

Involvement of chloride anion in photocatalytic process

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Abstract: The effect of Cl^- on photocatalytic degradation (PCD) of pollutants is an important factor since it is ubiquitous in nature. In general, Cl^- showed an inhibition on photodegradation due to its scavenging $\text{HO}\cdot$ radicals. In this paper, experiments were carried out to examine the effects of Cl^- on the PCD of Methylene Blue (MB) and Orange II (OII) in aqueous TiO_2 suspensions under UV light illumination. It was found that low concentration of Cl^- (< 0.01 mol/L) showed little influence on both dyes, however, high concentration of Cl^- (> 0.10 mol/L) had a very different influence on the decolorization of dyes: a significant inhibition for MB but a great promotion for OII. In the presence of 0.50 mol/L Cl^- , the rate decreased by 70% for MB while increased 7.5-fold for OII. Furthermore, two bands in the ultraviolet region of OII were rapidly broken down. The proposed mechanism was discussed in detail.

Keywords: photocatalytic degradation; TiO_2 ; dye pollutants; chloride ion; mechanism

Introduction

Recently, there have been considerable attentions from worldwide in the utilization of advanced oxidation processes (AOPs) for the remediation of water containing organic pollutants (Andreozzi, 1999). Among AOPs, heterogeneous photocatalysis is considered as one of the most emerging destructive technologies. It is a minute but complex photoelectrochemical process, in which the illumination of catalyst produces strongly active species, e.g. hole or $\text{HO}\cdot$ radicals, and these species go on to attack organic contaminants and subsequently cause mineralization (Fox, 1993; Hoffmann, 1995; Fujishima, 2000).

However, there is no significant commercial application of photocatalytic technology at present. From the fundamental point view, there are still open questions concerning the reaction mechanism and the utilization to treat real wastewater (Hufschmidt, 2004). When photocatalysts are utilized to treat natural waters, catalyst deactivation has been observed (Crittenden, 1996; Hu, 2003). The presence of inorganic ions has been shown to affect the kinetics and mechanism of the transformation processes of organic compounds.

Chloride ion is such a common inorganic ion that frequently present in the nature water or anthropogenic wastewater. In addition, chloride ion may be present as reaction product in the degradation of organic compounds (Hidaka, 1994). The increasing concentration of this anion will play a crucial role in the degradation of the parent compound.

In general opinion, the existence of Cl^- retards the photocatalytic degradation rate of contaminants (Abdullah, 1990; Zhu, 1995; Burns, 1999; Chen, 1997; Wang, 1999; Wang, 2000; Xia, 2002; Guillard, 2003). It has been found an efficient scavenger for photocatalytic process by competing radicals or surface active sites. Despite the contributions from these research groups, detailed mechanisms of the photocatalytic oxidation processes at the TiO_2 surface remain elusive (Hufschmidt, 2004).

On the other hand, very little attention has been given to the organic wastewaters containing high salinity (Piscopo, 2001). In some wastewater, the concentration of chloride can reach more than 0.5 mol/L. Hence, it would be of both

academic and practical interest to look into this problem and an experimental study of the photocatalytic treatment of high saline wastewater is in order.

Dye is a significant portion of wastewaters generated from the textile industry. The dyeing process often requires high concentration of sodium chloride. NaCl performs the function of shielding the surface charge of the fiber allowing the dye to achieve an improved bonding onto the fiber. The study of NaCl in the dyebath is important in photocatalysis. Information about the effect of inorganic ions and reaction mechanisms is very important in the view of practical applications.

In this paper, experiments were conducted to examine the effects of Cl^- (up to 0.50 mol/L) on the photocatalytic degradation of two dyes, Methylene Blue (MB) and Orange II (OII), in aqueous TiO_2 suspensions under UV light illumination. It was found, for the first time, that OII was rapidly transformed at high concentration of Cl^- . And the mechanism was also discussed in detail.

1 Materials and methods

1.1 Chemicals

Methylene Blue (MB) and Orange II (OII) as shown in Fig.1 were obtained from Sigma Chemical Co. TiO_2 (P_25 , ca. 80% anatase, 20% rutile; BET area, ca. 50 m^2/g ; mean particle size, ca. 30 nm) was supplied by Degussa Co.

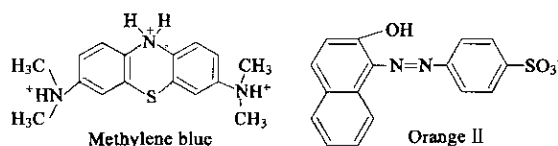


Fig.1 Molecular structures of dye

1.2 Photocatalytic experiments

A detailed description of the experimental arrangement was reported previously (Chen, 2005). In brief, photodegradation was conducted in a quartz reactor of 450 ml capacity at batch mode as shown in Fig. 2, and all comparisons were made using the same batch. Two 6 W UV lamps ($\lambda_{\text{max}} = 365$ nm) were used as the UV light source. The initial concentration of TiO_2 was fixed at 1.0 g/L. At

given intervals of irradiation, the dispersion was sampled, centrifuged, and then filtered through a Millipore filter (pore size $0.22 \mu\text{m}$) in order to remove the TiO_2 particles.

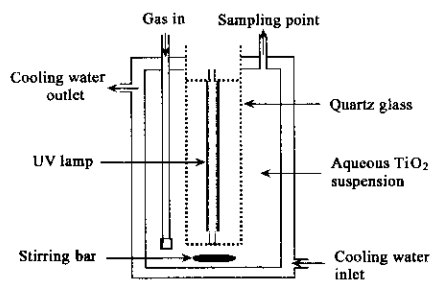


Fig.2 Schematic diagram of photocatalytic degradation experiment apparatus

1.3 Analysis methods

The filtrates were analyzed for UV-Vis absorbance with a Shimadzu UV1206 spectrophotometer. The degradation of dyes was monitored by measuring absorbances at 664 nm (MB) and 484 nm (OII) as a function of irradiation time. The photodegradation rates were described by pseudo-first-order model.

2 Results

2.1 Effects of chloride ion on PCD of MB

MB has been selected as a model compound in this oxidation process. It is a basic dye extensively used for dyeing and printing cotton, silk, and so on. The effect of the concentration of chloride ion on PCD of MB is shown in Fig.3. It was found that increasing the Cl^- concentration led to the decrease of rate constants. In the absence of any additives, the rate constant was 1.20 h^{-1} . And it was well described by pseudo-first-order model ($R^2 = 0.99$). In the presence of 0.01 mol/L Cl^- , the rate constant decreased to $k = 1.10 \text{ h}^{-1}$. When the concentration of Cl^- reached 0.50 mol/L , the rate constant decreased significantly by 70% ($k = 0.36 \text{ h}^{-1}$).

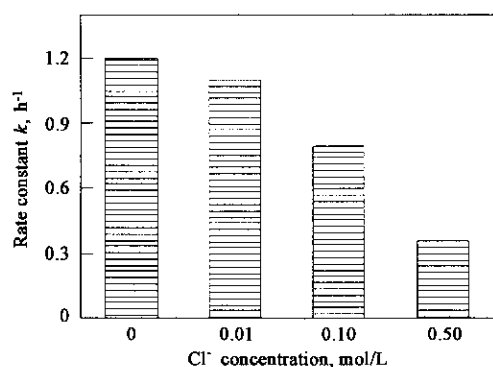


Fig.3 Effect of the concentration of chloride ion on PCD of MB(20 mg/L)

2.2 Effects of chloride ion on PCD of OII

OII has commonly been used as a model compound for the photodegradation of dyes (Stylidi, 2004). Experiments (Fig.4) were carried out to examine the effects of Cl^- on the decolorization of OII in aqueous TiO_2 suspensions. It was observed that the intensity of the visible light chromophore band of OII (azo-linkage, 484 nm) decreased with time and followed apparent first-order kinetics with a rate constant of $k = 0.50 \text{ h}^{-1}$. At low concentration (0.01 mol/L Cl^-)

showed a little inhibition and the rate constant decreased to 0.45 h^{-1} . However, when Cl^- concentration increased to 0.10 mol/L , a promotion was found ($k = 0.60 \text{ h}^{-1}$). It was more interesting that 0.50 mol/L Cl^- showed a significant enhancement for the decolorization of OII. The rate constant increased more than 7.5-fold ($k = 3.74 \text{ h}^{-1}$).

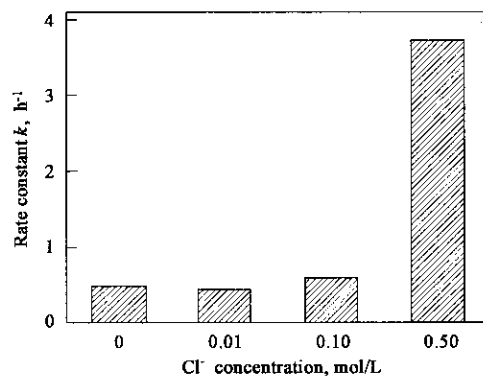


Fig.4 Effect of the concentration of chloride ion on the decolorization of OII (40 mg/L)

The bands in the ultraviolet region, located at 228 and 310 nm, correspond to $\pi-\pi^*$ transitions in benzoic and naphthalene rings of OII, respectively. Considering Fig.5, it was clear that the degradations of benzene ring and naphthalene ring were also as a function of the chloride concentration, with a slower rate compared to that of decolorization. With 0.01 mol/L Cl^- the rate constant decreased a little, but with 0.10 mol/L Cl^- it increased, and when the chloride ion concentration reached 0.50 mol/L , it was rapidly enhanced about 9-fold.

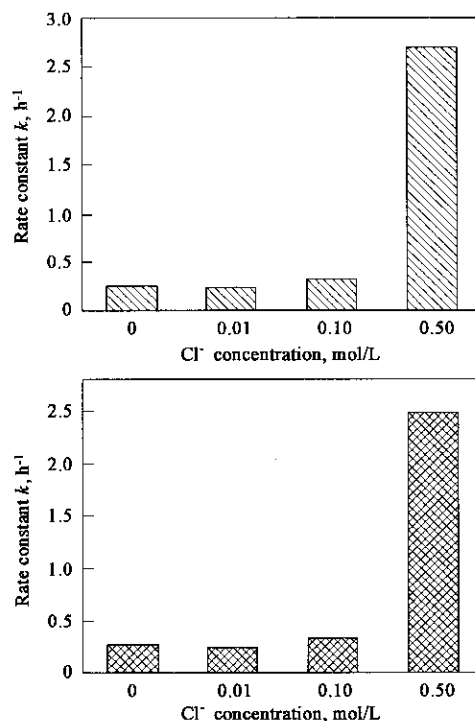


Fig.5 Effect of chloride ion on the degradation of benzene ring (top) and naphthalene ring (bottom) of OII(40 mg/L)

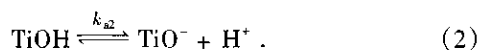
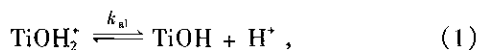
It should be noted that our control experiments under otherwise identical conditions but in the absence of the

semiconductor showed that no degradation of both visible and ultraviolet regions of OII was observed when the experiments were conducted with 0.50 mol/L chloride ion. Therefore, both chloride ion and TiO_2 were indispensable for the significant enhancement for the PCD of OII. From the improvement effect of Cl^- , it was deduced that Cl^- played an important role in the photodegradation of OII under UV light irradiation.

3 Discussion

3.1 Reaction mechanism without chloride ion

It is well known that TiO_2 surfaces are readily hydrated in aqueous solution. Its surface groups are amphoteric and the surface acid-base equilibria can be written as Eqs. (1), (2).



In our study, the pH was in the range of 5–6 which was less than the point of zero charge of the TiO_2 (6.8 for Degussa P-25) (Jaffrezic-Renault, 1986), so the TiO_2 surface is weakly positive due to predominant species TiOH_2^+ and TiOH .

In the case of PCD of MB, the electropositive MB molecules could not easily transport to the electropositive surface from the solution. It is believed that firstly the photogenerated hole reacts with surface hydroxyl groups or water molecule to form a "trapped hole" on the surface or bulk free HO^\cdot , and the formed HO^\cdot radicals subsequently oxidize MB molecules. So it is HO^\cdot radical-mediated mechanism, which can be proved by the significant inhibition of 0.10 mol/L isopropanol (*i*-PrOH) on its photodegradation (Fig. 6), since alcohols could scavenge HO^\cdot radicals effectively (Sun 1995; Richard, 1997; El-Morsi, 2000). These processes can be depicted by Eqs. (3)–(5).

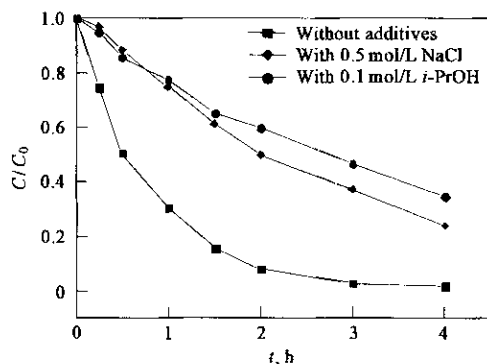
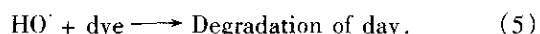
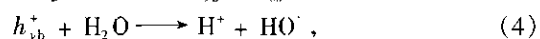
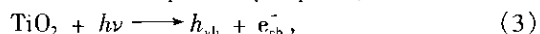


Fig.6 Effect of *i*-PrOH addition on degradation of MB(20 mg/L) in TiO_2 suspension

We had focused our attentions on the role of primary active species and TiO_2 surface characteristic in UV-illuminated photodegradation of OII (Chen, 2005). The PCD of OII performed a hole-dominated surface reaction mechanism (Eq. (6)), since little influence of *i*-PrOH on its photodegradation was found (Fig. 7). The strong adsorption of

OII on TiO_2 surface forms an inner-sphere complex (Bauer, 1999), so OII molecules are able to directly interact with valence band holes.

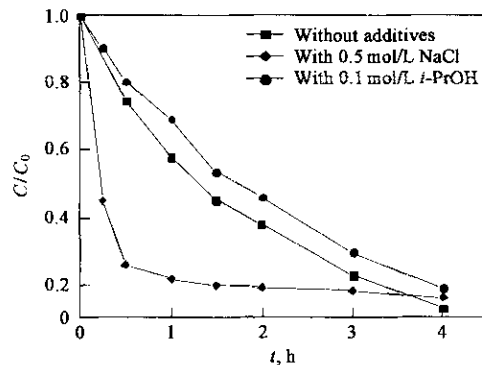


Fig.7 Effect of *i*-PrOH addition on degradation of OII(40 mg/L) in TiO_2 suspension

3.2 Proposed reaction mechanism with chloride ion

The possible effects of Cl^- on TiO_2 photocatalysis include scavenging the oxidizing radical species or holes and competing with contaminant molecules for adsorption sites.

It has been demonstrated that Cl^- has a most detrimental effect on the TiO_2 photocatalysis of various compounds (Abdullah, 1990; Zhu, 1995; Burns, 1999; Chen, 1997; Wang, 1999; 2000; Xia, 2002; Guillard, 2003). Some reported that Cl^- had no effect on organic degradation.

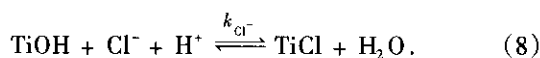
In fact, the influence of Cl^- is dependent on the pH of the aqueous solution. At $\text{pH} > \text{pH}_{\text{PZC}}$ (point of zero charge), chloride ion was found to have no effect on the initial rate of disappearance of 2-chlorobiphenyl (Wang, 1999) since the chloride concentration near the TiO_2 surface is lower than that in the bulk of the solution. At $\text{pH} < \text{pH}_{\text{PZC}}$, the surface is positively charged. The study by Wang *et al.* (Wang, 1999) indicated that at pH 3, the Cl^- was strongly adsorbed on the TiO_2 surface and reduced the photodegradation rate.

In our experiments of PCD of MB, the competition of MB with Cl^- for active sites was negligible because of the weak adsorption of MB on the surface of TiO_2 . Thus, the inhibition of Cl^- was mainly due to its scavenging oxidizing radical species, i. e. HO^\cdot radicals as Eq. (7). The inorganic radical anion shows a much lower reactivity than HO^\cdot radicals. It does not take part in the dye decomposition (Galindo, 2001). So the higher concentration of chloride ion was, the lower concentration of HO^\cdot radicals was achieved, and the greater inhibition was obtained. This result is similar to other report (Piscopo, 2001).

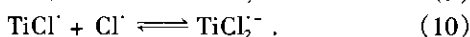
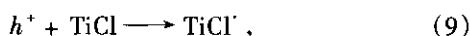


It is interesting to note that the behavior of OII is sensitively different at low and high chloride concentrations. At low chloride concentration, the slowdown also caused by the combination of Cl^- with radicals as Eq. (7) since the oxidation of OII was partly by HO^\cdot radicals.

In contrast, the participation of high concentration of Cl^- greatly enhanced the PCD process. In the presence of Cl^- , another event may happen: chloride ligands are able to form inner-sphere surface complexes:

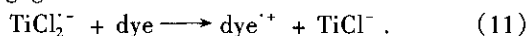


According to Kormann *et al.* (Kormann, 1991), the formation of TiCl complexes is significant only at low pH, while at pH > 6.2 the attachment Cl⁻ to the surface is negligible. In our experiments (pH 5–6) with high chloride concentration, the Cl⁻ ions have more chances to migrate to the TiO₂ surface and the concentration of TiCl complexes would be considerable. Once Cl⁻ adsorbed on a TiO₂ surface, the following hole scavenging becomes more significant as Eqs. (9), (10) (Hwang, 1998; Yamazaki, 2004):

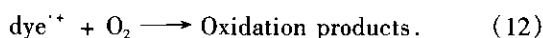


In principle, the formed chloride radical, with a potential + 2.47 V (vs. NHE) (Hirakawa, 2002), is capable of oxidizing organic compounds (Eq. (11)). Hwang *et al.* (Hwang, 1998) described that Cl radical played an important role in the trichloroethylene photodegradation. Yamazaki *et al.* (Yamazaki, 2004) indicated that the accumulation of Cl on the TiO₂ surface promoted a Cl radical-initiated reaction for the photodegradation of chlorinated ethylenes.

For MB, the electropositive molecules could not transport to the inner surface and the oxidation by chloride radical is negligible.



But for OII, the adsorption on TiO₂ surface is very strong. Though the competition of Cl⁻ with OII for adsorption sites may occur, numerous chloride radicals should increase the availability of oxidation species and the degradation rate of OII, since OII molecules are able to directly interact with chloride radical at inner-sphere surface. In the presence of O₂, dye^{·+} is further oxidized into lower molecular weight organics and carbon dioxide, as shown in Eq. (12). Subsequently, azo-linkage, benzoic and naphthalene rings are rapidly transformed. The rate enhancement is suggested due to a surface chain-transfer mechanism involving chloride radical.



In a very recent study (Tang, 2004) the presence of high dissolved oxygen (15 mg/L) and NaCl (up to 80 g/L) was found to enhance the decolorization and mineralization rate of Reactive Black 5, a sulfonated azo dye. It was proposed that Cl⁻ ions have a higher affinity for the holes than HO· radicals, and thus, further inhibit the electron-hole pair recombination favoring the reactions.

3.3 Prospects

Many industrial wastewaters have been found to be highly saline, such as gas oil wastewater, landfill leachates, meat-peaking wastewater, contaminated ground water, and mining wastewater, and so on. Treatment of saline wastewater is not easy. The overall efficiency of the biological treatment, even employing well acclimated microorganisms, is far from satisfactory.

According to our results, high concentration of Cl⁻ could enhance the PCD process. It may provide a new method to rapidly decompose some kinds of organic pollutants with strong absorbability on the surface of TiO₂. It would be

a very interesting subject for further study and it would be discussed in detail in our later papers.

4 Conclusions

Effects of chloride ion (up to 0.5 mol/L) on the TiO₂ photocatalytic degradation (PCD) of Methylene Blue (MB) and Orange II (OII) were investigated. The electropositive MB shows poor adsorption on the TiO₂ surface and its degradation is of HO· radical-mediated mechanism. Chloride ion slows down the PCD rate of MB by scavenging HO· radicals. OII forms an inner-sphere complex on the surface and its degradation is of hole-mediated mechanism. In the presence of low concentration chloride ion, it is the same as the case of MB. But high concentration of Cl⁻ could greatly enhance the PCD process of OII, which may due to the participation of chloride radicals that oxidize adsorbed OII molecules directly on the TiO₂ surface. Thus, chloride ion could be used as a diagnostic tool to study the complex reaction mechanism of photocatalysis. On the other hand, information about our conclusions would be useful in view of practical applications of photocatalytic technology.

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