

Short communication

# Simultaneous photocatalytic reduction of Cr(VI) and oxidation of bisphenol A induced by Fe(III)–OH complexes in water

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## Abstract

Simultaneously photocatalytic reduction of Cr(VI) and oxidation of bisphenol A (BPA) in aqueous solution in the presence of Fe(III)–OH complexes were investigated under a 250 W metal halide lamp ( $\lambda \geq 365$  nm). Synergy effect of the simultaneous photocatalytic oxidation and reduction of both pollutants was achieved. The effects of initial pH value, initial concentration of BPA, Cr(VI) and Fe(III) were preliminarily investigated. The results showed that both photocatalytic reduction of Cr(VI) and degradation of BPA could occur simultaneously in the Fe(III)/Cr(VI)/BPA ternary system, and the rates of photocatalytic reduction of Cr(VI) and the oxidation of BPA were more rapid at a low pH range of 2.0–3.0. The increase of the initial concentration of Fe(III) was favorable to both photocatalytic reduction of Cr(VI) and oxidation of BPA. The reduction efficiency of Cr(VI) decreased with increasing initial concentrations of Cr(VI) and BPA, but the degradation efficiency of BPA was not changed obviously at different Cr(VI) concentrations.

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**Keywords:** Photoreduction; Photooxidation; Cr(VI); Bisphenol A (BPA); Fe(III)–OH complexes

## 1. Introduction

Chromium is an important industrial metal that is considered a priority pollutant, which is a known carcinogen and mutagen and can be acutely toxic. Chromium exists in two major oxidation states in aquatic environments. One is Cr(VI), which is considered to be the most toxic form of Cr, and the other is Cr(III), which is less mobile, less toxic and even essential for human and animal [1]. For these reasons, Cr(VI) reduction processes are the major focus of the environmental behavior of chromium. Organic matter, Fe(II) and sulfides are capable of reducing Cr(VI) [2,3]. Fe(II) is one of the dominant reductants of Cr(VI) used in treating industrial-generated Cr wastes [4].

Many studies have recognized that the photochemical cycling of Fe(III)/Fe(II) plays an important role in fresh, marine, and atmospheric waters [5]. Photoexcitation of Fe(OH)<sup>2+</sup> leads to

formation of •OH, which can take an active part in many environmental pollutants decomposition [6–8]. The photochemical reduction Cr(VI) in the presence of Fe(III)–OH complexes was reported to be influenced by both Cr(VI) and Fe(III)–OH concentrations and pH [9]. Thus, the photoexcitation of Fe(OH)<sup>2+</sup> can lead to formation of •OH and Fe(II) in water since the photolysis of Fe(III)–OH complexes can induce degradation of organic compounds as well as reduction of Cr(VI). A question is certainly proposed whether the two processes occur simultaneously in the photoredox system of Fe(III)–OH complexes to treat both organic and Cr(VI) pollutants. Actually, organic and inorganic pollutants usually coexist in the natural environment; it is necessary to concern decontamination simultaneously for applications [10,11]. In this work, we have studied the possible synergy effect of the simultaneous photocatalytic oxidation and reduction of organic and inorganic pollutants in the presence of Fe(III)–OH complexes. The photocatalytic reactions using a representative endocrine disrupter bisphenol A (BPA) and Cr(VI) were investigated in the ternary system consisted of Fe(III)/Cr(VI)/BPA. The influence factors, such as pH values, initial concentrations of Fe(III), Cr(VI) and BPA on the degradation were examined.

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## 2. Experimental

### 2.1. Materials

Fe(III) solution was prepared by dissolving  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Cr(VI) solution was prepared by using analytical grade potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). Chemically pure BPA was purchased from Damao Chemicals Co. (Tianjin, PRC) and used without purification. Acetonitrile was spectroscopic grade (Lingfeng Chemical Reagent Co., Shanghai, PRC). Hydrochloric acid and sodium hydroxide were used to adjust the pH values of the solutions. All of the other reagents were analytical grade. Pure water used was treated with an ultrapure water system (Liyuan Electric Instrument Co., Beijing, PRC).

### 2.2. Photochemical experiment

The photoreactor was designed with a cylindrical cell of 500 ml capacity, and a glass-jacket reactor surrounded an internal light source where the solution completely surrounded the light source. The temperature of the solution was maintained at  $25 \pm 2^\circ\text{C}$  by cooling water circulation. The light source was a 250 W metal halide lamp ( $\lambda \geq 365\text{ nm}$ , Chenguang Illumination Instrument, Jinzhou, PRC). The pH values of reaction solutions of 250 ml prepared were adjusted with hydrochloric acid and sodium hydroxide. The solution was put into the photoreactor and mixed with a magnetic stirrer placed at the bottom. Samples were collected at specific time intervals and analyzed immediately in order to avoid further reaction.

### 2.3. Analyses

The BPA concentration in aqueous solution was determined by high-pressure liquid chromatography (HPLC) [Shimadzu LC-6A pump, HP Zorbax SB-C18 column (4.6 mm  $\times$  150 mm, 5  $\mu\text{m}$ )] with a flow rate of  $1.0\text{ ml min}^{-1}$  and the UV absorbance was detected (Waters 481 detector) at 280 nm. The mobile phase was a mixture of acetonitrile and water (50/50, v/v). The injection volume was 20  $\mu\text{l}$ . The retention time of BPA was about 5.0 min. The concentration of Cr(VI) was determined at 540 nm by 1,5-diphenylcarbazide methods with a Shimadzu UV-160A UV-vis spectrophotometer [12].

All the measurements of BPA and Cr(VI) were carried out three times and the relative errors were all less than 5%.

## 3. Results and discussion

### 3.1. Synergistic effect among Fe(III), Cr(VI), and BPA

Figs. 1 and 2 show a comparison of photoreduction Cr(VI) and photooxidation BPA under different conditions. The results show that both reduction of Cr(VI) and oxidation of BPA have not noticeable change in single system at pH 3.0 before and after irradiation. In the two-component system with Cr(VI) and BPA, the photodecomposition rates of Cr(VI) and BPA are low; both of the decomposition efficiencies are about 20% after 120 min irradiation. In this system, Cr(VI) reduction is described via pho-

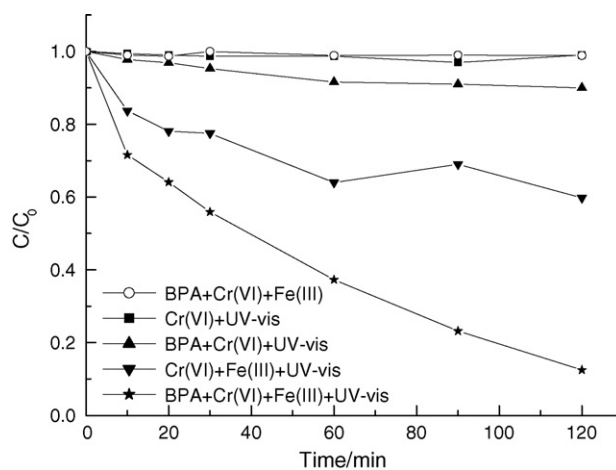
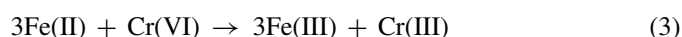
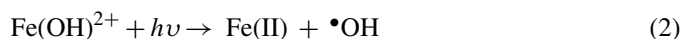


Fig. 1. Photoreduction of Cr(VI) under different conditions ( $[\text{BPA}]_0 = 20\ \mu\text{mol l}^{-1}$ ,  $[\text{Fe(III)}]_0 = 50\ \mu\text{mol l}^{-1}$ ,  $[\text{Cr(VI)}]_0 = 20\ \mu\text{mol l}^{-1}$ , pH 3.0).

toinduced electron transfer (PET) [13]. The reduction of Cr(VI) is accompanied by simultaneous oxidation of BPA, which plays a role of sacrificial electron donor. In acidic medium, Cr(VI) is reduced to Cr(III) according to the following reaction:



In the presence of Fe(III)–OH complexes, both the rates of photochemical reduction of Cr(VI) and oxidation of BPA are more rapid. In the Fe(III)/Cr(VI)/BPA system,  $\text{Fe(OH)}^{2+}$  acts as an effective photocatalyst in the degradation of BPA and reduction of Cr(VI), which provides an important source of  $\bullet\text{OH}$  and Fe(II) (reaction (2)) [14]. The  $\bullet\text{OH}$ , one of the most powerful oxidizing agents, would be thus responsible for the fast oxidation of the BPA while the simultaneous reduction of Cr(VI) to Cr(III) is attributed to Fe(II) (reaction (3)).



Consequently, in the Fe(III)/Cr(VI)/BPA ternary system, Cr(VI) is reduced via two pathways: (a) by PET and (b) by the

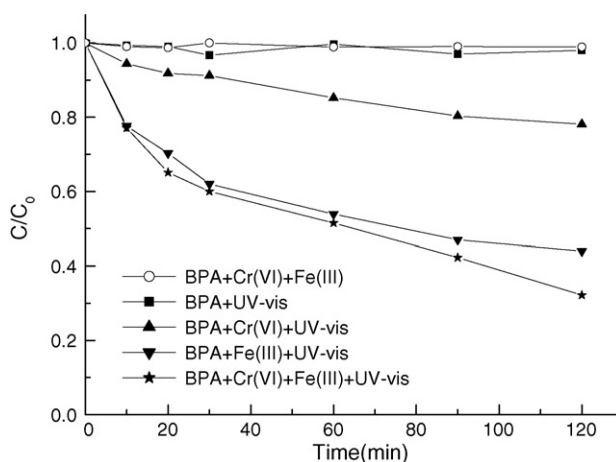


Fig. 2. Photodegradation of BPA under different conditions ( $[\text{BPA}]_0 = 20\ \mu\text{mol l}^{-1}$ ,  $[\text{Fe(III)}]_0 = 50\ \mu\text{mol l}^{-1}$ ,  $[\text{Cr(VI)}]_0 = 20\ \mu\text{mol l}^{-1}$ , pH 3.0).

Table 1  
Effect of the initial concentration of Fe(III), Cr(VI), and BPA and pH value on photoredox in ternary system (pH 3.0; exposure time 120 min)

Effect	pH	[Fe(II)] <sub>0</sub> (μM)	[Cr(VI)] <sub>0</sub> (μM)	[BPA] <sub>0</sub> (μM)	Photocatalytic decomposition			
					Rate of Cr(VI) (×10 <sup>5</sup> , μM s <sup>-1</sup> )	Rate of BPA (×10 <sup>5</sup> , μM s <sup>-1</sup> )	Ratio of Cr(VI) (%)	Ratio of BPA (%)
pH effect	2.0	50	20	20	6.66	6.02	99.1	98.2
	2.5				6.44	7.14	87.1	99.1
	3.0				5.71	3.38	87.5	67.8
	4.0				2.00	1.96	53.4	48.5
	5.0				1.76	1.58	49.9	44.9
	6.0				1.64	1.06	49.0	31.0
	7.0				1.02	0.68	31.4	26.1
Initial Fe(III) Concentration effect	3.0	10	20	20	0.62	0.66	31.3	34.8
		20			1.98	1.88	47.8	46.9
		50			14.25	13.45	87.5	67.8
		100			42.40	40.20	95.0	94.5
Initial Cr(VI) Concentration effect	3.0	50	10		4.31	1.75	99.23	69.8
			20		5.71	3.38	87.5	67.8
			50		7.71	7.55	66.2	62.0
Initial BPA Concentration effect	3.0	50	20	20	5.71	3.38	87.5	67.8
				40	9.64	4.12	79.6	51.6
				80	18.64	4.64	77.7	30.2

redox reactions (2) and (3). The photocatalytic reduction rate of Cr(VI) in the ternary system is faster than that in the single or two-component system with photoreduction efficiency of about 90% after 120 min irradiation. The simultaneous cycling of Fe(III)/Fe(II) is also accelerated, which results in the effective photodegradation of BPA. The results show a synergism among the photocatalytic redox reactions.

### 3.2. Effect of the initial concentration of Fe(III), Cr(VI), and BPA and pH value on photocatalytic redox in ternary system

In order to examine the changes of reaction rates as a function of Cr(VI) and BPA decomposition, the effects of initial pH value and the initial concentration of Fe(III), Cr(VI), BPA on rate of Cr(VI) photoreduction and BPA photooxidation at pH 3.0 within 120 min illumination time are summarized in Table 1. The photocatalytic reaction with Fe(OH)<sup>2+</sup> under these experimental conditions was estimated to follow a pseudo-first-order kinetic law [8,9].

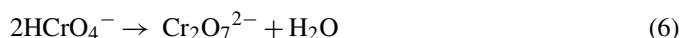
Fe(OH)<sup>2+</sup> is the predominant photoreactive species in the aqueous solutions. The pH value affects the formation rate of Fe(II) and •OH in the photochemical reactions [15].

As shown in Table 1, both the photocatalytic reduction rate of Cr(VI) and the degradation rate of BPA increase with decreasing pH values. An explanation for the pH effect is that the speciation of Cr(VI), Fe(III), and the intermediates change with the pH values.

At the pH range of 2.0–3.0, the degradation rates have not obvious changes. However, when the pH values increase from 4.0 to 7.0, both the photoreduction rate of Cr(VI) and the degradation rate of BPA decreased rapidly. It is possibly related to the iron speciation since Fe(III) will hydrolyze and form a pre-

cipitate at higher pH values. The Fe(OH)<sup>2+</sup> concentration and its photoactivity decrease, which result in the decrease of the photoreduction rate of Cr(VI) and the degradation rate of BPA.

Moreover, in aqueous solution the Cr(VI) species distribution is the function of pH values based on the following reactions:



The neutral chromic acid molecule, H<sub>2</sub>CrO<sub>4</sub> was the dominant speciation at pH less than 2.0, HCrO<sub>4</sub><sup>-</sup> at pH 2.0–5.0 and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions at medium to low pH values. Redox potential of Cr(VI) species is different at different pH medium with higher potential of HCrO<sub>4</sub><sup>-</sup> than that of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, so it can react with Fe(II) more easily [1,16].

Iron plays an important role in the degradation reaction. The rates of photocatalytic Cr(VI) reduction and BPA oxidation increase with the Fe(III) concentration from 10 to 100 μmol l<sup>-1</sup>. The conversion efficiency of Cr(VI) increases from 31.4 to 95% and the degradation efficiency of BPA increases from 34.8 to 94.5% after 120 min irradiation in the photocatalytic processes.

We can also observe that the initial reduction rate of Cr(VI) increases with its concentration from 20 to 50 μmol l<sup>-1</sup>. Moreover, the photodecomposition efficiency of Cr(VI) is much higher than that of BPA.

When simultaneous photocatalytic reaction takes place, the photooxidation efficiency of BPA decrease with increasing its concentrations, but the effect on the reduction efficiency of Cr(VI) is not evident.

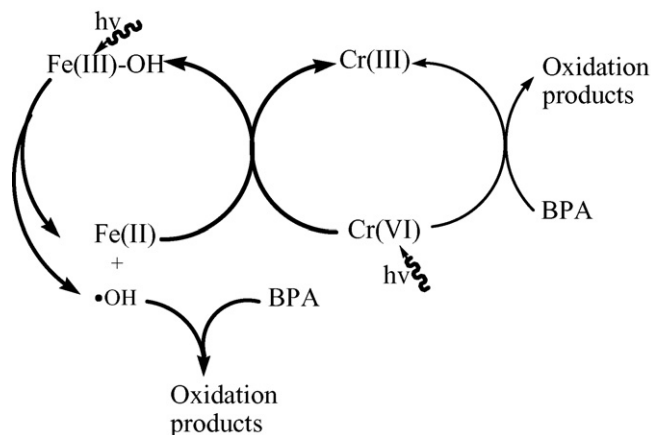


Fig. 3. Proposed dominant mechanism of simultaneous photodegradation of both pollutants in Fe/Cr/BPA ternary system.

### 3.3. Proposed dominant mechanism of simultaneous photodecomposition of both pollutants in the Fe(III)/Cr(VI)/BPA ternary system

Based on the above results, the proposed mechanism of photoreduction Cr(VI) and photooxidation BPA is shown in Fig. 3. In the absence of Fe(III)–OH complexes, the Cr(VI) photoreduction is accompanied by simultaneous oxidation of BPA via PET. In the presence of Fe(III)–OH complexes, photoexcitation of Fe(OH)<sup>2+</sup> leads to formation of abundant •OH and Fe(II) in acidic solution. The •OH would be thus responsible for the fast oxidation of BPA and simultaneously Fe(II) would reduce the Cr(VI) to Cr(III) easily. At the same time, the cycling of Fe(III)/Fe(II) is accelerated, which results in the more effective photooxidation of BPA and Cr(VI) reduction.

## 4. Conclusions

We can draw a preliminary conclusion that both photocatalytic Cr(VI) reduction and BPA degradation can occur simultaneously in aqueous solutions in the presence of Fe(III)–OH complexes. Both the photoreduction rate of Cr(VI) and the oxidation rate of BPA are strongly affected by the pH values and the initial concentrations of Fe(III), Cr(VI) and BPA. Based on these results, high degradation and conversion efficiencies for both BPA and Cr(VI) under irradiation can be achieved in the ternary system (Fe(III)/Cr(VI)/BPA). The photocatalytic system could be a useful pathway for the treatment of pollutants in the natural aqueous environment.

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## References

- [1] J. Kotaś, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, *Environ. Pollut.* 107 (2000) 263–283.
- [2] J.D. Makos, D.C. Hrcir, Chemistry of Cr(VI) in a constructed wetland, *Environ. Sci. Technol.* 29 (1995) 2414–2419.
- [3] M.S. Elovitz, W. Fish, Coupled iron corrosion and chromate reduction: mechanisms for subsurface remediation, *Environ. Sci. Technol.* 29 (1995) 1913–1922.
- [4] L.E. Eary, D. Rai, Chromate removal from aqueous wastes by reduction with ferrous ion, *Environ. Sci. Technol.* 22 (1988) 972–977.
- [5] P. Bchra, Sigg, Evidence for redox cycling of iron in atmospheric droplets, *Nature* 344 (1990) 419–421.
- [6] Y. Zuo, J. Hoigné, Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)–oxalato compounds, *Environ. Sci. Technol.* 26 (1992) 1014–1022.
- [7] B.C. Faust, R.G. Zepp, Photochemistry of aqueous iron(III)–polycarboxylate complexes: roles in the chemistry of atmospheric and surface waters, *Environ. Sci. Technol.* 27 (1993) 2517–2522.
- [8] N.S. Deng, W. Fang, S. Tian, Photodegradation of dyes in aqueous solutions containing Fe(III)–hydroxy complex I. Photodegradation kinetics, *Chemosphere* 33 (1996) 547–557.
- [9] Z. Zhang, F. Wu, N.S. Deng, Photochemical reduction of Cr(VI) in aqueous solutions containing Fe(III)–hydroxy complexes, *Toxicol. Environ. Chem.* 82 (2001) 129–137.
- [10] S.G. Schrak, H.J. José, R.F.P.M. Moreira, Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO<sub>2</sub> slurry reactor, *J. Photochem. Photobiol. A: Chem.* 147 (2002) 71–76.
- [11] B. Sun, E.P. Reddy, P.G. Smirniotis, Visible light Cr(VI) reduction and organic chemical oxidation by TiO<sub>2</sub> photocatalysis, *Environ. Sci. Technol.* 39 (2005) 6251–6259.
- [12] APHA, AWWA, WEF, Standard Methods for Examination of Water and Wastewater, 19th ed., Publication Office, American Public Health Association, Washington, 1995.
- [13] P. Mytych, Z. Stasicka, Photochemical reduction of chromium(VI) by phenol and its halogen derivatives, *Appl. Catal. B: Environ.* 52 (2004) 167–172.
- [14] B.C. Faust, J. Hoigné, Photolysis of Fe(III)–hydroxy complex as sources of OH radicals in clouds, fog and rain, *Atmos. Environ. A* 24 (1990) 79–89.
- [15] H.J. Benkelberg, P. Warneck, Photodecomposition of iron(III) hydroxo and sulfato complexes in aqueous solution: wavelength dependence of OH and SO<sub>4</sub><sup>2-</sup> quantum yields, *J. Phys. Chem.* 99 (1995) 5214–5221.
- [16] I.J. Buerge, S.J. Hug, Kinetics and pH dependence of chromium(VI) reduction by iron(II), *Environ. Sci. Technol.* 31 (1997) 1426–1432.