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Fe-catalyzed photoreduction of Cr(VI) with dicarboxylic acid (C_2–C_5): divergent reaction pathways

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ABSTRACT

Reduction of carcinogenic hexavalent chromium (Cr(VI)) by ferrous iron (Fe(II)) to essentially nontoxic trivalent chromium (Cr(III)) is a simple and effective method for Cr(VI) decontamination. In this study, the photoreduction efficacy of Cr(VI) in acidic Fe(III)/Fe(II) solutions was examined in the presence of dicarboxylic acids (DCA) (i.e. oxalic acid (Oxal), malonic acid (Mal), succinic acid (Suc), and glutaric acid (Glu)). Rates of Cr(VI) reduction under UV irradiation depend on the photochemistry of Fe(III)/Fe(II) complexes with DCA, following the order of Oxal > Suc ≈ Glu > Mal. Fe(III)-oxalato complexes are favorable for transforming Cr(VI) due to the formation of relative abundance of Fe(II) and reductive radicals such as $CO_2^{\cdot-}$, $O_2^{\cdot-}$ after photoreaction, whereas Fe(III)-Mal complexes upon UV irradiation generate the lowest amount of Fe(II) among all the Fe-DCA complexes, and thus have poor capacity for Cr(VI) reduction. The effects of Suc and Glu on the Cr(VI) reduction are insignificant since the Fe(III)-OH complexes are still the main Fe(III) species due to their weak chelating abilities with Fe(III). This work has important implications for selecting the favorable ligands of Fe(III) for light-induced Cr(VI) transformation and designing the methods for treating wastewater with low-molecular-weight acids and Cr(VI).

Keywords: Iron redox cycling; Photochemistry; Fe speciation; Reaction mechanism

1. Introduction

Chromium is an indispensable metal and widely used in industrial processes such as electroplating, pigments, and leather tanning [1]. Improper waste disposal and discharge may have a large environmental and economic impact [2–4]. Chromium exists mainly in two major oxidation states: hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) [5–7]. These two oxidation states are quite different in chemical property and toxicity. Cr(VI) has a high mobility in the environment and is toxic to humans, animals, plants, and micro-organisms. However, Cr(III) is quite immobile and much less toxic unlike Cr(VI), and even is essential in living nutrition. Therefore, one of the most important strategies to detoxify chromium is to convert Cr(VI) to Cr(III).

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Reduction of Cr(VI) by ferrous iron (Fe(II)) has been proven effective in natural and engineered systems [8,9]. However, this stoichiometric reaction consumes massive Fe(II) reagent and cannot sustain once Fe(II) is completely exhausted. Fe-catalyzed photoreduction of Cr(VI) is much more efficient because Fe(II) can be continuously regenerated by photolysis of Fe(III) complexes such as Fe(III)-aquo ions (Eqs. (1) and (2)) or a dye-sensitized reaction [10–12]. However, the rates of reduction of Cr(VI) are constrained from the poor quantum yield of Fe(III)-OH complexes due to their weak UV absorption [13]. The addition of low-molecular-weight acids significantly accelerates the reduction of Cr(VI) in the presence of Fe(III) (Eq. (3)) [14,15]. Carboxylate is one of the abundant functional groups presented in low-molecular-weight acids [16]. Most Fe(III)-polycarboxylate complexes have higher molar absorption coefficients, relative higher quantum yields in the near UV and visible regions, and broader working pH ranges than simple aquated Fe(III) species [17,18].

$$\mathrm{FeOH}^{2+} + h\nu \rightarrow \mathrm{Fe(II)} + {}^{\bullet}\mathrm{OH} \tag{1}$$

$$\mathrm{Cr(VI)} + 3\mathrm{Fe(II)} \rightarrow \mathrm{Cr(III)} + 3\mathrm{Fe(III)} \tag{2}$$

$$\begin{aligned}\mathrm{R\text{-}CO_2\text{-}Fe(III)} + h\nu &\rightarrow \mathrm{R\text{-}CO_2^{\bullet}} + \mathrm{Fe(II)}\\ &\rightarrow \mathrm{R^{\bullet}} + \mathrm{CO_2} + \mathrm{Fe(II)}\end{aligned} \tag{3}$$

Oxalate (Oxal), as a classic dicarboxylate-type ligand of Fe(III), has been shown to effectively promote the transformation Cr(VI) to Cr(III) and reduce the toxicity of chromium [19,20]. Hug and his co-worker investigated the role of Oxal and citrate as organic ligands of Fe(III) on the reduction of Cr(VI) [21]. They discovered the Cr(VI) reduction with Oxal in the presence of Fe(III) was extremely quick (Eqs. (4)–(6)). However, little information on the efficiency of Cr(VI) reduction by the Fe(III) complexes with the other dicarboxylic acid (DCA) is available. Based on the catalytic effect of Fe(III)-oxalato complexes, we hypothesize that the other DCAs (i.e. malonic acid (Mal), succinic acid (Suc), and glutaric acid (Glu)) may have a similar effect on the reduction of Cr(VI) like Oxal.

$$\mathrm{Fe(III)\text{-}Oxalato} + h\nu \rightarrow \mathrm{Fe(II)\text{-}Oxalato} + \mathrm{CO_2^{\bullet -}} + \mathrm{CO_2} \tag{4}$$

$$\mathrm{CO_2^{\bullet -}} + \mathrm{O_2} \rightarrow \mathrm{O_2^{\bullet -}} + \mathrm{CO_2} \tag{5}$$

$$\mathrm{Cr(VI)} + \mathrm{Fe(II)}, \mathrm{CO_2^{\bullet -}}, \mathrm{O_2^{\bullet -}} \rightarrow \mathrm{Cr(III)} + \mathrm{Fe(III)}, \mathrm{CO_2}, \mathrm{O_2} \tag{6}$$

Therefore, in the present work, a series of batch experiments were carried out to investigate the photoreduction efficiency of Cr(VI) in the addition of Fe(III) and DCA. To the best of our knowledge, the systematic investigation on photo-induced reduction of Cr (VI) by the series of DCAs is not reported. Hence, the aim of this study was to study the effects of DCAs (C_2–C_5) on the Fe(III) photocatalytic reduction of Cr(VI). The reaction mechanisms in UV/Fe(III)/DCA/Cr(VI) systems were discussed.

2. Materials and methods

2.1. Materials

Fe(III) perchlorate hydrate ($Fe(ClO_4)_3 \cdot xH_2O$) and Fe(II) perchlorate hydrate ($Cl_2FeO_8 \cdot xH_2O$) were supplied by Aldrich. The DCAs, oxalic acid ($C_2H_2O_4 > 99\%$), malonic acid ($C_3H_4O_4 > 99\%$), succinic acid ($C_4H_6O_4 > 99\%$), and glutaric acid ($C_5H_8O_4 > 99\%$) were purchased from Tokyo Chemical Industry Co., Ltd. Potassium dichromate ($K_2Cr_2O_7$, ≥99.8%), perchloric acid ($HClO_4$, >99%), 1, 10-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$, >99%), acetic acid (CH_3COOH, >99%), sodium acetate ($C_2H_3O_2Na \cdot 3H_2O$, >99%), ammonium fluoride (NH_4F, >99%), and sodium hydroxide (NaOH, >99%) were all purchased from Sinopharm Chemical Reagent Co., Ltd., China. The chemicals used in this work were all of analytical grade and used without further purification. Deionized water (18.3 MΩ cm, Barnstead UltraPure water) was used throughout the experiments. All stock chemical solutions were freshly prepared. Prior to every experiment, aliquots were transferred to the reactor tubes to obtain the specific concentrations.

2.2. The photoreaction setup

All photocatalytic experiments were conducted in a photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China). A medium-pressure Hg lamp (100 W) surrounded by a quartz well was placed in the center of the reactor. The spectrum distribution and relative energy of UV lamp are shown in Table 1 [22]. The water jacket was connected to an electric-heated thermostatic water bath to cool the reactor and the temperature was maintained at 26 ± 2°C. The Hg lamp was turned on and allowed to stabilize for 30 min prior to each photochemical experiment.

2.3. Cr(VI) reduction

The pH was adjusted to 3.0 with dilute perchloric acid and sodium hydroxide. All experiments were

Table 1
Spectrum distribution and relative energy of medium-pressure Hg lamp

Wavelength (nm)	265.2–265.5	296.7	302.2–302.8	312.6–313.2	365.0–366.3
Relative energy (%)	15.3	16.6	23.9	49.9	100
Wavelength (nm)	404.5–407.8	435.8	546.1	577.0–579.0	
Relative energy (%)	42.2	77.5	93	76.5	

conducted in 60 mL Pyrex tubes. One milliliter reaction solution was withdrawn at a time interval to determine the concentrations of Cr(VI) and Fe(II). All the experiments were conducted in duplicate. The calculated relative error was shown in the figures.

2.4. Analytical methods

The concentrations of Cr(VI) and Fe(II) were determined spectrophotometrically using diphenylcarbazide reagent at 540 nm [20] and 1,10-phenanthroline method at 510 nm [23], respectively. A UV–visible spectrophotometer (Hitachi Model U-2910) was used to measure absorbance of solutions in a 1 cm quartz cell. The pH was measured with Muti-340i multi-parameter water quality monitoring instrument with a SenTix 41 pH-electrode (Germany). A Shimazu TOC-V_{CPH} analyzer was employed for TOC measurement. MEDUSA software, a chemical equilibrium program, was used to simulate the aqueous Fe speciation [22,24].

3. Results and discussion

3.1. Cr(VI) reduction in UV/Fe(III)/DCA

The photoreduction of Cr(VI) in different Fe(III)/DCA (C_2–C_5) systems at pH 3.0 was illustrated in Fig. 1. Fe(III) alone exhibited a weak capacity for Cr(VI) reduction under UV light illumination. 16.9% of initial Cr(VI) was converted within 40 min. However, the Cr(VI) reduction was markedly improved as Oxal was added to Fe(III) solution. Complete reduction of Cr(VI) was observed in the first 8 min. Among the DCAs, Mal was found to be most inefficient for the photoreduction of Cr(VI), while the rates of Cr(VI) transformation in the presence of Suc or Glu nearly remained the same as compared to control experiment.

3.2. Effects of DCAs concentrations in UV/Fe(III)/Cr(VI)

The effects of DCAs concentrations on Cr(VI) reduction and photoproduction of Fe(II) in solution were investigated. Fig. 2 demonstrated that the reduction of Cr(VI) was obviously enhanced with an increase in Oxal concentration. The Cr(VI) reduction

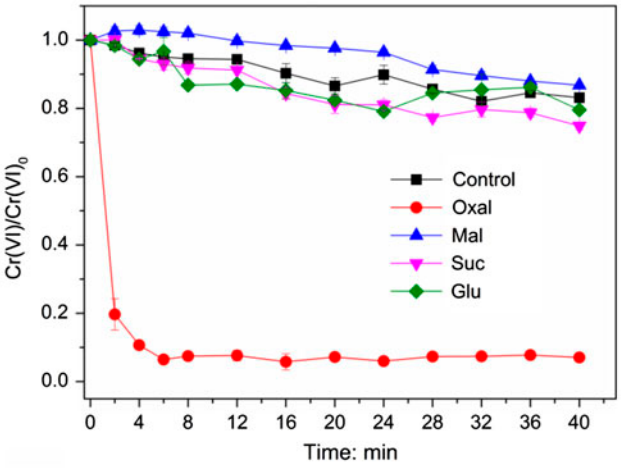

Fig. 1. Cr(VI) reduction in UV/Fe(III)/Cr(VI) system with DCA. (Experimental conditions: $[Cr(VI)]_0 = 80$ µmol/L, $[Fe(III)]_0 = 100$ µmol/L, $[DCA]_0 = 200$ µmol/L (if any), and $pH_{ini} = 3.0$.).

rate was approximately 100% in 4 min when Oxal concentration was more than 600 µmol/L. The influences of concentrations of the other DCAs (C_3–C_5) on Cr(VI) reduction were insignificant. Only approximately 20% of initial Cr(VI) was reduced in 40 min. The changes of Fe(II) concentration was also measured (see Fig. 3) and a rapid production of Fe(II) was observed with Oxal. In contrast, increasing Mal concentration led to a reduced generation of Fe(II) (Fig. 3). There was nearly no Fe(II) detected when Mal concentration was more than 600 µmol/L. However, addition of excess Suc or Glu to the photolyzed Fe(III) solutions did not change the generation rates of Fe(II).

3.3. Photochemistry of Fe(III)/DCA

Fe(II) as a reductant has been proven effective for remediation of Cr(VI) [25–27]. The photolysis of Fe(III)-complexes is a key source of Fe(II) generation. However, it is known that different Fe(III) complexes have different photoreactivities, and also lead to different photochemical production rates of Fe(II). Hence, the photochemistry of Fe(III)/DCA system was also investigated in this work.

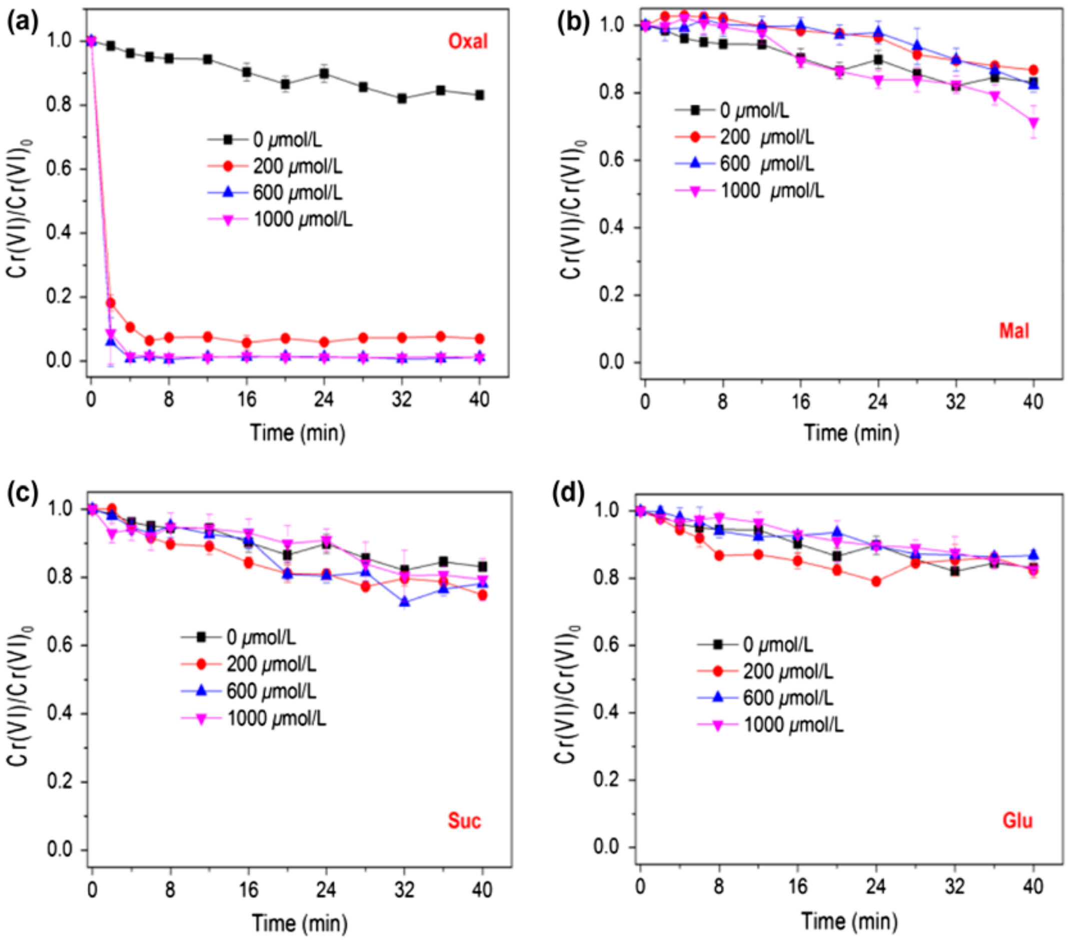

Fig. 2. Effects of DCA concentrations on Cr(VI) reduction in UV/Fe(III)/Cr(VI) system. (a) UV/Fe(III)/Cr(VI)/Oxal system, (b) UV/Fe(III)/Cr(VI)/Mal system, (c) UV/Fe(III)/Cr(VI)/Suc system, and (d) UV/Fe(III)/Cr(VI)/Glu system. (Experimental conditions: $[Cr(VI)]_0 = 80$ μmol/L, $[Fe(III)]_0 = 100$ μmol/L, $[DCA]_0 = 0$–1,000 μmol/L (if any), and $pH_{ini} = 3.0$.).

3.3.1. Photoproduction of Fe(II)

Changes of photoproduction of Fe(II), depending on the photochemistry of Fe(III) complexes, were investigated in the presence of DCAs at pH 3.0. Fig. 4 showed that photocatalytic production of Fe(II) significantly increased with the addition of Oxal. The highest amount of Fe(II) was 33.2 μmol/L when 1,000 μmol/L Oxal was added in the system in a short reaction time. However, among all DCAs, only Mal had an opposite effect on the Fe(II) production. The Fe(II) concentration was decreased with the amount of Mal added. Only less than 5.0 μmol/L Fe(II) was produced as Mal concentration was more than 600 μmol/L.

3.3.2. DCA mineralization

The photolysis of Fe(III)-polycarboxylates complexes was always accompanied by the decomposition of polycarboxylate ligands [28]. In order to study the photochemistry of Fe(III)/DCA system, the mineralizations were further measured by TOC analysis instead of ion chromatography in the present study (Fig. 5). The TOC removal of Oxal and Mal was 46.7 and 3.4%, respectively, demonstrating that a part of Oxal and Mal was photodecarboxylated by the photocatalysis of Fe(III)-Oxal and Fe(III)-Mal complexes. However, there was approximately no TOC removal (≤1.1%) with the addition of Suc and Glu under the similar condition. It indicates that no photodecarboxylation occurred in Fe(III)-Suc and Fe(III)-Glu solutions.

3.4. Cr(VI) reduction by Fe(II)/DCA

The overall photoduction rates of Cr(VI) not only depend on the Fe(III) photochemistry, but also on the

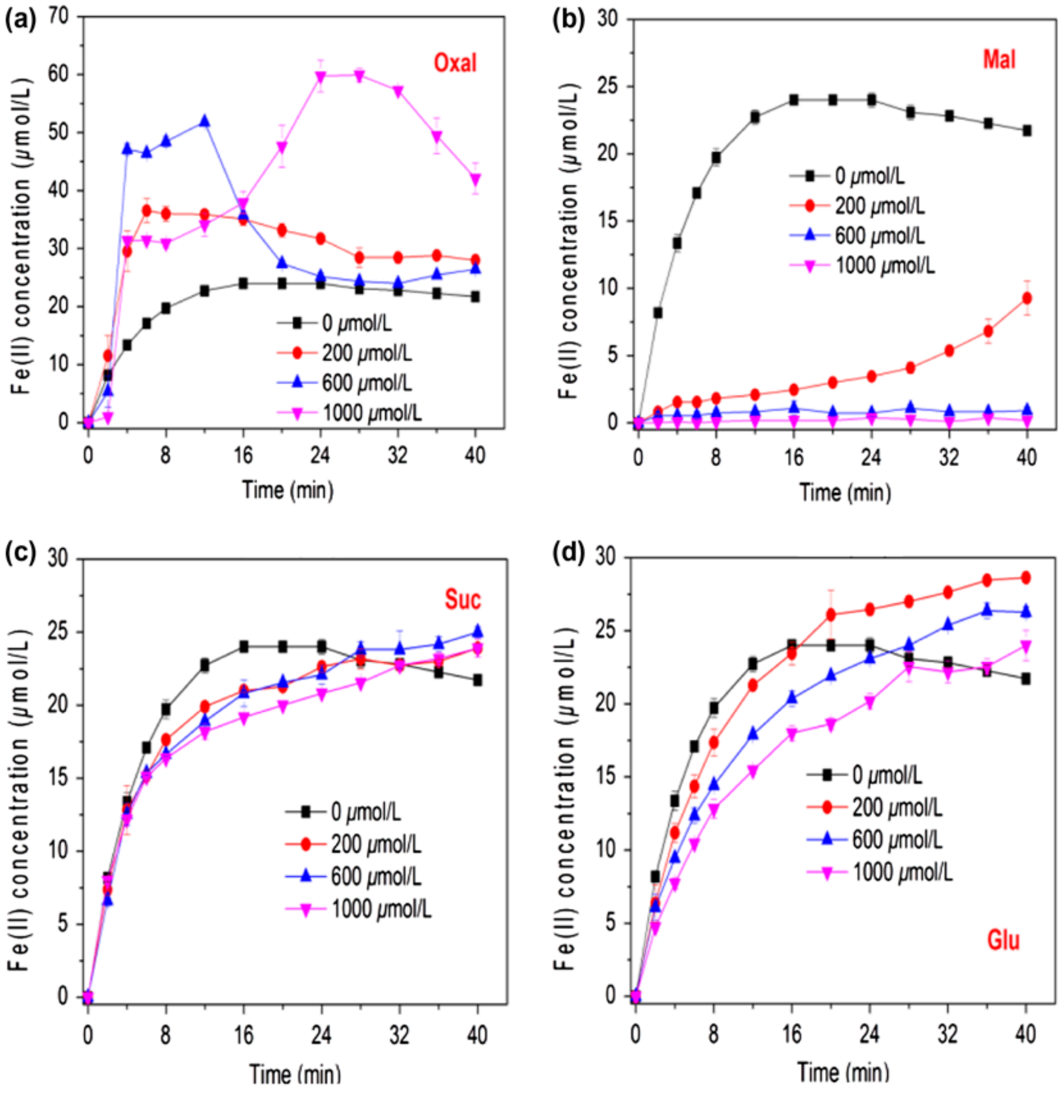

Fig. 3. Effects of DCA concentrations on Fe(II) reduction in UV/Fe(III)/Cr(VI) system. (a) UV/Fe(III)/Cr(VI)/Oxal system, (b) UV/Fe(III)/Cr(VI)/Mal system, (c) UV/Fe(III)/Cr(VI)/Suc system, and (d) UV/Fe(III)/Cr(VI)/Glu system. (Experimental conditions: $[Cr(VI)]_0 = 80$ μmol/L, $[Fe(III)]_0 = 100$ μmol/L, $[DCA]_0 = 0$–1,000 μmol/L (if any), and $pH_{ini} = 3.0$.).

reactivities of Fe(II)-DCA complexes. Hence, we further monitored the efficiency of Cr(VI) reduction in the dark Fe(II)/DCA system. As shown in Fig. 6, the Cr(VI) reduction was approximately 100% in Oxal and Mal systems within 1 min, whereas the addition of Suc and Glu did not improve the reduction efficiency of Cr(VI) as compared to the control experiment.

3.5. Discussion and mechanistic interpretation

In UV/Fe(III) system, Cr(VI) reduction has been demonstrated due to the generation of Fe(II) in UV-irradiated Fe(III) solutions. The level of Fe(II) is controlled by photochemistry of $Fe(OH)^{2+}$, which has relative weaker UV absorbance and has a lower quantum yield ($\Phi_{360\ nm} = 0.017$) [29]. Therefore, the Cr(VI) reduction efficiency is not significant.

In UV/Fe(III)/Oxal system, Cr(VI) decreases rapidly due to the efficient production of a high amount of Fe(II) by Fe-oxalato complexes under irradiation (Fig. 4). The mechanism of Cr(VI) reduction by Fe(III) catalysis in the presence of Oxal is very complicated due to the complete reduction of Cr(VI) to Cr(III) is a three-electron reduction. Moreover, photolysis of Fe-oxalato complexes not only

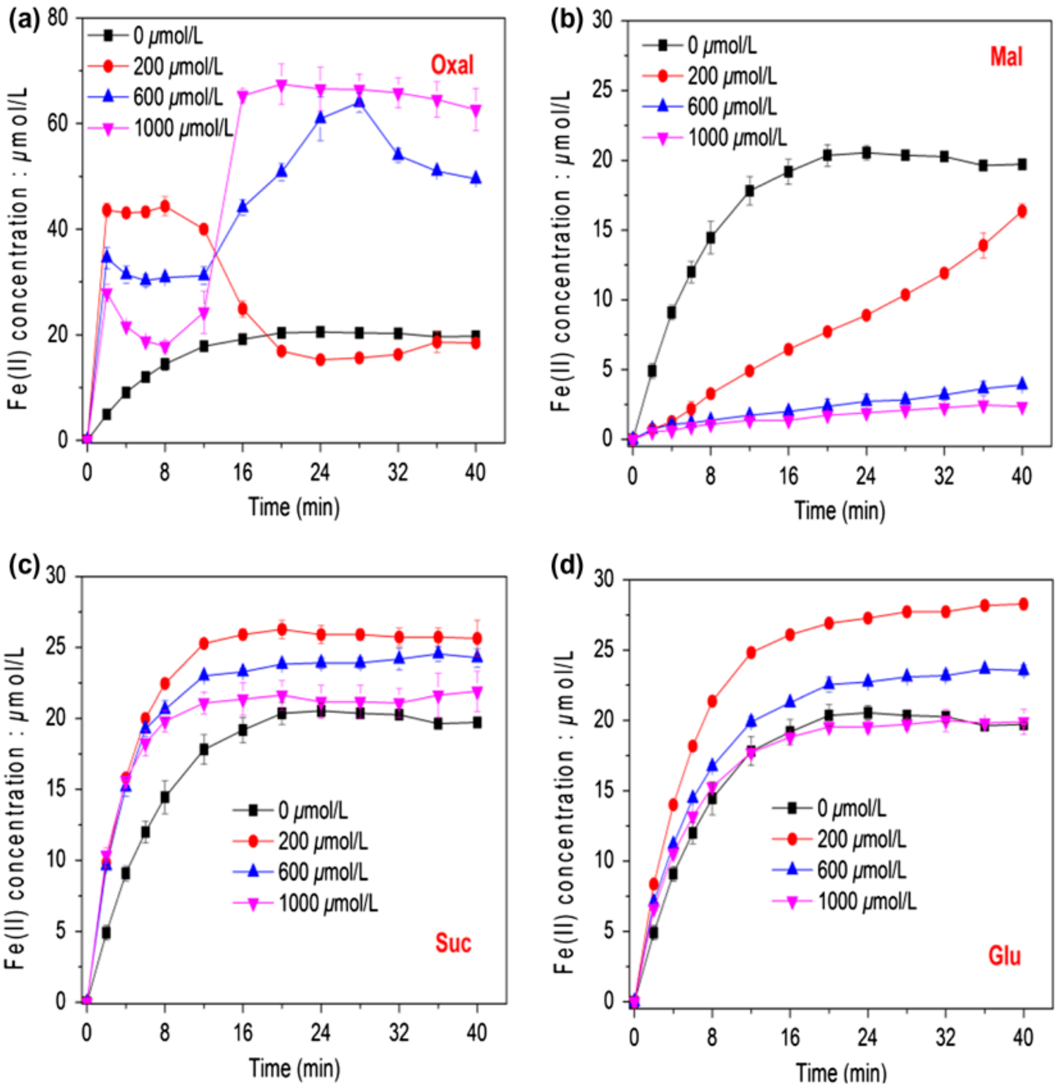

Fig. 4. Effects of DCA concentrations on Fe(II) production in UV/Fe(III) system. (a) UV/Fe(III)/Oxal system, (b) UV/Fe(III)/Mal system, (c) UV/Fe(III)/Suc system, and (d) UV/Fe(III)/Glu system. (Experimental conditions: $[Fe(III)]_0 = 100$ μmol/L, $[DCA]_0 = 0$–1,000 μmol/L (if any), and $pH_{ini} = 3.0$.).

generated Fe(II) but also produced reductive radicals such as $CO_2^{\cdot -}$, $O_2^{\cdot -}$ after a series of reactions. Fe(II) together with reductive radicals converted Cr(VI) into Cr(III), accompanied with the production of Fe(III) and Fe(III)-oxalato formed again. Thus, a redox cycling process of Fe(III)/Fe(II) was established in this system (Eqs. (4)–(6)).

In UV/Fe(III)/Mal system, the production of Fe(II) is the lowest when compared to the other DCA system (Fig. 3). The speciation of Fe(III) as a function of total DCA concentration at pH 3.0 was studied and shown in Fig. 7. The results from Fig. 7(a) and (b) demonstrate that both Oxal and Mal can form relatively stable Fe(III) complexes. All the Fe(III)-OH complexes decreased significantly with the addition of Oxal and Mal. Fe(III)-oxalato and Fe(III)-Mal predominated the Fe(III) speciation at a high concentration of Oxal and Mal in each system. It was found photo activities of Fe(III)-oxalato and Fe(III)-Mal were quite different in our previous work, depending on the nature of Fe(II) and the radicals formed by photodecarboxylation [30,31]. Therefore, we could conclude that the less Fe(II) generated by the photolysis of Fe(III)-Mal lead to the lower efficiency of Cr(VI) reduction.

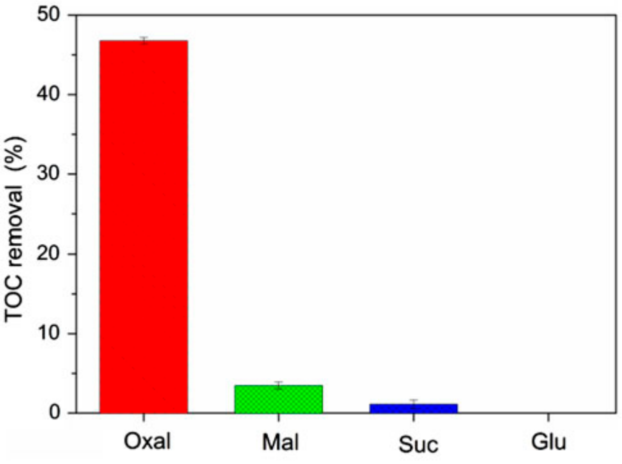

Fig. 5. Mineralization of DCA in UV/Fe(III)/DCA system after 40 min irradiation. (Experimental conditions: $[Fe(III)]_0 = 100$ μmol/L, $[DCA]_0 = 1{,}000$ μmol/L, and $pH_{ini} = 3.0$.).

In UV/Fe(III)/Suc and UV/Fe(III)/Glu system, these two systems have a similar efficiency of Cr(VI) reduction to that without DCA. It is mainly due to the poor complexation capacity of Suc and Glu with Fe(III). The main speciation of Fe(III) with the addition of Suc and Glu was given in Fig. 7(c) and (d). The results showed that Fe(III)-OH complexes dominate the primary speciation even the Suc and Glu in a high concentration. Consequently, the well-known photocatalysis of Fe(III)-OH complexes could be attributed to the Cr(VI) reduction in this two systems.

In Fe(II)/DCA system, Oxal and Mal could form stable five-member and six-member chelate rings with Fe(II) at the ligand concentrations used in this study [32,33]. The formation of Fe(II)-oxalato and Fe(II)-Mal complexes may enhance the activity of Fe(II) [34]. Therefore, the Cr(VI) reduction by Fe(II) with Oxal and Mal is significant when compared to Fe(II) alone. The reduction efficiencies of Cr(VI) with Suc and Glu are similar to the control experiment, since Suc and Glu could not change the Fe(II) speciation in aqueous solution.

The significance of the current study is the correlation linking Cr(VI) reduction with the Fe(III)/Fe(II) in the presence of DCAs, which has several important implications for environmental application of Fe(III) photochemistry. Although Oxal is capable of promoting the Cr(VI) reduction, not all the DCAs could be added to improve the reductive abilities of UV/Fe(III) systems especially Mal. Moreover, Oxal is frequently detected as intermediates or final products in the oxidative degradation of high-molecular-weight aromatic hydrocarbons in wastewater treatment [17,18,35], while chromium is an indispensable metal and widely used in many industrial processes. The Fe(III) photocatalytic technique could be selected for enhancing the treatment efficiency by mixing wastewaters of Cr(VI) and organics. In addition, if Mal is the possible predominant component of the Cr(VI)-containing wastewaters, the Fe(III) photocatalytic technique should not be selected.

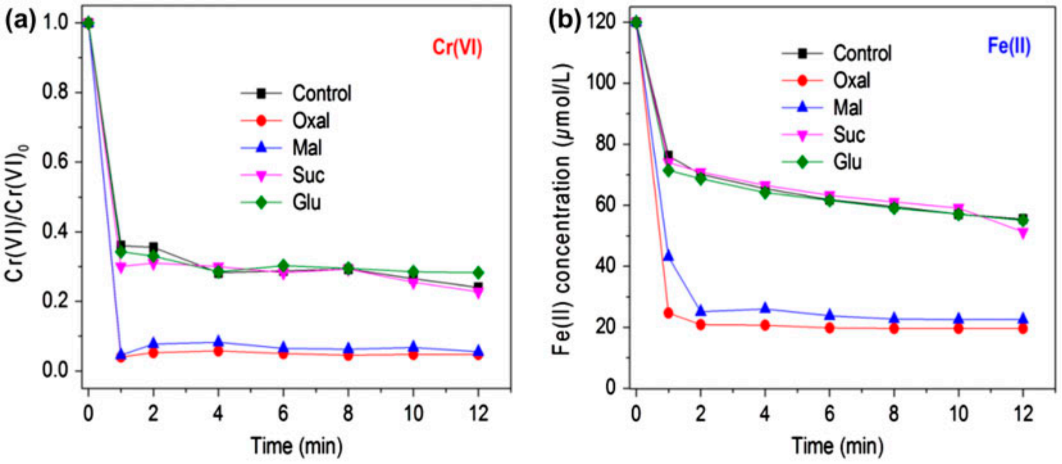

Fig. 6. Cr(VI) reduction and Fe(II) concentration in Fe(II)/Cr(VI) system without light in the presence of DCA. (a) Cr(VI) reduction and (b) Fe(II) concentration. (Experimental conditions: $[Cr(VI)]_0 = 40$ μmol/L, $[Fe(II)]_0 = 120$ μmol/L, $[DCA]_0 = 1{,}000$ μmol/L (if any), and $pH_{ini} = 3.0$.).

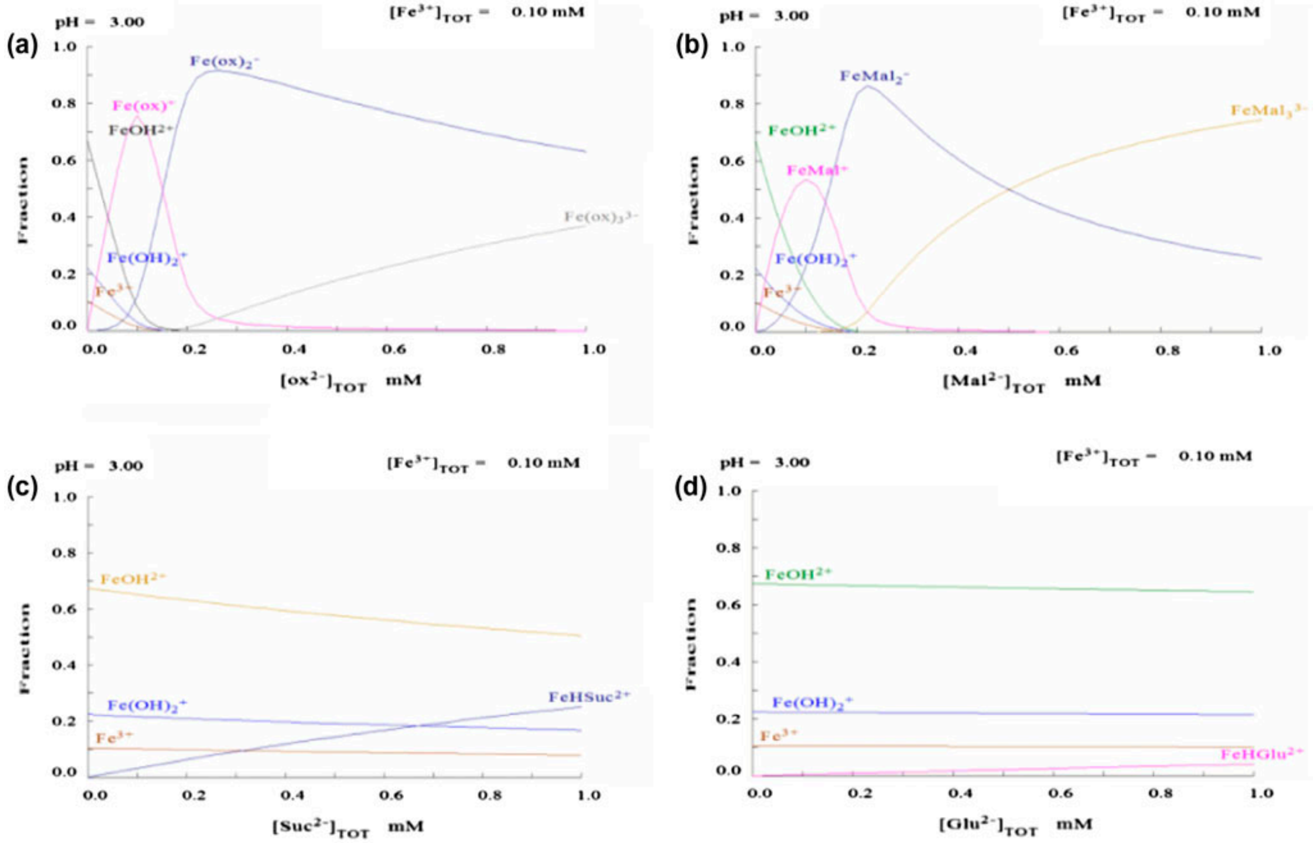

Fig. 7. Fe(III) speciation in (a) Fe(III)-Oxal, (b) Fe(III)-Mal, (c) Fe(III)-Suc, and (d) Fe(III)-Glu system. (Experimental conditions: $[Fe(III)]_0 = 100$ μmol/L, $[DCA)]_0 = 1{,}000$ μmol/L (if any), and $pH_{ini} = 3.0$.).

4. Conclusion

The Fe-catalyzed Cr(VI) photoreduction in the presence of DCA (C_2–C_5) was examined. The effects of DCA on Cr(VI) reduction were rather different. The order of the Cr(VI) removal in UV/Fe(III)/DCA systems was Oxal > Suc ≈ Glu > Mal. Oxal was found to be the most effective Fe ligand for chromate transformation, while Mal exhibited poor capability for Cr(VI) removal. The effects of other DCA, such as Suc and Glu, were insignificant in UV/Fe(III)/Cr(VI) system. Both Oxal and Mal are capable of forming stable Fe(III) complexes, but the different photochemistry of Fe-oxalato and Fe-Mal complexes leads to the distinct effects on Cr(VI) reduction. Photolysis of Fe(III)-oxalato complexes generates a large amount of Fe(II) and reductive radicals as $CO_2^{\cdot-}$, $O_2^{\cdot-}$, but a relatively less quantity of Fe(II) was produced in a photolyzed Fe(III)/Mal solution. In addition, the formation of Fe(III)-Suc and Fe(III)-Glu complexes is negligible and the Fe(III)-OH complexes are still the main Fe(III) speciation in their Fe(III)/DCA solutions. Therefore, the presence of Suc and Glu did not improve the photoreduction efficiency of Cr(VI) by Fe(III) complexes.

Acknowledgments

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