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Simultaneous reduction of hexavalent chromium and decolorization of orange II in photo/ferricarboxylate system

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ABSTRACT

Simultaneous reduction of hexavalent chromium (Cr(VI)) and decolorization of orange II (OII) was mainly investigated in homogeneous photo/ferricitrate system utilizing a metal halide lamp as the primary light source. It has been found that under certain conditions, the percentage reduction for Cr(VI) and percentage decolorization for OII reaches 85% and 51% after 60 min, respectively, indicating that the photo/ferricitrate system is effective for simultaneous reduction of Cr(VI) and decolorization of OII. The percentage reduction for Cr(VI) and percentage decolorization for OII in such system strongly depends on the operating parameters, such as light intensity, initial pH and initial concentrations of Fe(III) and citric acid, and the influence of initial concentrations of Fe(III) and citric acid on reduction of Cr(VI) differs from decolorization of OII. Photo/ferricitrate system only under solar light also has certain photoactivity for those reactions. Homogeneous photo/ferritartarate system is also effective for simultaneous reduction of Cr(VI) and decolorization of OII.

Keywords: Hexavalent chromium; Orange II; Carboxylic acid; Photoreduction; Photodecolorization

1. Introduction

Hexavalent chromium (Cr(VI)) is a carcinogenic contaminant in wastewaters arising from industrial processes such as electroplating, leather tanning or paint manufacture [1]. Several methods have been used to treat wastewaters containing Cr(VI), such as membrane filtration, extraction, ion exchange, adsorption and various kinds of reduction (e.g., chemical, electrochemical, biological and photocatalytic). The preferred treatment is chemical reduction of Cr(VI) to the less harmful Cr(III), the other stable species of chromium, which can be precipitated in neutral or alkaline solutions as $Cr(OH)_3$ and removed as a solid waste [2]. Salts of S(II) and Fe(II) are often used as reducing agents [3]. Recently, transformation of Cr(VI) to Cr(III) using dissolved organic acids as reductants has also been reported [4–6]. However, in many cases, the reduction of Cr(VI) by those compounds is a slow process [7]. Fortunately, transition metal ions (e.g., Fe(III)) can significantly catalyze the photochemical reduction of Cr(VI) by carboxylic acids [8]. For example, Xu et al. [4] reported on the efficient photocatalytic reduction of Cr(VI) by citric and oxalic acids over biogenetic jarosite. More recently, we have found that iron corrosion products collected from the cast iron pipes have significant photocatalytic effect on reduction of Cr(VI) by tartaric acid [9].

Azo dyes, characterized by an azo group (N=N) are also industrial pollutants in wastewaters from the production of textiles, paper, cosmetics and pharmaceuticals [10]. There are a number of treatment techniques for azo dyes contained in wastewaters, including chemical coagulation/flocculation, membrane separation, activated carbon adsorption, biodegradation and advanced oxidation processes (AOPs) [11]. AOPs are based on the formation of hydroxyl radical (·OH) able to oxidize almost all organic matters and mineralize them to carbon dioxide and water owing to its high oxidation potential [12]. Photo-Fenton process based on complexes of Fe(III) and carboxylate anions (without artificial addition of H_2O_2) as an important AOPs technology has received considerable attention in photodegradation of organic compounds

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such as dyes [13]. Cheng et al. reported on the decolorization of reactive dye using a photo/ferrioxalate system with brick grain-supported iron oxide [11]. In a previous work, we found that iron corrosion products can also be effectively used for decolorization of orange II (OII) in the presence of oxalic acid under simulated natural light or solar light [14].

Since Cr(VI) and azo dye may co-exist in some industrial effluents [15], it is of great interest to investigate the co-treatment of these two pollutants present in the wastewaters. Compared with extensive studies on respective treatment of Cr(VI) and azo dye, the co-treatment remains a great challenge. In recent years, the studies on co-treatment of Cr(VI) and azo dye have focused on physical adsorption [16], photochemistry [17], electrochemistry [10] and microbiology [15]. More recently, simultaneous reduction of Cr(VI) and decolorization of azo dye in zero-valent iron/carboxylic acids system has been reported [18,19]. Based on the above discussion, simultaneous reduction of Cr(VI) and decolorization of azo dye with photo/ferricarboxylate system may be feasible. However, little information is available on such co-treatment of Cr(VI) and azo dye [9].

The main objective of the current study was to assess the feasibility of simultaneous reduction of Cr(VI) and decolorization of OII (an azo dye, molecular structure of which is shown in Fig. 1) in homogeneous photo/ferricitrate system, and to examine the influence of some key operating parameters. Simultaneous reduction of Cr(VI) and decolorization of OII in photo/ferritartarate system was also preliminarily investigated.

2. Experimental

All chemical reagents were of analytic reagent grade and used as received. Except OII (from Reagent No. 3 Factory of Shanghai Chemical Reagent Co. Ltd., China), the other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Stock solutions of Cr(VI) (0.2 M), OII (1 g/L) and citric acid (or tartaric) (0.2 M) were prepared by, respectively, dissolving $K_2Cr_2O_7$, OII and citric acid (or tartaric) into distilled water and all stored under dark conditions. Stock solutions of Fe(III) (0.01 M) were prepared by dissolving $Fe_2(SO_4)_3{\cdot}9H_2O$ in dilute H_2SO_4 solution, and kept at pH < 2 in order to prevent hydrolysis.

UV–Vis absorption spectra for Cr(VI) and for OII solution were recorded on a Shimadzu UV-2501 PC spectrometer. The experiments on simultaneous reduction of Cr(VI) and decolorization of OII were performed in a cylinder quartz tube (3.0 cm diameter × 8.0 cm height) filled with reaction solution (20 mL) under illumination of light. The concentration of Cr(VI) and OII in the mixed solution was 0.2 mM and 10 mg/L, respectively. The initial pH of the solution was adjusted by sodium hydroxide (1 M) or sulfuric acid (0.2 M). A 300 W metal halide lamp was used as the primary light source, and the distance between the lamp and the solution was 15 cm. The experiments only under solar light were carried out at solar noon in September. The light intensity available in the solution was measured to be about 14 and 1.2 mW/cm^2, respectively.

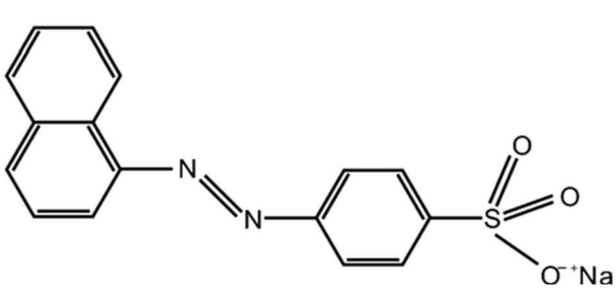

Fig. 1. Molecular structure of OII.

Unless stated otherwise, the experiments were carried out by utilizing a metal halide lamp as the primary light source. All the experiments were conducted at room temperature with the reactor open to the air.

At given time interval (10 min), samples were withdrawn from the solution. The concentration of Cr(VI) and OII during the reaction period was determined by measuring the absorbance of the samples at 349 and 486 nm, respectively, using a spectrophotometer [9,14]. The change in Cr(VI) concentration during the reaction period is given by the percentage conversion of Cr(VI) and it is calculated according to the following formula:

$$\text{Percentage conversion} = [(C_0 - C)/C_0]\%$$

where C_0 and C are the concentration of Cr(VI) before and after reaction, respectively. Similarly, percentage conversion for decolorization of OII was obtained.

Each kinetics experiment was carried out in triplicate; the reproducibility of the results was within an acceptable limit (±2%) and the reported data were expressed as a mean value.

3. Results and discussion

3.1. UV–Vis spectra for Cr(VI) and for OII solution

The UV–Vis absorption spectra for Cr(VI) and for OII solution were presented in Fig. 2. Cr(VI) is characterized by the intense bands at 258 and 352 nm. OII shows a strong absorbance band at 486 nm due to the n–π* transition of –N=N– group [20]. Other characteristic bands observed at 310, 230 nm and the shoulder at 256 nm are assigned to π–π* transition related to aromatic rings [21].

3.2. Simultaneous reduction of Cr(VI) and decolorization of OII in photo/ferricitrate system

Initially, an experiment on simultaneous reduction of Cr(VI) and decolorization of OII in ferricitrate system under dark condition was carried out. Negligible change in concentrations of both Cr(VI) and OII was observed in such case (data not shown). This means that photoirradiation is crucial for the redox process in ferricitrate system. When the photoirradiation from the metal halide lamp was introduced into the system (i.e., in the photo/ferricitrate system), simultaneous reduction of Cr(VI) and decolorization of OII significantly occurred. It can be seen from the results shown in Fig. 3 that the concentrations of both Cr(VI) and OII were decreased with the reaction time, and the percentage reduction for Cr(VI) and the percentage decolorization for OII after 60 min reached 85% and 51%, respectively. The results indicate that the photo/ferricitrate system is effective for simultaneous reduction of Cr(VI) and decolorization of OII. Because the interaction between Cr(VI) and OII under photoirradiation is quite limited [18], the resulting significant Cr(VI) reduction and OII decolorization in the photo/ferricitrate system are not caused by the direct redox reaction of Cr(VI) with OII. The mechanism for the simultaneous reduction of Cr(VI) and decolorization of OII in such system can be discussed as follows.

In ferricitrate system, Fe(III)–citrate complexes ($\mathrm{Fe^{III}(Cit)}$) are formed. Under photoirradiation, a ligand-to-metal charge transfer (LMCT) occurs in the complex molecule to form Fe(II) and citrate radical ($\mathrm{Cit^{\cdot 2-}}$; Eq. (1)). The latter reacts with the dissolved oxygen to form 3-oxoglutarate and superoxide ion ($\mathrm{O_2^{\cdot -}}$; Eq. (2)) [13]. Photonation of $\mathrm{O_2^{\cdot -}}$ produces hydroperoxyl radical ($\mathrm{HO_2\cdot}$; Eq. (3)). $\mathrm{H_2O_2}$ is formed by dismutation of $\mathrm{O_2^{\cdot -}/HO_2\cdot}$ (Eq. (4)). Fe(II) reacts with the formed $\mathrm{H_2O_2}$ to form hydroxyl radical (·OH) following the classic Fenton reaction (Eq. (5)) [14].

$$\mathrm{Fe^{III}(Cit)} + h\nu \rightarrow \mathrm{Fe(II)} + \mathrm{Cit^{\cdot 2-}} \tag{1}$$

$$\mathrm{Cit^{\cdot 2-}} + \mathrm{O_2} \rightarrow \text{3-oxoglutarate} + \mathrm{O_2^{\cdot -}} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{H^+} + \mathrm{O_2^{\cdot -}} \rightarrow \mathrm{HO_2} \tag{3}$$

$$\mathrm{O_2^{\cdot -}/HO_2\cdot} + \mathrm{H^+} + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + \mathrm{H_2O_2} \tag{4}$$

$$\mathrm{H_2O_2} + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + \cdot\mathrm{OH} + \mathrm{OH^-} \tag{5}$$

Both Fe(II) and $\mathrm{Cit^{\cdot 2-}}$ formed through LMCT (Eq. (1)) in the ferricitrate system can reduce Cr(VI) to Cr(III) (Eqs. (6) and (7)) [22].

$$\mathrm{3Fe(II)} + \mathrm{Cr(VI)} \rightarrow \mathrm{Cr(III)} + \mathrm{3Fe(III)} \tag{6}$$

$$\mathrm{Cr(VI)} + \mathrm{Cit^{\cdot 2-}} \rightarrow \mathrm{Cr(III)} + \mathrm{CO_2} + \text{Products} \tag{7}$$

In fact, Cr(VI) to Cr(III) conversion is quite complex because such conversion is a three-electron reduction. Cr(V) and Cr(IV) are the intermediates for the reactions expressed by Eqs. (6) and (7) [8]. The formed $\mathrm{O_2^{-}}$ (Eq. (2)) may also be an efficient reductant for Cr(V) and Cr(IV) intermediates [23]. Meanwhile, the formed ·OH in the same system is able to oxidize OII, resulting in its decolorization.

The results are shown in Fig. 1 that during the reaction period of 60 min, the concentration of OII continuously decreased, while that of Cr(V) dramatically decreased before 30 min, subsequently appeared stabilized without further reduction. Appearance of steady state for Cr(V) may be due to the fact that ·OH present in the system may also reoxidize Cr(III) to Cr(VI) in the late stage of reaction (Eq. (8)) [22], which fully offsets the reduction of Cr(VI) by Fe(II) and $\mathrm{Cit^{\cdot 2-}}$.

$$\mathrm{Cr(III)} + 3\cdot\mathrm{OH} \rightarrow \mathrm{Cr(IV)} + \mathrm{3OH^-} \tag{8}$$

In mechanism investigation of the organic compounds degradation in a heterogeneous photocatalytic system, isopropanol and benzoquinone are often used as scavengers for ·OH and for $\mathrm{O_2^{\cdot -}}$, respectively [24,25]. In order to verify the

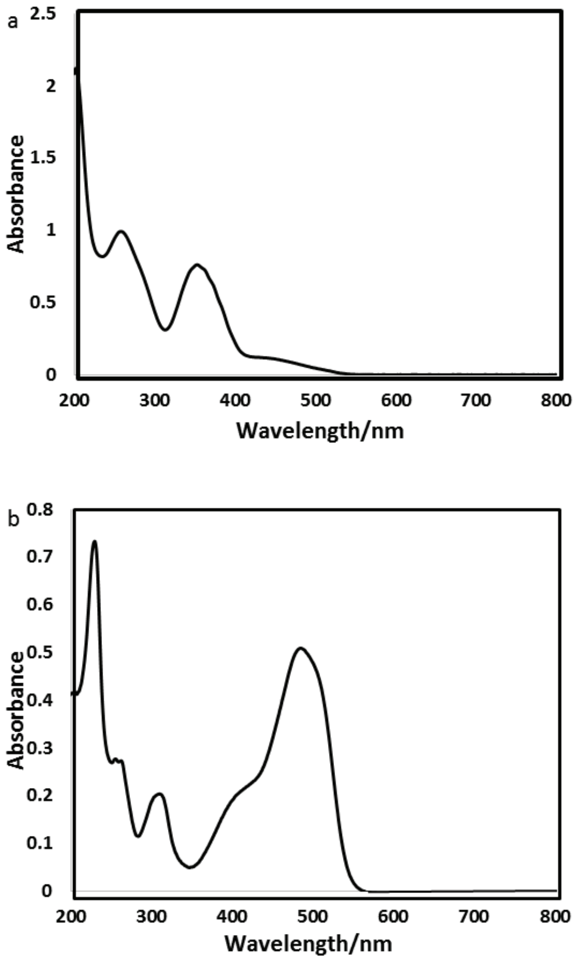

Fig. 2. UV–Vis absorption spectra for Cr(VI) (a) and for OII (b) solution. Experimental conditions: [Cr(VI)] = 0.2 mM, [OII] = 10 mg/L and pH = 3.0.

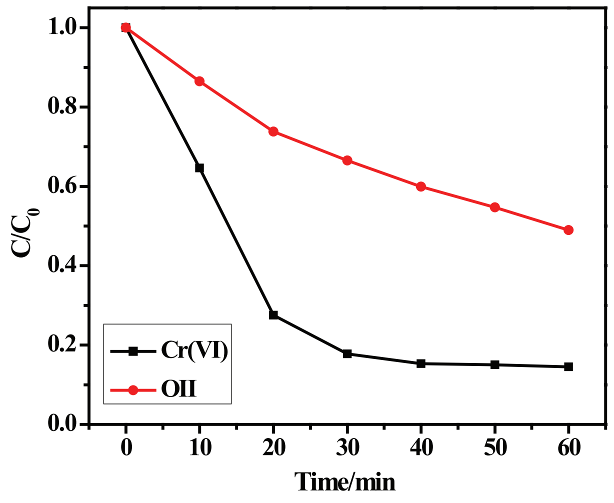

Fig. 3. Simultaneous reduction of Cr(VI) and decolorization of OII in photo/ferricitrate system. Experimental conditions: [Fe(III)] = 0.2 mM, [Cr(VI)] = 0.2 mM, [OII] = 10 mg/L, [Cit] = 2.4 mM and pH = 3.0.

action of the active free radicals such as ·OH and $O_2^{\cdot-}$ of the ferricitrate system in simultaneous reduction of Cr(VI) and decolorization of OII, the effects of isopropanol and benzoquinone on photocatalytic performance of the photo/ferricitrate system were investigated. It was found that after adding isopropanol into the photo/ferricitrate system (concentration of isopropanol being 0.1 mM), the percentage reduction for Cr(VI) and the percentage decolorization for OII after 60 min were changed to 95% and 26%, respectively. The increase in percentage reduction of Cr(VI) and the decrease in percentage decolorization of OII due to the addition of isopropanol indicate that ·OH plays a crucial role in decolorization of OII, and it may reoxidize Cr(III) to Cr(VI). After addition of benzoquinone into the system (concentration of benzoquinone also being 0.1 mM), it was found that the percentage reduction for Cr(VI) after 60 min remained 85%, indicating that $O_2^{\cdot-}$ plays a dual role in the reduction of Cr(VI). On the other hand, the addition of benzoquinone led to the decrease in percentage decolorization of OII (percentage decolorization of OII after 60 min being 30%), which implies that dissolved O_2 is important for decolorization of OII in the photo/ferricitrate system.

A more environmentally friendly process is the use of solar light to simultaneously reduce Cr(V) and decolorize OII in ferricitrate system. Therefore, a relevant experiment only under solar light was conducted and the results were shown in Fig. 4. The concentrations of both Cr(VI) and OII were also decreased with the reaction time in ferricitrate system only under solar light, and the percentage reduction for Cr(VI) and the percentage decolorization for OII after 60 min reached 57% and 32%, respectively. This means that solar light can also induce the redox reactions within the ferricitrate system. Nevertheless, the reduction and decolorization efficiency was lower than that under illumination of the metal halide lamp. Those different results also indicate that the simultaneous reduction of Cr(VI) and decolorization of OII in ferricitrate system strongly depend on the illuminated light intensity.

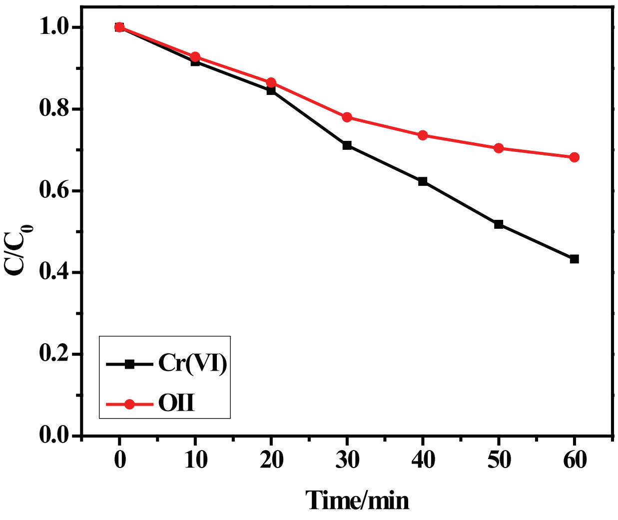

Fig. 4. Simultaneous reduction of Cr(VI) and decolorization of OII in photo/ferricitrate system only under solar light. Experimental conditions: [Fe(III)] = 0.2 mM, [Cr(VI)] = 0.2 mM, [OII] = 10 mg/L, [Cit] = 2.4 mM and pH = 3.0.

3.3. Effect of initial pH

As an important parameter, pH affects photo-Fenton reaction and Fe(III) catalyzed photochemical reduction of Cr(VI) by carboxylic acids. In order to evaluate the influence of pH on the simultaneous reduction of Cr(VI) and decolorization of OII in the photo/ferricitrate system, corresponding experiments were conducted at pH = 5.0 and 7.0, respectively. The obtained results, including those at pH = 3.0 were all shown in Fig. 5. Both percentage reduction of Cr(VI) and percentage decolorization of OII were decreased with increasing pH levels.

This pH dependence of Cr(VI) reduction in the photo/ferricitrate system may be related to the change of speciation of Cr(VI) and Fe(III) with pH. For example, $HCrO_4^-$ is the dominant species for Cr(VI) under acidic conditions, while CrO_4^{2-} is the major species at pH = 7. CrO_4^{2-} is less reactive than $HCrO_4^-$ [8]. For Fe(III), Fe^{III}(Cit) is the dominant species under acidic conditions, while $[Fe(OH)_2]^+$ is the major species at pH = 7 [13]. Because the photoactivity of $[Fe(OH)_2]^+$ is worse than Fe^{III}(Cit) [26], less reductants for Cr(VI) would be produced at higher pH. On the other hand, under acidic conditions, production of·OH is mainly caused by the photolysis of Fe^{III}(Cit) [27], while at pH = 7, the major source of ·OH is the photolysis of $[Fe(OH)_2]^+$ (Eq. (9)) [28].

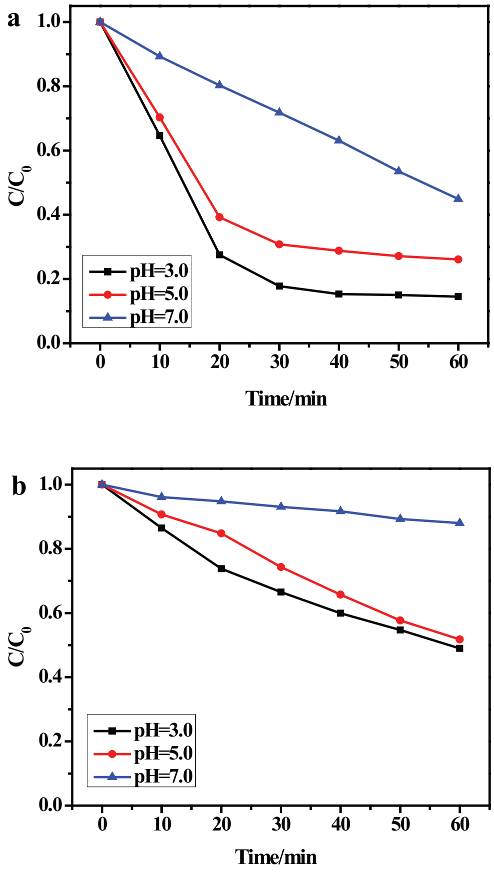

Fig. 5. Effect of initial pH on simultaneous reduction of Cr(VI) (a) and decolorization of OII (b) in photo/ferricitrate system. Experimental conditions: [Fe(III)] = 0.2 mM, [Cr(VI)] = 0.2 mM, [OII] = 10 mg/L and [Cit] = 2.4 mM.

$$[\mathrm{Fe(OH)_2}]^+ + h\nu \rightarrow \mathrm{Fe(II)} + \cdot\mathrm{OH} \tag{9}$$

Considering the difference in photoactivity between $[\mathrm{Fe(OH)_2}]^+$ and $\mathrm{Fe^{III}(Cit)}$, one would expect the percentage decolorization for OII to be lower at pH = 7 due to the production of less ·OH. In addition, Fe(II) may form insoluble ferrous hydroxide at pH > 6, which also inhibits the production of ·OH through Fenton reaction (Eq. (5)) [10].

Over the tested pH range, Fe(III) may hydrolyze into $\mathrm{Fe(OH)_3}$ in the aqueous solution. The formed $\mathrm{Fe(OH)_3}$ may remove Cr(VI) and OII through the adsorption followed by the co-precipitation. However, in the absence of citric acid at pH = 3.0, removal of Cr(VI) and OII was very limited (see the results shown in Fig. 7). This means that $\mathrm{Fe(OH)_3}$ plays a minor role in removal of Cr(VI) and OII at lower pH in the photo/ferricitrate system. The removal of Cr(VI) and OII caused by $\mathrm{Fe(OH)_3}$ may become more important at higher pH [29].

3.4. Effect of initial Fe(III) concentration

As can be seen from the mechanism mentioned above, the photodecomposition of $\mathrm{Fe^{III}(Cit)}$ complex (leading to the production of Fe(II) and citrate radical) (Eq. (1)) initiates the simultaneous reduction of Cr(VI) and decolorization of OII in the photo/ferricitrate system. The formed Fe(II) is both a reductant for Cr(VI) (Eq. (6)) and a catalyst for Fenton reaction (Eq. (5)); the reduction of Cr(VI) (Eq. (7)) and the production of ·OH (Eqs. (2)–(6)) are also related to the formed citrate radical. This means that the initial Fe(III) concentration may play an important role in the photo/ferricitrate system. Therefore, simultaneous reduction of Cr(VI) and decolorization of OII were conducted at different initial Fe(III) concentrations. All the results were shown in Fig. 6.

It can be seen that in the absence of Fe(III) (i.e., [Fe(III)] = 0), no change in concentration of Cr(VI) was observed during the reaction period, and that of OII was decreased only slightly after 60 min. Such limited decolorization of OII may be caused by its direct photolysis. When Fe(III) concentration was increased to 0.04 mM, the concentration of Cr(VI) was dramatically decreased with time and its percentage reduction reached 81% after 60 min. Further increasing Fe(III) concentration to 0.2 and 1.0 mM, little influence on percentage reduction for Cr(VI) after 60 min was observed (corresponding percentage reduction being 85% and 87%, respectively). At higher Fe(III) concentration, more reductants (e.g., Fe(II) and $\mathrm{Cit^{\cdot 2-}}$) would be produced and consequently more Cr(VI) would be reduced. However, higher Fe(III) concentration also leads to the production of more ·OH, which may reoxidize Cr(III). It is worth noting that in a reaction stage (about from 10 to 45 min), the decrease in Cr(VI) concentration at [Fe(III)] = 1.0 mM was less than [Fe(III)] = 0.2 mM. No clear explanation can be provided for this behavior, but it may be related to the reoxidization of Cr(III) by ·OH. Compared with the reduction of Cr(VI), the influence of initial Fe(III) concentration on decolorization of OII is simple. Over the tested range, percentage decolorization for OII was always increased with increasing the initial Fe(III) concentration.

3.5. Effect of initial citric acid concentration

Based on the discussion on the mechanism for simultaneous reduction of Cr(VI) and decolorization of OII in the photo/ferricitrate system, the initial citric acid concentration might also be an important factor affecting the photochemical activity of this system. Therefore, simultaneous reduction of Cr(VI) and decolorization of OII in the photo/ferricitrate system were conducted at other initial citric acid concentrations and the results were shown in Fig. 7.

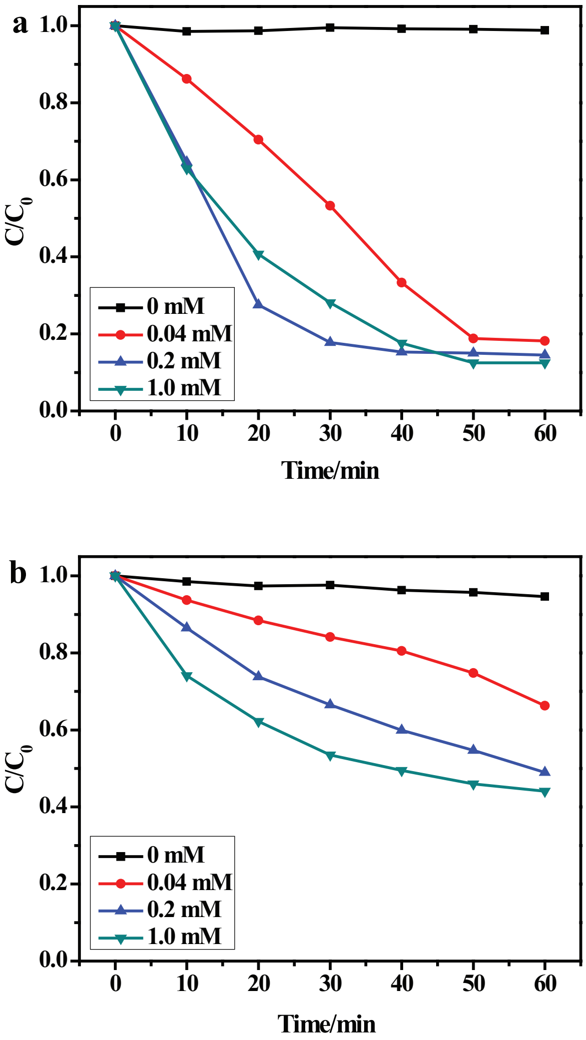

Fig. 6. Effect of initial Fe(III) concentration on simultaneous reduction of Cr(VI) (a) and decolorization of OII (b) in photo/ferricitrate system. Experimental conditions: [Cr(VI)] = 0.2 mM, [OII] = 10 mg/L, [Cit] = 2.4 mM and pH = 3.0.

It can be seen that in the absence of citric acid (i.e., [Cit] = 0), decrease in both Cr(VI) and OII concentrations was observed (percentage reduction and decolorization after 60 min being 13% and 17%, respectively). This may be due to the reaction of Cr(VI) and OII with the products from the photolysis of $[\mathrm{Fe(OH)_2}]^+$ (Eq. (9)). Over the range of 0–1.2 mM, the percentage reduction for Cr(VI) was increased with increasing citric acid concentration (e.g., percentage reduction after 60 min being 85% at 1.2 mM). The reason is similar to that with regard to Fe(III), that is to say, more Fe(II) and $\mathrm{Cit^{\cdot 2-}}$ are produced at higher citric acid concentration. However, when the citric acid concentration was further increased from 1.2 to 4.8 mM, the percentage reduction after 60 min was decreased

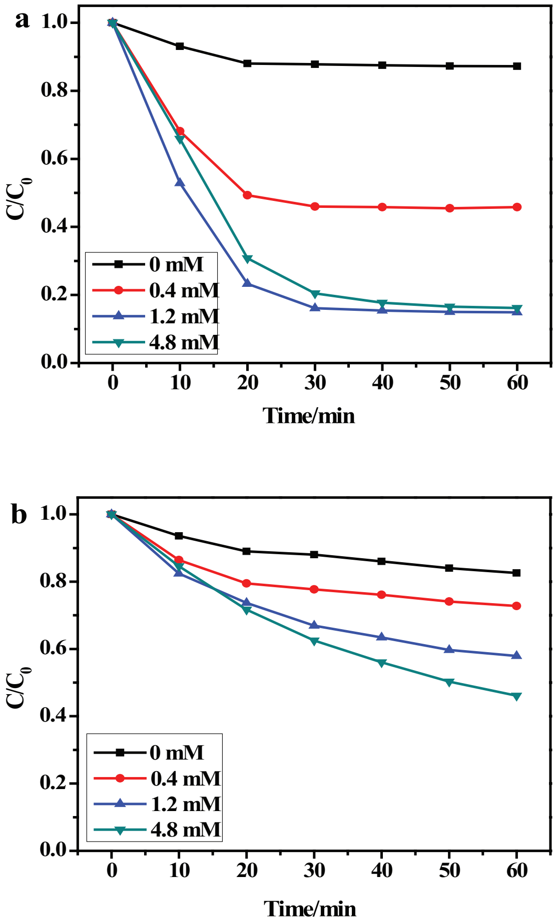

Fig. 7. Effect of initial citric acid concentration on simultaneous reduction of Cr(VI) (a) and decolorization of OII (b) in photo/ferricitrate system. Experimental conditions: [Fe(III)] = 0.2 mM, [Cr(VI)] = 0.2 mM, [OII] = 10 mg/L and pH = 3.0.

from 85% to 83%. This behavior may also be related to the reoxidization of Cr(III) by ·OH. Different from Cr(VI), percentage decolorization for OII was always increased with increasing the initial Fe(III) concentration over the tested range.

3.6. Simultaneous reduction of Cr(VI) and decolorization of OII in photo/ferritartarate system

Tartaric acid is also a carboxylic acid and can form ferricarboxylate complex with Fe(III). Photo/ferritartarate system has been used, respectively, to reduce Cr(VI) and to decolorize OII [9,14]. In the present work, simultaneous reduction of Cr(VI) and decolorization of OII in the photo/ferritartarate system were also performed and the results are shown in Fig. 8.

It can be seen that the concentrations of both Cr(VI) and OII were also decreased with the reaction time, and the percentage reduction for Cr(VI) and the percentage decolorization for OII after 60 min reached 91% and 50%, respectively. The results indicate that the photo/ferritartarate system is also effective for simultaneous reduction of Cr(VI) and decolorization of OII. It is worth noting that in the initial stage, Cr(VI) concentration was sharply decreased and the percentage reduction reached 83% only after 10 min, which is much higher than that in Fe(III)/Cit system (35%). Such difference may be due to the fact that tartaric acid has higher Fe(III) photoreductivity than citric acid [23].

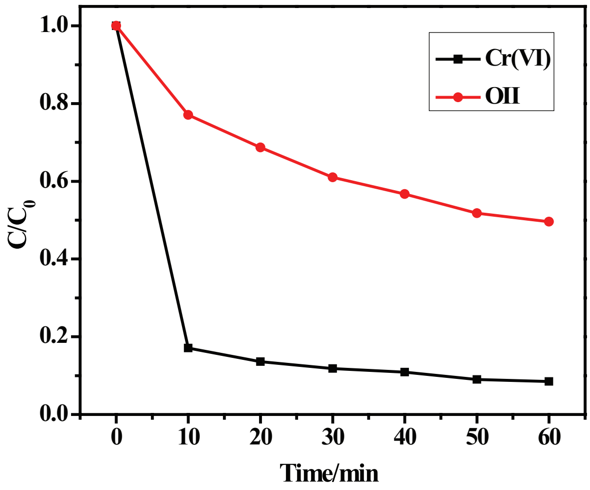

Fig. 8. Simultaneous reduction of Cr(VI) and decolorization of OII in photo/ferritartarate system. Experimental conditions: [Fe(III)] = 0.2 mM, [Cr(VI)] = 0.2 mM, [OII] = 10 mg/L, [Cit] = 2.4 mM and pH = 3.0.

Although simultaneous reduction of Cr(VI) and decolorization of OII in the photo/ferricitrate and photo/ferritartarate systems are effective, the decolorization efficiency for OII is relatively low. Further investigation is needed for improvement of the decolorization efficiency and will be the subject of future publications.

4. Conclusions

The following conclusions can be withdrawn from the results obtained in the present work: homogeneous photo/ferricitrate system is effective in simultaneous reduction of Cr(VI) and decolorization of OII. The percentage reduction for Cr(VI) and percentage decolorization for OII in such system strongly depends on the operating parameters, such as light intensity, initial pH and initial concentrations of Fe(III) and citric acid. The influence of initial concentrations of Fe(III) and citric acid on reduction of Cr(VI) differs from decolorization of OII. Homogeneous photo/ferritartarate system is also effective in such co-treatment. Photo/ferricitrate system only under solar light also has certain activity for simultaneous reduction of Cr(VI) and decolorization of OII.

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