



## A mechanism study of light-induced Cr(VI) reduction in an acidic solution

Shan-Li Wang<sup>a</sup>, Chung-Chi Chen<sup>b</sup>, Yu-Min Tzou<sup>a,\*</sup>,  
Chia-Lian Hsu<sup>a</sup>, Jen-Hshuan Chen<sup>a</sup>, Chen-Fang Lin<sup>a</sup>

<sup>a</sup> Department of Soil & Environmental Sciences, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung 40227, Taiwan, ROC

<sup>b</sup> Department of Life Science, National Taiwan Normal University, Taipei 116, Taiwan, ROC

### ARTICLE INFO

#### Article history:

Received 17 March 2008

Received in revised form 31 May 2008

Accepted 31 July 2008

Available online 9 August 2008

#### Keywords:

Photolysis

Chromium

Photo-reduction

Reaction rate

### ABSTRACT

The mechanisms of photo-catalytic reduction of Cr(VI) were investigated in acidic solutions with and without Fe(III). In a system without Fe(III), no Cr(VI) reduction was observed in dark conditions; conversely, under light conditions, the reduction reaction rate increased to 0.011 and 0.020  $\mu\text{M min}^{-1}$  at pH 2 and pH 1, respectively, indicating the occurrence of Cr(VI) photo-reduction. The Cr(VI) photo-reduction reaction was induced by the photolysis of water molecules, leading to  $\text{O}_2$  production. Upon the addition of Fe(III), the photo-reduction rate of Cr(VI) was significantly enhanced due to the formation of Fe(II), which is the photolytic product of  $\text{FeCl}_2^+$  and the electron donor for Cr(VI) reduction. However, with the same concentration of FeCl complexes, a strong inhibition of Cr(VI) reduction at pH 2 was observed, compared with pH 1. A possible explanation is that  $\text{FeOH}^{2+}$  becomes predominant with increasing pH and that its photolytic product, the OH free radical, is an oxidant for Fe(II) and Cr(III) and can compromise Cr(VI) reduction. The kinetic result of each photo-reduction reaction pathway shows zero-order kinetics, suggesting that the photolysis reaction of  $\text{H}_2\text{O}$  or  $\text{FeCl}_2^+$  is the rate-determining step in each pathway. The results also show the potential of developing a homogeneous photo-catalytic method to treat Cr(VI)-containing water.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Chromium(VI) is one of the major toxic contaminants threatening water supplies worldwide. The occurrence of Cr(VI) in the environment is generally anthropogenic. Its major sources include wastewaters from electroplating and tanning processes and the disposal of Cr(VI)-containing wastes [1,2]. In aqueous solutions, the main chemical species of Cr(VI) are  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{HCr}_2\text{O}_7^-$ , depending on the total Cr concentration and pH [3,4]. These anionic species have relative high mobility due to the preponderance of reactive, negatively charged mineral surfaces and organic functional groups in soils and sediments. The exclusion of these anions from negatively charged mineral surfaces may actually enhance their mobility. Because Cr(VI) is highly toxic to living organisms [5–7], its fate in the environment needs to be clarified in order to evaluate its threat to ecosystems and public health [8,9].

Chromium(VI) can be reduced to Cr(III), which is less harmful to living organisms. The reduction of Cr(VI) to Cr(III) subsequently

restricts the distribution of Cr because of the formation of Cr(III) oxides with low solubility. In soils and sediments, potential reductants for the conversion of Cr(VI) to Cr(III) are organic matter and chemical species containing S(I), S(II) and Fe(II) [10–16]. Cr speciation in waters has been extensively reviewed by Calder [1] and Kotas and Stasicka [4]. In an oxic environment, such as shallow water and surface soil, the concentrations of reductive forms of Fe or S are extremely low, so they may not contribute to Cr(VI) reduction to any observable extent. In contrast, organic substances are ubiquitous in soils and surface waters. The reduction of Cr(VI) by organic reductants may be one of the major pathways for Cr(VI) attenuation in the surface environment; however, previous studies had suggested that the reduction rate of Cr(VI) by organics was relatively low in the pH range of 4–8 [17,18]. Meanwhile, in some cases, the organic content in an open ditch or river close to the discharge outlet of Cr(VI)-containing wastewater was found to be low [19]; thus, the rapid disappearance of Cr(VI) was hypothesized to be the result of a photo-catalytic pathway of reductive transformation not related to organics [20].

Cr(VI)-containing wastewaters usually contain many inorganic components, such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and Fe(III), associated with a very low pH (i.e., pH less than 2) [21]. We speculate that the

\* Corresponding author. Tel.: +886 4 2284 0373x4206; fax: +886 4 2285 5167.  
E-mail address: [ytmzou@dragon.nchu.edu.tw](mailto:ytmzou@dragon.nchu.edu.tw) (Y.-M. Tzou).

photo-reduction of Cr(VI) may involve inorganic electrolytes and proceed immediately upon the release of the effluent from the electroplating factories in sunlight. If this reaction indeed occurs, the detrimental impacts of Cr(VI) to an ecosystem with low organic content may be overestimated. Our previous study showed that the photolysis of Fe(III)–Cl complexes would lead to Cr(VI) reduction in a system without an apparent reductant [20]. In this work, the effect of pH on Cr(VI) photo-reduction by Fe(III)–Cl complexes with a fixed concentration was further investigated. The objectives of this work are to clarify the reaction mechanism by a detailed examination of the photo-induced Cr(VI) reduction in the presence of Fe(III) and Cl<sup>-</sup> and by the direct detection of photolytic products of H<sub>2</sub>O and Fe(III)–Cl complexes. The results may be applied to develop homogeneous photo-catalytic methods for treating wastewater containing Cr(VI).

## 2. Materials and methods

### 2.1. Reactor setup

Photo-catalytic experiments were conducted in a water-jacketed reactor. A 100 W, medium-pressure mercury UV lamp inserted in a borosilicate well (borosilicate filters out  $\lambda \leq 290$  nm) was centered in the reactor (Fig. 1). The lamp emits mostly in the range 310–1000 nm, with the most intense lines at 303, 313, 366, 405, 436, 546, and 578 nm. The well and the reactor were both connected to a circulating bath to maintain their temperature at  $24.5 \pm 0.5^\circ\text{C}$ . This temperature setting was suggested by the UV lamp manufacturer (ACE Glass Incorporated) to light the lamp and to obtain stable irradiation. The UV lamp was warmed up for 20 min prior to the addition of reactants and initiation of photo-catalytic experiments. To avoid any possible interferences of inflowing sunlight or ceiling light, the reactor was covered with Al foil and placed in a stainless-steel chamber throughout the experiments.

In order to monitor the O<sub>2</sub> concentration during the experiments, a peristaltic pump was used to circulate the sample solution in a closed loop between the reaction vessel and a flask with an O<sub>2</sub> probe (Dissolved Oxygen Meter, HANNA HI 9143) (Fig. 1). The dissolved O<sub>2</sub> concentration was monitored continuously, and special care was taken to ensure that the sample was not exposed to the air. A preliminary dark study indicated that the adsorption of Cr(VI) on the glass wall and tube wall is low and can be ignored.

### 2.2. Cr(VI) photo-reduction as influenced by Fe(III)

All chemicals used in this work were of analytical grade. The Cr(VI) solutions of 0.19–192  $\mu\text{M}$  were made from a stock solution of 1.92 mM Cr(VI), prepared by dissolving K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 1.0 M HCl. The Fe(III) solutions of 0, 35.8, 89.5, and 179.1  $\mu\text{M}$  were obtained from the stock solutions of 500 mg L<sup>-1</sup> FeCl<sub>3</sub>. The final volume of the mixture containing Cr(VI) and Fe(III) was brought to 250 mL using 0.1 M HCl (pH 1) and 0.01 M HCl (pH 2). A 5-mL aliquot was withdrawn prior to the exposure to the UV light for determining the initial Cr(VI) and Fe(III) concentrations. Once the UV light was switched on, a 5 mL aliquot was also periodically withdrawn from the reactor and passed through a syringe filter. The residual Cr(VI) concentration in the filtrates was measured using the diphenylcarbazide (DPC) method on a Cary 50 UV-vis spectrophotometer [22]. The potential interference of the Fe(III) used in the study on Cr(VI) measurement by the DPC method was less than  $\pm 1\%$  [23]. A control experiment was conducted with the same experimental settings and procedures, except that the light was turned off.

In a separate set of the same experiments, the possible photo-reduction of Fe(III) to Fe(II) was examined to clarify whether the formation of Fe(II) resulted in the rapid Cr(VI) reduction under irradiation. Since the change of pH observed during the experiments was low (i.e., deviation <0.02 in pH value), no buffer was needed to maintain a constant pH. The changes in Cr(VI), Fe(III), and Fe(II) concentrations were measured using colorimetric methods. Chromium(VI) concentrations were measured by the DPC method. The Fe(II) and Fe(III) concentrations were determined colorimetrically by 1,10-phenanthroline at 510 nm. Since 1,10-phenanthroline would readily form complexes with Fe(II), leading to a strong absorbance at 510 nm, Fe(II) could be measured directly upon the addition of the indicator. By converting Fe(III) to Fe(II) using a reductant, hydroxylamine, prior to 1,10-phenanthroline addition, total Fe was obtained. The Fe(III) concentration was then calculated by subtracting the Fe(II) concentration from the corresponding total Fe concentration.

## 3. Results and discussion

### 3.1. Photo-reduction of Cr(VI)

The photo-reduction kinetics of Cr(VI) with Fe(III) addition was investigated at pH 1 (Fig. 2a) and pH 2 (Fig. 2b). The top curves in Fig. 2a and b, corresponding to the change of Cr(VI) under

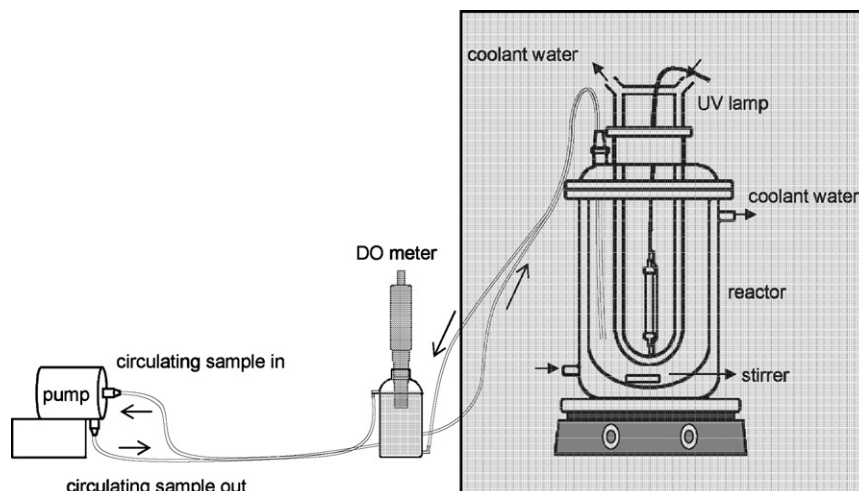
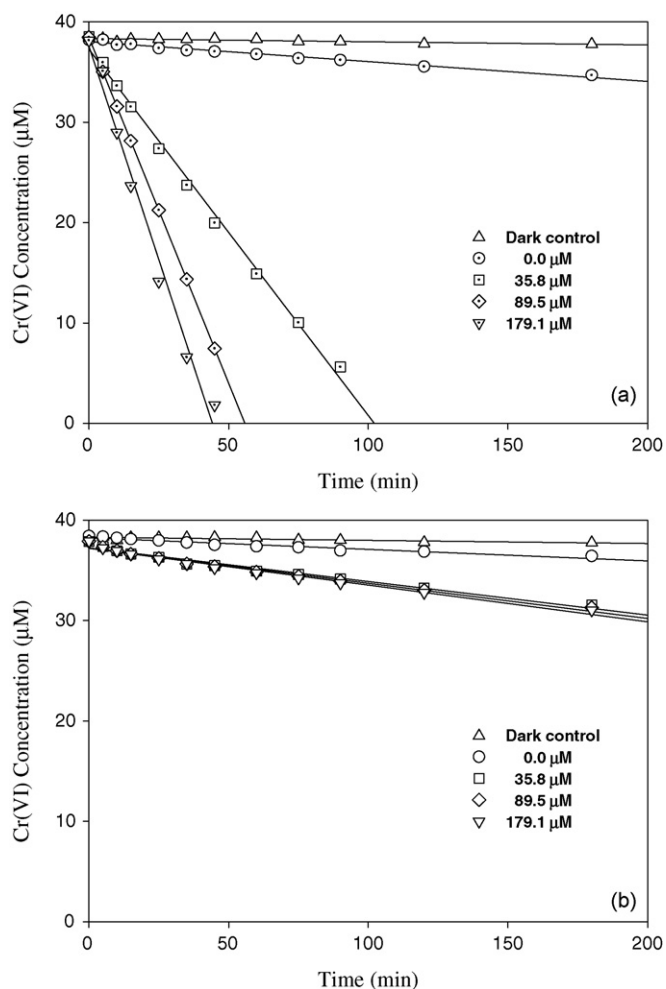


Fig. 1. Schematic setup for in situ measurement of the production of dissolved oxygen (DO) during the irradiation of reactants.



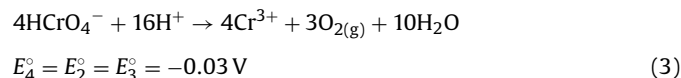
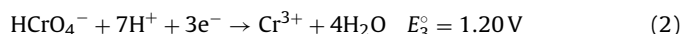
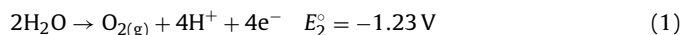
**Fig. 2.** Influences of light and Fe(III) addition (0–179.1  $\mu\text{M}$ ) on 38.5  $\mu\text{M}$  Cr(VI) photo-reduction at (a) pH 1 and (b) pH 2 as a function of time.

dark conditions at these two pH values, show that Cr(VI) reduction was negligible and indifferent to solution pH when no light was applied to the system. Conversely, when light was applied to the system, more rapid decreases in Cr(VI) concentration were observed, and the decreasing rate was correlated with the Fe(III) concentration. The experimental data could be fit well with the zero-order equation,  $d[\text{Cr(VI)}]/dt = k$  ( $R^2 > 0.98$ ) (Table 1). The reaction order indicated that the overall reaction rate was independent of Cr(VI) concentration. The reaction rate constant increased as the Fe(III) concentration was increased. Thus, the results show that

light energy is of crucial importance in Cr(VI) reduction and that the photo-reduction reaction is enhanced at lower pH and higher Fe(III) concentration.

### 3.1.1. Effect of pH on Cr(VI) photo-reduction in the absence of Fe(III)

In the absence of Fe(III) at both pH 1 and pH 2, Cr(VI) was able to be photo-reduced (Fig. 2), and the reaction rate was dependent on pH (Table 1). At pH 2 and pH 1, the rate constant was determined to be 0.011 and 0.020  $\mu\text{M min}^{-1}$ , respectively. The reaction rate increased as the pH decreased. Since no reductants existed in the systems, we speculate that the electron source for Cr(VI) reduction was  $\text{H}_2\text{O}$  photolysis (reactions (1) and (2)). Although the negative redox potential shown in reaction (3) suggests that the reaction will not occur spontaneously, the application of UV light may provide energy for  $\text{H}_2\text{O}$  photolysis and subsequently resulted in Cr(VI) reduction (Fig. 2). Because the reaction rate was dependent on pH but not on Cr(VI) concentration, reaction (1) may be the rate-determining step for Cr(VI) photo-reduction.



### 3.1.2. Effects of pH and Fe(III) on Cr(VI) photo-reduction

The presence of Fe(III) enhanced the Cr(VI) photo-reduction rate, and the reaction was also favorable at a lower pH. For example, compared to the rapid Cr(VI) reduction at pH 1, more than 31  $\mu\text{M}$  Cr(VI) could still be detected after a 3-h irradiation with Fe(III) addition at pH 2 (Fig. 2). Moreover, as the Fe(III) concentration was increased from 0 to 179.1  $\mu\text{M}$ , the reaction rate constant increased from 0.020 to 0.934  $\mu\text{M min}^{-1}$  at pH 1 and from 0.011 to 0.037  $\mu\text{M min}^{-1}$  at pH 2 (Table 1). Thus, Fe(III) ions play a key role in the photo-reduction of Cr(VI), and the positive effect of Fe(III) on the Cr(VI) photo-reduction rate was more significant at lower pH.

Using the MINTEQA2 program [24], the distributions of Fe(III) species in a solution with various concentrations at pH 1 and 2 were calculated. These are presented in Table 1. The Fe(III) species were determined to be  $\text{Fe}^{3+}$ ,  $\text{Fe}(\text{OH})_2^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{FeCl}_2^+$ , and  $\text{FeCrO}_4^+$ . The  $\text{Fe}^{3+}$  ion is at its highest oxidation state; thus, it is apparently not a reductant for Cr(VI) photo-reduction, ruling out the  $\text{Fe}^{3+}$  ion and its complex with Cr(VI) (i.e.,  $\text{FeCrO}_4^+$ ) as potential reductants for Cr(VI) reduction. The other predominant species are  $\text{Fe}(\text{OH})_2^{2+}$  and  $\text{FeCl}_2^+$ .

Photolysis of  $\text{Fe}(\text{OH})_2^{2+}$  is a well-known reaction, which leads to the production of Fe(II) and OH radicals (reaction (4)) at pH 2.5–4.5

**Table 1**

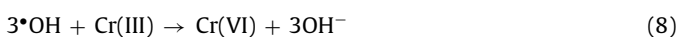
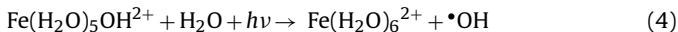
The influence of Fe concentrations on the zero-order rate constant for the photo-reduction of 35.8  $\mu\text{M}$  Cr(VI) at pH 1 and 2

	Fe <sup>a</sup> ( $\mu\text{M}$ )	$k$ ( $\mu\text{M min}^{-1}$ )	Fe <sup>3+</sup> ( $\mu\text{M}$ ) <sup>b</sup>	Fe(OH) <sub>2</sub> <sup>+</sup> ( $\mu\text{M}$ ) <sup>b</sup>	FeCl <sub>2</sub> <sup>+</sup> ( $\mu\text{M}$ ) <sup>b</sup>	FeOH <sub>2</sub> <sup>2+</sup> ( $\mu\text{M}$ ) <sup>b</sup>	FeCrO <sub>4</sub> <sup>+</sup> ( $\mu\text{M}$ ) <sup>b</sup>
pH 1.0	0.0	0.020	–	–	–	–	–
	35.8	0.365	21.4	4.9E–4	13.8	0.57	0.01
	89.5	0.689	53.5	12.1E–4	34.6	1.41	0.02
	179.1	0.934	107.0	24.2E–4	69.2	2.82	0.05
pH 2.0	0.0	0.011	–	–	–	–	–
	35.8	0.033	20.5	0.16	3.3	11.5	0.41
	89.5	0.035	51.3	0.38	8.3	28.5	0.99
	179.1	0.037	102.7	0.76	16.9	56.6	1.91

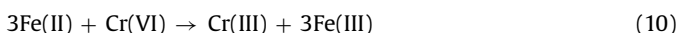
<sup>a</sup> The initial Fe(III) level added.

<sup>b</sup> The distribution of Fe species in the solution was calculated by MINTEQA2 program.

[25–27]. Although the formation of Fe(II) may result in the reduction of Cr(VI), Fe(II) could also be readily oxidized by OH radicals back to Fe(III) (reaction (5)) or perform as a Fenton reagent, leading to the production of OH radicals (reactions (6) and (7)). In particular, OH radicals were proposed as an efficient oxidant for Cr(III) (reaction (8)) [25]; thus, the photolysis of Fe(OH)<sup>2+</sup> and the subsequent formation of OH radicals may actually prevent the photo-reduction reaction of Cr(VI) by increasing the reaction rate in the opposite direction (i.e., Cr(III) oxidation). In this case, the photolysis of Fe(OH)<sup>2+</sup> has a negative effect on Cr(VI) photo-reduction, and the effect is dependent on solution pH. As suggested by Zhang and Bartlett [25], Cr(VI) formation may be maximized at pH 2.5–4.5, while the production of Cr(III) due to Cr(VI) reduction is low.



The potential electron donor for Cr(VI) reduction is FeCl<sup>2+</sup> in the current system. The photochemical reduction of Fe(III) to Fe(II) and the formation of Cl radicals were reported to occur in an acidified solution (reaction (9)) [28]. It was further demonstrated that the optimum pH range of reaction (9) was between 1 and 2. Following Fe(II) formation, Cr(VI) was subsequently reduced (reaction (10)). The reaction order indicated that the overall reaction rate was independent of the Cr(VI) concentration; thus, the rate-determining step may be the photolysis reaction of FeCl<sup>2+</sup> (reaction (9)).



The photolytic products of FeOH<sup>2+</sup> and FeCl<sup>2+</sup> have antagonistic effects on Cr(VI) photo-reduction. It is clear that pH is an important factor controlling Cr transformation by controlling the relative concentrations of FeOH<sup>2+</sup> and FeCl<sup>2+</sup> in the systems. At pH 1, other than Fe<sup>3+</sup>, FeCl<sup>2+</sup> is the major species, and its concentration is 24-fold higher than that of FeOH<sup>2+</sup> at each added Fe(III) concentration. When FeCl<sup>2+</sup> becomes the predominant species, the photolysis of FeCl<sup>2+</sup> (reaction (9)) dominates the competition with the photolysis of FeOH<sup>2+</sup> (reaction (4)) on Cr transformation at pH 1, and its photolytic product facilitates Cr(VI) reduction. Conversely, when the pH of a Fe(III)/Cl-containing solution was increased, more FeOH<sup>2+</sup> was formed and provided a beneficial environment for Cr(III) oxidation. At pH 2, the concentration of FeOH<sup>2+</sup> becomes three-fold greater than that of FeCl<sup>2+</sup> (Table 1). The photolysis of FeOH<sup>2+</sup> (reaction (4)) may become dominant relative to the photolysis of FeCl<sup>2+</sup>, and the production of OH radicals subsequently inhibits Cr(VI) photo-reduction (Fig. 2b).

### 3.1.3. Rate constants of Cr(VI) photo-reduction as influenced by pH and Fe(III)

In the presence of Cl<sup>-</sup>, a slight increase in the rate constant from 0.01 to 0.02 μM min<sup>-1</sup> was observed with decreasing solution pH from 2 to 1 in the absence of Fe(III). With the addition of 35.8 μM Fe(III), the reaction rate increased sharply to 0.365 and 0.033 μM min<sup>-1</sup> at pH 1 and 2, respectively, which explained the 12-fold increments of Cr(VI) reduction with decreasing pH from 2 to 1 (Table 1). The increase resulted from an increase in FeCl<sup>2+</sup> concentration from 3.30 to 13.8 μM and from a decrease in Fe(OH)<sup>2+</sup> concentration from 11.5 to 0.56 μM. When the initial addition of Fe(III) was increased to 179.1 μM, the rate constants for Cr(VI) reduction increased from 0.037 to 0.934 μM min<sup>-1</sup> with decreasing

pH from 2 to 1 (Table 1). Thus, this result demonstrated again that the effect of changing pH on Cr(VI) reduction in the presence of Fe(III) and Cl<sup>-</sup> is the result of a combination of the promoting and inhibiting reactions induced by the photolytic products of FeCl<sup>2+</sup> and Fe(OH)<sup>2+</sup>, respectively. In addition, the increment of the Cr(VI) reduction rate gradually decreased with increasing initial Fe(III) concentration (Table 1). This result is probably due to an increase in the rate of the back reaction due to the gradual build-up of reaction products over the course of irradiation [28].

Because HCl was used to adjust solution pH, the concentrations of Fe–Cl complexes were different at pH 1 and 2. To clarify further the real effect of pH on Cr(VI) photo-reduction, a corresponding experiment was conducted by holding the concentration of FeCl<sup>2+</sup> approximately constant. This was done by adding a specific amount of Fe(III) to the pH 1 or 2 solution based on the simulated results of the MINTEQA2 program. The results, presented in Fig. 3a, show that Cr(VI) photo-reduction was strongly inhibited at pH 2. That is, even with the same concentration of FeCl<sup>2+</sup> (~14 μM), a large decrease in Cr(VI) photo-reduction was observed at a higher pH value (i.e., pH 2). Moreover, with the adjustment of the FeCl<sup>2+</sup> concentrations from 0 to near 14 μM, a slight increase in the Cr(VI) reduction rate from 0.01 to 0.04 μM min<sup>-1</sup> was observed at pH 2 (Fig. 3b). These results indicate that Fe(III) led to more efficient Cr(VI) photo-reduction at a low pH in the presence of Cl<sup>-</sup>. With the same Fe(III) and Cl<sup>-</sup> concentrations, a higher relative concentration of Fe(OH)<sup>2+</sup>, which was photolyzed to form OH radicals and

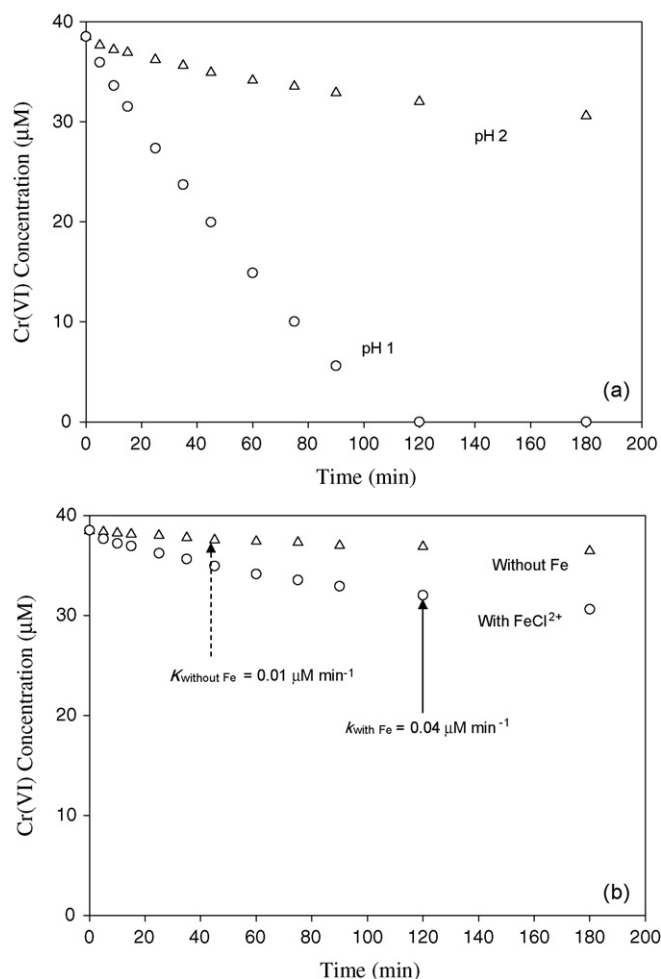
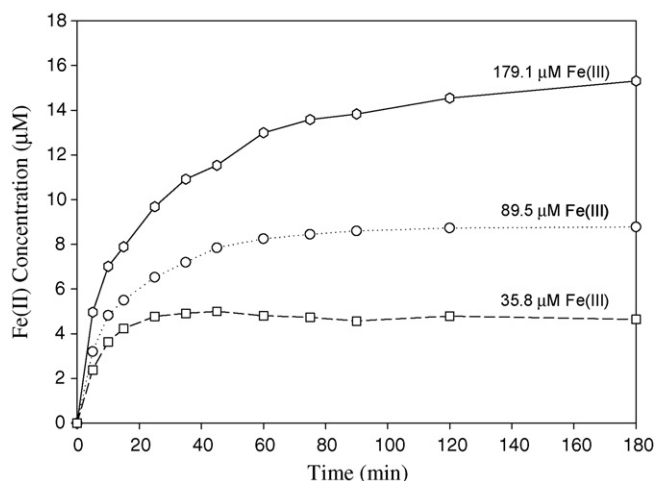


Fig. 3. Light-induced 38.5 μM Cr(VI) reduction (a) in the presence of 14 μM FeCl<sup>2+</sup> at pH 1 and pH 2 and (b) in the absence or presence of 14 μM FeCl<sup>2+</sup> at pH 2.



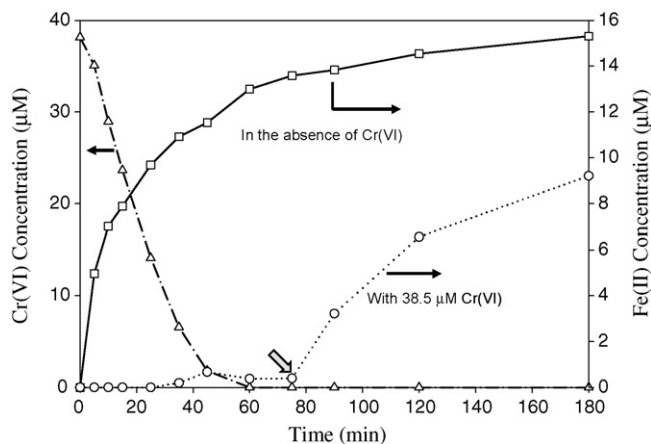


**Fig. 4.** Influence of initial Fe(III) concentrations (35.8–179.1  $\mu\text{M}$ ) on light-induced Fe(II) formation in a solution with 0.1 M  $\text{Cl}^-$  at pH 1.

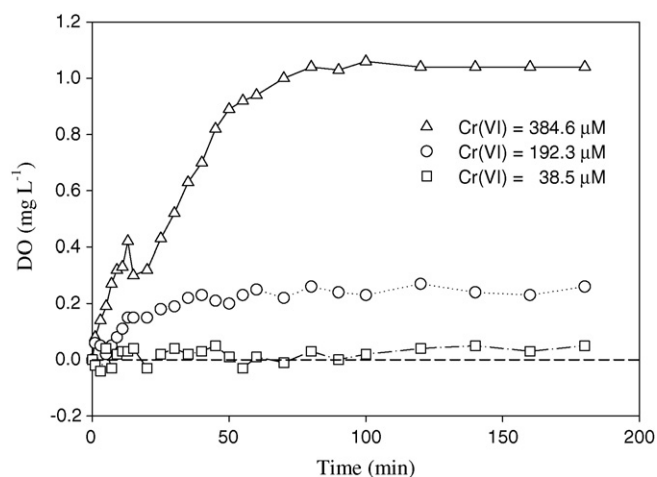
subsequently re-oxidized the photo-reduction products, i.e., Cr(III), may explain the low reaction rate at pH 2.

### 3.2. Evidence for the proposed mechanisms

As demonstrated above, Cr(VI) photo-reduction was greatly enhanced by the addition of Fe(III) to a solution with  $\text{Cl}^-$ . This was due to Fe(II) formation, as proposed by Lim et al. [28], and it was further shown here in Fig. 4. The Fe(II) concentration increased with the addition of Fe(III). A low increase in Fe(II) concentration was observed with the addition of 35.8  $\mu\text{M}$  Fe(III), a result that is consistent with the lower rate of Cr(VI) reduction (Fig. 2a). Since Fe(II) oxidation by Cr(VI) was extremely rapid at low pH, no Fe(II) could be detected when Cr(VI) was present in the solution (Fig. 5). Therefore, in Fig. 4, Fe(II) was measured under irradiation without the addition of Cr(VI). Although an observable amount of Fe(II) was detected when the added Cr(VI) was nearly reduced, the rate of Fe(II) production was lower than in the system without Cr(VI) addition (Fig. 5). The reason for this is unclear. We hypothesized that the re-oxidization of Cr(III) back to Cr(VI) by trace  $\cdot\text{OH}$  or  $\cdot\text{Cl}$  radicals, which indirectly consumed the produced Fe(II), may have contributed to the result.



**Fig. 5.** Influence of 38.5  $\mu\text{M}$  Cr(VI) on Fe(II) formation in a solution with 179.1  $\mu\text{M}$  Fe(III) and 0.1 M  $\text{Cl}^-$  at pH 1. The open arrow indicates the point of Cr(VI) disappearance accompanied by an apparent increase in Fe(II).



**Fig. 6.** Changes in dissolved oxygen (DO) as a function of irradiation time with various concentrations of Cr(VI) (38.5–384.6  $\mu\text{M}$ ) with 0.1 M  $\text{Cl}^-$  at pH 1.

The detection of dissolved oxygen (DO) content as a function of irradiation time is shown in Fig. 6. In the presence of  $\text{Cl}^-$  with Fe(III), the photolysis of the Fe–Cl complex mainly controlled the Cr(VI) reduction. Therefore, Cr(VI) reduction induced by  $\text{H}_2\text{O}$  photolysis, releasing  $\text{O}_2$  based on reaction (2), was low and not readily observed under these conditions. Although we proposed that the product of  $\text{H}_2\text{O}$  photolysis may dominate Cr(VI) photo-reduction in the presence of  $\text{Cl}^-$  electrolytes without Fe(III), the low Cr(VI) reduction rate (Fig. 2) explained the unobservable change in dissolved  $\text{O}_2$  (Fig. 6). However, an observable change in dissolved  $\text{O}_2$  was found when the initial Cr(VI) concentration was brought to 384.6  $\mu\text{M}$  or higher (Fig. 6). These results suggest that Cr(VI) reduction could indeed be promoted by a redox mechanism through photolysis of  $\text{H}_2\text{O}$  molecules as shown in reaction (1). Nonetheless, the reaction is readily overwhelmed by the rapid photolysis of the Fe–Cl complex, limiting its overall contribution to Cr(VI) reduction.

## 4. Conclusions

Under irradiation, the photolytic products of  $\text{H}_2\text{O}$  and  $\text{FeCl}_2^+$  were the electron donors for Cr(VI) reduction in systems without and with the presences of Fe(III) and  $\text{Cl}^-$ , respectively. Because the Cr(VI) photo-reduction reaction rate was independent of Cr(VI) concentration and higher at lower pH, the rate-determining step was, therefore, proposed to be the photolysis of  $\text{H}_2\text{O}$  or  $\text{FeCl}_2^+$ . With the addition of Fe(III), the Cr(VI) photo-reduction rate slowed as the pH was increased from 1 to 2. At pH 2,  $\text{FeOH}^{2+}$  is the predominant species of Fe, and its photolytic product, OH radicals, is an oxidant of Cr(III). Therefore, Cr(VI) photo-reduction was greatly inhibited in a solution with a higher pH value. This study suggests a potential pathway for reductive transformation of Cr(VI) to Cr(III) after an acidic electroplating waste containing Cr(VI) and Fe(III) is discharged to an environment in sunlight. In addition, a remediation technique may be developed by applying light energy directly to the electroplating wastewater, which commonly contains Fe(III),  $\text{Cl}^-$ , and Cr(VI), to induce reductive transformation of Cr(VI) to less harmful Cr(III).

## Acknowledgement

This work was financially supported by the National Science Council, ROC under Project No. 95-2313-B-005-047-MY3 and, in part, by the Ministry of Education, R.O.C. under the ATU plan.

## References

- [1] L.M. Calder, Chromium contamination of groundwater, in: J.O. Nriagu, E. Nieboer (Eds.), *Chromium in the Natural and Human Environments*, John Wiley and Sons, New York, 1988, pp. 215–229.
- [2] Y.M. Tzou, R.H. Loeppert, M.K. Wang, Light-catalyzed Cr(VI) reduction by organic compounds and soil minerals, *J. Environ. Qual.* 32 (2003) 2076–2084.
- [3] Y.M. Tzou, R.H. Loeppert, M.K. Wang, Organic ligand-enhanced photochemical reduction and immobilization of chromium(VI) on TiO<sub>2</sub> particles in acidic aqueous media, *Soil Sci.* 169 (2004) 413–422.
- [4] J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, *Environ. Pollut.* 107 (2000) 263–283.
- [5] M. Loutit, P. Bremer, J. Aislabie, *The Significance of the Interactions of Chromium and Bacteria in Aquatic Habitats*, John Wiley & Sons, New York, 1988, pp. 317–334.
- [6] M.A. Turner, R.H. Rust, Effects of chromium on growth and mineral nutrition of soybeans, *Soil Sci. Soc. Am. Proc.* 35 (1971) 755–758.
- [7] D.A. Holdway, The toxicity of chromium to fish, in: J.O. Nriagu, E. Nieboer (Eds.), *Chromium in the Natural and Human Environments*, John Wiley & Sons, New York, 1988, pp. 360–397.
- [8] Y.M. Tzou, Y.R. Chen, M.K. Wang, Chromate sorption by acidic and alkaline soils, *J. Environ. Sci. Health A* 33 (1998) 1607–1630.
- [9] S.A. Katz, H. Salem, The toxicology of chromium and its compounds, in: S.A. Katz, H. Salem (Eds.), *The Biological and Environmental Chemistry of Chromium*, VCH Publishers, New York, 1994, pp. 65–119.
- [10] D.W. Blowes, C.J. Ptacek, J.L. Jambor, In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: laboratory studies, *Environ. Sci. Technol.* 31 (1997) 3348–3357.
- [11] M.L. Peterson, G.E. Brown Jr, G.A. Parks, Direct XAFS evidence for heterogeneous redox reaction at the aqueous chromium/magnetite interface, *Colloids Surf.* 107 (1996) 77–88.
- [12] S.E. Fendorf, G. Li, Kinetics of chromate reduction by ferrous iron, *Environ. Sci. Technol.* 30 (1996) 1614–1617.
- [13] B. Deng, A.T. Stone, Surface-catalyzed chromium(VI) reduction: reactivity comparisons of different organic reductants and different oxide surfaces, *Environ. Sci. Technol.* 30 (1996) 2484–2494.
- [14] A. Ozer, H.S. Altundogan, M. Erdemli, A study of the Cr(VI) removal from aqueous solutions by steel wool, *Environ. Pollut.* 97 (1997) 107–112.
- [15] R.R. Patterson, S. Fendorf, Reduction of hexavalent chromium by amorphous iron sulfide, *Environ. Sci. Technol.* 31 (1997) 2039–2044.
- [16] M.L. Peterson, A.F. White, G.E. Brown, G.A. Parks, Surface passivation of magnetite by reaction with aqueous Cr(VI): XAFS and TEM results, *Environ. Sci. Technol.* 31 (1997) 1573–1576.
- [17] C.A. Johnson, L. Sigg, L.U. Lindauer, The chromium cycle in a seasonally anoxic lake, *Limnol. Oceanogr.* 37 (1992) 315–321.
- [18] P.R. Wittbrodt, C.D. Palmer, Reduction of Cr(VI) in the presence of excess soil fulvic acid, *Environ. Sci. Technol.* 29 (1995) 255–263.
- [19] EPA, The investigation in effects of the irrigation water and sediment on the heavy metal contaminate of rice land, EPA-94-GA12-03-A187, Taiwan, 2006.
- [20] C.L. Hsu, S.L. Wang, Y.M. Tzou, Photocatalytic reduction of Cr(VI) in the presence of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> electrolytes as influences by Fe(III), *Environ. Sci. Technol.* 41 (2007) 7907–7914.
- [21] V. Orescanin, L. Mikelic, S. Lulic, K. Nad, N. Mikulic, M. Rubcic, G. Pavlovic, Purification of electroplating wastewaters utilizing waste by-product ferrous sulfate and wood fly ash, *J. Environ. Sci. Health, Part A* 39 (2004) 2437–2446.
- [22] A.D. Eaton, L.S. Clesceri, A.E. Greenberg, *Standard Methods for the Examination of Water and Wastewater*, APHA, Washington, DC, 1995, p. 1325.
- [23] R.J. Bartlett, B.R. James, Chromium, in: D.L. Sparks (Ed.), *Methods of Soil Analysis*, SSSA, Madison, WI, 1996, pp. 683–701.
- [24] J.D. Allison, D.S. Brown, K.J. Novo-Gradac, MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, U.S. Environmental Protection Agency, Athens, GA, 1990, EPA/600/3-91/021.
- [25] H. Zhang, R.J. Bartlett, Light-induced oxidation of aqueous chromium(III) in the presence of iron(III), *Environ. Sci. Technol.* 33 (1999) 588–594.
- [26] V. Balzani, V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, London, 1970, pp. 145–184.
- [27] B. Faust, J. Hoigne, Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in cloud, fog, and rain, *Atmos. Environ.* 24 (1990) 79–89.
- [28] M. Lim, K. Chiang, R. Amal, Photochemical synthesis of chlorine gas from iron(III) and chloride solution, *J. Photochem. Photobiol. Chem.* 183 (2006) 126–132.