

## Influence of inorganic anion on Cr(VI) photo-reduction in the presence of ferric ion

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### Abstract

Photo-reduction of Cr(VI) in a solution with single or multi-inorganic anions was evaluated. The results show that 38.5  $\mu\text{M}$  Cr(VI) is photo-reduced in the presence of  $\text{NO}_3^-$  at pH 1. The photolysis of  $\text{NO}_3^-$ , producing  $\text{NO}_2^-$  or  $\text{H}_2\text{O}_2$ , may contribute to Cr(VI) reduction. The addition of 0.001–0.1 M chlorite to  $\text{NO}_3^-$  enhanced Cr(VI) photo-reduction when 35.8  $\mu\text{M}$  Fe(III) was present. This enhancement was the combinative result of photolysis of  $\text{NO}_3^-$  and Fe–Cl complexes, leading to the formation of  $\text{NO}_2^-$  and Fe(II), respectively, for Cr(VI) reduction. On the contrary, a significant decrease in Cr(VI) photo-reduction was observed with the addition of  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ . This decrease was due to their strong competition with Fe(III) from  $\text{Cl}^-$ , resulting in a marked decrease in the concentrations of Fe–Cl complexes. The results suggest that a direct irradiation of acidic wastewaters containing  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and Fe(III) is a feasible strategy for eliminating Cr(VI).

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**Keywords:** Photolytic reaction; Fe–Cl complex; Inorganic anion

### 1. Introduction

Chromium is commonly found as a contaminant in water and soil as a result of extensive use in industry. Chromium exists in two major oxidation states: Cr(III) and Cr(VI). An interchange of these two Cr species can occur, depending on the redox potential and the pH of the medium. Chromium(III) occurs naturally; a dietary supplement of 50–200  $\mu\text{g}$  of Cr(III) per day is recommended for people with adult-onset diabetes or insulin resistance [1,2]. Trivalent Cr is readily hydrolyzed in solution at pH values above 5.5, leading to the formation of chromium hydroxide ions such as  $\text{Cr}(\text{OH})_2^{2+}$  and  $\text{Cr}(\text{OH})_2^+$ . Trivalent forms of Cr ions carry a positive charge and are readily adsorbed on negatively charged soil particles; thus, Cr(III) is not very mobile in soil [3]. By contrast, Cr(VI) is generally produced by industrial activities and is commonly found at contaminated sites. Chromium(VI) is of interest to scientists because of its high toxicity to both plants

[4] and animals [5] as well as its carcinogenicity to humans [6]. Due to electrical repulsion, the anionic type of Cr(VI) is barely retained by negatively charged clay minerals in soils. This property expedites its mobility in the soil profile and can potentially represent a detrimental impact on groundwater. Therefore, direct removal of Cr(VI) from contaminated sites for further treatment or the conversion of Cr(VI) to Cr(III) on-site is the alternatives for attenuating Cr toxicity to the ecosystem.

The separation or extraction of Cr(VI) from Cr(VI)-contaminated soils and sediments with a fine texture or passive structure can be an incomplete or a long-term process, and the cost of Cr(VI) removal from these sites can be high. On the other hand, the addition of some reductants, such as Fe(II), dithionite, and  $\text{H}_2\text{S}$ ,  $\text{FeS}_x$  [7–11], into the Cr(VI)-contaminated medium followed by immobilizing the redox products on-site is considered to be a feasible strategy for eliminating Cr(VI). However, this technique usually leads to the accumulation of redox by-products as coating materials or discrete solids in soil pores, resulting in a decrease of aeration or water movement in the soil profile. In addition, these by-products are amorphous and have large surface areas, which may serve as new adsorption sites

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for non-reducible Cr(VI) or other toxic contaminants [12]. As a result, the integral function of an ecosystem can be significantly spoiled by the addition of a great number of reductants. Therefore, the development of a clean and efficient technique is still necessary because none of the above-mentioned techniques has achieved much success for remediating Cr(VI)-contaminated sites.

Unlike inorganic reductants, naturally occurring organic compounds have been recognized as benign reductants of Cr(VI) in an acid medium. Nonetheless, the results of previous studies suggest that the rate of Cr(VI) reduction by organics was relatively low in the pH range of 4–8 [13,14]. To accelerate the reduction of Cr(VI) by organics, ultraviolet/visible light, including sunlight, has been applied in laboratory-scale studies in attempts to overcome the energy barrier for Cr(VI) reduction [15,16]. In addition, it has been suggested that the presence of ferric ions may expedite Cr(VI) photo-reduction by organics due to the enhancement of electron transfer between Cr(VI) and organics through the Fe(III)/Fe(II) redox couple [17,18]. Unfortunately, light-induced Cr transformation is not always beneficial for Cr(VI) reduction. Zhang and Bartlett [19] proposed that light would induce Cr(III) oxidation in an organic-free solution with Fe(III) and suggested an optimal pH range of 3.2–4.4 for the reaction, and they proposed that the photolysis of  $\text{Fe}(\text{OH})^{2+}$ , leading to OH radical formation, was responsible for Cr(III) oxidation. Thus, other than Mn hydr(o)oxides, Fe(III)-induced Cr(III) photo-oxidation provides an alternative for the conversion of Cr(III) to toxic Cr(VI). Accordingly, the results of these studies suggested that the species interacted with Fe(III) would influence Cr abiotic transformation under illumination.

In preliminary studies, we found that the presence of Fe(III) and inorganic anions had a strong effect on Cr photo-transformation. For instance,  $\text{Fe}(\text{OH})^{2+}$  facilitated Cr(III) oxidation, but a tendency to increase on Cr(VI) photo-reduction

was observed in the presence of  $\text{FeCl}^{2+}$ . Furthermore, Fe(III) exhibited a very limited effect on Cr(VI) photo-reduction when indifferent electrolytes such as  $\text{NO}_3^-$  were present. Wastewaters, particularly from electroplating industries, may contain different kinds of anions and cations, including Cr(VI) and Fe(III). The influence of anions on Cr(VI) photo-reduction in the presence of Fe(III) needs to be evaluated if the photo-catalytic technique is selected for treating Cr(VI)-containing wastewaters. That is, the elucidation of the details of Cr transformation as influenced by anions and Fe(III) may be helpful to enhance the efficiency of a photo-involved technique.

The work seeks to obtain a better understanding of the transformation and transportation of Cr once it is released into the environment under sunlight. The objectives of this study are to investigate the kinetic results of Cr transformation in a solution with single or mixed anions in the presence of Fe(III); clarify the details of the reaction mechanism; and evaluate the potential use of a photo-catalytic technique to treat Cr(VI)-containing wastewater with multiple anions and Fe(III).

## 2. Materials and methods

### 2.1. Reagents

The chemicals and reagents used in this work were all of analytical grade. All solutions were prepared with 18 M $\Omega$  Millipore water. All glassware was cleaned with 6 M HCl, followed by thorough rinsing with 18 M $\Omega$  Millipore water.

### 2.2. The reactor

Each photo-catalytic experiment was conducted in a 500 mL, double-walled water-jacketed reactor. A 100 W, medium-pressure mercury UV lamp in a quartz well was placed in the

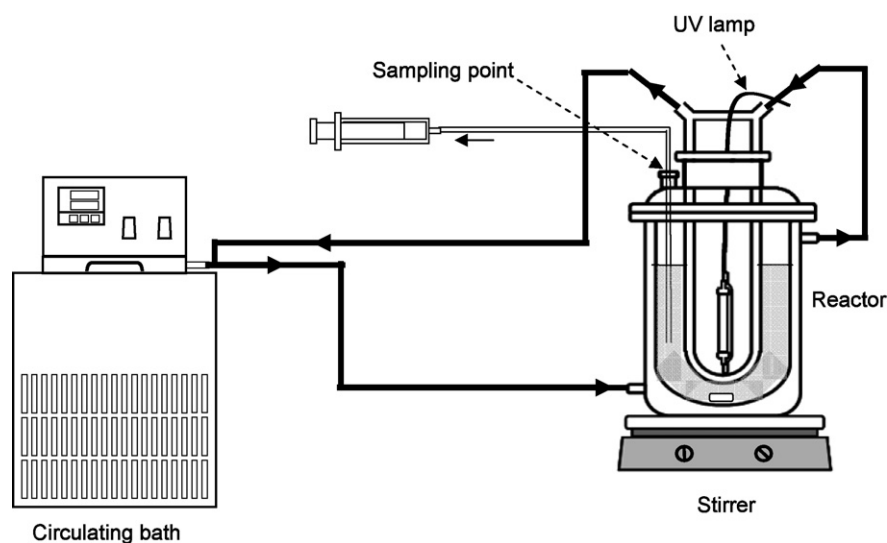


Fig. 1. Schematic illustration of the setup of the photolytic reactor consisting of a centered UV lamp, a close-loop waterbath, and a plastic tube connecting to a syringe for extracting sample solution.

center of the reactor (Fig. 1). The well and the reactor were connected to a circulating waterbath to maintain the temperature at  $24.5 (\pm 0.5) ^\circ\text{C}$ ; this temperature is suggested by the manufacturer (ACE Glass Incorporation) for lamp ignition. To obtain a stable emission, the UV lamp was switched on at least 20 min before conducting the photo-experiments. The reactor was covered with Al foil and placed inside a stainless steel chamber throughout the experiments to avoid any possible interference by natural or artificial light. One end of the plastic tube was inserted into the reactor with the other end connected to a syringe to extract the sample solution (Fig. 1). The tube was pumped and purged several times before sample collection and emptied before the next run.

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

Stock solutions of  $100 \text{ mg L}^{-1}$  Cr(VI) and  $50 \text{ mg L}^{-1}$  Fe(III) were prepared by dissolving  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{Fe}(\text{NO}_3)_3$ , respectively, in  $0.1 \text{ M HNO}_3$ . The photo-catalytic reaction of  $38.5 \mu\text{M}$  Cr(VI) was investigated by adding appropriate amounts of stock solutions to  $0.1 \text{ M HNO}_3$  (i.e. at pH 1) with and without  $35.8 \mu\text{M}$  Fe(III). No buffer was needed to maintain a constant pH, since the change of pH was insignificant ( $<0.02$  pH unit) during the experiments. A  $5 \text{ mL}$  aliquot was withdrawn before each run for determining the initial concentration of Cr(VI) or Fe(III). After the photo-catalytic experiment began,  $5 \text{ mL}$  samples of solution were withdrawn from the reactor periodically, and the concentrations of Cr(VI) were measured by the diphenylcarbazide (DPC) method [20]. Control experiments were conducted using the same experimental settings but without UV light.

In another set of experiments, the influence of  $0.001$ – $0.1 \text{ M Cl}^-$  (as KCl) on photo-reduction of  $38.5 \mu\text{M}$  Cr(VI) was first evaluated in  $0.1 \text{ M HNO}_3$  with  $35.8 \mu\text{M}$  Fe(III). Then,  $100 \text{ mM}$  anionic ligands ( $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{SO}_4$ ) or indifferent anions ( $\text{KClO}_4$ ) were added to the solution with  $10 \text{ mM Cl}^-$ ,  $38.5 \mu\text{M}$  Cr(VI), and  $35.8 \mu\text{M}$  Fe(III) in  $0.1 \text{ M HNO}_3$ . The influence of the competition among the anions to Fe(III) on Cr(VI) photo-reduction was investigated. The remaining procedures, such as sample extraction and measurement, were conducted as previously described.

### 2.4. The reduction of Cr(VI) by $\text{NO}_2^-$

Our preliminary experiments showed that Cr(VI) was photo-reduced in the presence of  $\text{NO}_3^-$  even when Fe(III) was absent. We attributed this to photolysis of  $\text{NO}_3^-$ , leading to the production of  $\text{NO}_2^-$ , which served as a reductant for Cr(VI) reduction. To confirm this reaction,  $0.5 \text{ mM NO}_2^-$  (as  $\text{KNO}_2$ ) was added to  $96.2 \mu\text{M}$  Cr(VI) in  $0.1 \text{ M HNO}_3$ . Since  $\text{NO}_2^-$  affects the measurement of Cr(VI) by the DPC method [21], each extracted sample was transferred directly to a  $1 \text{ cm}$  path-length optical cell, and wavelength scans were conducted from  $200$  to  $600 \text{ nm}$ . The changes of intensity of the Cr(VI) absorption peak at  $\sim 350 \text{ nm}$  were recorded and plotted as a function of irradiation time [15,22] to obtain a qualitative result for Cr(VI) reduction by  $\text{NO}_2^-$ .

### 2.5. Analytical methods

Concentrations of Cr(VI) were determined by the DPC method, measuring absorbance at  $540 \text{ nm}$  except in the presence of  $\text{NO}_2^-$  [21]. Although the potential interference of Fe(III) in the DPC method has been proposed [21], the variation in the standard solutions of Cr(VI) before and after the addition of  $35.8 \mu\text{M}$  Fe was found to be less than  $\pm 1\%$ . Thus, the interference of Fe(III) in the Cr(VI) measurement was ignored. The concentrations of Fe(II) and Fe(III) were determined using the 1,10-phenanthroline method measuring absorbance at  $510 \text{ nm}$  with a Cary 50 UV–vis spectrophotometer. Ferrous ions were determined by reaction with 1,10-phenanthroline in the absence of hydroxylamine. Because 1,10-phenanthroline cannot form a complex with Fe(III), hydroxylamine was added to the samples to reduce Fe(III) to Fe(II) in order to obtain the total concentration of Fe. The concentration of Fe(III) was determined by subtracting the concentration of Fe(II) from the corresponding total concentration of Fe.

## 3. Results and discussion

### 3.1. Cr(VI) photo-reduction in $0.1 \text{ M NO}_3^-$ solution

As shown in Fig. 2, no significant decrease in the concentration of Cr(VI) with a prolonged reaction time was observed in the absence of light. In contrast,  $38.5 \mu\text{M}$  Cr(VI) was rapidly reduced when exposed to light. The reaction followed zero-order kinetics with a rate constant of  $0.099 \mu\text{M min}^{-1}$ . The photolysis of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  [23,24] as indicated in reaction (1) may be responsible for Cr(VI) reduction because of the positive value of the redox potential in reaction (2) [25].

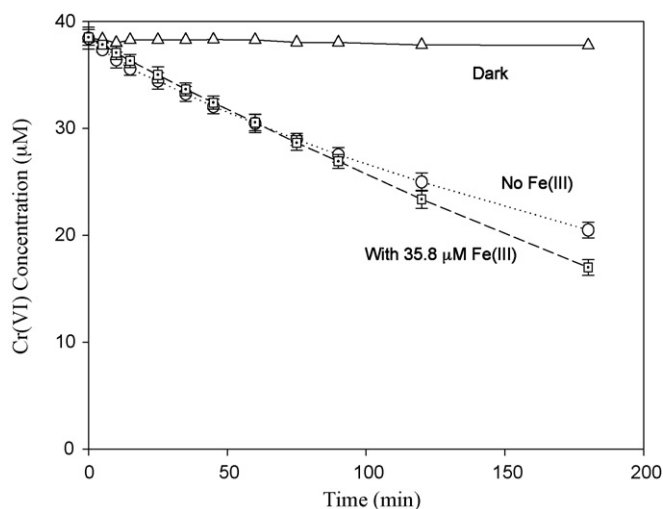
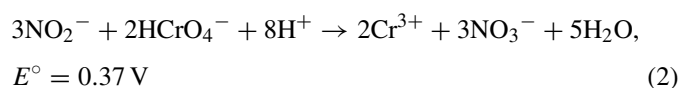
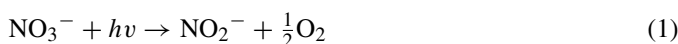


Fig. 2. The photo-reduction of  $38.5 \mu\text{M}$  Cr(VI) in the presence of  $0.1 \text{ M NO}_3^-$  at pH 1 with or without  $35.8 \mu\text{M}$  Fe(III).

Because the photolytic product of  $\text{NO}_2^-$  was consumed rapidly by Cr(VI), the measurement of  $\text{NO}_2^-$  and the stoichiometric evaluation of reaction (2) was not possible. To provide a direct experiment evidence of reaction (2), 0.5 mM  $\text{NO}_2^-$  was added to 38.5  $\mu\text{M}$  Cr(VI) in 0.1 M  $\text{NO}_3^-$ . The reduction of Cr(VI) by  $\text{NO}_2^-$  was examined through observation of the changes in the absorbance at  $\sim 350$  nm because of the interference of  $\text{NO}_2^-$  with color development using the DPC method [21]. Cr(VI) has a strong UV/visible spectrum with a very large molar absorption coefficient ( $\epsilon$ ) of  $1550 \text{ M}^{-1} \text{ cm}^{-1}$  at 350 nm [26]. Nonetheless, the absorption spectra of  $\text{NO}_2^-$  contain a relatively weak  $n \rightarrow \pi^*$  band at 360 nm ( $\epsilon = 22.5 \text{ M}^{-1} \text{ cm}^{-1}$ ) [27]. Therefore, upon the reduction of Cr(VI) by  $\text{NO}_2^-$ , the decrease in absorbance at  $\sim 350$  nm results predominantly from a decrease in the concentration of Cr(VI), indicating Cr(VI) reduction.

Fig. 3a shows a decrease in the intensity of the spectra measured at  $\sim 350$  nm with a prolonged reaction time. Cr(VI) reduction by  $\text{NO}_2^-$  was not readily observed from the spectra because  $\text{NO}_3^-$  formation through reaction (2) may be greatly

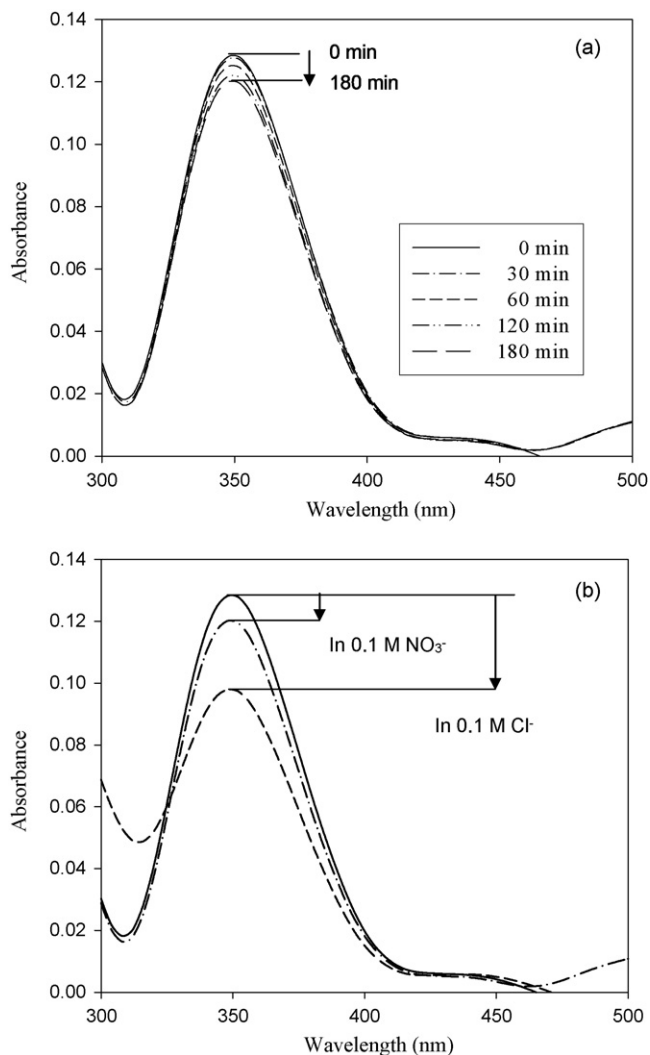
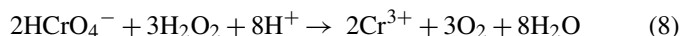
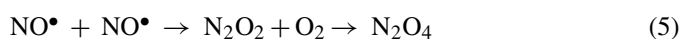


Fig. 3. The decrease in the intensity of spectra measured at  $\sim 350$  nm with 0.5 mM  $\text{NO}_2^-$  and 96.2  $\mu\text{M}$  Cr(VI) (a) in 0.1 M  $\text{NO}_3^-$  with a prolonged reaction time and (b) in 0.1 M  $\text{NO}_3^-$  or 0.1 M  $\text{Cl}^-$  after 180 min at pH 1.

inhibited in the presence of 0.1 M  $\text{NO}_3^-$ . However, a significant decrease in absorbance at 350 nm was observed after 3 h of reaction when 0.1 M  $\text{Cl}^-$  replaced  $\text{NO}_3^-$  as the electrolyte (Fig. 3b). These results demonstrate clearly that Cr(VI) reduction by  $\text{NO}_2^-$  resulting from the photolysis of  $\text{NO}_3^-$  is a possible pathway for detoxifying Cr(VI) in solution.

Although  $\text{NO}_2^-$  is capable of reducing Cr(VI) in the dark, Cr(VI) disappears more rapidly when the  $\text{NO}_2^-$ -containing solution is exposed to light (Fig. 4). The photolysis of  $\text{NO}_2^-$  (reactions (3)–(6)) [27] results in the formation of  $\text{H}_2\text{O}_2$  (reaction (7)) [19,28], which may lead to rapid reduction of Cr(VI) (reaction (8)) [29]. The pathways are given below:



The influence of Fe(III) on Cr(VI) photo-reduction in 0.1 M  $\text{NO}_3^-$  solution was shown in Fig. 2. Cr(VI) photo-reduction followed zero-order kinetics upon the addition of 35.8  $\mu\text{M}$  Fe(III), with a slight increase of reaction rate from 0.099 to 0.121  $\mu\text{M min}^{-1}$ . This might be the result of the production of Fe(II) ( $\sim 1.06 \mu\text{M}$  measured in the absence of Cr(VI) at 180 min), resulting from the photolysis of  $\text{H}_2\text{O}$  (reaction (9)). In addition, we found that less than 1.5  $\mu\text{M}$  Fe(II) could be produced after irradiation for 3 h, even when 179.1  $\mu\text{M}$  Fe(III) was added initially. Therefore, it is clear that Fe(III) influences slightly Cr(VI) photo-reduction in the presence of  $\text{NO}_3^-$ , probably due to the lack of a strong interaction between Fe(III) and  $\text{NO}_3^-$ . Although the reduction of Cr(VI) by Fe(II) was rapid at

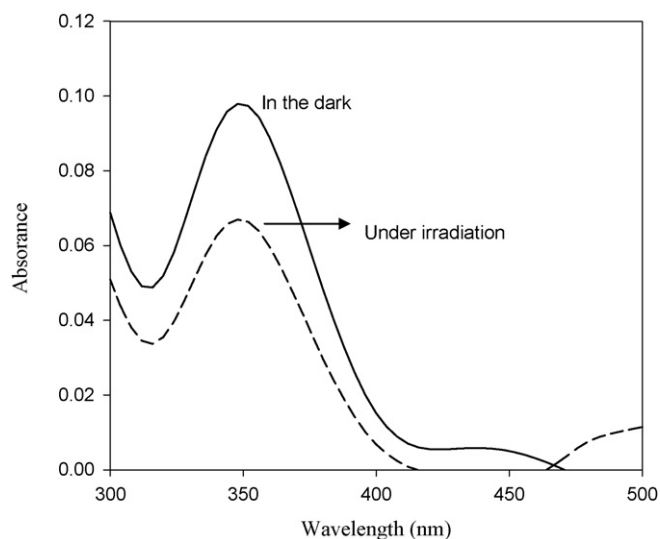


Fig. 4. Comparison of the decrease in intensity of the spectra at  $\sim 350$  nm measured in the dark or under light in a solution with 0.5 mM  $\text{NO}_2^-$  and 96.2  $\mu\text{M}$  Cr(VI).



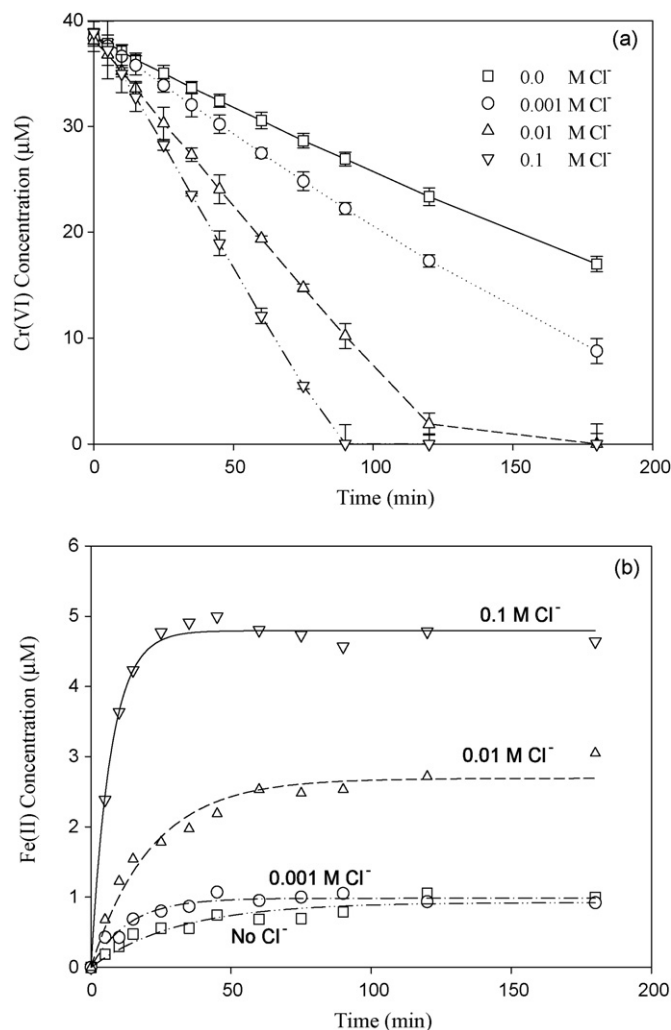
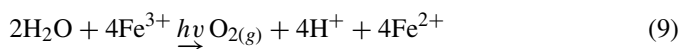


Fig. 5. (a) Photo-reduction of 38.5  $\mu\text{M}$  Cr(VI) with the addition of 0.001–0.1 M  $\text{Cl}^-$  in the presence of 35.8  $\mu\text{M}$  Fe(III) and 0.1 M  $\text{NO}_3^-$  at pH 1 and (b) influence of  $\text{Cl}^-$  concentration on the kinetic formation of Fe(II) measured in the absence of Cr(VI) with 0.1 M  $\text{NO}_3^-$  at pH 1.

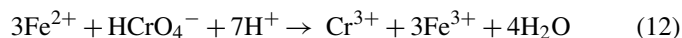
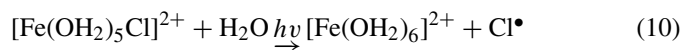
acidic pH, the redox reaction does not significantly contribute to Cr(VI) reduction due to a low Fe(II) production rate through reaction (9).



### 3.2. Effects of $\text{Cl}^-$ on Cr(VI) photo-reduction in the presence of 0.1 M $\text{NO}_3^-$ and Fe(III)

Fig. 5 shows that Cr(VI) photo-reduction was greatly enhanced when  $\text{Cl}^-$  was added to a solution with Fe(III) and

$\text{NO}_3^-$ . The rate of Cr(VI) photo-reduction increased with the increase in initial concentration of  $\text{Cl}^-$  from 0.001 to 0.1 M. For example, 38.5  $\mu\text{M}$  Cr(VI) was reduced completely within 90 min with 0.1 M  $\text{Cl}^-$ ; however, more than 15  $\mu\text{M}$  Cr(VI) was still present in the solution after 180 min with 0.001 M  $\text{Cl}^-$  (Fig. 5a). The results demonstrate that the addition of  $\text{Cl}^-$  promoted the overall photo-reduction of Cr(VI). The results are consistent with our previous works with the addition of various concentrations of Fe(III) [27]. In addition, we found no observable change of Cr(VI) concentration when  $\text{Cl}^-$  was added to a solution of  $\text{NO}_3^-$  in the absence of Fe(III). Therefore, we speculated that the rapid disappearance of Cr(VI) upon the addition of  $\text{Cl}^-$  might be due to the formation of Fe–Cl complexes when Fe(III) is present. Upon the photolysis of  $\text{FeCl}^{2+}$  (reaction (10)),  $\text{Fe}^{2+}$  and  $\text{Cl}_2^{\bullet-}$  were produced rapidly at acidic pH (reaction (11)) [30]. Consequently, Cr(VI) was reduced rapidly by  $\text{Fe}^{2+}$  (reaction (12)). The  $\text{Cl}_2^{\bullet-}$  forms molecular chlorine or reacts with Fe(II) back to  $\text{Cl}^-$  (reaction (14), see below).



Reaction (10) suggests that Fe(II) formation results from the photolysis of Fe–Cl complexes; thus, raising the concentrations of the Fe–Cl complexes enhances the formation of Fe(II) and the subsequent photo-reduction of Cr(VI). With an increase in initial concentration of  $\text{Cl}^-$  from 0.001 to 0.1 M, calculation of the distribution of Fe species using the MINTQA2 program [31] suggested a corresponding increase in the percentage of Fe–Cl complexes from 0.62 to 35.2. The rate of Cr(VI) photo-reduction was greatly enhanced (Fig. 5a, Table 1) due to the significant increase in Fe–Cl complexes with increasing concentrations of  $\text{Cl}^-$ , leading to the production of more Fe(II) ions (Fig. 5b). Nonetheless, the amount of Fe(II) formed was not correlated stoichiometrically to that of Cr(VI) reduction because the measurement of Fe(II) was conducted in the absence of Cr(VI). Even if the rate of Cr(VI) photo-reduction increased with increasing concentrations of  $\text{Cl}^-$  (Table 1), the photo-reduction of Cr(VI) still followed zero-order kinetics, indicating that the reaction mechanism does not depend on the concentration of  $\text{Cl}^-$ .

### 3.3. Effect of other anions on Cr(VI) photo-reduction with Fe–Cl complexes in 0.1 M $\text{NO}_3^-$

Previous results indicated that Fe–Cl complexes would enhance Cr(VI) photo-reduction in 0.1 M  $\text{NO}_3^-$ . However,

Table 1  
The influences of inorganic anions on the zero-order kinetic constants of photo-reduction of 38.5  $\mu\text{M}$  Cr(VI) in the presence of 0.1 M  $\text{NO}_3^-$  and 35.8  $\mu\text{M}$  Fe(III)

Anions	[ $\text{Cl}^-$ ] (mM)				10 mM [ $\text{Cl}^-$ ]				
	0	1	10	100	Control <sup>a</sup>	100 mM $\text{PO}_4^{3-}$	100 mM $\text{SO}_4^{2-}$	100 mM $\text{ClO}_4^-$	100 mM $\text{NO}_3^-$
$k$ ( $\mu\text{M min}^{-1}$ )	0.12	0.17	0.31	0.44	0.31	0.14	0.21	0.34	0.34
$r^2$	1.00	1.00	1.00	1.00	1.00	0.96	0.99	1.00	1.00

<sup>a</sup> No extra anions addition.

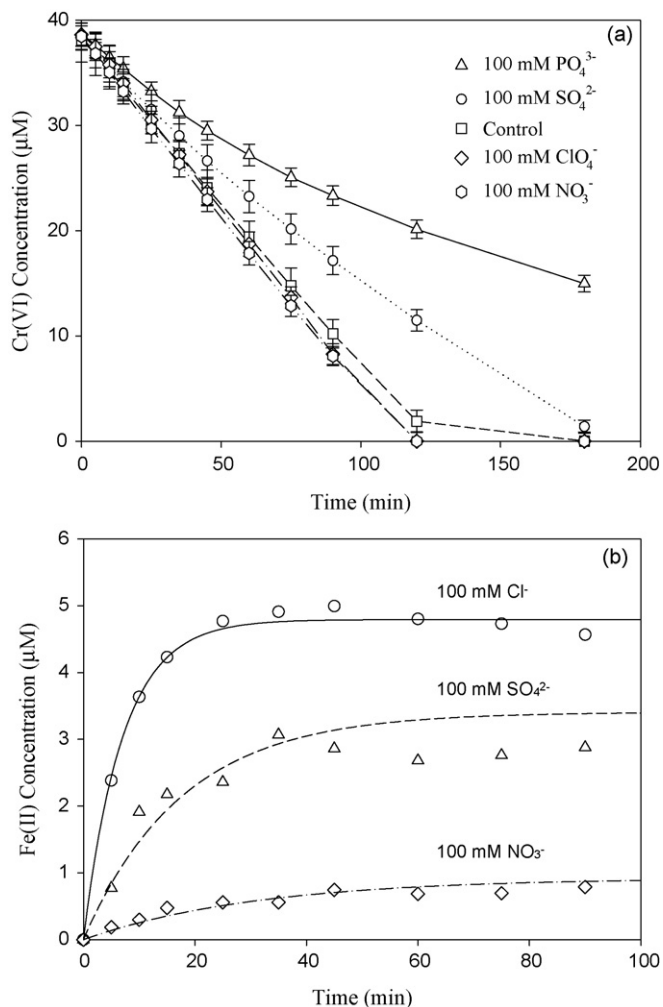


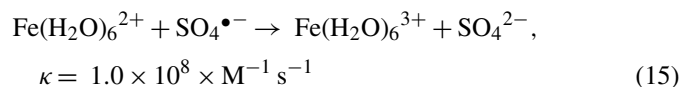
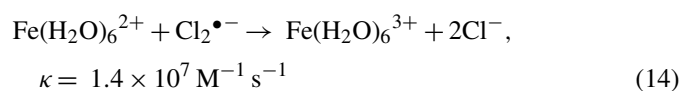
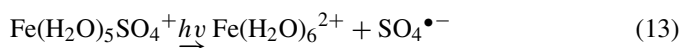
Fig. 6. (a) Photo-reduction of 38.5 μM Cr(VI) with the addition of various anions at a final concentration of 100 mM to a solution with 10 mM Cl<sup>-</sup>, 35.8 μM Fe(III), and 0.1 M NO<sub>3</sub><sup>-</sup> at pH 1, and (b) the kinetic formation of Fe(II) in the presence of various anions at pH 1.

Fe–Cl complexes are not stable, and some complexation ligands may replace Cl<sup>-</sup> through ligand exchange, influencing Cr(VI) photo-reduction indirectly. Therefore, 100 mM PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, or ClO<sub>4</sub><sup>-</sup> was added to 10 mM Cl<sup>-</sup>, 35.8 μM Fe, 0.1 M NO<sub>3</sub><sup>-</sup> to further investigate whether Cr(VI) photo-reduction was affected by the presence of these specific anions. These anions were selected because they have different abilities to form complexes with Fe(III). For example, the stability constants as logarithmic forms for PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> with Fe(III) are 22.5 and 4.0, respectively; however, ClO<sub>4</sub><sup>-</sup> complexes only weakly with Fe(III) in solution [32]. Thus, upon the addition of these anions, Cr(VI) photo-reduction may be affected due to their different competitive abilities with Fe(III), leading to the re-distribution of photo-activated Fe species, such as Fe–Cl complexes. The influence of anions on Cr(VI) photo-reduction is shown in Fig. 6a and Table 1.

As compared with the control experiment, the addition of 100 mM ClO<sub>4</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup> increased Cr(VI) photo-reduction slightly, corresponding to an increase in the zero-order reaction rate from 0.31 to 0.34 μM min<sup>-1</sup> (Table 1). A slight increase

in Fe(II) formation and photolytic reaction in the presence of ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, respectively, may explain the results (data not shown). In contrast, a significant decrease in Cr(VI) photo-reduction was observed with the addition of 100 mM PO<sub>4</sub><sup>3-</sup> or SO<sub>4</sub><sup>2-</sup> (Fig. 6a). The decrease in Cr(VI) photo-reduction upon the addition of PO<sub>4</sub><sup>3-</sup> or SO<sub>4</sub><sup>2-</sup> was due to their strong competition with Fe(III) from Cl<sup>-</sup>, resulting in a marked decrease in the concentrations of Fe–Cl complexes. For example, with the addition of PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>, the FeCl<sub>2</sub><sup>+</sup> complexes decreased from 2.08 to 0.057 μM and 0.151 μM, respectively. As previously mentioned, the Fe–Cl complex was a photo-activated species; nonetheless, there was no evidence that Fe–PO<sub>4</sub> could be photolyzed, producing Fe(II) or reducible radicals for Cr(VI) reduction. Therefore, the decrease of Cr(VI) photo-reduction upon the addition of PO<sub>4</sub><sup>3-</sup> was due to the decrease in the concentrations of Fe–Cl complexes and subsequent photolytic reactions. In addition, according to calculations with MINTEQA2, PO<sub>4</sub><sup>3-</sup> forms a precipitate with Fe(III), which may partially explain the decrease in Cr(VI) photo-reduction and the slight deviation from a zero-order reaction (Table 1).

With the addition of 100 mM SO<sub>4</sub><sup>2-</sup>, Fe–SO<sub>4</sub><sup>+</sup> becomes the major species in solution (~84.3% of total 35.8 μM Fe). Although photolysis of the Fe–SO<sub>4</sub><sup>+</sup> complex may also produce Fe(II), as shown in reaction (13) [33,34], the rate of Fe–SO<sub>4</sub><sup>+</sup> photolysis may be slower than that of Fe–Cl (reaction (10)). Therefore, the overall Cr(VI) photo-reduction decreased with the addition of SO<sub>4</sub><sup>2-</sup>. In addition, Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> reacts rapidly with Cl<sub>2</sub><sup>•-</sup> and SO<sub>4</sub><sup>•-</sup> radicals back to Fe(III), as shown in reactions (14) [30] and (15) [34]. Because the rate of oxidation of Fe(II) by Cl<sub>2</sub><sup>•-</sup> is lower than that by SO<sub>4</sub><sup>•-</sup>, Fe(II) obtained from the photolysis of the Fe–Cl complex may last longer for Cr(VI) reduction.



Thus, in the absence of Cr(VI), we observed that the amount of Fe(II) resulting from the photolysis of Fe–Cl was greater than Fe(II) resulting from the photolysis of Fe–SO<sub>4</sub><sup>+</sup> (Fig. 6b). Accordingly, due to the decrease in Fe–Cl complexes upon the addition of 100 mM SO<sub>4</sub><sup>2-</sup>, the overall efficiency of Fe(II) production was decreased, which resulted indirectly in a low level of Cr(VI) photo-reduction.

#### 4. Conclusions

This study shows that Cr(VI) can be reduced in the presence of NO<sub>3</sub><sup>-</sup> at acidic pH under irradiation. Photolysis of NO<sub>3</sub><sup>-</sup>, leading to the production of intermediates (NO<sub>2</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub>) may contribute to rapid reduction of Cr(VI). The addition

of ferric ions to a solution with an indifferent electrolyte such as  $\text{NO}_3^-$  did not influence the photo-reduction of Cr(VI). Nonetheless, when  $\text{Cl}^-$  was present in the solution, a significant increase in Cr(VI) photo-reduction was observed. The increase in Cr(VI) photo-reduction was attributed to the formation and subsequent photolysis of Fe–Cl complexes, producing Fe(II) for Cr(VI) reduction. On the contrary, the addition of  $\text{PO}_4^{3-}$  to a solution containing Fe–Cl complexes inhibit Cr(VI) photo-reduction. The result is likely due to strong competition between Fe(III) and Cl, leading to a decrease in the concentration of Fe–Cl complexes. Although the addition of  $\text{SO}_4^{2-}$  decreased the rate of Cr(VI) reduction, its influence was lower, because the photolysis of Fe– $\text{SO}_4^+$  may also produce Fe(II) for Cr(VI) reduction.

The results of this study indicate that the direct exposure to light of acidic electroplating wastewater containing Fe(III) and other anions is a potential strategy for eliminating toxic Cr(VI) from solution. However, different anions exhibit different abilities to form complexes with Fe(III); these complexes have various photo-activities. Therefore, the influence of anions on Cr(VI) photo-reduction needs to be clarified to enhance the efficiency of the proposed technique.

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