Adsorption and photo-induced reduction of Cr(VI) ion in Cr(VI)–4CP(4-chlorophenol) aqueous system in the presence of TiO₂ as photocatalyst

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Abstract

Dark adsorption of Cr(VI) ion on TiO₂ is mainly dependent on Cr(VI) concentration and the system acidity. 4-Chlorophenol (4CP) has no interference on Cr(VI) adsorption. Cr(VI) can easily be photocatalytically reduced under UV irradiation with TiO₂ as catalyst. The reduction is in accord with the Langmuir–Hinshelwood (L–H) kinetic equation. Under the UV irradiation, photo-induced Cr(VI) reduction is observed in either Cr(VI)–4CP or Cr(VI)–4CP–TiO₂ system. Light intensity and system acidity are two main roles influencing both reactions. The linear decrease in Cr(VI) concentration reveals the zero order of Cr(VI) reduction rate in both systems. Two different reactions are involved in Cr(VI)–4CP–TiO₂ system under the experimental UV irradiation: the photo-induced homogeneous reaction between Cr(VI) and 4CP, and the photocatalytic reaction on TiO₂ semiconductor photocatalyst. In the condition of excluding homogeneous reactions between Cr(VI) and 4CP, the promotive effect of 4CP on photocatalytic reduction of Cr(VI) in Cr(VI)–4CP–TiO₂ system is distinguished and confirmed. Under the sunlight irradiation, no reaction is observed in Cr(VI)–4CP system. Photocatalytic reduction efficiency of Cr(VI) ion on TiO₂ in Cr(VI)–4CP–TiO₂ system under the sunlight irradiation is much larger than that in Cr(VI)–TiO₂ system.   © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cr(VI) adsorption; Cr(VI) reduction; Cr(VI)–4CP-TiO₂ system; Photocatalysis

1. Introduction

As an efficient means for pollution treatment, semiconductor photocatalysis has attracted more and more attention [1–5]. A great deal of toxic and bioresistant organic and inorganic compounds in aqueous solutions have been reported to be transformed into harmless species. But unfortunately, many studies on photocatalytic decontamination concern only the single component systems. There are few papers concerning decontamination of complex systems, which, however, are the actual situations of the real environmental pollution. Many waste streams may contain mixtures of hazardous organic and inorganic species. The spontaneous reactions among them under environmental conditions are negligible. Photocatalysis has special advantages in decontamination in these pollution systems because, as we know, it can complete the reduction of metal ions and the oxidation of organic species. From the theory of photocatalysis, waste

metal ions and organic species can get photo-excited electrons and holes, respectively, and be decontaminated simultaneously. Being the redox half reactions of photocatalysis, these two processes must be influenced synergically.

In our study, Cr(VI)–chlorophenol co-existed system is considered because both of them are important industry pollution species and their mixture can be easily found in many waste streams. Cr(VI), as one of the toxic heavy metal ions, has attracted much attention because of its quite high toxicity and mobility. It is a suspected carcinogen and is difficult to be removed from water by other physical or chemical methods. Cr(III), another environmentally stable oxidation state of chromium, is relatively noncarcinogenic and less toxic. It is not so mobile like Cr(VI) and can be easily removed in alkaline medium. Photocatalytic reduction of Cr(VI) to Cr(III) has been studied in different suspensions and reactor systems [6–13]. Cr(VI) can easily accept photo-excited conduction band electrons and be reduced, especially in the acidic medium. But in related investigations, adsorption of Cr(VI)

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on the catalyst was neglected and the kinetic and mechanisms of Cr(VI) reduction were rarely studied.

Chlorophenols are another type of important pollutant. They are common chemical intermediates of many industrial processes and can be found in large amounts in waste streams. Many investigators have studied the photocatalytic degradation of chlorophenols. The conditions of the reaction, kinetics and mechanisms have been discussed in many papers [14–17].

In this paper, the results of Cr(VI) dark adsorption on TiO$_2$ and UV or sunlight-induced Cr(VI) reduction in Cr(VI)–TiO$_2$, Cr(VI)–4CP(4-chlorophenol), and Cr(VI)–4CP–TiO$_2$ systems are presented. In the condition of excluding other homogeneous reactions, the synergism between photocatalytic half reactions was distinguished and confirmed in Cr(VI)–4CP–TiO$_2$ system.

2. Experimental

2.1. Materials

Analytical grade K$_2$Cr$_2$O$_7$ was used to prepare Cr(VI) solution. Chemical pure 4CP was dissolved in water before reaction. The de-ionized water was used as solvent. P-25 TiO$_2$ was used as received. It has been reported to be a nonporous 70:30 anatase to rutile mixture, with BET surface area of about 55 ± 15 m^2/g and crystallite size of 30 nm in 0.1-μm diameter aggregates [1]. Dilute NaOH and HNO$_3$ were used to adjust pH of the reaction solution.

2.2. Reaction

All experiments were performed in quartz vials of approximate 150-ml capacity. Reaction suspensions were prepared by using 50 ml of 2 mmol/l freshly prepared Cr(VI) and 4CP solutions. Around 100 mg of TiO$_2$ was added. The reactor was sealed to prevent the volatilization of the solutes. In experiments investigating the effects of different atmospheres, O$_2$ or N$_2$ were purged into the reactor for about 30 min in darkness before and throughout the reaction. The mixture inside the reactor were magnetically stirred. Sunlight reactions were performed under the direct irradiation of the sun on June 22, 1996 (a sunny day), in Lanzhou, China, from 10:00 to 16:00 h. All experiments were carried out at room temperature except the thermal reaction experiments, in which the reactor was placed in a water bath with temperature regulation. Medium pressure 250-W and 125-W mercury lamps were used as UV light source, which have the radiation from about 300 nm to 600 nm, and peaks at 360 nm, 410 nm, 440 nm, 550 nm and 580 nm. Each group of experiment was performed at least three times.

2.3. Chemical analysis

The initial concentrations were determined before reaction. About 1 ml of suspension was removed as the sample at

suitable reaction time. After removing TiO$_2$ by centrifugation, Cr(VI) concentration was determined colorimetrically at 546 nm using diphenylcarbazide as color agent. Experimental results showed that other reactants and products in reaction systems had little interference on Cr(VI) determination. Concentration of 4CP was determined by HPLC using a Varian 5000 HPLC instrument with an ODS column. The detection wavelength were 254 nm. The eluent consists of a mixture of methanol and water (70:30 by volume). pH of the systems was measured using a Markson pH meter. UV-Vis spectra were taken on a Shimadzu UV-365. ESR characterization was performed on a Varian E-115.

3. Results and discussion

3.1. Cr(VI)–TiO$_2$ system

3.1.1. Cr(VI) dark adsorption on TiO$_2$

Experimental results showed that adsorption of Cr(VI) on TiO$_2$ surface reaches saturation in about 30 min. So Cr(VI) concentration in the suspension, after being stirred in darkness for 1 h, was determined as the equilibrium concentration. The amount of Cr(VI) adsorbed on TiO$_2$ can be calculated from the following equation:

$$[Cr(VI)]_{adsorbed} = [Cr(VI)]_{initial} - [Cr(VI)]_{suspension}$$

(1)

With different initial concentrations, Cr(VI) adsorption on TiO$_2$ was investigated at pH 2.5 in dark condition (see Fig. 1). It can be seen that the amount of Cr(VI) adsorbed on TiO$_2$ increases with Cr(VI) concentration up to 300 μmol/l. But at the Cr(VI) concentrations above 300 μmol/l, the amount of Cr(VI) adsorbed on TiO$_2$ decreases obviously. This is due to the alteration of Cr(VI) existence forms in different Cr(VI) concentration ranges, such as [18]:
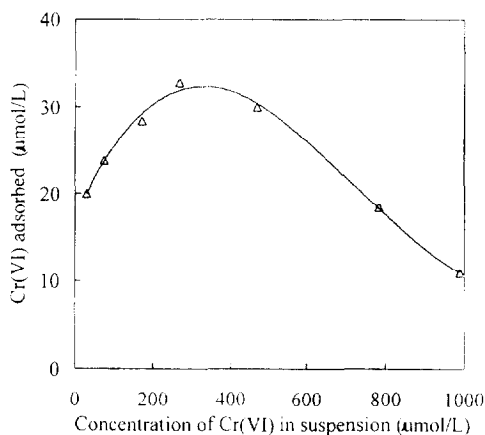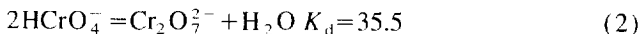
$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \quad K_d = 35.5$$

(2)

Fig. 1. Cr(VI) adsorption onto 1 g/l TiO$_2$ at pH 2.5, room temperature and air atmosphere.

With the increase in Cr(VI) concentration, more $Cr_2O_7^{2-}$ species are formed, which have weaker adsorption ability than $HCrO_4^-$ and is able to repel the adsorption of $HCrO_4^-$ species on TiO_2. The result is that Cr(VI) adsorption decreases with the increase in Cr(VI) concentration when it is larger than 300 μmol/l. Only at the Cr(VI) initial concentration below 30 μmol/l, Cr(VI) adsorption on TiO_2 can be simplified to a linear adsorption isotherm:

$$[Cr(VI)]_{adsorbed}=S+k[Cr(VI)]_{suspension} \qquad (3)$$

From Fig. 2, $S = 3.6$ μmol/l and $k = 0.97$ can be obtained.

With an initial concentration of 30 μmol/l, the influences of pH, atmosphere and temperature on Cr(VI) adsorption were investigated. The pH of suspension affects Cr(VI) adsorption dramatically. If pH is increased to 6, only 5% of 30 μmol/l Cr(VI) was adsorbed on TiO_2, about 10 times smaller than that at pH 2.5. This is due to the alteration of Cr(VI) existence forms with the change of system pH, such as [18]:

$$HCrO_4^- =H^+ +CrO_4^{2-} \quad pK_a=6.52 \qquad (4)$$
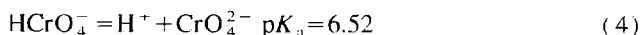
The change of the amount of OH^- on the surface of TiO_2 may be another reason of such pH influence. It is reported that PZC of P-25 TiO_2 is about pH 6.25 [1]. So at pH below 6.25, the surface is electropositive, which favors the adsorption of Cr(VI) anions. On the contrary, when pH is above 6.25, the surface is electronegative, the adsorption of Cr(VI) anions is decreased with the increase in system pH.

The effect of atmosphere on Cr(VI) adsorption is not observed, which means that oxygen and any other components in the atmosphere have no competitive adsorption with Cr(VI) ions. The influence of temperature on Cr(VI) adsorption is also very small. When the temperature is increased from 15°C to 50°C, the efficiency of Cr(VI) adsorption only increases from 50% to 56%.

3.1.2. Photocatalytic Cr(VI) reduction in Cr(VI)–TiO₂ system

Photocatalytic Cr(VI) reduction has been studied by many investigators using semiconductor catalyst such as CdS, WO_3
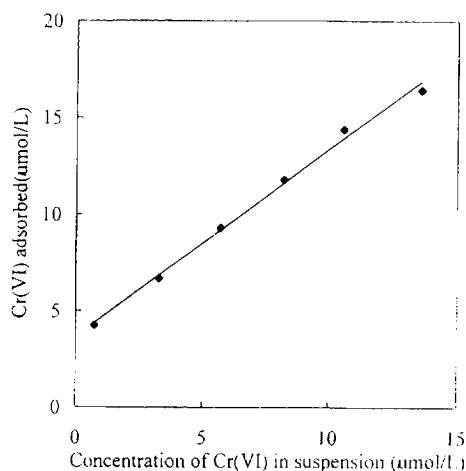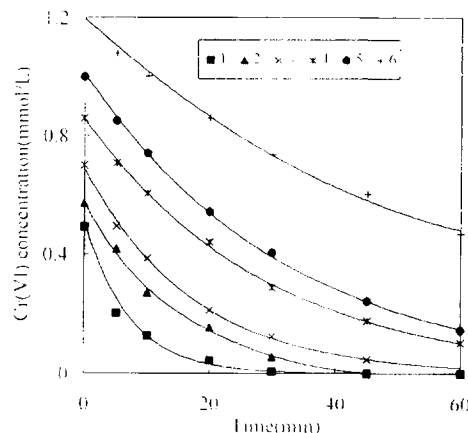

Fig. 3. Photocatalytic reduction of Cr(VI) ion on TiO_2 with different Cr(VI) initial concentrations under UV irradiation. Reaction conditions: TiO_2 concentration: 1 g/l; pH 2.5; room temperature; air atmosphere; light source: 250-W mercury lamp; Cr(VI) initial concentrations (mmol/l): (1) 0.48; (2) 0.57; (3) 0.70; (4) 0.86; (5) 1.00; (6) 1.23.
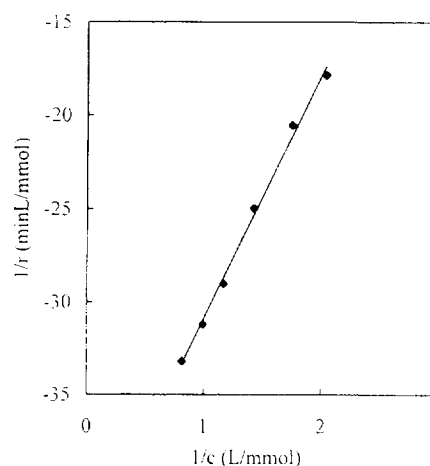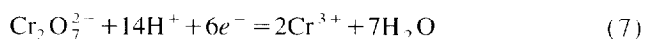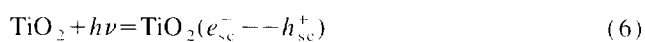

Fig. 4. A Langmuir–Hinshelwood plot of photocatalytic Cr(VI) reduction.

and TiO_2 [6–13]. The general results are that Cr(VI) can be easily photocatalytically reduced under UV irradiation. The reaction is mainly dependent on the light intensity and the system acidity. In our lab, P-25 TiO_2 was used as photocatalyst, about 80% of 1 mmol/l Cr(VI) is reduced in 1 h at pH 2.5, room temperature and air condition, with a 250-W mercury lamp as light source. It is found that the system atmosphere has no influence on Cr(VI) reduction in either acidic or neutral media. Kinetic studies showed that Cr(VI) reduction under UV irradiation is in accord with Langmuir–Hinshelwood equation:

$$1/r=1/CkK+1/k \qquad (5)$$

as shown in Figs. 3 and 4. Under the reaction conditions mentioned above, the apparent binding constant $K = 3.35$ l/mmol and the reaction rate constant $k = 0.023$ mmol/l per minute are obtained, respectively. The mechanism of photocatalytic Cr(VI) reduction is not very clear, but the redox process is always outlined as follows: Cr(VI) captures the

Fig. 2. Linear isotherm of Cr(VI) adsorption onto TiO_2.

photo-excited conduction band electrons and is reduced, H_2O gets the valence band holes, and the following photocatalytic redox cycle is fulfilled:

$$TiO_2 + h\nu = TiO_2(e_{cb}^- - - h_{vb}^+) \tag{6}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O \tag{7}$$

$$2H_2O + 4h^+ = O_2 + 4H^+ \tag{8}$$

3.2. Cr(VI)–4CP–TiO₂ system

3.2.1. Cr(VI) dark adsorption on TiO₂ in Cr(VI)–4CP–TiO₂ system

The thermal reaction between Cr(VI) and 4CP reported by Elovitz and Fish [18,19] is not observed in acidic medium in the absence of TiO_2, even if the system is heated to 50°C and placed under the sunlight irradiation. This may be due to the fact that the concentrations of the reactants are much smaller than that reported in the literature, and the efficiency of thermal reduction of Cr(VI) in Cr(VI)–4CP homogeneous system is not large enough to be observed.

The effect of 4CP on Cr(VI) adsorption on TiO_2 was studied in acidic medium. Analyzed theoretically, the presence of organic molecules would decrease the adsorption efficiency of Cr(VI) because of the competitive adsorption on the active sites. A good example is that Mesuere and Fish [20] have reported the interference of oxalic acid on Cr(VI) adsorption on goethite. But in Cr(VI)–4CP–TiO₂ system, the interference of 4CP on Cr(VI) adsorption onto TiO_2 is not observed in either acidic or neutral medium, even the initial concentrations of Cr(VI) and 4CP are both decreased to 30 μmol/l. Deng and Stone also found that in TiO_2–Cr(VI)–Atrolatic Acid (A.A.) heterogeneous system, A.A. had little influence on Cr(VI) adsorption [21]. In many previous studies on photocatalytic degradation of 4CP, 4CP adsorption is thought to be the primary step of photocatalytic reaction process, though it is still ambiguous whether 4CP is oxidized indirectly by ·OH or directly through getting valence band holes, and whether it is oxidized at the catalyst surface or in the solution. The absence of interference of 4CP on Cr(VI) adsorption indicated that: (1) If 4CP adsorbs on TiO_2, its adsorption sites must be different from that for metal ions, and competitive adsorption does not take place; (2) 4CP can not be easily adsorbed on TiO_2. Even if it does, the adsorption must be negligible. Thus, the photocatalytic oxidation of 4CP must be an indirect process, in which ·OH diffuses into solution to oxidize and mineralize 4CP.

Adsorption process plays an important role in photocatalytic reactions. The studies on co-adsorption of metal ions and organic species on photocatalysts provide some information about the mechanism of photocatalysis. Further investigation about adsorption of metal ions and organic species onto oxide catalysts is needed and being planned in our lab.

3.2.2. UV-induced Cr(VI) reduction in Cr(VI)–4CP–TiO₂ system and Cr(VI)–4CP system

Under UV irradiation, Cr(VI) reduction is observed not only in Cr(VI)–4CP homogeneous system in the absence of TiO_2 catalyst, but also in Cr(VI)–4CP–TiO₂ system, as shown in Fig. 5. Light intensity and system acidity are two important factors affecting both reactions. Temperature changing from 15°C to 50°C has negligible influence on Cr(VI) reduction. Oxygen has a little enhancement for Cr(VI) reduction in Cr(VI)–4CP homogeneous system without TiO_2. But in the presence of TiO_2 as catalyst, the effect of reaction atmosphere is not observed. The linear decrease in Cr(VI) concentration shown in Fig. 5 indicated the zero order of Cr(VI) reduction rate in both reactions under UV irradiation. This is also the general kinetic characteristic of photo-induced reactions.

The UV-Vis absorption spectra of the mixtures during the UV-induced homogeneous reaction are shown in Fig. 6. The maximum absorption of Cr(VI) at about 380 nm decreases along with the reaction time. The products have absorption below 600 nm.

After reaction, the concentration of 4CP was determined and its conversion efficiency was given in Table 1. It can be seen that the photolysis of 4CP, which has obvious UV absorption at about 310 nm (see Fig. 6), takes place under the experimental UV irradiation. The presence of Cr(VI) and/or TiO_2 promote its conversion efficiency.

3.2.3. UV-induced Cr(VI) reduction in Cr(VI)–4CP homogeneous system

The UV-induced reactions in homogeneous Cr(VI)–4CP system may result from thermal or photo-induced redox reactions between Cr(VI) and the photolysis products of 4CP.
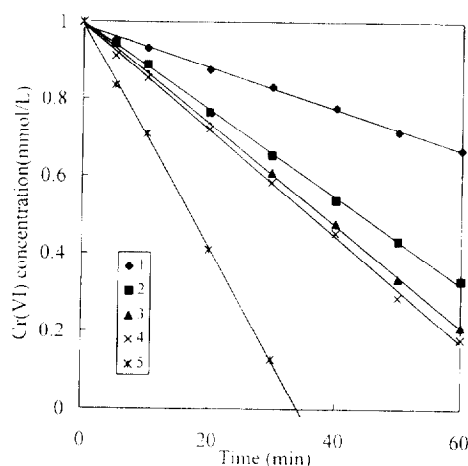

Fig. 5. UV induced Cr(VI) reduction in Cr(VI)–4CP and Cr(VI)–4CP–TiO₂ systems. Reaction conditions: TiO_2 concentration: 1 g/l; room temperature: air atmosphere; Cr(VI) and 4CP initial concentrations: 1 mmol/l. (1) Cr(VI)–4CP system; pH 6; light source: 125-W mercury lamp. (2) Cr(VI)–4CP system: pH 2.5; light source: 125-W mercury lamp. (3) Cr(VI)–4CP system: pH 2.5; light source: 250-W mercury lamp. (4) Cr(VI)–4CP–TiO₂ system: pH 6; light source: 125-W mercury lamp. (5) Cr(VI)–4CP–TiO₂ system: pH 2.5; light source: 125-W mercury lamp.
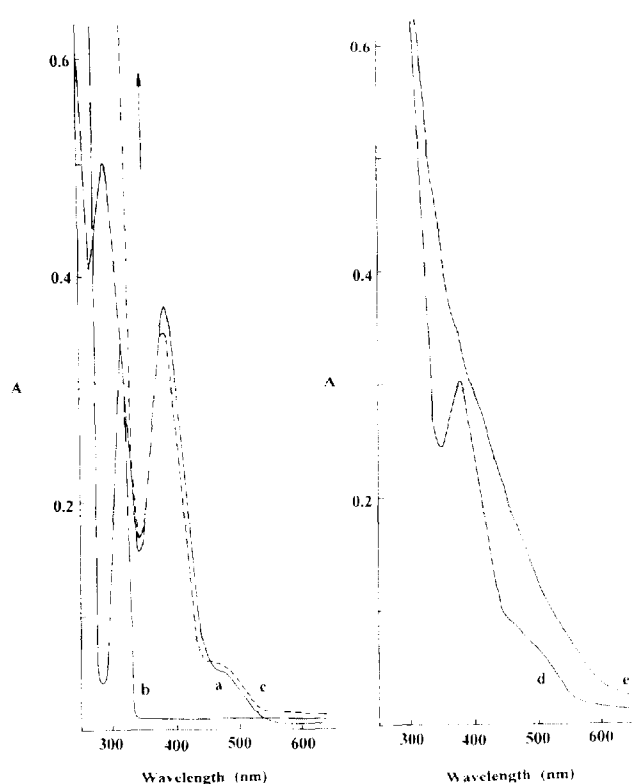
Fig. 6. UV-Vis absorption spectra of Cr(VI)–4CP mixtures during the UV-induced reaction. Reaction conditions: pH 2.5; light source: 125-W mercury lamp; Cr(VI) and 4CP initial concentrations: 1 mmol/l. (a) Cr(VI); (b) 4CP; (c) Cr(VI) + 4CP without irradiation; (d) Cr(VI) + 4CP irradiated for 10 min; (e) Cr(VI) + 4CP irradiated for 60 min.

Table 1
Conversion efficiencies of 4CP in different reaction systems[a]

No.	Reactants	Atmosphere	Conversion efficiency (%)
1	4CP	N_2	34
2	4CP	O_2	42
3	Cr(VI) + 4CP	N_2	51
4	Cr(VI) + 4CP	O_2	57
5[b]	Cr(VI) + 4CP + TiO_2	air	76

[a]Reaction conditions: Cr(VI) and 4CP initial concentrations: 1 mmol/l; TiO_2 concentration: 1 g/l; pH 2.5; reaction time: 1 h.
[b]Reaction time: 40 min.

Although Cr(VI) has no obvious thermal redox reactions with 4CP, it would be reduced by the photolysis products of 4CP. In other experiments, Cr(VI) is UV irradiated for 30 min, 4CP is then added and placed in darkness at pH 2.5. Concentrations of both Cr(VI) and 4CP do not decrease. When 4CP is firstly subjected to UV irradiation for 30 min, and then Cr(VI) is added and placed in darkness at pH 2.5, 10% Cr(VI) is reduced in about 1 min, and 21% Cr(VI) is reduced after 1 h. After 5 h, Cr(VI) concentration does not decrease any more. Its reduction efficiency is 30%. The concentration of 4CP does not change during the dark process. This verified the existence of dark thermal reactions between Cr(VI) and the photolysis products of 4CP. When Cr(VI)–

4CP system is UV irradiated for 30 min and then placed in darkness, only a little decrease of Cr(VI) concentration is observed. After 15 min, Cr(VI) reduction efficiency has a 5% increase, and an 8% increase after 3 h and then changes little any more. Concentration of 4CP does not change when the UV irradiation is stopped. This means that the photolysis of 4CP is fast, but the reactions between Cr(VI) and the photolysis products of 4CP are slow, which continue even after the UV irradiation is stopped.

Oxygen promotes the photolysis of 4CP, so it enhances Cr(VI) reduction in Cr(VI)–4CP system under UV irradiation. But in Cr(VI)–4CP–TiO_2 heterogeneous system, due to the quite large reduction rate of Cr(VI), the effect of oxygen is concealed and could not be observed.

4CP conversion efficiency is increased in Cr(VI)–4CP system, which means that the presence of Cr(VI) promotes 4CP conversion. Cr(VI) reduction efficiency in Cr(VI)–4CP system under UV irradiation is much larger than that in the dark reaction with the photolysis products of 4CP. These results indicate that besides the dark thermal reactions between Cr(VI) and the photolysis products of 4CP, other photoreactions between Cr(VI) and 4CP or the photolysis products of 4CP also take place in Cr(VI)–4CP system under UV irradiation.

3.2.4. UV-induced Cr(VI) reduction in Cr(VI)–4CP–TiO_2 system

In the presence of TiO_2, the reduction rate of Cr(VI) and the conversion efficiency of 4CP are both increased in Cr(VI)–4CP–TiO_2 system comparing with Cr(VI)–4CP system. From Section 3.1.2, we can easily understand that TiO_2 is an efficient photocatalyst in Cr(VI)–4CP–TiO_2 system. Cr(VI) ion and 4CP can be photocatalytically reduced or oxidized on TiO_2. So two different reactions would be involved in Cr(VI)–4CP–TiO_2 heterogeneous system under experimental UV irradiation: the photo-induced homogeneous reaction between Cr(VI) and 4CP, and the photocatalytic reaction of Cr(VI) and 4CP on TiO_2 semiconductor photocatalyst. It is difficult to separate the contribution of them to the overall Cr(VI) reduction under the above experimental conditions.

The ESR spectrum of product Cr(III) on TiO_2 catalyst after the UV-induced reactions in Cr(VI)–4CP–TiO_2 system is given in Fig. 7, in which $g = 1.984$ and $\Delta Hpp = 60$ mT were obtained.

Al_2O_3 was also used in this system instead of TiO_2. The experimental results showed that the decrease in Cr(VI) concentration are composed of Cr(VI) adsorption on Al_2O_3 and Cr(VI) reduction from the UV-induced Cr(VI)–4CP homogeneous reaction, which indicates that heterogeneous surface catalytic reaction does not happen on Al_2O_3. These results further confirmed the photocatalytic reaction on TiO_2 in Cr(VI)–4CP–TiO_2 system under UV irradiation.

Although the direct photolysis of 4CP under UV irradiation and the photocatalytic degradation of 4CP in 4CP–TiO_2 system have been investigated in many papers [1,22–25], the
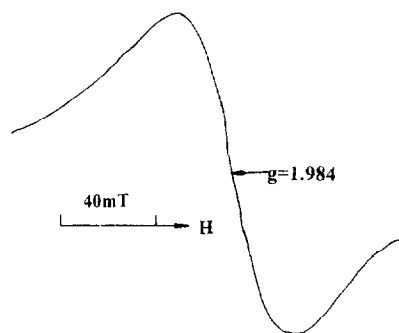
Fig. 7. ESR spectrum of the reaction product Cr(III) on TiO₂ in Cr(VI)–4CP–TiO₂ system. Reaction conditions: pH 2.5; light source: 125-W mercury lamp; TiO₂ concentration: 1 g/l; Cr(VI) and 4CP initial concentrations: 1 mmol/l; reaction time: 60 min.

details of the mechanism of photo-induced reactions in Cr(VI)–4CP and Cr(VI)–4CP–TiO₂ systems and the products of 4CP oxidation are much complicated. In this paper, photo reactions in Cr(VI)–4CP and Cr(VI)–4CP–TiO₂ systems are only discussed from the aspect of Cr(VI) reduction. Further investigation on the oxidation of 4CP are needed in order to completely understand the photo-behavior in these systems, which is in progress in our lab and is expected to be discussed in a forthcoming paper.

3.2.5. Photocatalytic Cr(VI) reduction in Cr(VI)–4CP–TiO₂ system

Analyzed from the theory of photocatalysis, part of Cr(VI) reduction induced by photocatalytic reactions on TiO₂ in Cr(VI)–4CP–TiO₂ system under UV irradiation must be more efficient than that in Cr(VI)–TiO₂ system because of the promotive effect by photocatalytic degradation of 4CP. In such metal ion–organic compound coexisted system, 4CP gets holes from valence band directly or indirectly and is oxidized. This oxidation process consumes photo-excited holes promptly and efficiently, which attenuates electron-hole recombination and promotes photocatalytic Cr(VI) reduction on TiO₂.

Such promotive effects have been proposed by Prairie et al. [26]. They ascribed it to the synergism between photocatalytic redox half reactions. But the results they presented were not very exact, because in their experiments, thermal and UV-induced homogeneous reactions between Cr(VI) and many organic compounds, such as EDTA and 4CP, had not been considered. This means that although the synergism does exist between photocatalytic half reactions, the effect is not so much as they suggested because it has been concealed by thermal or UV-induced homogeneous reactions between reactants.

In order to confirm the photocatalytic reaction in Cr(VI)–4CP–TiO₂ system and prove the synergism between photocatalytic half reactions, experiments under the light with wavelength above 340 nm (using glass to absorb part of light with wavelength below 340 nm) were performed in Cr(VI)–4CP, Cr(VI)–TiO₂, and Cr(VI)–4CP–TiO₂ systems. No reaction is observed in Cr(VI)–4CP system, which indicates

that no homogeneous reaction takes places between Cr(VI) and 4CP when photolysis of 4CP can not occur. After reaction for 1 h in acidic media, about 42% and 63% of Cr(VI) ions are reduced in Cr(VI)–TiO₂ and Cr(VI)–4CP–TiO₂ systems, respectively. No homogenous reaction takes place in Cr(VI)–4CP–TiO₂ system, so the decrease in Cr(VI) concentration can only be ascribed to the photocatalytic reduction on TiO₂. Photocatalytic reduction efficiency of Cr(VI) in Cr(VI)–4CP–TiO₂ system is much larger than that in Cr(VI)–TiO₂ system. This indicated the promotive effect of 4CP on photocatalytic reduction of Cr(VI) ions. Thus, in the condition of excluding homogeneous reactions, the photocatalytic reaction and the synergism between photocatalytic half reactions are distinguished and confirmed in Cr(VI)–4CP–TiO₂ system.

Further experiments were performed to study the photobehavior in Cr(VI)–4CP–TiO₂ system under the sunlight irradiation.

3.3. Sunlight induced photocatalytic Cr(VI) reduction in Cr(VI)–4CP–TiO₂ system

Semiconductor based photocatalytic process for removing water contamination has been studied for about 20 years. One goal of these studies is to use the sun as light source. For TiO₂ catalyst which has been widely used in photocatalysis, UV irradiation with wavelength below 387.5 nm is necessary for the activation because of its pretty large bandgap (3.2 eV). At the ground level, solar irradiation starts at a wavelength of about 300 nm. Therefore, part of sunlight with wavelength 300–387.5 nm can be used by TiO₂ photocatalytic systems [5].

Under the sunlight irradiation, decrease in Cr(VI) concentration is observed in both Cr(VI)–TiO₂ and Cr(VI)–4CP–TiO₂ systems (see Table 2). The presence of 4CP increases the reduction efficiency of Cr(VI) remarkably. The same influence of the pH, temperature and atmosphere on Cr(VI) reduction are found as that in the reactions under UV irradiation.

No other homogeneous reactions occur between Cr(VI) and 4CP under the sunlight irradiation, even the pH is

Table 2
Conversion efficiencies of Cr(VI) and 4CP in different sunlight reaction systems

No.	Reactants	pH	Cr(VI) reduction efficiency (%)	4CP conversion efficiency (%)
1	Cr(VI)	2.5	37	
2	Cr(VI)	6	13	
3	Cr(VI) + 4CP	2.5	74	12
4	Cr(VI) + 4CP	6	43	11

Reaction conditions: Cr(VI) and 4CP initial concentrations: 1 mmol/l; TiO₂ concentration: 1 g/l; air atmosphere; room temperature; reaction time: 3 h. Sunlight reactions were performed on June 22, 1996 (a sunny day), in Lanzhou, China.

decreased to 2.5. This may be due to the fact that the sunlight is too weak to induce such reactions. So the reduction of Cr(VI) ion in Cr(VI)–4CP–TiO₂ system under the sunlight irradiation could result only from the photocatalytic reactions on TiO₂. The remarkable increase in Cr(VI) reduction efficiency in the presence of 4CP comparing with Cr(VI)–TiO₂ system can only be ascribed to the promotive effect of 4CP on photocatalytic reduction of Cr(VI) ion.

For comparison, Al₂O₃ and SiO₂ were also used respectively in this system instead of TiO₂. Adsorption equilibrium of Cr(VI) ion was achieved rapidly. But no any further reaction is observed. This also confirmed the photocatalytic effect of TiO₂ in Cr(VI)–4CP–TiO₂ system.

Experiments were also performed under room-light to test the influence of the light intensity. Reduction of Cr(VI) is also observed, but the efficiency is much smaller than that of the sunlight reaction. This dramatic decrease is due to the weakness of the light intensity and the decrease in the UV amount after the sunlight passes through window glass.

We wish to mention here that papers published recently by Deng and Stone [21,27], in which the thermal heterogeneous surface catalytic reactions on suspended TiO₂ in Cr(VI)–TiO₂–organic species systems were studied. We found that they have not paid attention to the comparative studies on dark reactions and photo induced reactions in these systems under the sunlight or room-light irradiation. So whether the reactions result from thermal catalysis or photocatalysis under room-light of their lab is still not very clear, because, the sunlight or room-light induced photocatalytic reactions in these systems would also take place as discussed above. The organic compounds they used, such as mandelic acid, methyl mandelate and atrolatic acid, are active organic species and can be easily photocatalytically oxidized, especially in the presence of strong oxidant like Cr(VI) ion.

4. Conclusions

System pH and Cr(VI) concentration affect Cr(VI) dark adsorption on TiO₂ remarkably. With the increase in pH, Cr(VI) adsorption efficiency decreases. The maximum adsorption of Cr(VI) on TiO₂ is achieved when its concentration is about 300 μmol/l. Only when the initial concentration is below 30 μmol/l, Cr(VI) adsorption can be simplified to a linear isotherm. Cr(VI) ion can be easily photocatalytically reduced under UV irradiation with TiO₂ as catalyst. The reduction is in accord with the L–H equation. The pH of the system and the light intensity are important factors, but atmosphere has no influence on Cr(VI) reduction.

The presence of 4CP in Cr(VI)–TiO₂ system has no interference on Cr(VI) adsorption on TiO₂. Under UV irradiation, the reactions in Cr(VI)–4CP–TiO₂ system are much complicated and two different reactions are important for the overall Cr(VI) reduction: the photo-induced homogeneous reaction between Cr(VI) and 4CP, and the photocatalytic reduction of Cr(VI) by TiO₂ as semiconductor catalyst. The

promotive effect of 4CP on photocatalytic Cr(VI) reduction is distinguished and confirmed in the condition of excluding homogeneous reactions in Cr(VI)–4CP–TiO₂ system.

Under the sunlight irradiation, obvious photocatalytic reduction of Cr(VI) by TiO₂ is observed in both Cr(VI)–TiO₂ and Cr(VI)–4CP–TiO₂ systems. Cr(VI) reduction efficiency in Cr(VI)–4CP–TiO₂ system is much larger than that in Cr(VI)–TiO₂ system.

The results presented above not only described the photobehavior of multi-component complex pollution systems which are more similar to the real environmental situations than single component systems studied before, but also revealed the possibility of efficient photocatalytic decontamination using the sunlight directly as light source. The synergism effect demonstrated in this work gives us an enlightenment to optimize both half reactions of photocatalysis in order to get an efficient pollution treatment, and indicates that photocatalytic decontamination may be more useful when applying directly to the waste water naturally containing both toxic heavy metal ions and hazardous organic species.

More investigation on the oxidation of 4CP products, kinetics and mechanism, are needed and are in progress in our lab. The results will help us further understand the photobehavior in metal ions–organic compounds co-existed pollution systems.

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