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A COMPARATIVE STUDY OF SONOLYTIC, PHOTOCATALYTIC AND SONOPHOTOCATALYTIC DEGRADATION OF CRYSTAL VIOLET

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ABSTRACT

The degradation of crystal violet (CV) in aqueous suspension was studied by sonolysis, photocatalysis and sonophotocatalysis. The bleaching of dye was monitored spectrophotometrically. The effect of various parameters like concentration of dye, pH, amount and particle size of semiconductor (ZnO) on the rate of degradation has also been observed. It has been reported that combination of ultrasound and photocatalysis in the aqueous phase increases the rate due to an increased concentration of reactive radicals. A tentative mechanism for the sonophotocatalytic bleaching of crystal violet has been proposed.

Key words: Sonophotocatalysis, Photocatalysis, Sonolysis, Crystal violet, Ultrasound, Zinc oxide.

INTRODUCTION

The treatment of dye containing wastewater by conventional methods, such as flocculation, air sparging and activated carbon adsorption are relatively less effective in decolourization of wastewater since dyestuffs are recalcitrant and difficult to remove by these processes due to their low molecular weight and high water solubility. Moreover, these chemical treatment options merely transfer the pollutant from water to another phase. Alternative biological treatment is difficult to control in order to achieve the desired degree of removal. Over the last decade, there has been a growing interest in the sonophotocatalytic degradation.

Ultrasonic degradation of 2, 4, 6-trichlorophenol in presence of TiO_2 catalyst was reported by Pandit et al.[1] Stavarache et al.[2] studied sonolysis of chlorobenzene in Fenton-

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type aqueous systems. Effect of Fenton-like oxidation on enhanced oxidative degradation of para-chlorobenzoic acid by ultrasonic irradiation have been investigated by Neppolian et al.[3] Okitsu et al.[4] proposed sonochemical degradation of azo dyes in aqueous solution. Tiehm and Neis[5] reported ultrasonic dehalogenation and toxicity reduction of trichlorophenol.

Tanaka et al.[6] studied photocatalytic degradation of commercial azo dyes while Matsuda et al.[7] carried out photocatalytic decomposition of acetaldehyde with anatase nanocrystals-dispersed silica films prepared by the sol–gel process with hot water treatment. An et al.[8] investigated heterogeneous photocatalytic degradation of methylene blue aqueous solution under coexistence of metelloporphyrine polymer and air. Kinetics of photocatalytic degradation of aniline in water over TiO_2 supported on porous nickel has been reported by Leng et al.[9] Chen et al.[10] observed photocatalytic decolourization of methyl orange in aqueous suspension of TiO_2 and Ag/TiO_2 immobilized on γ-Al_2O_3. Liu et al.[11] used a new type of nitrogen doped TiO_2 nanocrystals for photocatalytic degradation of azo dyes (acid orange 7 and reactive black 5).

A synergic effect on degradation of formic acid using new photoelectrochemical reactor was observed by An et al.[12] Stock et al.[13] used combinative sonolysis and photocatalysis for textile degradation. Complete mineralization of propyzamide in aqueous solution containing TiO_2 particles and H_2O_2 by simultaneous irradiation of light and ultrasonic waves has been reported by Yano et al.[14] while Harada[15] carried out sonophotocatalytic decomposition of water using TiO_2 photocatalyst. Gonzalez and Martinez[16] reported the sonophotocatalytic degradation of basic blue 9 industrial textile dye over slurry titanium dioxide and observed the influencing factors. The effect of carbon tetrachloride on reaction rates has been investigated by Bejarano-Perez and Suarez-Herrera.[17]

Behnajady et al.[18] investigated the effect of ultrasonic waves on the efficiency of direct photolysis and photooxidation processes i.e. on the removal of a model contaminant from textile industry. Sonophotocatalytic activity of methyl orange over Fe (III)/TiO_2 was reported by Wantala et al.[19] Hayashi et al.[20] investigated the effect of the sonophotocatalytic pretreatment on the volume reduction of sewage sludge and enhanced recovery of methane and phosphorous. Pankaj and Verma[21] observed sonophotocatalytic behaviour of cerium doped salts of Cu (II), Co (II) and Mn (II) in the degradation of phenol.

Sonophotocatalytic degradation of methyl orange by carbon nanotube/TiO_2 particles in aqueous solutions was carried out by Wang et al.[22] Vinu and Madras[23] reported kinetics of sonophotocatalytic degradation of anionic dyes with nano-TiO_2. Integrated heterogeneous sono-photo-Fenton processes for the degradation of phenolic aqueous solutions was described by Segura et al.[24] Wu[25] studied the effect of sonication with changing pH and temperature on decolourization of reactive red 2 in UV/TiO_2 system.

EXPERIMENTAL

Materials and apparatus

Crystal violet (SdS) and zinc oxide (Merck) have been used as received. All solutions were prepared in doubly distilled water.

Ultrasonic bath (Systronics Model 392) has been used as ultrasound radiation source. A 200 Watt tungsten lamp (Sylvania Laxman) was used for irradiation purpose. A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics Model 324). A G-2 sintered glass crucible was used for filtration. A UV-VL spectrophotometer (Systronics Model 108) was used for measuring optical density of reaction mixture at different time intervals.

Procedure

A stock solution of crystal violet (1.0×10^{-3} moles/litre) was prepared in doubly distilled water. The degradation of dye was observed using 50 mL of dye solution (2.5×10^{-5}M) and 0.20 g of ZnO semiconductor. The lamp and/or the ultrasonic bath filled with water were always switched on at least 30 minutes before starting the run. All runs were carried out under atmospheric conditions and by continuous stirring the reaction mixture.

Optical density of samples was observed before starting the run and at different intervals of time, at 590 nm (λ_{max} of crystal violet). Prior to measurement of optical density, ZnO was separated using a G-2 sintered glass crucible.

RESULTS AND DISCUSSION

Kinetic analysis

Preliminary kinetic runs carried out in an aqueous solution of crystal violet, demonstrated that it does not degrade without the use of ZnO under visible light and also under sonication at low ultrasound frequency (392 Hz). However, in the presence of ZnO semiconductor, degradation occurred at different rates, by employing visible light (VL) or ultrasound (US), either separately or simultaneously. A regular decrease in optical density was observed with increasing time of exposure.

The concentration of crystal violet (in terms of optical density) was found to decrease following a first order rate law. The experimental behaviour obtained under standard conditions has been reported in Table 1 and graphically represented in Fig. 1 (typical run). Both; photocatalysis and sonolysis induce the degradation of dye in water mainly through their oxidation initiated by $^{\bullet}OH$ radicals.

Table 1: Kinetic analysis

[Crystal violet] = 2.50×10^{-5} M
ZnO = 0.20 g
pH = 7.5

Time (min.)	D + US + PC 2 + log O. D.	D+ VL + PC 2 + log O. D.	D + US + VL + PC 2 + log O. D.
0	1.4857	1.4857	1.4857
10	1.4672	1.4240	1.3979
20	1.4440	1.3711	1.2934
30	1.4211	1.3155	1.2041
40	1.3989	1.2647	1.0755
50	1.3801	1.2005	0.9494
60	1.3757	1.1332	0.7851
70	1.3578	1.0219	0.6425
80	1.3384	0.9493	0.5865
90	1.3222	0.8339	0.4771
k Rate constant (s^{-1})	0.69×10^{-4}	2.78×10^{-4}	4.31×10^{-4}

D = Dye, US = Ultrasound, VL = Visible light, PC = Photocatalyst

As ZnO remains suspended in the reaction mixture and therefore, for accurate measurement of optical density, a G-2 sintered glass crucible was used for filtration to remove the suspended particles of semiconductor. Use of centrifuge and Whatmann filter paper were not preferred because comparatively more time is required for centrifugation and when reaction mixture was filtered through Whatmann filter paper, some particles still remained in filtrate, which may create a problem in determination of optical density.

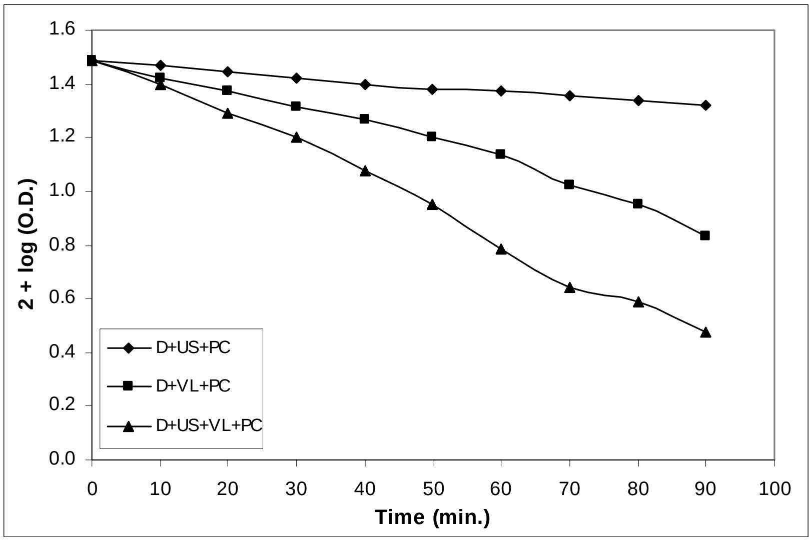

Fig. 1: A typical run

In the presence of ultrasound, $^{\bullet}OH$ and other radical species were generated from water scission under the extreme pressure and temperature conditions created by the implosion of cavitation bubbles.

However, under photocatalytic conditions, the principal source of $^{\bullet}OH$ radicals is the oxidation of hydroxide anions or water molecules adsorbed on the semiconductor surface by the holes of the semiconductor in valence band, which are generated due to the photoinduced promotion of electrons into the conduction band. Moreover, conduction band electrons interact with adsorbed dioxygen, leading to the sonication of superoxide anion $O_2^{-\bullet}$ and hydroperoxide radical $HO_2^{\bullet}$. All these species may play important role in the photocatalytic oxidation of organic compounds.

The results show that in the presence of ZnO and ultrasound, the dye underwent a slower degradation. Under photocatalysis (VL + ZnO), the degradation of the dye occurred at a comparatively higher rate. Further, a significant increase in the rate of reaction was found leading to complete degradation of crystal violet within 3 hrs, when the dye solution was sonicated alongwith the photocatalytic treatment i.e. under sonophotocatalysis (VL + US + ZnO).

Effect of pH variation

The pH of the medium is likely to play a significant role on rate of degradation. Therefore, the effect of pH on the degradation rate of dye was investigated in the pH range 5.5 – 9.0. The results are reported in Table 2.

Table 2: Effect of pH

[Crystal violet] = 2.50 x 10^{-5} M ZnO = 0.20 g

pH	D + US + PC k x 10^4 (s^{-1})	D + VL + PC k x 10^4 (s^{-1})	D + US + VL + PC k x 10^4 (s^{-1})
5.5	0.49	1.51	3.01
6.0	0.53	1.82	3.52
6.5	0.61	2.09	3.87
7.0	0.65	2.47	4.11
7.5	0.69	2.78	4.31
8.0	0.66	2.36	4.05
8.5	0.60	1.99	3.65
9.0	0.54	1.64	3.41

The first order rate constants were obtained under different experimental conditions. Degradation could not be studied in lower pH range (pH < 5.5) because in highly acidic medium, semiconductor ZnO was soluble in water and crystal violet dye is also degraded at lower pH. It has been observed that rate of degradation increases with increase in pH but after a certain value of pH (7.5), the rate of reaction decreases under all the three experimental conditions. However, it has been observed that under ultrasound and in the presence of zinc oxide, the reaction rate is slightly increased with increasing pH of the medium. Whereas, crystal violet degradation was much faster under both; photocatalysis and sonophotocatalysis. The degradation trends were same in sonolysis, photocatalysis and sonophotocatalysis.

The values of rate constants clearly demonstrate that the combined action of photocatalysis and sonolysis produced synergistic effect in this range of pH.

The increase in rate of degradation on approaching towards more alkaline medium may be explained by the fact that larger number of hydroxyl ions ($^{-}$OH ions) are available at higher pH values. OH^{-} ions will generate more $^{\bullet}$OH radicals by combining with the hole and these hydroxyl radicals are considered responsible for the degradation of dye. On increasing pH value of the medium in acidic range, again a decrease in the rate of reaction was observed. This may be attributed to the repulsion between cationic dye and the positively charged surface of the semiconductor due to adsorption of protons. There is a greater probability for the formation of hydroxyl radicals ($^{\bullet}$OH radicals) via combined effects of sonolysis and photocatalysis. These $^{\bullet}$OH radicals are actual oxidizing species responsible for the degradation of dye.

Effect of dye concentration

The effect of different initial concentrations of the dye on the degradation rate was also observed keeping all other parameters constant. The reaction rates with dye concentration are shown in Table 3. It was observed under sonolysis that in the presence of ZnO, the reaction rate first increases and then decreases with increasing dye concentration. The degradation of crystal violet was much faster under photocatalysis than sonolysis and very fast under sonophotocatalysis as compared to sonolysis and photocatalysis, separately.

Table 3: Effect of dye concentration

pH = 7.5 ZnO = 0.20 g

[CV] x 10^5 M	D + US + PC k x 10^4 (s^{-1})	D + VL + PC k x 10^4 (s^{-1})	D + US + VL + PC k x 10^4 (s^{-1})
1.0	0.23	1.77	3.35
1.5	0.38	2.05	3.63
2.0	0.52	2.49	4.01
2.5	0.69	2.78	4.31
3.0	0.58	2.34	3.86
3.5	0.40	2.13	3.22
4.0	0.29	1.62	2.57
4.5	0.18	1.31	2.19

It clearly demonstrates that the combined action of sonolysis and photocatalysis produced a synergistic effect. It has been observed that the rate of bleaching increases with an increase in the concentration of the dye. It may be due to the fact that as the concentration of crystal violet was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of degradation was observed. The rate of bleaching was found to decrease with a further increase in the concentration of the dye. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desired intensity to reach the semiconductor particles; thus, decreasing the rate of reaction..

However, this phenomenon occurs almost exactly in the same way in the presence and absence of ultrasound, indicating that under photocatalytic and sonophotocatalytic conditions, the reaction system is equally sensitive to the increase in the ratio of dye concentration and semiconductor.

Effect of amount of photocatalyst

First order rate constants were obtained for degradation under sonolysis, photocatalysis and sonophotocatalysis in the presence of different amounts of ZnO keeping all other factors identical. The results have been reported in Table 4.

Table 4: Effect of amount of photocatalyst

[Crystal violet] = 2.50×10^{-5} M pH = 7.5

Amount of ZnO (g)	D + US + PC $k \times 10^4$ (s^{-1})	D + VL + PC $k \times 10^4$ (s^{-1})	D + US + VL + PC $k \times 10^4$ (s^{-1})
0.05	0.44	1.92	3.37
0.10	0.51	2.18	3.53
0.15	0.59	2.43	3.99
0.20	0.69	2.78	4.31
0.25	0.63	2.52	4.08
0.30	0.54	2.27	3.84
0.35	0.49	2.01	3.65

The results of effect of amount of photocatalyst (ZnO) on the rate of bleaching reveal that the value of rate constant increases with increase in the amount of ZnO. This increase in the rate of bleaching may be attributed to increase in the exposed surface area of semiconductor. But after a certain limit (0.20 g), if the amount of ZnO was increased further, there will be no increase in the exposed surface area of the photocatalyst and hence, there is no increase in rate constant; however, there is a slight decrease in the rate of degradation, which may be due to possible electron-hole recombination with larger amounts of photocatalyst.

Effect of particle size of zinc oxide

The effect of particle size of ZnO on the rate of bleaching of crystal violet was also investigated. The results reveal that as the particle size of the semiconductor (0.80 μ) is increased (upto 4.00 μm), there is a corresponding decrease in the reaction rate. This may be due to the fact that on increasing the particle size (keeping the amount constant) of the semiconductor, the overall surface area of the semiconductor will decrease; thus, resulting into a decrease in the rate of bleaching of crystal violet.

MECHANISM

On the basis of the experimental observations, the following tentative mechanism has been proposed for sonophotocatalytic bleaching of crystal violet (CV).

The semiconductor (SC) is excited on exposure to visible light to give SC*. This excited state will provide an electron (e^-) in the conduction band and a hole in the valence band. The hole will generate hydroxyl radicals by abstracting an electron from the OH^- ions. Alternatively, hydroxyl radicals are also generated by sonolysis of water, which will oxidize the dye to its leuco form.

$$SC \rightarrow SC^* \quad ...(1)$$

$$SC^* \rightarrow SC^+ \text{ (or } h^+\text{)} + e^- \quad …(2)$$

$$h^+ + {}^-OH \rightarrow {}^{\bullet}OH \quad …(3)$$

$$H_2O \xrightarrow{\bullet)))} {}^{\bullet}OH + {}^{\bullet}H \quad …(4)$$

$$CV + {}^{\bullet}OH \rightarrow \text{Leuco CV} \rightarrow \text{Gaseous products} \quad …(5)$$

The generation of more ${}^{\bullet}OH$ radicals in presence of ultrasound by sonolysis of water will add to degradation rate of crystal violet.

The participation of $^{\bullet}$OH radicals as an active oxidizing species was confirmed by carrying out same reaction in presence of some hydroxyl radical scavengers like isopropanol, where rate of bleaching was drastically reduced.

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REFERENCES

1. A. B. Pandit, P. R. Gogate and S. Mujumdar, Ultrason. Sonochem., **8**, 227 (2001).
2. Stavarache, B. Yim, M. Vinatoru and Y. Maeda, Ultrason. Sonochem., **9**, 291 (2002).
3. Neppolian, J. S. Park and H. Choi, Ultrason. Sonochem., **11**, 273 (2004).
4. K. Okitsu, K. Iwasaki, Y. Yobiko, H. Bandow, R. Nishimura and Y. Maeda, Ultrason. Sonochem., **12**, 255 (2005).
5. A. Tiehm and U. Neis, Ultrason. Sonochem., **12**, 121 (2005).
6. K. Tanaka, K. Padermpole and T. Hisanaga, Water Res., **34**, 327 (2000).
7. A. Matsuda, Y. Kotani, T. Kogure, M. Tatsumisago and T. Minami, J. Sol-Gel Sci. Tech., **22**, 41 (2001).
8. T. C. An, J. Z. Gao, H. Chen and X. H. Zhu, Chem. J. Internet, **3**, 14 (2001).
9. W. H. Leng, H. Liu, S. A. Cheng, J, Q. Zhang and C. N. Cao, J. Photochem. Photobiol., **131A**, 125 (2000).
10. L. C. Chen, F. R. Tsai and C. M. Huang, J. Chem. Soc. Faraday Trans., **170A**, 7 (2005).
11. Y. Liu, X. Chen, J. Li and E. Burda, Chemosphere, **61**, 11 (2005).
12. T. An, Y. Xiong, G. Li, C. Cha and X. Zhu, J. Photochem. Photobiol., **152A**, 155 (2002).
13. N. L. Stock, J. Peller, K. Vonodgopal and V.Kamat, Environ. Sci. Technol., **34**, 1747 (2000).
14. J. Yano, J. Matsuura, H. Ohura and S. Yamasaki, Ultrason. Sonochem., **12**, 197 (2005).
15. H. Harada, Ultrason. Sonochem., **8**, 55 (2001).

16. A. S. Gonzalez and S.S. Martinez, Ultrason. Sonochem., **15**, 1038 (2008).

17. N. J. Bejarano-Perez and M. F. Suarez-Herrera, Ultrason. Sonochem., **15**, 612 (2008).

18. M. A. Behnajady, N. Modirshahla, M. Shokri and B. Vahid, Global Nest J., **10**, 8 (2008).

19. K. Wantala, D. Tipayaram, L. Laokiat and N. Grisdanurak, React. Kin. Catal. Lett., **97**, 249 (2009).

20. N. Hayashi, S. Koike, R. Yasutomi and E. Kasai, J. Environ. Engg., **135**, 1399 (2009).

21. Pankaj and M. Verma, Indian J. Chem., **48A**, 367 (2009).

22. R. Vinu and G. Madras, Environ. Sci. Technol., **43**, 473 (2009).

23. S. Wang, Q. Gong and J. Liang, Ultrason. Sonochem., **16**, 205 (2009).

24. Y. Segura, R. Molina, F. Martinez and J. A. Melero, Ultrason. Sonochem., **16**, 417 (2009).

25. D. H. Wu, J. Hazard. Mater., **169**, 1179 (2009).

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