



Effect of dye-metal complexation on photocatalytic decomposition of the dyes on TiO₂ under visible irradiation

MAHMOOD Tariq¹, CHEN Chuncheng¹, LIU Lili¹, ZHAO Dan¹,
MA Wanghong¹, LIN Jun², ZHAO Jincai^{1,*}

1. Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: jczhao@iccas.ac.cn
2. Department of Chemistry, Renmin University of China, Beijing 100872, China.

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Abstract

The photocatalytic degradation of dyes (Acid Chrome Blue K (ACBK) and Alizarin Red (AR)) with strong complexation ability was investigated in the presence of metal ions under visible light irradiation. It was found that, at low dye-metal ratio, the photodegradation of ACBK was markedly inhibited by the addition of high oxidative potential Cu²⁺. However, at high dye-metal ratio, the presence of Cu²⁺ enhanced the photodegradation of ACBK. The negative effect of Cu²⁺ on the photodegradation of AR was observed for all dye-metal ratios. The relative chemical inert Zn²⁺ tended to enhance the photodegradation of both anionic dyes. The mechanism underlying the different effect of Cu²⁺ was discussed from the different roles of surface-adsorbed and dye-coordinated Cu²⁺ in the photodegradation of dyes.

Key words: photocatalysis; degradation of dye pollutants, metal ions; TiO₂

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Introduction

Titanium dioxide (TiO₂) is a well-known semiconductor with strong photocatalytic ability to decompose a wide range of organic compounds in water or in air (Sauer and Ollis, 1994; Nimlos *et al.*, 1996; Mills and Hunte, 1997; Peral and Ollis, 1997; Muggli and Falconer, 1998; Martra *et al.*, 1999). However, this material is only active upon UV excitation because of its large energy band gap of 3.2 eV. Thus, it constrains the use of sunlight as the irradiation source (Goswami, 1997). During the last decade, to utilize the sunlight more effectively for decomposing color organic pollutants, extensive work has been done to study the photocatalytic degradation of dye pollutants on TiO₂ under visible irradiation (Vinodgopal *et al.*, 1996; Zhang *et al.*, 1998; Zhao *et al.*, 1998a, 1998b; Wu *et al.*, 1999; Liu *et al.*, 1999). The visible-induced degradation of dye pollutants is initiated by the electron injection from the excited dyes in the conduction band of TiO₂, and thereby the formation of dye radical cation and reactive oxygen species would lead the degradation of the dyes. In the previous study, through the investigation of the metal ions effects (e.g., Cu²⁺, Fe³⁺, Zn²⁺, Al³⁺) on the TiO₂-assisted photodegradation of dyes under the visible light irradiation, it was found that surface-adsorbed

copper(II) and iron(III) have a strong inhibiting effect on the photodegradation due to their ability of changing the pathway of electron injection (Chen *et al.*, 2002). The effect of metal ions on heterogeneous photocatalysis is of worth discussion because they are widely present in the wastewaters, and more importantly, are capable of changing the degradation mechanisms. Considering that widely used dyes such as Acid Chrome Blue K (ACBK) and Alizarin Red (AR) can form stable complexes with metals, the effect of complexes of dye-metal on the photocatalytic degradation rates and mechanism is important from both the practical and fundamental viewpoints. After our investigation on the effect of surface-adsorbed metal ions, where the complex between the dye and metal was not deeply concerned, the unique influence of dye-coordinated metal ions upon photodegradation of the dyes has attracted our attention. In this study, we examined the photodegradation of the dyes (AR and ACBK) with strong complex ability in the presence of the metal ions and TiO₂ (P-25) under visible irradiation. It was found that, although the surface-adsorbed Cu²⁺ can depress the photocatalytic degradation, the dye-coordinated Cu²⁺ was able to accelerate the degradation. The result provides further understanding on the electron transfer pathway of dyes and dye-metal complexes on the TiO₂ surface.

* Corresponding author. E-mail: jczhao@iccas.ac.cn

1 Experiments

1.1 Materials

TiO₂ (P-25, Anatase 80%, Rutile 20%, BET area 50 m²/g) was obtained from Degussa, Germany. The dyes ACBK, AR, and other chemicals were all of analytical grade and used without further purification. Doubly distilled and deionized water were used through the study. The solution pH where needed was adjusted using dilute HClO₄ and NaOH.

1.2 Photo reactor and light source

A 250-W tungsten lamp (Institute of Electric Light Source, China) was used as the light source and positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket for cooling the lamp. A cutoff filter was also placed outside the Pyrex jacket to remove the radiation below 450 nm completely and to ensure irradiation of dispersion only by visible light wavelengths.

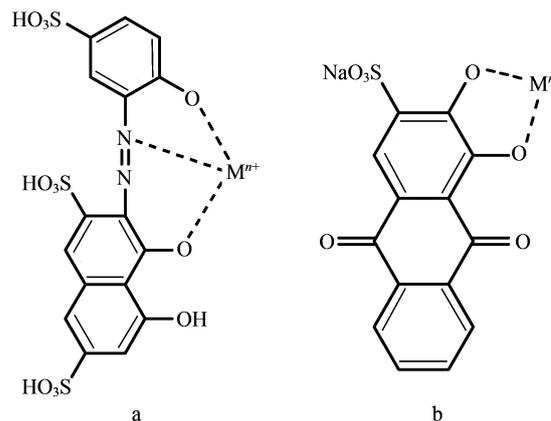
1.3 Procedures and analyses

Aqueous solution (50 mL) of dyes with a known amount of TiO₂ powder was put in a Pyrex vessel. Prior to irradiation the suspensions were magnetically stirred in the dark for one hour to ensure the establishment of an adsorption-desorption equilibrium of dye on the TiO₂ surface. At given intervals of illumination, the TiO₂ powder was separated off by centrifugation and filtration through a filter (pore size < 0.22 μm), the filtrates were analyzed by UV-Visible Spectrophotometer (Lambda 20, Perkin Elmer, USA).

2 Results and discussion

2.1 Coordination between dye and metal

The azo dye ACBK can strongly coordinate with the metals through N atom of the azo bond, and the two hydroxyl groups on naphthalene ring and phenyl ring. The anthraquinone dye AR, which can chelate with metals via the two hydroxyl groups (Scheme 1). The formation



Scheme 1 Structure of Acid Chrome Blue K (ACBK) (a) and Alizarin Red (AR) (b).

of dye-metal complexes can result in a marked change in the absorption spectra. In this study, Cu²⁺ and Zn²⁺ were chosen as coordination metals. As shown in Fig. 1, the addition of Zn²⁺ had little effect on the absorption spectra, indicating that Zn²⁺ has a weak complex ability with both dyes. However, the addition of Cu²⁺ markedly changed absorption spectra, indicating the strong coordination between the Cu²⁺ and the dyes. The dye-Cu²⁺ complex exhibited generally absorption band at the longer wavelength (red shift) than the uncoordinated dyes, and the absorbency of the complexes (especially for ACBK-Cu²⁺) also became larger. In ACBK solution, the addition of Cu²⁺ at 3:1 molar ratio of the dye to metal shifted the overall spectrum from 518 nm for the pure ACBK to 551 nm for the complex, indicating that all the dye was chelated to the metal. However, in the AR system, the absorption peak of the AR-Cu²⁺ complex only appeared as a shoulder (about at 532 nm) of the absorption band of pure AR (431 nm) at 3:1 molar ratio of the dye to metal, indicating the existence of a lot of free AR. Therefore, the chelating ability of ACBK with Cu²⁺ is much stronger than that of AR. In addition, both dyes and its metal complexes are stable in the wide pH range under visible light irradiation without TiO₂.

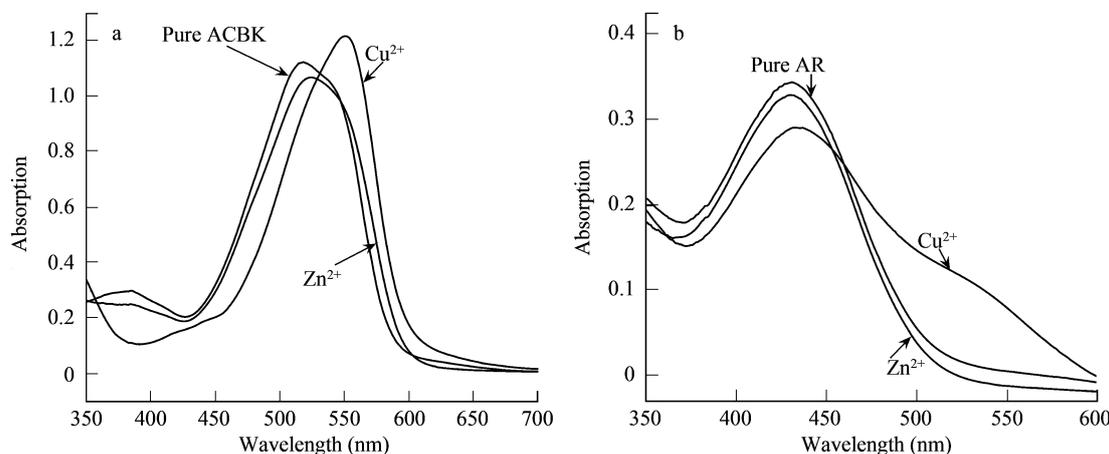


Fig. 1 Absorption spectra of different dye-metal complexes before and after the addition of metals. (a) ACBK 20 μmol/L; (b) AR 100 μmol/L; molar ratio of the dye to metal 3:1.

TiO₂ was added into the solution after the mixing of given concentrations of dyes and metal, which can assure the formation of dye-metal complexes before the adsorption of metal ions on the surface of TiO₂. The effect of metals on the degradation was examined in the presence of metals with different dye-metal molar ratios (1:1, 3:1, 10:1, and 100:1) at the constant concentration of dye (ACBK 20 μmol/L and AR 100 μmol/L). In this way, the amount of surface-adsorbed and the dye-chelated metal ions can be controlled. When dye-metal ratio is 1:1 there are excess free metal ions. In contrast, when dye-metal ratios are 10:1 or 100:1, the excess dyes (ligands) existed along with the pertinent dye-metal complexes.

2.2 Degradation of Acid Chrome Blue K and metal complex

Figure 2 shows the effect of different metal ions on the photocatalytic degradation of ACBK with different dye-metal ratios in the presence of TiO₂ under visible light irradiation. It was found that, when dye-metal ratio is 1:1, the photocatalytic degradation of ACBK was completely suppressed by the addition of Cu²⁺ (Fig. 2a). Apparently, at this dye-metal ratio, the amount of metal ions was excess dye, which allows the existence of the unchelated metal ions. These free metal ions would adsorb on the surface of TiO₂. As proposed in our earlier reports (Chen *et al.*, 2002), surface-adsorbed Cu²⁺, due to its high redox activity, can trap the injected electron prior to molecular oxygen, which would suppress the formation of reactive oxygen species (O₂^{•-}/•OOH), and hence depress the dye photodegradation. However, a promotive effect of relatively inert Zn²⁺ on the dyes degradation was observed, which can be attributed to the enhancement of the anionic ACBK adsorption due to electrostatic interaction with the adsorbed positively-charged Zn²⁺.

When dye-metal ratio is 3:1, the presence of Cu²⁺ enhanced the degradation at the early stage of the irradiation. However, the degradation became slow after 30 min, and then kept at constant (Fig. 2b). In this case, as shown by the adsorption spectrum in Fig. 1a, nearly all the Cu²⁺ formed as ACBK-Cu²⁺ complex at the beginning of the photodegradation. Accordingly, little amount of Cu²⁺ can adsorb on the TiO₂ surface. On the other hand, Cu²⁺ can be released due to the degradation of the complex at this

moderate dye-metal ratio. These results imply that the surface-adsorbed Cu²⁺ and dye-coordinated Cu²⁺ affect the dye photodegradation in different ways.

Interestingly, when dye-metal ratio is 10:1, the effect of Cu²⁺ was completely opposite to that with 1:1 ratio. The addition Cu²⁺ at low metal percentage was able to accelerate the photodegradation of ACBK during irradiation in first 2 h, although the degradation somewhat slowed down at the end (Fig. 2c). It is evident that the extreme excess of the dye can assure that the Cu²⁺ is in the dye-coordinated form and little surface-bound metals presented during the photodegradation process. This result suggests that the dye-coordinated Cu²⁺ can promote the photodegradation of the dyes.

2.3 Effect of metal complexes on the photodegradation rate of Alizarin Red

To further clarify effect of the metal-dye complexation, the degradation of AR in the presence of metal ions was also examined. Figure 3 shows that the kinetics of AR degradation, where TiO₂ was used as the photocatalyst with dye-metal ratio 3:1 and pH 5 under visible light irradiation. After about 60 min of irradiation, similar to Chen (2002), we observed that the AR photodegradation rates were in the order Zn²⁺ > AR only > Cu²⁺. The presence

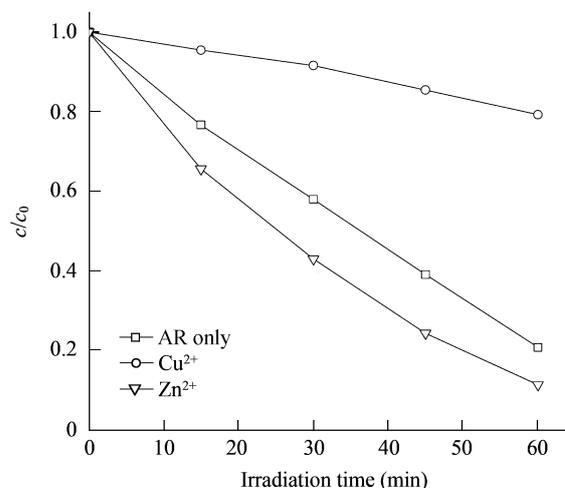


Fig. 3 Photodegradation of AR with different metal ions with AR-metal ratio 3:1 in the TiO₂ dispersions. AR 100 μmol/L; TiO₂ 1 g/L.

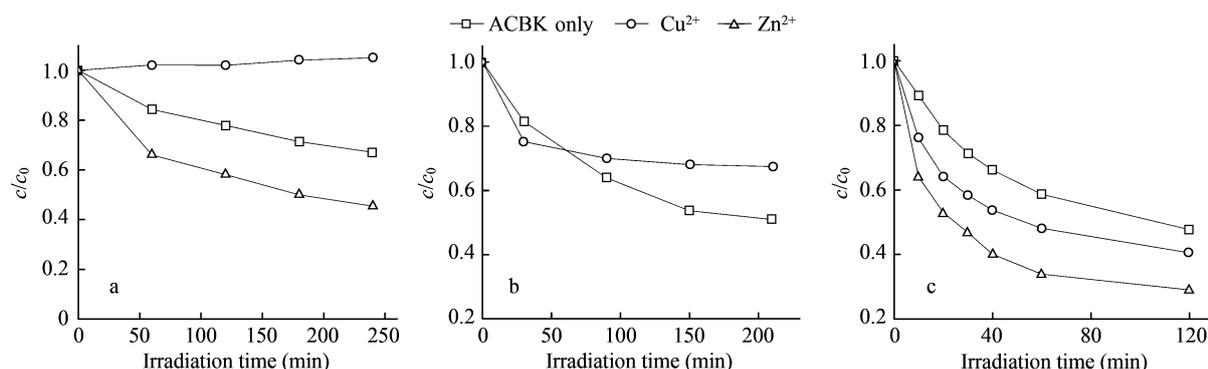


Fig. 2 Visible light assisted photo degradation profile of ACBK and its metal complexes in the presence of TiO₂. (a) dye-metal ratio 1:1; (b) dye-metal ratio 3:1; (c) dye-metal ratio 10:1 (excess dye). ACBK 20 μmol/L; TiO₂ 1 g/L; pH 5.0.

of Zn^{2+} was able to promote the day photodegradation, while the copper at the same concentration suppressed the photodegradation markedly. In contrast, AR has a weaker complexation with Cu^{2+} than ACBK. At a dye-metal ratio of 3:1, it is possible that there is some uncoordinated free Cu^{2+} adsorbed on the surface of TiO_2 . Accordingly, the depressive effect can be ascribed to the surface-adsorbed Cu^{2+} .

The effect of Cu^{2+} on ACBK degradation was in great dependence on the added Cu^{2+} concentration (Fig. 2). To further check the effect of Cu^{2+} on the photodegradation of AR, the influence of the different molar ratios of AR to copper was examined (Fig. 4). It was found that the photocatalytic degradation rate of AR decreased generally with the decreasing dye-metal molar ratio, even at ratio 100:1. It should be emphasized that the dynamic effect of Cu^{2+} on the dye degradation and its complex exhibited similar trends to that in the ACBK system. When AR- Cu^{2+} ratio was larger than 3:1, the AR was slowly decreased with linear relationship. However, at moderate ratio (10:1), although the initial degradation rate was still slower somewhat than the system without Cu^{2+} , it was significantly larger than that at the end stage of degradation. When Cu^{2+} concentration was significantly low (100:1), no obvious change in the rate was observed. Such changes in degradation rate could be explained by the Cu^{2+} releasing from the dye-metal complex. At high dye-metal molar ratio, there is too much adsorbed Cu^{2+} . The amount of Cu^{2+} released during the slow degradation is incomparable to the adsorbed one. As a result, the effect of released Cu^{2+} is insignificant. At moderate ratio, a fraction of Cu^{2+} are adsorbed on the surface of TiO_2 before the photodegradation, which is responsible for the low initial degradation relatively to that in absence of Cu^{2+} , while there are a lot of dye-coordinated Cu^{2+} . This kind of Cu^{2+} can be released from the complex after the complex degradation, which can greatly increase the amount of surface-bound Cu^{2+} . Accordingly, the degradation rate at the end stage could slow down.

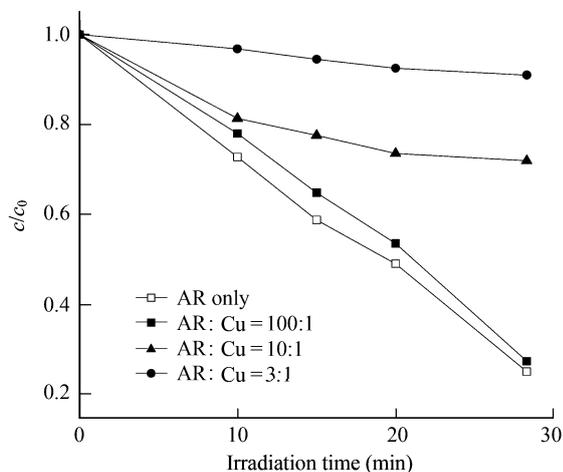


Fig. 4 Effect of Cu^{2+} concentration on AR degradation in the presence of TiO_2 . AR 100 $\mu\text{mol/L}$; TiO_2 1 g/L.

3 Conclusions

The experimental results on the degradation of ACBK and AR demonstrate that, depended on the coordination ability and the dye-metal ratio, Cu^{2+} have two different and competitive effects on the photocatalytic degradation of dyes under visible irradiation. One is the depressive effect, which is attributed to the surface-adsorbed Cu^{2+} . This effect is predominated under the three situations: (1) at high Cu^{2+} concentration; (2) for the target dye with weak coordination ability; (3) at the end stage of the degradation. The other is the promotive effect, which results from the dye-coordinated Cu^{2+} . This effect tends to become dominant when the dye has strong chelating ability and high concentration. However, the detailed mechanism of promotive effect on dye-coordinated Cu^{2+} still needs to be further studied.

Acknowledgments

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