the iron is corroded; d) products, i.e., $H_2(g)$ and Fe^{2+}, diffuse from liquid film into the bulk solution; and e) H^+ diffuses from the bulk solution into the liquid film to refill that have been consumed. Any one or a combination of these steps may be the rate limiting and, therefore, controls the overall reaction rate.

As a result, although the overall corrosion reaction of the Fe^0 seems to be simple as shown in Eq. (4), the actual reaction kinetics can be very complicated. Nonetheless, it is generally believed that the overall kinetic rate for dissolution is controlled by either: a) the transport step of either reactant(s) or product(s) through a liquid film layer which can be represented by an exponential rate law as shown in Eq. (5); or b) surface reaction step as described by a zero-order rate law (Eq. (6)) when approaching the steady-state condition at the surface [13].

$$r = \frac{dC}{dt} = k_w \times t^{-\frac{1}{2}} \tag{5}$$

$$r = \frac{dC}{dt} = k_w \times [Area] \tag{6}$$

where "k_w" and "k_w'" are the reaction rate constants and "[Area]" is the iron surface area concentration. The observed non-linear behavior of the time-related Fe^{2+} concentrations in Fig. 1 suggest that the diffusion of Fe^{2+} and/or hydrogen gas through the aqueous film to the bulk solution rather than the surface reaction was the rate-controlling step. Therefore, Eq. (5) was used to fit the observed data by following the non-linear least squares procedure as described previously. In this case, $M_{obs,i}$ and $M_{pred,i}$ are the measured and calculated (from Eq. (5)) Fe^{2+} concentrations, respectively, at corresponding time "i". The results are shown as solid lines in Fig. 1 which found to fit data satisfactorily. The optimum k_w from the non-linear least squares regression for all Fe^0 concentrations are summarized in Table 1. Since the optimum k_w varied with initial Fe^0 concentration or should rather be the surface area concentration, it implies that these optimum k_w were apparent rate constants not the intrinsic values. Further analysis as shown in Fig. 2 indicated that the optimum k_w was a linear function of surface area concentration. With the linear correlation of 0.99, it is strongly suggested that:

$$k_w = 5.9 \times [\text{Area}] \tag{7}$$

Table 1. Rate constants for water reduction by Fe^0.

Metallic iron concentration (g/l)	**Optimum k_w (min^{-1})**
2	12.2
5	26.6
10	60.5

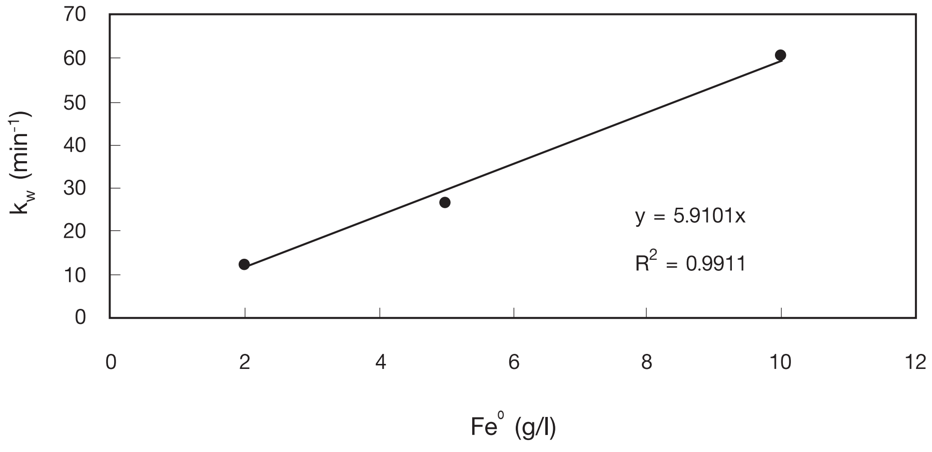

Fig. 2 Reaction rate constant as a function of Fe^0 concentration.

This result is comprehensible which can be explained by the effect of velocity gradient, $\overline{G}$, and film thickness. In this study, the mixing speed was kept constant for all experiments regardless on Fe^0 concentration. As the number of the iron particles increased, the apparent density of the mixed liquor increased which leading to a significant increase in $\overline{G}$. As a result, the aqueous film thickness became thinner as iron dose increased; hence, accelerating the overall mass transfer. Eq. (5) which is the oxidation rate of Fe^0 in water at pH 2, then, became:

$$r = \frac{d[Fe^{2+}]}{dt} = 5.9 \times [Area] \times t^{-\frac{1}{2}} \qquad \textbf{(8)}$$

where "t" is in min, "[Area]" is in $m^2.l^{-1}$, and intrinsic rate constant is in $mg.m^{-2}.min^{-0.5}$.

3.2 Determination of Cr(VI) reduction kinetics

During Cr(VI) reduction experiments, pH of the solution was quite steady as opposed to the corrosion study. In fact, it was found that an increase in pH began when most of Cr(VI) was reduced to Cr(III). This implies that the reduction of Cr(VI) by Fe^0 was far more rapid and dominant than that of water. Hence, the iron reactions took place initially with Cr(VI) and sequentially, upon the completion of Cr(VI) reduction, with water rather than in a competitive manner. As a result, the Cr(VI) reduction kinetics could be determined precisely and autonomously without any interferences from water molecules. In addition, further analysis revealed that the end products of Cr(VI) reduction by Fe^0 were Cr(III) and Fe^{2+} only which agreeing with several other studies [4, 8, 14-17]. The oxidation-reduction of Cr(VI) by Fe^0 can be described by the following equations.

Reduction-half reaction: $HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.20$ volt **(9)**

Combining with the oxidation-half reaction in equation (1); the overall redox reaction becomes:

$$3Fe^0 + 2HCrO_4^- + 14H^+ \rightarrow 3Fe^{2+} + 2Cr^{3+} + 8H_2O \qquad E^0 = +1.64 \text{ volt} \qquad \textbf{(10)}$$

The measured Fe^{2+} concentrations in the mixture agreed adequately with the values calculated from the stoichiometric Eq. (9) as shown in Fig. 3. Gould [8], using 245±3 μm-diameter iron wire, found the reduction of Cr(VI) by Fe^0 followed a pseudo-half-order reaction with respect to Cr(VI) concentration as shown in the following equation:

$$\frac{d[Cr(VI)]}{dt} = -k_{Cr} \times [Cr(VI)]^{0.5} \qquad \textbf{(11)}$$

where "k_{Cr}" is the psedo-half-order rate constant. On the other hand, Ponder et al. [7] using Fe^0 nanoparticles, and Alowitz and Scherer [4], using 18-35 mesh Fe^0 obtained from Peerless Metal Powders and Abrasive (Detroit, MI) and Connelly GPM, Inc. (Chicago, IL) and 40 mesh laboratory-grade Fe^0 from Fisher Scientific, found the reduction of Cr(VI) to be a pseudo-first order reaction as shown in the Eq (12):

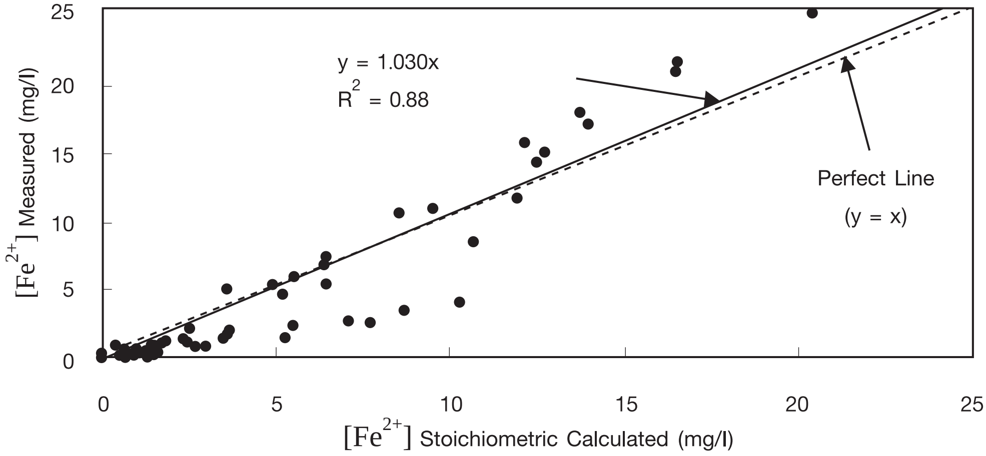

Fig. 3 $[Fe^{2+}]$ measured versus $[Fe^{2+}]$ stoichiometric calculated.

$$\frac{d[Cr(VI)]}{dt} = -k'_{Cr} \times [Cr(VI)] \qquad \textbf{(12)}$$

where "k'_{Cr}" is the pseudo first-order rate constant. At low Cr(VI) concentration range as used in this study, it was found that both half- and first-order-reaction equations provide very similar fit to the observed data. However, by using a non-linear least squares technique, Eq. (12) consistently gave lower ESS than Eq. (11) as illustrated in Table 2; hence, the pseudo first-order reaction should be a more suitable model to describe the reduction of Cr(VI) by the Fe^0 of this study. Fig. 4 illustrates a plot of residual Cr(VI) as a function of time and the best fit from pseudo-first-order kinetics model. Similar to iron corrosion experiment, further analysis on k'_{Cr} as shown in Fig. 5 indicated a linear dependence on iron surface area concentration which can be expressed by Eq. (13).

Table 2. Model comparison and rate constants for Cr(VI) reduction by Fe^0.

Metallic iron concentration (g/l)	half-order kinetics		first-order kinetics	
	Optimum k_{Cr} ($l^{0.5}.mg^{-0.5}.min^{-1}$)	ESS	Optimum k_{Cr} (min^{-1})	ESS
5	0.0114	5.624	0.0047	5.204
10	0.0488	10.878	0.0222	8.072
20	0.0855	5.877	0.0355	5.452

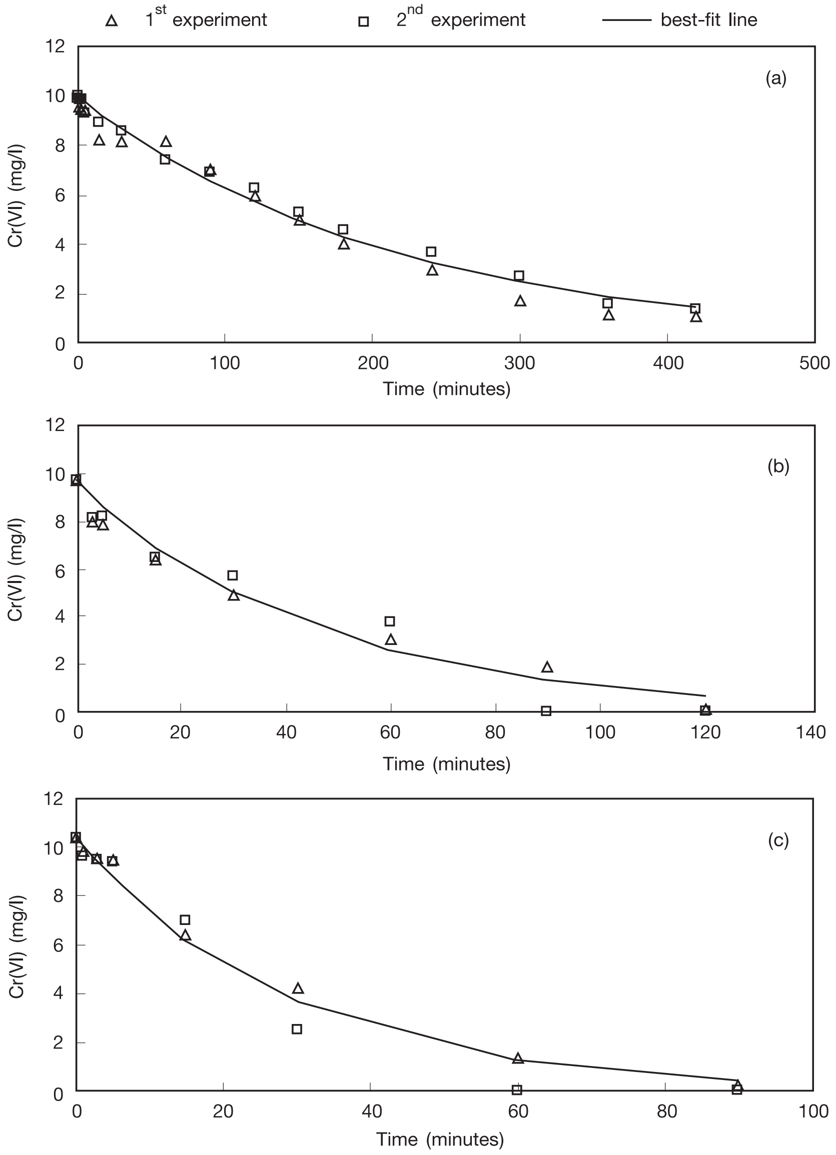

Fig. 4 Concentration of Cr(VI) versus time and best-fit line.

(a) 5 g/l of Fe^0

(b) 10 g/l of Fe^0

(c) 20 g/l of Fe^0

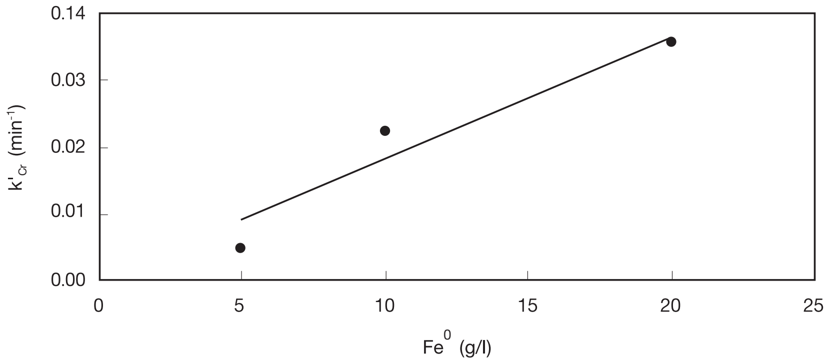

Fig. 5 Reaction rate constant as a function of Fe^0 concentration.

$$k'_{Cr} \quad = \quad 0.0018 \times [\mathrm{Area}] \tag{13}$$

where "[Area]" is the surface area of Fe^0 in $m^2.l^{-1}$. Based on this result, the reaction appears to be of the first order in iron surface area concentration and the overall kinetics can be expressed as follows:

$$\frac{d[\mathrm{Cr(VI)}]}{dt} = -0.0018 \times [\mathrm{Area}] \times [\mathrm{Cr(VI)}] \tag{14}$$

where "[Cr(VI)]" is in $mg.l^{-1}$, and surface area normalized rate constant is in $l.m^{-2}.min^{-1}$. This linear dependence of k'_{Cr} on iron surface area similar to this study has been previously reported by several others [4, 7, 8]; however, the value obtained in this study of 0.0018 is slightly lower than 0.0027-0.0042 $l.m^{-2}.min^{-1}$ reported by Alowitz and Scherer [4]. This deviation maybe due to the differences in pH, temperature, source of Fe^0, and system configuration.

3.3 Validation of kinetic rate equation

Since the experiments were all duplicated, it is possible to perform a Goodness of Fit Test to determine whether or not there is a significant lack of fit [18]. This analysis is based on an analysis of variance in which the ESS with N - P degree of freedom (N is the total number of data points including replicate, P is the number of the estimated parameters) were broken down into the pure error or replication sum of squares, RSS, which equal to the total of squares of deviations of the replicate values from their averages with N - G degree of freedom (G is the number of data points in each experiment), and the lack of fit sum of squares, LSS, which equal to the difference between ESS and RSS with G - P degree of freedom. The ratio of the lack of fit mean squares over the replication mean squares was, then, compared to the appropriate value in F distribution table. The results from

Goodness of Fit Test for both Fe^0 corrosion and Cr(VI) reduction experiments are summarized in Tables 3 and 4, respectively. The results indicate that there was no significant lack of fit with 95% confidence in all optimization runs. This means that the obtains rates of Fe^0 corrosion in Eq. (8) and Cr(VI) reduction by Fe^0 in Eq. (14) are justified and valid.

Table 3. Goodness of fit test for Fe^0 corrosion kinetics.

Source	**Metallic iron concentration (g/l)**								
	2			**5**			**10**		
	ESS	**LSS**	**RSS**	**ESS**	**LSS**	**RSS**	**ESS**	**LSS**	**RSS**
Sum of squares	1,264	715	549	13,292	6,634	6,658	18,837	10,867	7,970
Deg. of freedom	11	6	5	11	6	5	11	6	5
Mean squares	-	143	92	-	1,327	1,110	-	2,174	1,328
F	-	1.56	-	-	1.20	-	-	1.64	-
p	-	0.29	-	-	0.40	-	-	0.27	-

Table 4. Goodness of fit test for Cr(VI) reduction kinetics.

Source	**Metallic iron concentration (g/l)**								
	5			**10**			**20**		
	ESS	**LSS**	**RSS**	**ESS**	**LSS**	**RSS**	**ESS**	**LSS**	**RSS**
Sum of squares	5.204	3.187	2.017	8.072	5.626	2.447	5.452	2.882	2.570
Deg. of freedom	29	14	15	15	8	7	15	8	7
Mean squares	-	0.228	0.135	-	0.804	0.306	-	0.412	0.321
F	-	1.69	-	-	2.63	-	-	1.28	-
p	-	0.16	-	-	0.10	-	-	0.37	-

4. Conclusions

The kinetics for iron corrosion and Cr(VI) reduction were successfully established as expressed in Eq. (8) and (14), respectively. Corrosion of Fe^0 in aqueous solution at pH 2 is controlled by the liquid-film-layer transport step of redox products from iron surface to bulk solution. Reaction of Fe^0 with Cr(VI) which is far more rapid than with water, on the contrary, is restrained by surface reaction with the first order with respect to Cr(VI) and Fe^0 surface area concentrations leading to the overall second order reaction. The results from Goodness of Fit Test indicate no significant lack of fit at 95% confidence for both rate equations for iron corrosion and Cr(VI) reduction; hence, both equations are valid. These two kinetic equations can form a solid platform for engineering application for chrome-plating wastewater treatment.

5. Acknowledgement

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