

TiO₂-assisted photo-catalysis degradation process of dye chemicals

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Abstract: The photo-catalytic degradation pathway and degradation products of methylene blue, rhodamine B, methyl orange, and malachite green in aqueous TiO₂ suspension irradiated by high pressure mercury lamp by means of UV-visible absorption spectra and ion chromatography were investigated. The photo-catalysis degradation of dye solutions with charges was greatly effected by pH value owing to the electrostatic model. The photo-degradation rate of dyes anion increased with the decrease of pH value, in contrast, the photo-degradation rate of dyes cation increased with the increase of pH value. And the absorption peaks diminished with a blue shift. After illuminated for 30 minutes, a part of dye chemicals were completely mineralized and transferred into inorganic species including chloride ion, ammonium ion, nitrate ion, sulfate ion. And the addition of 100 mmol/L H₂O₂ promoted the formation of inorganic species. In this study, the quantity of ammonium ion was much more than that of nitrate ion. That indicated the formation of nitrate is from ammonium. The purification rate of COD in four kinds of dye solution was 71.7%—88.7%. The decrease of COD of dyes solution implies the feasibility of the environmental application of photo-catalyzed process.

Key words: photo-catalysis; dye; electrostatic absorption; degradation; titanium dioxide

Introduction

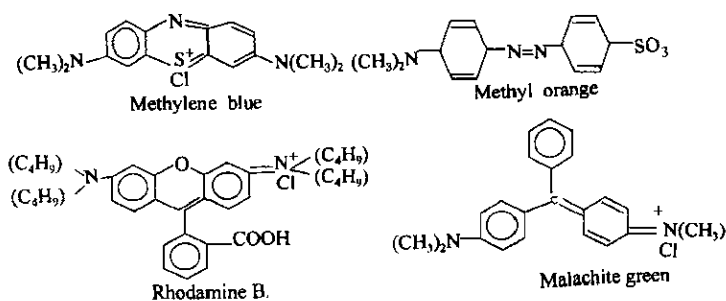
As one of the main pollution sources in China, the textile dyeing and finishing industry annually creates 9—12 × 10⁸ m³ wastewater with high organic strength and colour (Li, 1999b). Dyes are the most important class of synthetic organic chemicals. In general, conventional biological treatment processes have certain difficulties in degrading those dye chemicals with high COD and colour in the effluent. Therefore, it is necessary to develop a new process to effectively degrade those dye chemicals. Heterogeneous photo-catalysis, a special form of photolysis induced by semiconductor such as titanium dioxide, has been proposed as an important process for the degradation of non-degraded chemicals (Hoffmann, 1995). Published literature have been reported that heterogeneous photo-catalysis is a promising process for degrading some kinds of dye chemicals, including eosin (Zhang, 1998), methylene blue (Lakshimi, 1995), malachite green (Zhao, 1998), acid orange (Hustert, 1992) and methyl orange (Wang, 1999). The aim of those papers is to investigate the degradation kinetic and factors influencing the decomposition efficiency of dyes. However, few of literature relate to comparison investigation of the effect of pH value of solution on different dyes photo-degradation. Generally, the absorption of dyes on the surface of titanium dioxide particles is indispensable for degradation of dyes with charges. It was noted that dyes with positive charges is difficult to be absorbed on the surface of titanium dioxide particles in acidic solution, and hence can not undergo photo-induced electron transfer from the excited state to the conduction band. In contrast, it is difficult for dyes with negative charges to be adsorbed in alkaline solution.

The aim of this study is to investigate the photo-catalysis degradation pathway and the formation of inorganic species from dyes with charges on the condition of different pH value and the addition of hydrogen peroxide.

1 Experimental

1.1 Materials

Methylene blue, rhodamine B, methyl orange and malachite green (made by Guangzhou Chemicals and Reagent Co. Ltd.) were of analytical grade. Titanium dioxide was self-prepared by sol-gel process. The sol was prepared by mixing titanium tetraisopropoxide, ethanol, H₂O and CH₃COOH, at room temperature with stirring. The gel was calcined at 700°C for 2h. X-ray



power diffraction measurements was performed on a D/MAX-III A power X-ray diffractometer ($\text{CuK } \alpha$ 0.154 nm), as a result of titanium dioxide gel to anatase transformation. The mean particle size of 23.5 nm was measured by JEOL-100 CX II transmission electron microscopy. The specific surface area of 91.1 m²/g was measured by AMI-100 analysis-BET. Distilled water was used throughout this study.

1.2 Photo-reactor and light source

Irradiation was performed with a 125W high-pressure mercury lamp (Foshan Lamp, Guangdong). Photo-reactor had been described in details by Li *et al.* (Li, 1999a; 1999b). The volume of solution is 200 ml.

1.3 Experimental procedure

Aqueous suspensions of titanium dioxide containing dyes were irradiated with constant magnetic stirring. The optimum dosage of titanium dioxide is 1 g/L (Wang, 1998). In 5-minute time intervals samples of the suspension were taken. The samples were immediately centrifuged at 400 r/min for 30 minutes and the supernatant was analyzed by UNICAM UV-visible spectroscopy at the range of 250nm–750 nm. The concentration of chloride ion, ammonium ion, nitrate ion, and sulfate ion formed was determined by ion chromatography (Shimadzu LC-10 AS). The pH value of the solution was adjusted with H₃PO₄ or NaOH (analytical grade) as required and determined with a PHS-3C pH meter. COD was measured by the national standard methods.

2 Results and discussion

2.1 Effect of pH on dyes with charges

The adsorption spectra of aqueous solution of methylene blue, malachite green, methyl orange, and rhodamine B at various intervals is shown in Fig. 1, Fig. 2, Fig. 3 and Fig. 4, respectively. The adsorption peaks corresponding to dyes diminished and would be finally disappeared. That indicates the degradation of dyes. It was found that methyl orange and rhodamine B were photo-degraded at a much greater speed in acidic solution than in alkaline solution. In contrast, methylene blue and malachite green was degraded at a much greater speed in alkaline solution than in acidic solution. In fact, because of the amphoteric behavior of most semiconductors, an important parameter in reaction taking place on semiconductor particles surface is the pH value of the dispersions, which influences the surface charge properties of the photo-catalyst. The pH effect can be explained on the basis of the point of zero charge (pH_{pzc}) of titanium dioxide. Zhao *et al.* (Zhao, 1990) reported pH_{pzc} of titanium dioxide particles is 6.8. Titanium surface is positively charged in acidic media ($\text{pH} < 6.8$), whereas it is negatively charged under alkaline condition ($\text{pH} > 6.8$). On the other hand, Lakshimi *et al.* (Lakshimi, 1995) reported the pH_{pzc} of titanium dioxide particles is 3.5–6.7. However, the effect of pH on the photo-catalyzed degradation of dyes can be rationalized on the basis of the electrostatic adsorption model where cations are more readily accommodated at negative sites on titanium dioxide. Methyl orange and rhodamine B are anionic dye in aqueous solution because of its sulphony or hydroxyl with negative charges. Electrostatic interactions between the positive titanium dioxide surface and methyl orange anions or rhodamine B anions leads to strong adsorption of the latter on the metal oxide support under the condition of pH 3. It is difficult for methyl orange anions or rhodamine B anions to be

adsorbed on the negative titanium dioxide surface under the condition of pH 7. That is to say that the photo-catalyzed degradation of methyl orange or rhodamine B more quickly undergo in acidic solution than in alkaline solution. In contrast, methylene blue cation or malachite green cation is more easily adsorbed on the negative titanium dioxide surface in alkaline solution (pH 12) than in neutral solution (pH 7). In fact, the photo-catalysis process only occurs on the semiconductor surface, and not in bulk solution. The lifetime of $\cdot\text{OH}$ ($\cdot\text{OOH}$) radicals are relatively short and they unlikely migrate far from the titanium surface, and hence the photo-catalysis process occurs at the surface or within a few monolayers around the photo-catalyst surface.

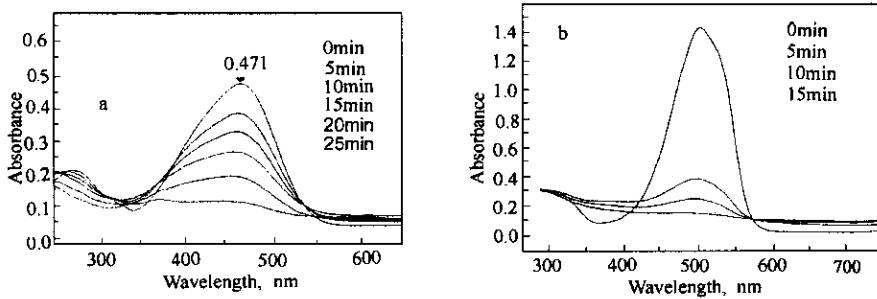


Fig. 1 The ultraviolet visible absorption spectra of methyl orange recorded at different time intervals (a) the initial concentration of 7.5 mg/L, pH 7; (b) the initial concentration of 15 mg/L, pH 3

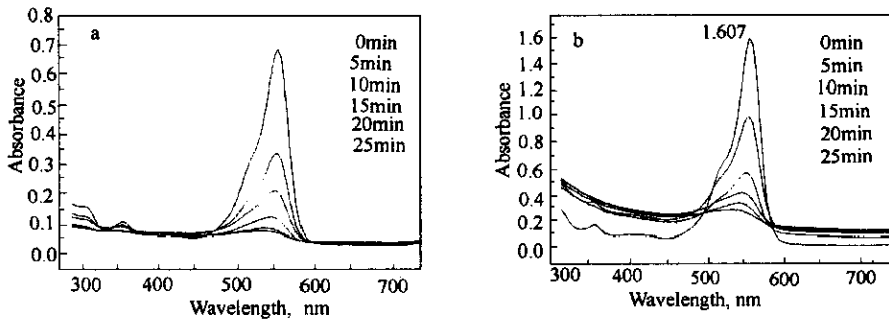


Fig. 2 The ultraviolet visible absorption spectra of rhodamine B recorded at different time intervals (a) the initial concentration of 5 mg/L, pH 7; (b) the initial concentration of 11.5 mg/L, pH 3

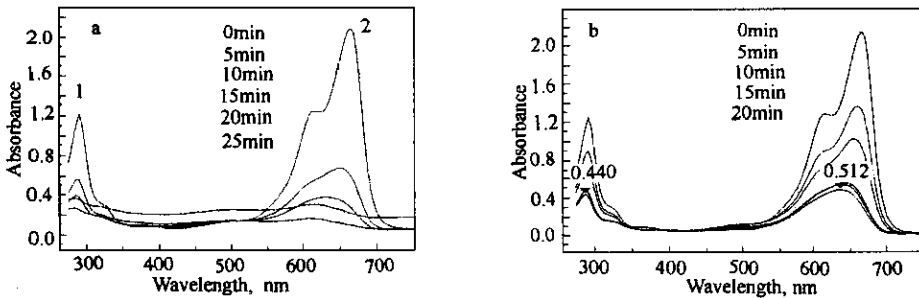


Fig. 3 The ultraviolet visible absorption spectra of methylene blue recorded at different time intervals (a) the initial concentration of 12.5 mg/L, pH 12; (b) the initial concentration of 7.5 mg/L, pH 7

2.2 The shift of absorption peaks

The UV-visible adsorption spectra of four kinds of dyes showed blue shift adsorption peaks. The adsorption peaks of four kinds of dyes at different time intervals are listed in Table 1 and described in Fig. 1—Fig. 4. The UV-visible adsorption spectra of methylene blue showed the most significantly blue shift absorption peak in visible spectra zone. This kind of blue shift would be

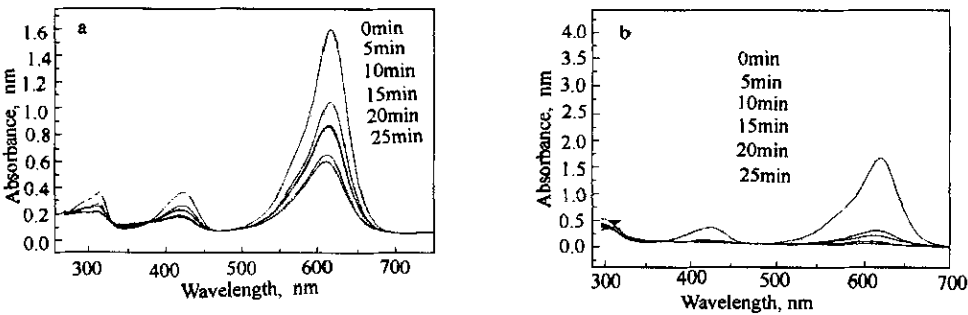


Fig. 4 The ultraviolet visible absorption spectra of malachite green(the initial concentration of 10 mg/L) recorded at different time intervals (a) pH 7; (b) pH 3

caused by the demethylation dyes molecular. The blue shift in ultraviolet spectra zone would be caused by the deamination. That indicated the photo-catalyzed degradation pathway of dyes molecular to some extent.

Table 1 The peak shift of UV-visible adsorption spectra of dye chemicals(nm)

Time, min	Methylene blue		Methyl orange	Rhodamine B	Malachite green		
	I	II	I	I	I	II	III
0	664	292	508	556	616	424	316
5	608	284	505	552	616	424	300
10	604	280	500	550	616	420	300
15	600	280	496	548	612	420	300
20	596	280	492	540	612		

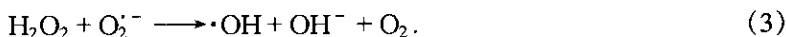
Notes: I , II and III represents the first-, the second- and the third maximum peak respectively

2.3 Formation of inorganic species from dyes

Inorganic species from photo-catalytic oxidation of dyes are listed in Table 2. It showed that a part of organic compounds molecular had been completely mineralized and inorganic species including chloride ion, ammonium ion, nitrate ion and sulfate ion formed. Generally, ammonium ion formed at first from nitrogen-containing organic compounds. Then, ammonium ion was oxidized and transferred into nitrate ion. Ohtani *et al.* (Ohtani, 1988) reported the formation of ammonia from nitrate when they photo-catalytically oxidized 2-propanol in a nitrate solution that was previously delrated with argon. However, in this study, the quantity of ammonia produced was more than that of nitrate. Especially, the formation of only ammonia from methyl orange after the photo-catalytic oxidation having been lasted 30 minutes implied the formation of ammonia at first in this study. Ammonia and nitrate ion all formed in addition to hydrogen peroxide in methyl orange solution. These results all indicated the formation of nitrate ion from ammonia.

In this study, another aim is to determine the factors influencing the relative yields of inorganic species. Low *et al.* (Low, 1991) reported the effect of illumination time and initial concentration of solution on the rate of formation of ammonia and nitrate from containing-nitrogen compounds. The results in Table 2 show that the quantity of formation inorganic species was greatly influenced by pH value of solution and the addition of hydrogen peroxide. There was a sharp rise of the concentration of inorganic species in addition to hydrogen peroxide, which acts as the direct electron acceptor or a direct source of hydroxyl radicals, and can inhibit the recombination reaction of electron and hole. The mechanism of hydrogen peroxide behavior can be explained as following equation.

On the other hand, lowering the pH value of methyl orange anion solution from 3 to 7 or rising the pH value of methylene blue solution from 7 to 12 resulted in increasing the quantity of inorganic species. The effect of pH on the formation of inorganic species can experimentally verify the mechanism of electrostatic adsorption model.

**Table 2** The formation of inorganic species from dyes chemical (mg/L)

	Dye chemicals	Cl ⁻	NO ₃ ⁻	NH ₄ ⁺	SO ₄ ²⁻
Rhodamine B	25 min, pH 7	0.678	0.141	0.645	—
	25 min, pH 7, 100 mmol/L H ₂ O ₂	0.781	0.268	0.958	—
Methyl Orange	30 min, pH 7	—	—	0.250	1.361
	30 min, pH 3	—	0.056	0.487	1.651
	30 min, pH 7, 100 mmol/L H ₂ O ₂	0.341	0.937	1.040	—
Malachite	35 min	0.840	0.125	0.315	—
	30 min, pH 7, 100 mmol/L H ₂ O ₂	1.690	0.447	0.612	—
Methylene	25 min, pH 7	1.153	0.124	0.929	0.546
	30 min, pH 12	1.681	0.164	1.085	0.785
	25 min, pH 7, 100 mmol/L H ₂ O ₂	1.810	0.186	1.212	1.170

2.4 The removal of COD of dyes solution

The variation of COD is listed in Table 3 at different time intervals in addition to 100 mmol/L hydrogen peroxide and pH adjustment. The results in Table 3 show COD of dye solutions significantly decreased in the process of photo-catalysis oxidation. Although a small part of organic molecular and their intermediates were not photo-degraded, a large of organic molecular had been completely mineralized. These results imply the feasibility of the environmental application of photo-catalysis process.

Table 3 The removal of chemical oxygen demand of dye solution in addition to 100 mmol/L hydrogen peroxide

Dye solutions	pH	COD, mg/L				Removal rate, %
		0 min	20 min	40 min	60 min	
Methylene blue	10.0	195.4	107.9	76.3	41.6	78.7
Methyl orange	3.0	181.3	117.8	85.7	51.3	71.7
Rhodamine B	3.0	225.5	126.3	83.4	48.7	78.4
Malachite green	12.0	216.7	101.2	50.3	24.4	88.7

3 Conclusion

Under titanium dioxide mediated photo-catalytic oxidation, all elements of dye molecular were converted to their inorganic forms. Organic carbon was transformed to carbon dioxide halogen to halides, sulfur to sulfate, nitrogen to both ammonium and nitrate. The pH value and addition to hydrogen peroxide greatly effected the formation of inorganic species. The degradation rate of methyl orange and rhodamine B was much greater in acidic than its in neutral media, while the degradation rate of methylene blue and malachite green was much greater in alkaline than its in neutral media. The decrease of COD of dye solution implies the feasibility of the environmental application of photo-catalysis process.

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