

Photocatalytic decolourization of reactive dyes

You Daoxin, Xie Huasheng and Dai Shugui

Department of Environmental Science, Nankai
University, Tianjin 300071, China

Abstract.— The photocatalytic degradation of reactive dyes with solar-irradiated TiO₂ was investigated in these experiments which showed that: (1) the decolourization efficiency are determined by pH value, catalyst amount and light intensity; (2) the reactive dyes decolourized rapidly (cleavage of the azo linkage), but the intermediates needed more time to transform to further degradation products, and finally to produce CO₂; (3) the main products were identified to be alkanes and alkyl amines which could be biologically degraded more easily, the toxicity decreased considerably after photodegradation.

The results demonstrated that the photocatalytic process would become an efficient and safe method for colour wastewater treatment and would be very useful for explaining the reaction mechanism and decolourising structure-reactivity relationship.

Keywords: reactive dyes; photocatalytic degradation; wastewater treatment.

INTRODUCTION

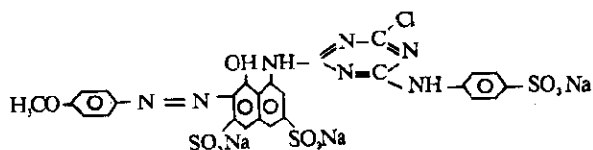
The photocatalytic degradation of pollutants is a new research field developed recently. In the presence of semiconductor catalysts almost all kinds of organic chemicals can be converted to CO₂, H₂O and inorganic ions (Matthews, 1986; Pelizzetti, 1986). The photocatalytic process could be an efficient method for the degradation of refractory organic chemicals including dye which is a vexed problem in its environmental toxicity and in the treatment of colour wastewater.

The research on photodegradation of soluble dye with TiO₂ powder and UV-light obtained satisfactory results: the dye solution decolourized speedily and COD decreased (Fan, 1989). The photodegradation of dye with other catalysts was also reported (Chen, 1990).

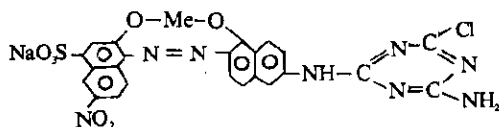
In this experiment, dye was photocatalytically degraded by solar-illuminated TiO₂ instead of TiO₂/UV, so in order to avoid the use of high energy to generate UV-light. Some factors affecting the transformation of organic species and the toxicity change were investigated.

The two dyes chosen here were representatives for reactive dyes, their structural formula are shown in the following. As the light fastness of dye is often improved in the presence of metal ions (Graves, 1988) such as Co (II), Co (III), Ni (II) and Cu (II) which can react with triplet dye to suppress singlet oxygen formation almost completely and, therefore inhibit the fading efficiency, so the research of metal-ion-complexed dye is also of interest.

Reactive Violet H-2R:



Reactive Black K-BG:



Me=Cr+Co, Cr : Co = 2 : 1

EXPERIMENTAL

Materials

CH_2Cl_2 (A. R.), redistilled. Anhydrous Na_2SO_4 (A. R.). TiO_2 anatase powder. Stock of bacterial solution. The two dyes chosen were both commercial products. Redistilled water was used throughout.

Equipment

ZD-2 pH meter, 722 Spectrophotometer, Shimadzu UV Spectrometer, HH-3 COD Analyzer, Shimadzu TOC Analyzer (TOC-10B), NE-713G Water Quality Toxicity Monitor, Shimadzu GC-9A and 5988A GC-MS.

Measurement of decolourization ratio

After the pH was adjusted to the desired value, the absorbance was measured (A_1), for reactive violet solutions at 543 nm and reactive black solutions at 610nm. The desired volume of solution was mixed with certain amount of semiconductor powder, stirred vigorously and put in the sunlight for irradiation. After irradiation, centrifugalize the solution and the absorbance of the clear solution was measured (A_2), then decolourization ratio $(A_1 - A_2) / A_1 \times 100\%$ is calculated.

GC-MS analysis

30 mg TiO_2 powder was added to 300 ml pH 12.03, 21.7 ppm reactive violet solution (or 300 ml pH 12.01, 9.3 ppm reactive black solution). The suspension was irradiated in the sunlight for some time, and the photodegradation products were then extracted at different pH value (pH 2.0, 7.0 and 12.0) with 30 ml redistilled CH_2Cl_2 each time. The organic phase was transferred to a flask and some anhydrous Na_2SO_4 was added to absorb the water in the organic phase which was further concentrated to 0.5 ml at 38 °C (with nitrogen gas). The samples thus obtained were analyzed with GC and the degradation products were identified with GC-MS.

Toxicity analysis

The sample solution (dye solution after photodegradation) was mixed with 1 ml bacterial solution, kept at constant temperature (37 °C) for 5 minutes, then 1 ml methylene blue solution was added and the decolourization time was measured.

RESULTS AND DISCUSSION

Factors affecting the decolourization efficiency

1. The effect of pH

A common feature of the photocatalytic reaction by suspended semiconductor powders in

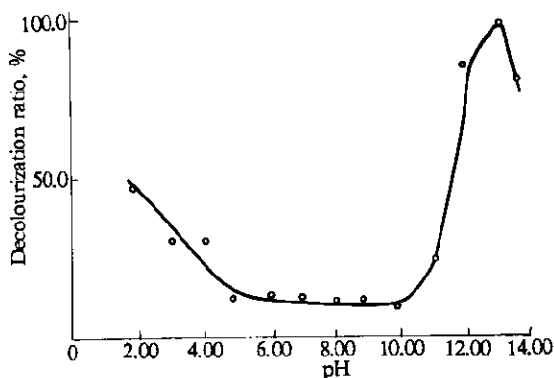


Fig.1 Decolourization ratio vs pH value
30 ppm reactive violet solution, temperature 31 °C,
illuminance 93200 lx, irradiated for 8 h

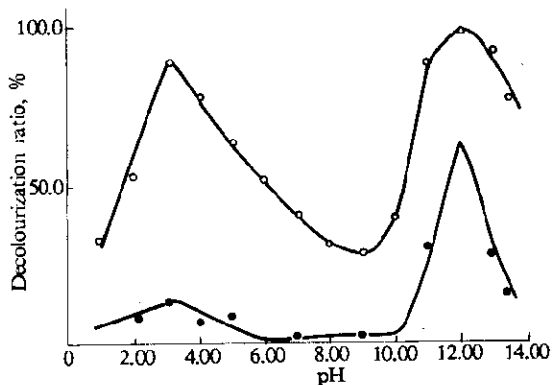
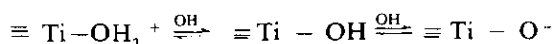


Fig.2 Decolourization ratio vs pH value
40 ppm reactive black solution; 1: non-stirred irradiated for 6 h
at temperature 15 °C, illuminance 41000 lx; 2: stirred irradiated
for 6 h more at temperature 15 °C, illuminance 48500 lx

aqueous is the remarkable pH dependence of the reaction rate. The results (Fig. 1 and Fig. 2) showed that these dyes can be decolourized more easily under acidic or basic condition and the optimal values for their degradation were 13.00 and 12.00. The effect of pH to photocatalytic reactions may be explained in the following ways:

(1) TiO_2 powders was found to distribute more uniformly in basic solution, especially when pH is 12.00 or 13.00. In the solution the following equilibria exist:

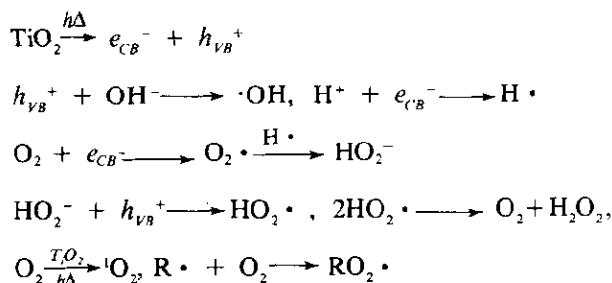


and TiO_2 powder having a larger surface area with a high proportion of strongly acidic surface sites rather than readily protonated hydroxyls is favourable for the photocatalytic (Ohtani, 1987).

(2) With increase of pH, the band-gap of TiO_2 semiconductor reduced, the band-gap energy decreased (Fox, 1983) and the part of light with longer wavelength can irradiate the semiconductor, so the sunlight utilization efficiency is increased.

(3) The dyes may be more easily broken under such pH condition. But the structure-reactivity relationship are not clear till now.

(4) OH^- and H^+ may be involved in the reactions. They trap the $h_{\nu\text{B}}^+$ or e_{CB}^- formed during irradiation, and make the other available for the reactions taking place at the surface of the semiconductor particles thereby preventing the $e_{\text{CB}}^- - h_{\nu\text{B}}^+$ recombinations. And generate some efficient oxidants such as OH , O_3 , $^1\text{O}_2$, H_2O_2 and $\text{RO}_2\cdot$ by which the pollutants are oxidized (Cunningham, 1988; Izuml, 1981; Kormann, 1988).



2. Effect of catalyst amount

The results are shown in Fig. 3 and Fig. 4. The decolourization ratio is a function of irradiation time and catalyst amount.

When irradiated time is short, the decolourization ratio increase with increasing of catalyst amount (in form of times of dye's weight); when irradiation time is longer enough, it increases with increasing of the catalyst amount and remained almost constant above a certain level.

The results can be explained as follows.

When irradiation time is short, the number of photons absorbed and the number of dye

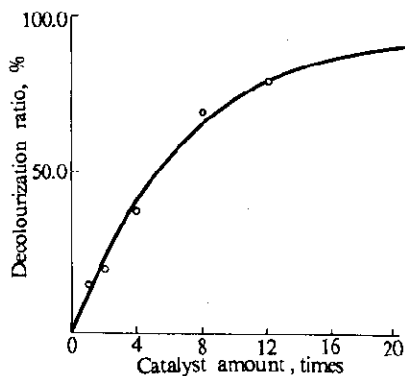


Fig. 3 Relation between decolourization ratio and catalyst amount
50 ppm reactive violet solution, irradiation for 6 h at temperature 18 °C; illuminance 40000 lx

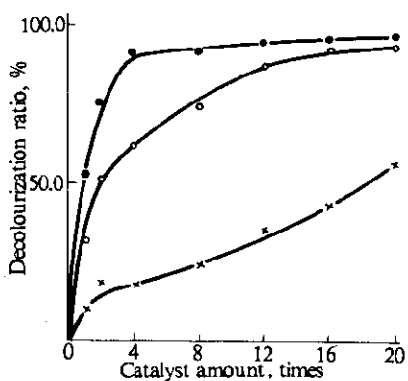


Fig. 4 Decolourization ratio vs catalyst amount
40 ppm reactive black solution 1: irradiated for 3 h at temperature 10 °C, illuminance 40600 lx 2: for 6 h at temperature 14 °C, illuminance 68000 lx 3: for 12 h at temperature 14 °C, illuminance 43000 lx.

The results also imply that the photoreaction rate ($r=kC$) increases with the increase of dye initial concentration, and higher concentration is better for increasing the decolourization efficiency.

4. Effect of irradiation time

Fig. 6 and Fig. 7 showed that the decolourization ratio increases with the increase of

molecules absorbed are increased owing to the increase in the number of TiO_2 particles. After irradiated for some time, the available dye molecules are not sufficient for adsorption by the increased number of TiO_2 particles. Hence the added amount of catalyst powders are not involved in catalytic activity and the ratio no longer increases with increase in catalyst amount beyond a certain limit.

Fig. 3 and Fig. 4 showed that the optimal amount of catalyst is determined by irradiated time and light intensity.

3. Effect of initial concentration

Fig. 5 showed the relationship between $\lg C$ and t . The linear correlation implies that the photodegradation reaction corresponds well with first order reaction.

$$\text{reactive violet: } \lg C = 1.460 - 0.110 t, r = -0.997$$

$$\text{reactive black: } \lg C = 1.635 - 0.348 t, r = -0.998$$

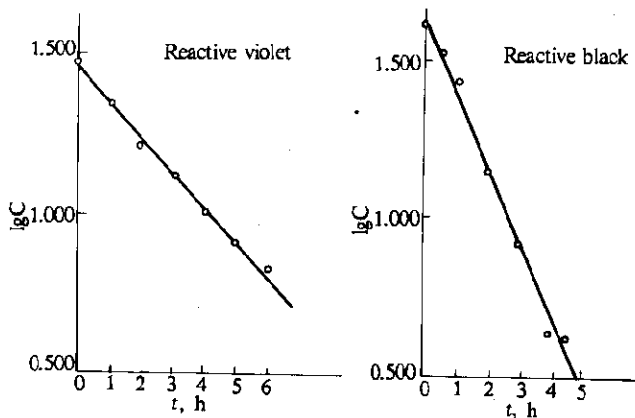


Fig. 5 Relationship between $\lg C$ and t

irradiation time and finally reached a constant level.

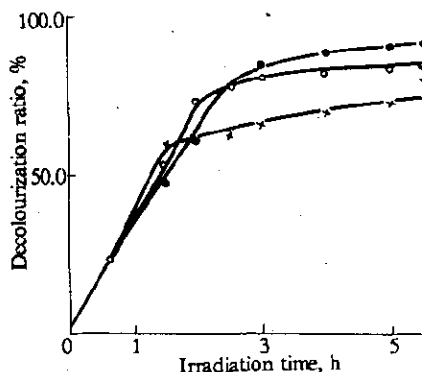


Fig. 6 Effect of irradiation time reactive black solution, catalyst amount: 6 times, pH 12.00, irradiated at temperature 14 °C, illuminance 41200 lx 1: 10 ppm 2: 20ppm 3: 40ppm

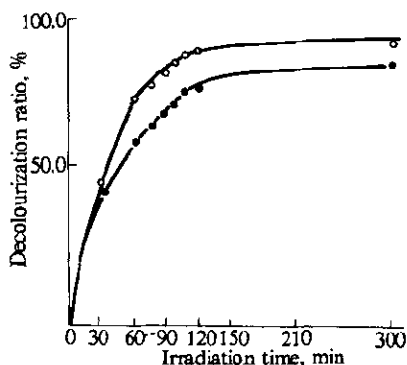


Fig. 7 Effect of irradiation time reactive violet solutions, catalyst amount: 6 times, pH 13.00, irradiated at temperature 11 °C, illuminance 51600 lx 1: 10ppm 2: 20 ppm

GC-MS analysis of photodegradation products

The samples were analyzed under the following condition and the chromatograms are shown in Fig. 8.

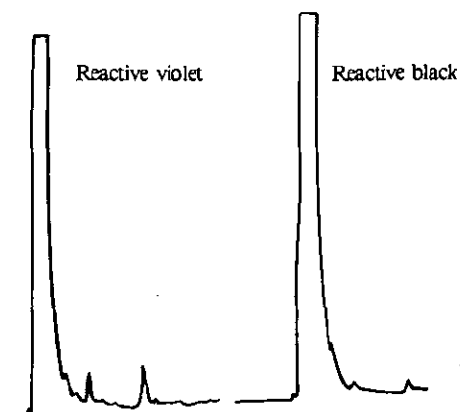
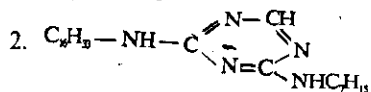


Fig. 8 Products GC analysis of dye photodegradation

GC condition: FID detector. Stationary phase OV-101. 25 m capillary column, i. d. 0.2 mm, injector temperature 300 °C. Column temperature programme initial 40 °C for 1 minute, rising at 10 °C min and final 200 °C for 1 minute. Injected sample volume is 5 µl.

Some products of photodegradation were identified:

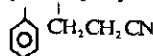
Reactive violet: 1. $C_{13}H_{27}C_2H_2O$



3. $C_{14}H_{30}$

4. $C_8H_{17}CH=CHNHCH_2NHC_5H_{11}$

Reactive black: 1. $CH_3CHCNCH_2NHOH$



2. $C_{14}H_{29}NHCH_2CH_2CH_2COOH$

It can be deduced from the photodegradation products that in the reactions the following processes may exist: (1) the elimination of nitrogen from azo-compounds. (2) the broken of benzene system. (3) rearrangement of photogenerated radicals.

Azo-compounds are extremely photoreactive as a result of the force for the elimination of molecular nitrogen which is a stable substance (Horspool, 1976).

The fact that the dye absorbance decreased beyond 230 nm also suggests that the azo linkage and the large π -electron system were destroyed (Fig. 9).

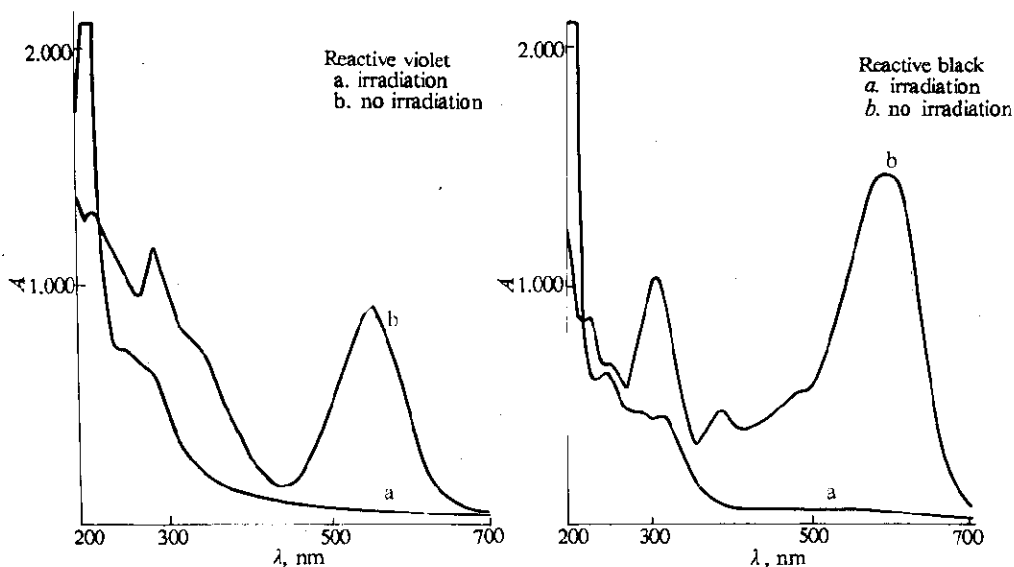


Fig. 9 Absorbance decrease of dye solution after photodegradation
a. after irradiation; b. before irradiation

The reaction of OH-radicals with aromatic substances is well documented. Phenol photocatalytic decomposition intermediates underwent further photocatalytic oxidation via acids and / or aldehydes and finally decomposed into CO_2 and H_2O (Okamoto, 1985).

The situation of toxicity change after the photolytic reaction

NAD (P) H (nicotinamide adenine dinucleotide or nicotinamide adenine dinucleotide-phosphate as hydrogen acceptor) can reduce methylene blue from blue to colourless. The decolourization time increases when the activity is inhibited by environmental toxicants. The results (Table 1) showed that the toxicity of the solution decreased obviously after photodegradation.

Table 1 The situation of toxicity change

Dye solution	pH	C, ppm	Decolourization ratio, %	EC_{100}
<i>RV</i>				
Before irradiation	7.55	13.3	0	77.2%
<i>RV</i>				
After irradiation	7.55	13.3	83.6	∞
<i>RB</i>				
Before irradiation	7.80	13.3	0	66.4%
<i>RB</i>				
After irradiation	7.80	13.3	74.0	85.6%

EC_{100} is used as an indicator of relative toxicity, which equals percent sample causing 100 percent effect

Transformation of organic species

300 ml 40 ppm dye solutions (with 30 mg TiO_2 powder) were adjusted to pH 13.00 for

Table 2 Transformation of organic species

Dye solution	COD_{Cr} , mg/L	IC, ppm	Decolourization ratio, %
<i>RV</i>			
Before irradiation	19.4	7.0	0
<i>RV</i>			
After irradiation	12.0	22.1	95.6
<i>RB</i>			
Before irradiation	21.9	2.3	0
<i>RB</i>			
After irradiation	10.6	8.7	96.7

COD_{Cr} (mg/L) means chemical oxygen demand using $\text{K}_2\text{Cr}_2\text{O}_7$ as oxidant, in form of decrease of oxygen concentration (mg/L). IC means inorganic carbon

reactive violet and pH 12.00 for reactive black and photodegraded by solar light, the following parameters were measured (Table 2).

The dye solutions decolourized rapidly which suggests that the dye can be easily photocatalytically degraded to other organic compounds. However the slow decrease of COD means that the intermediates need more time to transform to further degradation products, and the increase of IC implies that the photocatalytic reaction finally produced CO_2 .

CONCLUSION

There are many factors influencing the decolourization efficiency. For the decolourization of reactive violet and reactive black the optimal pH values are 13.00 and 12.00 respectively. The optimal amount of catalyst is determined by irradiation time and light intensity and the decolourization efficiency increases with increase of initial dye concentration.

Reactive dyes can be rather completely photocatalytically degraded by sunlight in the presence of TiO_2 catalyst, some products are identified to be alkanes or alkyl amines which could be biologically degraded more easily. The decrease of COD and increase of IC imply that dye can be photocatalytically mineralized.

The toxicity of the solutions decreased considerably after photodegradation, the results mean that the photocatalytic process could become a safe method for dye degradation and colour wastewater treatment.

The reaction mechanism and decolourizing structure-reactivity relationship are to be investigated in detail.

REFERENCES

- Cunningham, J. and Srijaranai, S., *J. Photochem. Photobio., A: Chem.*, 1988, 43 : 329
Chen Dezhi and Wen Xuemo, *Acta Energetica Solaris Sinica*, 1990, 11(3): 340
Fan Bangtang and Li Jin, *Environ. Poll. Contr.*, 1989, 11(4): 16; *ibid*, 11(6): 7
Fox, M. A., *Acc. Chem. Res.*, 1983, 16 : 314
Graves, H. M. and Johnston, L. G., *J. Photochem. Photobio., A: Chem.*, 1988, 43 : 183
Horspool, W. M., *Aspect of organic photochemistry*, London, New York, San Francisco: Academic Press, 1976 : 263
Izumil, I., Fan, F. and Bard, A. F., *J. Phys. Chem.*, 1981, 85 : 218
Kormann, C., Bahnmann, D. W. and Hoffmann, M. R., *ES&T*, 1988, 22 : 798
Matthews, R. W., *Water Res.*, 1986, 20 : 569
Phtani, B., Okugawa, Y., Nishimoto, S. and Kagiya, T., *J. Phys. Chem.*, 1987, 91 : 3550
Okamoto, K., Yamamoto, Y. and Tanaka, M., *Bull. Chem. Soc. Jpn.*, 1985, 58 : 2015
Pelizzetti, E., Serpone, N., *Homogeneous and heterogeneous catalysis*, Dordrecht, Boston, Lancaster, Tokyo: D. Reidel Publishing Company, 1986 : 593

(Received April 18, 1991)