Photocatalytic Reduction of Hexavalent Chromium Induced by Photolysis of Ferric/tartrate Complex

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Photocatalytic reduction of hexavalent chromium (Cr(VI)) in ferric-tartrate system under irradiation of visible light was investigated. Effects of light resources, initial pH value and initial concentration of various reactants on Cr(VI) photocatalytic reduction were studied. Photoreaction kinetics was discussed and a possible photochemical pathway was proposed. The results indicate that Fe(III)-tartrate system is able to rapidly and effectively photocatalytically reduce Cr(VI) utilizing visible light. Initial pH variations resulte in the concentration changes of Fe(III)-tartrate complex in this system, and pH at 3.0 is optimal for Cr(VI) photocatalytic reduction. Efficiency of Cr(VI) photocatalytic reduction increases with increasing initial concentrations of Cr(VI), Fe(III) and tartrate. Kinetics analysis indicates that initial Fe(III) concentration affects Cr(VI) photoreduction most significantly.

**Key Words :** Ferric, Tartrate, Chromium, Photocatalysis, Reduction

Introduction

Reduction of the extremely poisonous and cancerigenic Cr(VI) is a slow process lasting from several days to months in the natural water environment, thus hexavalent chromium may exist in the environment for a long time that leads to a large scale chromium pollution.[1,2] Investigations on Cr(VI) reduction pathway and Cr(VI) pollution remediation in the nature have attracted common concern since the last century.

General Cr(VI) reduction methods include chemical reduction, photoreduction, electrochemistry reduction and microorganism reduction, *etc*. In recent years, Cr(VI) photocatalytic reduction has been widely developed, and the methods employing TiO$_2$[3,4] and ZnO[5-7] as the photocatalysts are most common in heterocatalytic reaction systems. Meanwhile, studies on the new photocatalysts for Cr(VI) reduction are also continuously emerging.[8-10] However, research on Cr(VI) photoreduction in homogeneous system has seldom been referred.

Recently, photochemistry characteristics of Fe(III)-carboxylate complexes, such as Fe(III)-citrate and Fe(III)-oxalate, have received increasing attention due to higher sunlight utilization efficiency. These complexes not only play an essential role in the migration and transformation of pollutants in the environment, but also are feasible in disposing organic pollutants[11-14] and high valent heavy metals.[15,16] It has been previously revealed that some photoactive Fe(III)-carboxylate complexes could decompose into Fe(II) and carboxyl free radicals under irradiation, and then many intermediate products such as H$_2$O$_2$, HO$_2$·/O$_2^-$· and ·OH were produced from the secondary photochemcal process of carboxyl free radicals.[15] Therefore, high valent heavy metals can be reduced in the presence of reductive Fe(II) and intermediate products. The key reactions are shown in Eq. (1) to (2),

$$RCOO^- + Fe(III) \rightarrow RCOO\text{-}Fe(III) \qquad (1)$$

$$RCOO\text{-}Fe(III) + h\nu \rightarrow Fe(II) + RCOO· \qquad (2)$$
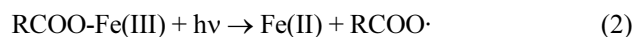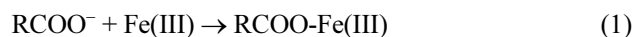
Fe(III)-carboxylate system outweighs TiO$_2$ photocatalysis in the utilization of visible light. Compared to the traditional chemistry method using ferrous sulfate as the reductant, this system is advantageous in saving Fe(III) quantity due to the cycling of Fe(II)/Fe(III) during photoreaction and reducing sediment capacity.

Both of Fe(III) and tartrate exist widely in the nature, which are able to form a 1:1 complex with the stability constant (logK) of 7.49 (25 °C).[17] In addition, photolysis of Fe(III)-tartrate complex has been investigated to determine quantitatively the concentration of hydroxyl radicals produced from photoreaction.[18] However, Cr(VI) photocatalytic reduction in ferric-tartrate system have not been reported systematically. In the present work, feasibility and basic principles of Cr(VI) photoreduction in ferric-tartrate system under the irradiation of visible light with daylight lamp or sunlight as the light resource were researched. The research facilitates the understanding of the photochemistry behaviors of Fe(III)-tartrate complex as well as its influences on the migration and transformation of high valent heavy metals in the natural environment, and also provides basis and new practical concepts for the reduction disposal of high valent heavy metals.

Experimental

Potassium dichromate was used to prepare Cr(VI) stock solution, FeCl$_3$·6H$_2$O and sodium tartrate were used as ferric and tartrate sources respectively. The concentration of working solution mainly were 20, 20, 100 µmol·L^{-1} for Fe(III),

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Cr(VI) and tartrate respectively. However, in order to improve the measurement accuracy, the higher concentration of working solution were used to measure the absorbance of Fe(III)-tartrate complex at 410 nm (the maximum wavelength of daylight lamps which were the main light source) under different pH values and Fe(II) concentration changes in photolysis process of Fe(III)-tartrate complex. HCl and NaOH were used to adjust pH values. All the used chemicals were of reagent grade and were used without further purification. Double-distilled water was used for all experiments.

A UV3010 spectrophotometer (Hitachi, Japan) was used to measure UV-Vis spectra of the solutions and concentrations of Cr(VI) and Fe(II). A pHS-3C pH meter (Chengdu, China) was used to determine pH values of the solutions. Two daylight lamps (30W, λ_{max} = 410 nm) were used as the main light source. In addition, sunlight was also used as the light source. Irradiation intensities of daylight lamp and sunlight were determined with TES1332 digital luxmeter (Taiwan).

The reaction solution containing ferric, Cr(VI) and tartrate was prepared and adjusted to the desired pH in a dark room, and then transferred into 9 colorimetric tubes with stopper (all tubes were calibrated). These tubes were irradiated under 2 daylight lamps or sunlight. At different time intervals during irradiation, one of the tubes was taken out to detect the remaining Cr(VI) concentration.

Cr(VI) concentration was determined by the diphenyl carbazide photometric method, and Fe(II) concentration was measured by 1,10-phenanthrolino photometric method.
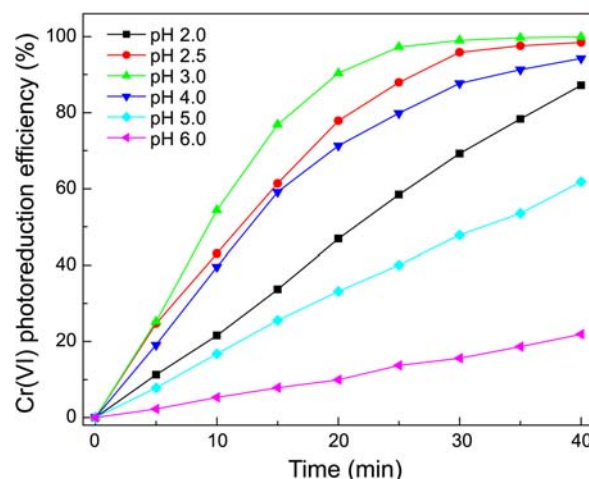
Cr(VI) photoreduction efficiency was calculated according to the following formula $E(\%) = (1-c/c_0) \times 100\%$, where c_0 represents initial Cr(VI) concentration and c represents Cr(VI) concentration at different irradiation time.

Results and Discussion

Cr(VI) Photoreduction in Fe(III)-tartrate System (Comparison Experiment). In previous studies, the presence of Fe(III)-tartrate complex in the given experimental condition was proved (see supplementary material). In this study, the comparison experiment of Cr(VI) photoreduction in Fe(III)-tartrate system was carried out. As shown in Figure 1, Cr(VI) concentration changed slightly when only sodium tartrate was added in Cr(VI) solution and then was irradiated for 40 min. When merely Fe(III) was added in Cr(VI) solution and was irradiated for 40 min, Cr(VI) concentration decreased by 1.9% due to the photolysis of Fe(OH)$^{2+}$ in Fe(III) solution following the reaction Fe(OH)$^{2+}$ + hν → Fe^{2+} + ·OH.[19] Since the light used is similar to sunlight that photolyzes Fe(OH)$^{2+}$ weakly, Cr(VI) reduction efficiency was relatively low. Dark reaction was also carried out for comparison. The mixed solution of Fe(III), Cr(VI) and sodium tartrate was placed in a darkroom for 40 min, and no change of Cr(VI) concentration was observed. However, after being irradiated for 40 min, Cr(VI) concentration in the mixed solution of Fe(III), Cr(VI) and sodium tartrate obviously decreased by 100%. Comparison experiments show
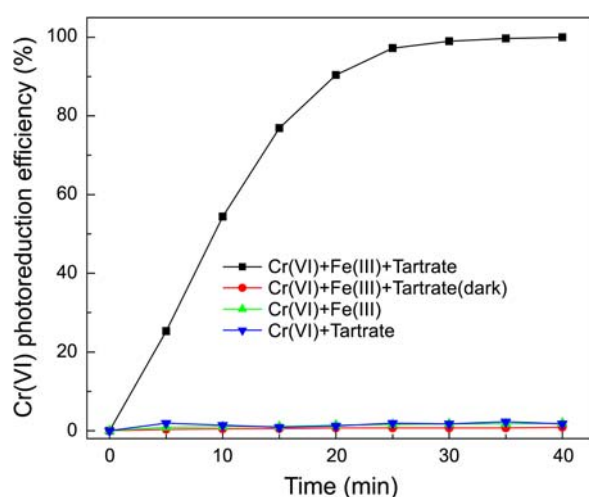
Figure 1. Dependence of Cr(VI) photoreduction efficiency on reaction time in comparison experiments. c_0(Cr(VI)) = 20.0 μmol·L^{-1}, c_0(Fe(III)) = 20.0 μmol·L^{-1}, c_0(tartrate) = 100.0 μmol·L^{-1}, pH 3.0.

Figure 2. Influence of initial pH value on Cr(VI) photoreduction efficiency. c_0(Cr(VI)) = 20.0 μmol·L^{-1}, c_0(Fe(III)) = 20.0 μmol·L^{-1}, c_0(tartrate) = 100.0 μmol·L^{-1}.

that Cr(VI) reduction in Fe(III)-tartrate system could only occur under light initiation.

Influence of Initial pH Value and pH Changes in the Reaction Process. As shown in Figure 2, initial pH value of the reaction solution significantly affected Cr(VI) photoreduction. Cr(VI) photoreduction efficiency gradually increased at the initial pH ranging from 2.0 to 3.0 and reached up to the optimum at pH 3.0, and then obviously reduced when pH ranged from 3.0 to 6.0.

Accordingly, the absorbances of Fe(III)-tartrate system under different initial pH values were measured at the wavelength of 410 nm. The results in Table 1 show that the absorbance firstly increases with pH ranging from 2.0 to 3.0 and then decreases with the increase of initial pH from 3.0 to 6.0, and the effects of initial pH value on solution absorbance are similar to those on Cr(VI) photoreduction efficiency. Absorbance represents Fe(III)-tartrate complex concentration in the system to a certain extent, so initial pH change actual-

Table 1. Absorbance of Fe(III)-tartrate complex at 410 nm under different pH values. c_0(Fe(III)) = 200.0 μmol·L^{-1}, c_0(tartrate) = 1 000.0 μmol·L^{-1}

pH	2.0	2.5	3.0	4.0	5.0	6.0
Abs	0.060	0.097	0.119	0.091	0.089	0.081

Table 2. Solution pH changes during photoreaction. c_0(Cr(VI)) = 20.0 μmol·L^{-1}, c_0(Fe(III)) = 20.0 μmol·L^{-1}, c_0(tartrate) = 100.0 μmol·L^{-1}

Time (min)	0	5	10	15	20	30	40	50
pH	4.00	4.09	4.16	4.22	4.25	4.28	4.29	4.29
pH	5.00	5.35	5.49	5.64	5.78	5.90	6.04	6.13

ly results in the concentration variation of Fe(III)-tartrate complex in the system.

Generally, chemical reaction rate depends on oxidative ability of oxidant and reductive ability of reductant. It has been previously reported that Cr(VI) photoreduction efficiency increased with decreasing initial pH value because Cr(VI) oxidative potential increased with decreasing initial pH value.[6,18] However, this phenomenon did not occur herein. In this system, initial pH change of the reaction solution enables Fe(III)-tartrate complex concentration variations by affecting Fe(III) hydrolysis equilibrium and tartaric acid dissociation equilibrium. Therefore, pH value affects Cr(VI) photoreduction owing to synergetic results of Cr(VI) oxidative potential, hydrolysis equilibrium of Fe(III) and dissociation equilibrium of tartaric acid.

Solution pH changes during Cr(VI) photoreduction were also measured at the initial pH ranging among 4.0 and 5.0. As shown in Table 2, solution pH value increases with elapsed irradiation time. This result indicates that H$^+$ consumption was involved in photoreduction process. When initial pH was 3.0, solution pH value almost kept unchanged in photoreduction process, which is attributed to the low H$^+$ consumption that was insufficient to affect pH value of the whole reaction solution.

Influence of Initial Reactants Concentrations on Cr(VI) Photoreduction and Reaction Kinetics Analysis. Dependence of Cr(VI) concentration on irradiation time was investigated under different initial concentrations of Fe(III), tartrate and Cr(VI), and the results are shown in Table 3.
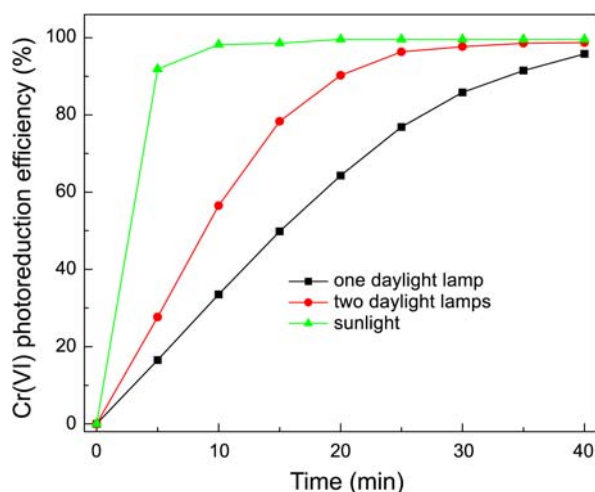
Variations of the residual Cr(VI) concentration with elapsed irradiation time was fitted to the first order reaction kinetics equation $\ln c/c_0 = -kt$, and the initial reaction rate v_0 was obtained under different initial conditions according to $v_0 = -(\mathrm{d}c/\mathrm{d}t)_{t=0} = kc_0$, where k is the apparent first order rate constant (min^{-1}).

As shown in Table 3, correlation coefficient r of each fitting equation is larger than the critically related coefficient r_c(n = 9, α = 0.001, r_c = 0.8982), which indicates that the photoreduction reaction under various reaction conditions is accordance with the first order reaction kinetics. The initial rate of Cr(VI) photoreduction reaction increases with increasing initial concentrations of various reactants.

To explore the effects of initial concentration of Fe(III) on initial Cr(VI) photoreduction rate, initial Fe(III) concent-

Table 3. Cr(VI) Photoreduction kinetics analysis. pH = 3.0

Concentration (μmol·L^{-1})			$\ln c/c_0 = -kt$	Correlation coefficient r (n = 9)	Initial rate v_0 (μmol·L^{-1}·min^{-1})	Kinetics Equation
Fe(III)	Tartrate	Cr(VI)				
2.5			-0.00875t	0.99621	0.1750	
5.0			-0.01775t	0.99481	0.3550	
10.0			-0.03390t	0.99167	0.6780	-dc(Cr(VI))/dt
15.0	40.0	20.0	-0.04951t	0.99356	0.9902	= 0.0694 × c(Fe(III))$^{0.99}$
20.0			-0.06735t	0.99133	1.3470	R^2 = 0.99983, n = 8
25.0			-0.08376t	0.98218	1.6752	
30.0			-0.10078t	0.98920	2.0156	
35.0			-0.11664t	0.98865	2.3328	
	10.0		-0.01901t	0.99529	0.3802	
	20.0		-0.03962t	0.99680	0.7924	
	30.0		-0.05518t	0.97685	1.1036	-dc(Cr(VI))/dt
20.0	40.0	20.0	-0.07385t	0.99133	1.4770	= 0.0669 × c(tartrate)$^{0.83}$
	50.0		-0.08626t	0.98539	1.7252	R^2 = 0.99743, n = 8
	60.0		-0.09987t	0.98268	1.9974	
	70.0		-0.11148t	0.99377	2.2296	
	80.0		-0.12296t	0.99312	2.4592	
		5.0	-0.06736t	0.99133	0.3368	
		10.0	-0.05424t	0.99092	0.5424	
		15.0	-0.04287t	0.99190	0.6431	
10.0	40.0	20.0	-0.03629t	0.96115	0.7258	-dc(Cr(VI))/dt
		25.0	-0.03142t	0.97967	0.7854	= 0.210 × c (Cr(VI))$^{0.40}$
		30.0	-0.02746t	0.98328	0.8239	R^2 = 0.96461, n = 8
		35.0	-0.02435t	0.99077	0.8523	
		40.0	-0.02187t	0.99274	0.8748	

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Figure 3. Influence of different light resources on Cr(VI) photo-reduction efficiency. c_0(Cr(VI)) = 20.0 μmol·L^{-1}, c_0(Fe(III)) = 20.0 μmol·L^{-1}, c_0(tartrate) = 100.0 μmol·L^{-1}, pH 3.0.

ration in Table 3 and the relevant initial rate v_0 were non-linearly fitted to the equation $v_0 = ac_0(Fe(III))^b$ to acquire a kinetics equation of Fe(III) concentration influence. Kinetics equations of tartrate and Cr(VI) concentration influences were also obtained in the similar way. Since the reaction orders of Fe(III), tartrate and Cr(VI) are 0.99, 0.83 and 0.40 respectively, it is reasonable to regard Fe(III) initial concentration as the major factor affecting reaction rate. Therefore, during Cr(VI) photoreduction disposal, Fe(III) concentration and tartrate quantity can be appropriately elevated and reduced respectively to lower Cr(VI) disposal cost.

Influence of Different Light Sources. The mixed solution of Cr(VI), Fe(III) and sodium tartrate was reacted under different light sources and different irradiation intensities. The results are shown in Figure 3. Cr(VI) concentration reduced by 99.6% under sunlight irradiation for 20 min (illumination was 3.2×10^4 Lux), while Cr(VI) concentrations reduced by 95.8% and 98.7% respectively under the irradiation of one (illumination was 3.3×10^3 Lux) and two daylight lamps (illumination was 6.2×10^3 Lux). It is clearly stated that Cr(VI) can be quickly reduced under sunlight, and a stronger illumination accelerates Cr(VI) reduction.

Photoreduction Pathway. In order to explain Cr(VI) reduction mechanism, the concentration of Fe(II) generated from the photolysis of Fe(III)-tartrate complex was measured. Results in Table 4 exhibit that Fe(II) concentration gradually increases with elapsed irradiation time, and Fe(III) conversion efficiency reaches 95.9% after 50 min of irradiation. Fe(II) concentration mainly varied within the first 20 minutes of irradiation and remained unchanged thereafter.

Comparing the dependences of Fe(II) concentration, Cr(VI) concentration and pH value on irradiation time during Cr(VI) photocatlytic reduction in Fe(III)-tartrate system reveal that they all changed mainly within the first 20 min of irradiation. Furthermore, kinetics analysis also indicates that Fe(III) concentration majorly affects reaction rate. As discussed above, it is reasonable to suggest that Fe(II) generated from

Table 4. Fe(II) concentration changes in photolysis process of Fe(III)-tartrate complex. c_0(Fe(III)) = 200.0 μmol·L^{-1}, c_0(tartrate) = 1 000.0 μmol·L^{-1}, pH = 3.0

Time (min)	0	5	10	20	30	40	50
c(Fe(II)) (μmol·L^{-1})	0	91.9	144.4	181.7	190.3	191.0	191.8

the photolysis of Fe(III)-tartrate complex primarily contributes to the reduction of Cr(VI).

According to the stoichiometry in following Eq. (3),

$$HCrO_4^- + 3Fe^{2+} + 7H^+ = 3Fe^{3+} + Cr^{3+} + 4H_2O \qquad (3)$$

3 mol Fe(II) is required to reduce 1mol Cr(VI). If Cr(VI) is only reduced by Fe(II) generated in photolysis of Fe(III)-tartrate complex, Cr(VI) photoreduction efficiency should be about 33% theoretically after 40 min of irradiation in the presence of 20.0 μmol·L^{-1} Cr(VI) and 20.0 μmol·L^{-1} Fe(III) initially. However, experiment results in Figure 2 showed that Cr(VI) was reduced completely, which implied an additional Cr(VI) reduction approach. In fact, Cr(VI) reduction rapidly converted Fe(II) into Fe(III), which re-formed the complex with excessive tartrate (in the above experiments, the input of tartrate was excessive for 1:1 Fe(III)-tartrate complex) for ongoing photolysis. Thus a a cycling of Fe(III) and Fe(II) in this system was formed. Accordingly, Cr(VI) reduction could be completed in the presence of relatively low concentration of Fe(III). Hug reported the reaction of iron(III) catalyzed photochemical reduction of chromium(VI) by oxalate and thought the reaction product with oxalate was mainly soluble Cr(III)-oxalate.

It has been previously reported that chromium(VI) can be photochemically reduced by carboxylate under catalysis of iron(III) and the reaction product with carboxylate was mainly soluble Cr(III)-carboxylate complex. In addition, HO$_2$·, O$_2^-$· and H$_2$O$_2$ produced in secondary photochemistry process were potential reductants for Cr(VI).[15]

By integrating the previous research results and the present work, the pathway profile of Cr(VI) photoreduction by Fe(III)-tartrate complex is suggested in Figure 4, and it can be described as follows:

(1) Fe(III)-tartrate complex formed in the reaction system
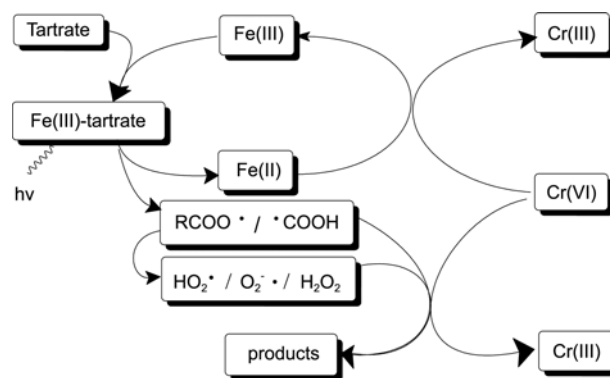
Figure 4. Suggested pathway of Cr(VI) photoreduction by Fe(III)-tartrate complex.

is photolyzed into Fe(II) and carboxyl radical under irradiation, and then Fe(II) mainly accounts for the reduction of Cr(VI). (2) Cr(VI) reduction accelerates the cycling of Fe(III)/Fe(II) in the system, and Fe(II, III) acts as a photocatalyst during Cr(VI) photoreduction. (3) Reductibility radicals such as $HO_2^{\cdot}$, $O^{2-}\cdot$ and H_2O_2 generated from the secondary photochemcal process of carboxyl radical are also potential Cr(VI) reductants.

Conclusions

(1) Fe(III)-tartrate system could rapidly and effectively reduce Cr(VI) utilizing visible light. With initial pH at 3.0 and initial concentrations of Cr(VI), Fe(III) and sodium tartrate at 20.0, 20.0 and 100.0 $\mu mol \cdot L^{-1}$ respectively, Cr(VI) photochemcal reduction efficiency reached up to 100% and 99.6% after being irradiated for 40 min under two daylight lamps and 20 min under sunlight. (2) Initial pH change resulted in the concentration change of Fe(III)-tartrate complex in the system, and pH 3.0 was optimal for Cr(VI) photoreduction. (3) Cr(VI) photoreduction rates increased with increasing initial concentrations of Cr(VI), Fe(III) and tartrate, and initial Fe(III) concentration mainly influenced Cr(VI) reduction. The photoreduction reaction was in accordance with the apparent first order reaction kinetics equation. (4) Fe(II) was quickly generated from the photolysis of Fe(III)-tartrate complex and behaved as the major reductant for Cr(VI) reduction. The cycling of Fe(III)/Fe(II) in the system accelerated photochemical reaction, which facilitated the complete reduction of Cr(VI) even under relatively low Fe(III) concentrations.

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