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Wat. Res. Vol. 34, No. 3, pp. 990–994, 2000
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Printed in Great Britain
0043-1354/00/\$ - see front matter

PII: S0043-1354(99)00210-9

SOLAR PHOTOCATALYTIC DEGRADATION OF EIGHT COMMERCIAL DYES IN TiO₂ SUSPENSION

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(First received 1 May 1998; accepted in revised form 1 May 1999)

Abstract—The photocatalytic degradation of eight commercial dyes with different structure and containing different substitute groups has been investigated using TiO₂ as photocatalyst in aqueous solution under solar irradiation. Decolorization rate, TOC decrease and inorganic ion production of the dye solution were detected. The experimental results indicate that eight commercial dyes could be degraded efficiently at different levels. The comparison of chloride and sulfate ions production rate from the cleavage of substitute groups in different structure positions reveals the dye compounds degradation pattern and decomposition pathway. © 2000 Elsevier Science Ltd. All rights reserved

Key words—solar photocatalysis, commercial dyes, decolorization, mineralization, degradation pattern, TiO₂

INTRODUCTION

Dyes are an abundant class of colored organic compounds that represent an increasing environmental danger. During dye production and textile manufacturing processes a large amount of wastewater containing dyestuffs with intensive color and toxicity can be introduced into aquatic systems. Due to the large degree of aromatics present in these molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolorization and degradation (Souther and Alspaugh, 1957; Hamza and Hamoda, 1980; Sheng and Chi, 1993). This had led to the study of other methods. Recent studies have demonstrated that photocatalysis can be used to destroy dye compounds using semiconductors such as the anatase form of titanium dioxide and UV light irradiation (Al-Ekabi *et al.*, 1991; Blake, 1994; Hoffmann *et al.*, 1995). Lately, the utilization of combining photocatalysis and solar technologies has been attracted increasing attention. It may be developed to a useful process for the reduction of water pollution caused by dying compounds because of the mild conditions required and their efficiency in the mineralization (Minero *et al.*, 1993, 1996; Daoxin *et al.*, 1994; Lindner *et al.*, 1995; Li and Zhang, 1996). In order to elucidate the photocatalytic decolorization mechanism and decomposition pattern of dye compounds in details, our study focus on the

investigation of inorganic ion production from degradation of substitute groups. It will provide the reaction pathways for eight commercial dyes with different molecular structures and containing different substitute groups under solar irradiation.

EXPERIMENTAL SECTION

Materials

Seven commercial dyes were obtained from the Dye Plant in Shanghai without further purification. Methylorange was purchased from the Beijing Chemical Industrial Company as an analytical reagent grade. Their classification and molecular formulas were listed in Table 1. The catalyst used in all testes was titanium dioxide reagent powder (from Beijing Chemical Industrial Company; predominantly anatase with specific surface areas of 9 m² g⁻¹).

Irradiation experiment

All photocatalytic experiments were carried out at the same conditions on October 14, 1996 from 11.00 a.m. to 15.00 p.m. The average insolation of the solar irradiation was 21.28 W m⁻² measured by an UV irradiance meter at the range of 375–475 nm, (model UV-A, made in photoelectric instrument factory of Beijing Normal University). A series of slurries of dyes solution of 1 l with 20 mg l⁻¹ initial concentration and 1 g l⁻¹ TiO₂ powder were mixed using magnetic stirrers in open Pyrex beakers. A series of certain volume of samples were withdrawn at selected times for analysis. To avoid a volume change due to the volatility of the solvent, a certain amount of distilled water was added into the system at different intervals.

Analytical determination

Samples were analyzed after centrifugation (1800 rpm for 10 min) and filtration by a 0.45 µm syringe filter. The

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Table 1. Description of eight commercial dyes

No.	Name ($\lambda_{\max}$)	Classification	Molecular formulas
1	reactive brilliant red K-2G ($\lambda_{\max}$ = 508 nm)	reactive	C ₂₅ H ₁₃ O ₁₃ N ₇ S ₄ ClNa ₄
2	reactive brilliant red K-BP ($\lambda_{\max}$ = 530 nm)	reactive	C ₂₅ H ₁₃ O ₁₀ N ₇ S ₃ Cl ₂ Na ₃
3	reactive yellow KD-3G ($\lambda_{\max}$ = 405 nm)	reactive	C ₅₀ H ₃₄ O ₂₀ N ₁₈ S ₆ Cl ₂ Na ₆
4	cationic pink FG ($\lambda_{\max}$ = 505 nm)	cationic	C ₂₂ H ₂₉ O ₄ N ₂ PCl
5	methyl orange ($\lambda_{\max}$ = 458 nm)	indicator	C ₁₄ H ₁₄ O ₃ N ₃ S
6	direct light red F-3B ($\lambda_{\max}$ = 522 nm)	direct	C ₄₅ H ₂₆ O ₁₉ N ₁₀ S ₆ Na ₆
7	direct light turquoise GL ($\lambda_{\max}$ = 620 nm)	direct	C ₃₂ H ₁₄ O ₆ N ₈ S ₂ Na ₂
8	acid red B ($\lambda_{\max}$ = 513 nm)	acid	C ₂₀ H ₁₂ O ₇ N ₂ S ₂ Na ₂

color removal of the dye solution was determined with the absorbance value at the maximum of the absorption spectrum for every dye by monitoring UV/VIS spectrum in 200–800 nm using a spectrometer (Beckman DU-650). The production of ions during photocatalytic degradation process was measured with a capillary ion analyzer (Waters CIA). The total organic carbon of the dye solution was determined with a TOC analyzer (Shimadzu TOC-500).

RESULTS AND DISCUSSION

Photocatalytic degradation of eight dyes

The experimental data of different photocatalytic degradation of eight dyes with different structures after 4 h solar irradiation are shown in Table 2. It indicates that, in general, the decolorization rate of the dye solution was more rapid than the mineralization rate identified by TOC removal. The latter will take longer time for further oxidation. The release of chloride ions and sulfate ions points to molecular structure cleavage during the solar photodegradation process. Nitrate and nitrite ions were detected in trace quantities in the degradation process of methylorange.

Photocatalytic oxidation of dyes with chloride substitute

Four dyes with chloride-substitutes in different positions listed in Table 1 from Nos. 1–4 are reactive brilliant red K-2G, reactive brilliant red K-2BP, reactive yellow KD-3G and cationic pink FG, respectively. The chlorides of compound Nos. 1 and 3 are linked to the 1,3,5-triazine ring only. For compound No. 2, one chloride connects with the benzene ring and the other one connects with the triazine ring being the same as compounds Nos. 1 and 3. For compound No. 4, the chloride is linked to the aliphatic lateral chain connected with the

nitrogen atom. The results of decolorization (Fig. 1) and TOC decrease (Fig. 2) provide the degree of photodegradation and mineralization for the four dyes with different structures during 4 h of solar irradiation. The chloride ion production rate (Fig. 3) reveals their degradation pattern. For the compounds Nos. 1 and 3, after 4 h of solar irradiation, there is no chloride ion detected although the color removal of the dye solution is almost complete (100 and 81.34%, respectively) and the TOC content decreased to 81.81 and 41.62%, respectively. The results indicate that the chloride being linked to the triazine as well as the ring structure containing three nitrogen atoms are stable in photocatalysis. Therefore, from the chloride ion production of compound No. 2, we could conclude that it is due to the cleavage of the chloride connected with the benzene ring. It is worth noting that there is a different chloride ion production rate for compound Nos. 2 and 4. Cleavage of the chloride is linked to the benzene ring in compound No. 2 started after 1 h of irradiation and increased slowly up to 10% until 4 h when the TOC degradation of the solution achieved about 72.52%. Clearly, benzene and chloro-benzene are stable intermediate products during the photocatalysis. It requires a longer time for full oxidation. In contrast, for compound No. 4, the chloride ion production rate delayed the rate of decolorization and the TOC decrease and started after 3 h but increased rapidly up to 36.01% in the last one hour. It reveals that the chloride group cleavage depends on its position in the molecular structure.

Photocatalytic oxidation of the dyes with sulfonic groups

The reactive brilliant red K-2G and the reactive

Table 2. Photocatalytic degradation data for eight dye solutions after 4hr solar irradiation

No.	Name of dye	Removal of color (%)	Removal of TOC (%)	Sulfate ion production (%)	Chloride ion production (%)
1	reactive brilliant red K-2G	100	82	53	0
2	reactive brilliant red K-2BP	93	73	25	9
3	reactive yellow KD-3G	81	42	27	0
4	Cationic pink FG	100	61	0	36
5	Methylorange	94	52	60	0
6	direct light red F-3B	100	70	25	
7	direct light turquoise GL	92	45	18	
8	acid red B	100	55	63

Fig. 1. Color removal of four dyes during 4 h of photocatalytic oxidation.

brilliant red K-2BP were also chosen as model compounds to investigate the photocatalytic degradation of the dyes containing sulfonic groups. There are three sulfonic groups in a molecule of reactive brilliant red K-2BP. They are linked to a naphthalene ring and a benzene ring, respectively. There are four sulfonic groups in one molecule of reactive brilliant red K-2G. In addition to the three sulfonic groups, which are the same as those of reactive brilliant red K-2BP, the other sulfonic group is linked to another benzene ring, which is not adjacent to the azo bond. According to the

results as shown in Fig. 4, the sulfate ion production rates for both dyes within 4 h show obviously different and the sulfate ion conversion for sulfonic groups are about 28 and 4%, respectively, for the first 2 h. Clearly, the rapid appearance of sulfate ion for reactive brilliant red K-2G is due to the cleavage of the special sulfonic group being different from the others in reactive brilliant red K-2BP. It is more reactive to photocatalysis than the other three sulfonic groups. The net amount of sulfate ion conversion is about 24% which is the expected quantity for the photocatalyzed oxidation

Fig. 2. TOC removal of four dyes during 4 h of photocatalytic oxidation.

Fig. 3. Chloride ion production of four dyes during 4 h of photocatalytic oxidation.

of one sulfonic group only rather than the total four sulfonic groups in the whole molecule. It indicates that this kind of sulfonic group degraded before the others. After 2 h, the rate of sulfate ion production is similar.

In the photocatalytic degradation of the acid red B, compound No. 8 according to the molecular formula in Table 1, the two sulfonic groups connect with the two kinds of naphthalene rings which are with or without a hydroxyl group. From the results shown in Fig. 5, the sulfate ion production rates in

the early part and the latter part of irradiation are obviously different. It reflects the difference in reactive property between two naphthalene ring structures. It still needs further identification of the other products in order to determine which naphthalene ring is more reactive in photocatalysis.

Comparison of photocatalytic decolorization of dyes with different substitute groups

The molecular structures of reactive brilliant red K-2G and reactive brilliant red K-2BP show differ-

Fig. 4. Sulfate ion production for two dyes during 4 h of photocatalytic oxidation.

Fig. 5. Sulfate ion production of acid red B during 4 h of photocatalytic oxidation.

ent substitute groups of chloride and sulfonic. The different decolorization rates and TOC decreasing rates of both dyes shown in Figs 1 and 2 indicate that the sulfonic-substituted dye is more reactive than the chloride-substituted dye in the photocatalytic process.

SUMMARY AND CONCLUSION

This study demonstrates that certain commercial dyes with different structure and different substitute groups can be decolorized and mineralized by solar photocatalysis. The experimental results indicate that during the photocatalytic degradation, the decolorization rate is faster than the mineralization rate. For chloride substituted dye, the chloride in the side chain is more active with respect to cleavage than the one connected with the benzene ring. The triazine ring and the groups connected with it are stable in photocatalysis. A naphthalene ring is more stable than benzene. The structures not adjacent to azo bond are more reactive.

Acknowledgements—This research has been supported by the National Natural Foundation of China (No. 29637010; 59878051) and partly supported by the Chinese Academy of Sciences (No: KZ952-S1-231). Liu Nian, a student of Beijing Industrial University, took part in the research within a training program.

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