Effects of acidity and inorganic ions on the photocatalytic degradation of different azo dyes

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Abstract

Effects of acidity and inorganic ions that are common in industrial effluent on the photocatalytic degradation of azo dyes, Procion Red MX-5B (MX-5B) and Cationic Blue X-GRL (CBX), have been investigated in UV illuminated TiO₂ dispersions. There are significant differences between adsorption and photodegradation of MX-5B and those of CBX to the change of solution pH. The results indicated that CBX photodegradation was favored at the surface of TiO₂, while that of MX-5B occurred in the aqueous phase. At pH 2.4, SO₄²⁻, H₂PO₄⁻, ClO₄⁻ and F⁻ in general increased the decolorization rates of MX-5B and CBX by enhancing the adsorption of the selected dyes on the surface of TiO₂. At pH 10.8, most of the selected anions inhibited the photocatalytic oxidation (PCO) to decolorize and degrade CBX and MX-5B. These results demonstrated that inorganic anions affect the photodegradation of dyes by their adsorption onto the surface of TiO₂ and trapping positive hole (h⁺) and •OH. Inorganic cationic ions, such as Cu²⁺ and Ni²⁺ had strong inhibition on the PCO decolorization of MX-5B at pH 10.8. On the contrary, no significant effect was observed at the same concentration of metal cations at pH 2.4.

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1. Introduction

Heterogeneous photocatalytic oxidation (PCO) for wastewater treatment has received much attention by various research groups. Numerous types of catalysts and contaminants have been investigated on laboratory scale [1,2]. However, very few commercial applications of this technology are available at present. One of the major reasons is the deactivation of the photocatalyst when photocatalysis is utilized

to treat real wastewater [3]. Therefore, information on the long-term activity of photocatalysts is needed for the application of photocatalysis. Heterogeneous photocatalysis is a process in which the illumination of an oxide semi-conductor, usually TiO₂ in the form of anatase or rutile, produces photo-excited electrons (e⁻) and positive charged holes (h⁺). The photo-excitation of the semi-conductor particles by UV light changes the energy state of the electrons from the valence band of the solid to the conduction band. The formation of active species was previously discussed in detail [4]. The effects of salty water on the PCO products of liquid 3-octanol and 3-octanone were studied [5]. A number of studies have examined

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the effect of various inorganic ions on TiO_2 slurry photocatalysts [6,7] and on fixed-bed photocatalysts where the TiO_2 was attached to a support, e.g. the inside wall of a borosilicate glass spiral [5,8], and the surface of porous silica gel or fiberglass mesh [9]. There seems to be a general consensus that the effect of organic ions on photocatalysis depends on geometric configuration of the reactor and the structures of the organic compounds to be degraded.

Organic dyes are one of the major groups of pollutants in wastewaters produced from textile and other industrial processes [10]. These wastewaters are highly colored. The more complex environmental problem associated with the textile industry is that organic dyes are resistant to microbial degradation and they can be converted to toxic or carcinogenic compounds [11]. Heterogeneous photocatalysis has been considered as a cost-effective alternative as pre- or post-treatment of the biological treatment process for the purification of dye-containing wastewater [11,12]. The occurrence of dissolved inorganic ions is rather common in dye-containing industrial wastewaters. They can significantly influence the photocatalytic reactions for the treatment of dyes. A study on the effects of inorganic ions on PCO degradation of dye will therefore be very useful for understanding the mechanism of the photocatalytic decolorization of dyes in TiO_2 dispersions under UV irradiation.

In this paper, we examined the effects of several types of inorganic ions (SO_4^{2-} , H_2PO_4^- , ClO_4^- , F^- , Cu^{2+} and Ni^{2+}) that are common in synthetic dye-containing effluent on the photodegradation of two selected azo dyes in TiO_2 aqueous dispersions under UV irradiation. These two azo dyes have different adsorption modes on the surface of TiO_2 .

The photodegradation rates showed different patterns with the changes of pH. In addition, the effects of different inorganic ions on and the mechanisms of photodegradation of these two azo dyes were discussed.

2. Experimental

2.1. Chemicals

TiO_2 (P-25, ca. 80% anatase, 20% rutile; BET area, ca. $50 \text{ m}^2 \text{ g}^{-1}$) was obtained from Degussa Co., Germany. The azo dye, Procion Red MX-5B (MX-5B), shown in Fig. 1A was manufactured by Imperial Chemicals Industries. Another azo dye, Cationic Blue X-GRL (CBX) shown in Fig. 1B, was provided by Shanghai Chemical Company, China. They were used without further purification. All other reagents were analytical grade. The pH of the solution was adjusted with HCl or NaOH.

2.2. Adsorption experiments

All equilibrium adsorption studies were performed in a 50 ml suspension with 25 mg of TiO_2 . The suspension was equilibrated overnight in a temperature-controlled incubation shaker at $23 \pm 2^\circ \text{C}$. The appropriate addition of acid (2N, HCl) or base (3N, NaOH) was made to adjust required pH, respectively. The samples were kept in the dark for the entire period of the experiments in order to avoid photo-excitation of the TiO_2 . The rate of dye decolorization was monitored by a Milton Roy Spectronic 3000 Array spectrophotometer.

Fig. 1. Structures of azo dyes: (A) MX-5B and (B) CBX.

2.3. Photocatalytic degradation experiments

A laboratory-scale photoreactor consisted of an open Pyrex glass column (430 mm height, 25 mm external diameter, and with a wall 1.5 mm thick) surrounded by eight 365 nm UV fluorescent tubes (Viber-lourmat, Model T-15 L/8D) with a power consumption rate of 15 W and an average UV output intensity of 2.13 mW cm^{-2} as determined at the center of the photoreactor [13]. The total UV intensity was controlled by turning on different number of UV lamps. During PCO reaction, the solution with TiO_2 and dye solution was continuously aerated by a pump in order to provide O_2 and complete mixing to reaction solution.

In dye degradation by PCO experiments, the TiO_2 aqueous dispersions were prepared by addition of 75 mg of TiO_2 to 150 ml aqueous solution containing the dyes and inorganic ions at different pHs. Prior to irradiation, the suspensions were mixed in dark for 30 min to ensure adsorption/desorption equilibrium. At given time intervals, 5 ml aliquots were sampled, centrifuged, and then filtered through a Millipore filter (pore size $0.22 \mu\text{m}$) in order to remove the TiO_2 particles. The filtrates were analyzed by recording variations of the adsorption band maximum (540 nm for MX-5B, 610 nm for CBX) in the UV-Vis spectra of the dyes using a Milton Roy Spectronic 3000 Array spectrophotometer.

Fig. 2. The adsorption and photocatalytic decolorization of (A) MX-5B (irradiation time: 20 min) and (B) CBX (irradiation time: 10 min) at different pHs ($[\text{TiO}_2] = 500 \text{ mg l}^{-1}$, $C_0 = 40 \text{ mg l}^{-1}$, $\text{UV} = 4.2 \text{ mW cm}^{-2}$).

3. Results and discussion

3.1. Effects of pH

Fig. 2A and B shows the changes of adsorption and decolorization of MX-5B and CBX with pH. Clearly, the adsorption of MX-5B decreased with pH increasing. However, the photodegradation rate of MX-5B increased under UV irradiation with the decrease of adsorption of MX-5B. We have confirmed in a pre-

vious study that, in the decolorization of MX-5B, the more active bonds including the C–N bonds linked to the benzene ring or the naphthalene ring were hydroxylated first [14]. The photodegradation of MX-5B therefore occurred in the bulk aqueous phase. On the contrary, the adsorption of CBX increased with pH, and the decolorization of CBX was also accelerated with the adsorption of CBX. Because of the high dependency on adsorption, the decolorization of CBX occurred mainly on the surface of TiO_2 [15].

Fig. 3. The effects of different concentrations of Na_2SO_4 on the adsorption and photocatalytic degradation of (A) MX-5B (irradiation time: 20 min) and (B) CBX (irradiation time: 10 min) at pH 2.4 ($[\text{TiO}_2] = 500 \text{ mg l}^{-1}$, $C_0 = 40 \text{ mg l}^{-1}$, $\text{UV} = 4.2 \text{ mW cm}^{-2}$).

The efficiencies of photocatalytic processes strongly depend upon the pH of the reaction solution. It was due to the amphoteric behavior of semi-conductor—TiO₂. The surface charge-property of TiO₂ changes with the change of solution pH. The point of zero charge (pzc) for TiO₂ is 6.5. The TiO₂ surface is positively charged in acidic solutions and negatively charged in basic solutions. The selected azo dyes had different adsorption behavior to the surface of TiO₂. MX-5B was adsorbed on the surface of TiO₂ by the sulfuric group [14], which was negatively charged,

and the acidic solution favored adsorption of the dye onto photocatalyst surface. CBX was strongly adsorbed to the TiO[−] site of the photocatalyst by a penta-heterocyclic-N group, which was positively charged, and the basic solution favored adsorption of the dye onto photocatalyst surface [15].

3.2. Effect of inorganic ions

Anions, such as SO₄^{2−}, ClO₄[−], H₂PO₄[−] could be adsorbed on the surface of TiO₂ in acidic conditions by

Fig. 4. The effect of Na₂SO₄ on the photodegradation of (A) MX-5B at pH 10.8 and (B) CBX at pH 8.0 ([TiO₂] = 500 mg l^{−1}, C₀ = 40 mg l^{−1}, UV = 4.2 mW cm^{−2}).

electrostatic attraction. In alkaline solutions, such adsorption would be unlikely because of repulsive electrostatic force. In order to investigate the effect of these inorganic ions on the decolorization of dyes, a series of experiments were carried out in the presence of TiO_2 with UV irradiation at different pH conditions.

3.2.1. Effect of SO_4^{2-} on the photodegradation of MX-5B and CBX

Fig. 3A and B shows the changes of the adsorption and photocatalytic degradation of MX-5B and

CBX with increasing Na_2SO_4 concentration at pH 2.4. Obviously, with the increase of the SO_4^{2-} concentration, the adsorption of MX-5B onto TiO_2 decreased, whereas the adsorption of CBX onto TiO_2 increased. The TiO_2 surface is positively charged at pH 2.4, SO_4^{2-} was adsorbed onto negatively charged TiO_2 surface by electrostatic attraction. Meanwhile, the TiO_2 surface charge becomes less positive due to the adsorption of SO_4^{2-} (SO_4^{2-} holds the positive site on the surface of TiO_2), leading to the increased adsorption of CBX onto TiO_2 . In the presence of

Fig. 5. The effects of different concentrations of NaH_2PO_4 on the adsorption and photodegradation of (A) MX-5B (irradiation time: 20 min) and (B) CBX (irradiation time: 10 min) at pH 2.4 ($[\text{TiO}_2] = 500 \text{ mg l}^{-1}$, $C_0 = 40 \text{ mg l}^{-1}$, $\text{UV} = 4.2 \text{ mW cm}^{-2}$).

0.1 M Na_2SO_4 , maximum photocatalytic decolorization was obtained for both MX-5B and CBX. When the Na_2SO_4 concentration was more than 0.1 M, the decolorization rates of MX-5B and CBX decreased. The addition of Na_2SO_4 played two roles in the photodegradation of the selected dyes. The first one was that SO_4^{2-} affected the PCO of the selected dyes by changing the surface charge of TiO_2 , resulting in a change of distribution of dye molecules between solution and TiO_2 surface. Another was that the adsorbed SO_4^{2-} reacted with the positive holes (h^+) and hydroxyl radical ($\bullet\text{OH}$), as shown in Eqs. (1) and (2):

$\text{SO}_4^{\bullet-}$ is less reactive than $\bullet\text{OH}$ and h^+ , therefore, the excess SO_4^{2-} hindered the photocatalytic decolorization of the selected dyes. Fig. 4A shows that the effect of different SO_4^{2-} concentrations on the photodecolorization of MX-5B at strongly basic conditions. Obviously, the photodecolorization of MX-5B was significantly inhibited at all SO_4^{2-} concentrations. For SO_4^{2-} does not adsorbed on the negatively

Fig. 6. The effect of NaH_2PO_4 on the photodegradation of MX-5B (A) at pH 10.8 and CBX (B) at pH 8.0 ($[\text{TiO}_2] = 500 \text{ mg l}^{-1}$, $C_0 = 40 \text{ mg l}^{-1}$, $\text{UV} = 4.2 \text{ mW cm}^{-2}$).

charged surface of TiO_2 at strong basic condition, the addition of SO_4^{2-} had no influence on the adsorption of the selected dyes to TiO_2 . Most of the SO_4^{2-} is available in the solution to trap $\bullet\text{OH}$, and the decolorization rate of dyes decreases. Fig. 4B shows an increase of the photocatalytic decolorization rate of CBX in the presence of SO_4^{2-} . At pH 8.0, SO_4^{2-} had no negative effect on the photodecolorization of CBX.

3.2.2. Effect of phosphates

The effects of H_2PO_4^- on PCO rates were studied by adding $\text{Na}_2\text{H}_2\text{PO}_4$ to solutions of MX-5B and

CBX. At pH 2.4, predominately H_2PO_4^- is present. The effects observed were due to the adsorption of H_2PO_4^- on the surface of the catalyst (Fig. 5A and B). As expected, with increasing H_2PO_4^- concentrations, the adsorption of MX-5B on TiO_2 decreased, while the adsorption of CBX increased. Abdullah et al. [5] have proposed an adsorption mechanism based on an exchange reaction between the surface hydroxyl groups of TiO_2 and H_2PO_4^- . As shown in Fig. 5A and B, the maximum photocatalytic decomposition rates of MX-5B and CBX were recorded at a NaH_2PO_4 concentration of 0.01 M. When NaH_2PO_4

Fig. 7. The effects of different concentrations of NaClO_4 on the adsorption and photodegradation of (A) MX-5B (irradiation time: 20 min) at pH 2.4 and (B) MX-5B under pH 10.8 ($[\text{TiO}_2] = 500 \text{ mg l}^{-1}$, $C_0 = 40 \text{ mg l}^{-1}$, $\text{UV} = 4.2 \text{ mW cm}^{-2}$).

concentration was more than 0.01 M, the photodegradation of MX-5B and CBX decreased with increasing NaH_2PO_4 concentrations. The behavior of H_2PO_4^- was similar to SO_4^{2-} in that photocatalytic activity first increased then decreases with H_2PO_4^- concentration. The H_2PO_4^- reacted with h^+ and $\bullet\text{OH}$ to form $\text{H}_2\text{PO}_4^\bullet$, which is similar to $\text{SO}_4^{\bullet-}$. However, both $\text{H}_2\text{PO}_4^\bullet$ and $\text{SO}_4^{\bullet-}$ are not as reactive as h^+ and $\bullet\text{OH}$. At strong basic conditions, the rates of photocatalytic decomposition of MX-5B and CBX were slowed down in the presence of NaH_2PO_4 (Fig. 6A and B). No significant adsorption influence was ob-

served at the selected NaH_2PO_4 concentration. In strong basic condition (pH 10.8 or 8.0), the main anions in solution were HPO_4^{2-} and PO_4^{3-} . They reacted with $\bullet\text{OH}$ to form $\text{HPO}_4^{\bullet-}$ and $\text{PO}_4^{\bullet2-}$, which are somewhat less reactive [16]. The phosphate has a stronger inhibition effect for the photodegradation of dyes at high pH conditions.

3.2.3. Effect of ClO_4^-

Fig. 7A and B shows the effect of NaClO_4 on the photodegradation of MX-5B at pH 2.4 and 10.8. At pH 2.4, the addition of NaClO_4 to solution decreased the

Fig. 8. The effects of different concentrations of NaF on the adsorption and photodegradation of (A) MX-5B (irradiation time: 20 min) and (B) CBX (irradiation time: 10 min) at pH 2.4 ($[\text{TiO}_2] = 500 \text{ mg l}^{-1}$, $C_0 = 40 \text{ mg l}^{-1}$, $\text{UV} = 4.2 \text{ mW cm}^{-2}$).

adsorption of MX-5B onto the surface of TiO_2 . Meanwhile, appropriate amounts of NaClO_4 enhanced the photocatalytic decolorization rate of MX-5B. ClO_4^- played the same role as those of SO_4^{2-} and H_2PO_4^- . At pH 10.8, ClO_4^- decreased the photoactivity of TiO_2 . The ClO_4^- in solution trapped $\bullet\text{OH}$ to decrease the decolorization rate of MX-5B.

3.2.4. Effect of F^-

F^- showed different effects for the photodegradation of MX-5B and CBX. In general, the adsorption of MX-5B decreased with F^- concentration at pH 2.4 (Fig. 8A). The maximum photocatalytic decolorization rate of MX-5B was observed at $10\text{ }\mu\text{M}$ of F^- . The

photodegradation rate started to drop in the presence of higher F^- concentrations. The behavior of F^- was similar to the above-mentioned effect of ions on photocatalytic activity. On the contrary, there was no correlation between the adsorption amount of CBX and F^- concentration at pH 2.4 (Fig. 8B). Moreover, the photocatalytic activity was markedly inhibited with the addition of F^- to solution. The result indicated that F^- mainly trapped h^+ and $\bullet\text{OH}$ affecting the photodegradation of MX-5B, while its adsorption on the surface of TiO_2 could not change the charge arrangement of TiO_2 surface at pH 2.4. Fig. 9A and B shows that the lowering F^- concentration decreases the photodegradation of MX-5B and CBX at strong basic conditions.

Fig. 9. The effect of NaF on the photodegradation of (A) MX-5B at pH 10.8 and (B) CBX at pH 8.0 ($[\text{TiO}_2] = 500\text{ mg l}^{-1}$, $C_0 = 40\text{ mg l}^{-1}$, $\text{UV} = 4.2\text{ mW cm}^{-2}$).

3.3. Effects of Cu^{2+} and Ni^{2+} on the photodegradation rates of dyes

Fig. 10A and B shows the changes of the photodegradation rates of MX-5B with $\text{Cu}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ concentrations at pH 2.4. The photocatalytic decolorization rate of MX-5B slightly increased in the presence of $1\ \mu\text{M}$ of Cu^{2+} and Ni^{2+} . No significant relationship between the adsorption of MX-5B and the addition of metal ions was observed in all experiments. Over the tested pH range, the principal cationic ions in the solution were Cu^{2+} and Ni^{2+} .

They affected the PCO of organics by trapping electrons. Their reduced forms could trap holes and that might explain the decrease of the e^-/h^+ recombination rate and a higher production of $\bullet\text{OH}$. Excess Cu^{2+} and Ni^{2+} led to the short-circuiting reactions, which created a cyclic process without generating active $\bullet\text{OH}$, and retarded the reaction. The reaction schemes are shown in the following equation (Eqs. (3) and (4)):

Fig. 10. The effects of (A) Cu^{2+} ($a = 0\ \mu\text{M}$, $b = 1\ \mu\text{M}$, $c = 10\ \mu\text{M}$ and $d = 33\ \mu\text{M}$), and (B) Ni^{2+} ($a = 0\ \mu\text{M}$, $b = 1\ \mu\text{M}$ and $c = 10\ \mu\text{M}$) on the photodegradation of MX-5B at pH 2.4 ($[\text{TiO}_2] = 500\ \text{mg l}^{-1}$, $C_0 = 40\ \text{mg l}^{-1}$, UV = $4.2\ \text{mW cm}^{-2}$).

Under acidic conditions, 63% of added MX-5B was adsorbed onto the surface of TiO_2 to inhibit trapping of e^- and h^+ by Cu^{2+} and Ni^{2+} . However, at pH 10.8, the photodegradation of MX-5B was completely inhibited by the trace quantities of Cu^{2+} and Ni^{2+} (Fig. 11A and B). Under this experimental condition, the principle ions in solution were Cu^{2+} and Ni^{2+} . No

significant adsorption of MX-5B onto the surface of TiO_2 was observed under the basic condition. Cu^{2+} and Ni^{2+} trapped the electron-hole pair more easily than that in acidic condition. Ni^{2+} showed a stronger influence than Cu^{2+} . It has been reported [17] that the following oxidation reaction is thermodynamically favored at $\text{pH} > 9$. Therefore, some Ni^{2+} formed NiO_2 deposition on the surface of TiO_2 , and deactivated the photocatalyst (Eq. (5)):

Fig. 11. The effects of (A) Cu^{2+} ($a = 0 \mu\text{M}$, $b = 10 \mu\text{M}$ and $c = 33 \mu\text{M}$) and (B) Ni^{2+} ($a = 0 \mu\text{M}$, $b = 10 \mu\text{M}$ and $c = 10 \mu\text{M}$) on the photodegradation of MX-5B under pH 10.8 ($[\text{TiO}_2] = 500 \text{ mg l}^{-1}$, $C_0 = 40 \text{ mg l}^{-1}$, $\text{UV} = 4.2 \text{ mW cm}^{-2}$).

4. Conclusions

Results in this study indicate that the adsorption and photocatalytic degradation (decolorization) of two azo dyes, namely, MX-5B and CBX, are very different. Aqueous phase reactions favored the decolorization of MX-5B, while photodegradation of CBX took place mainly on the surface of TiO₂. The difference was due to the difference in physico-chemical properties of two azo dyes. In order to efficiently treat target azo dyes by PCO, the appropriate pH should be used for specific azo dye.

In addition, the presence of various inorganic ions such as SO₄²⁻, H₂PO₄⁻, ClO₄⁻, F⁻, Cu²⁺ and Ni²⁺ that are frequently found to co-exist with azo dyes in industrial effluent. Anions such as SO₄²⁻, H₂PO₄⁻, ClO₄⁻ and F⁻ generally increased the photodegradation rates of MX-5B and CBX in acidic solutions, while these anions inhibited the activity of the photocatalyst (TiO₂) by trapping h⁺ and •OH under both acidic and basic conditions. Also the presence of trace quantities of Cu²⁺ and Ni²⁺ were detrimental for the photodegradation MX-5B at pH 10.8. In the presence of these inorganic ions, the optimum pH for specific azo dye degradation by PCO should be considered in order to achieve the maximal treatment efficiency.

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