Sonochemical degradation of brilliant cresyl blue – an ecofriendly approach

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Abstract : Dyestuffs which are often present in industrial waste water may have a serious impact on the environment as well as on the health of human beings. This report describes an ecofriendly method which has been developed for the degradation of brilliant cresyl blue. Ultrasonic frequency of 4 MHz was used for all experiments in order to find the best conditions for degradation. The effect of operating variables like pH, concentration of dye, solvent composition, temperature, nature and concentration of surfactant etc. on the reaction rate has been observed. The progress of the sonochemical degradation was monitored spectrophotometrically. The value of energy of activation was also computed for this sonochemical degradation. A suitable tentative mechanism for sonochemical degradation of brilliant cresyl blue has also been proposed.

Keywords : Sonochemical degradation, brilliant cresyl blue, spectrophotometry.

Introduction

Inspite of many uses, the dyes are toxic and carcinogenic in nature also. Environmental contamination by these toxic chemicals is emerging as a serious global problem. Coloured solution containing dyes from effluents of textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage. On the contrary, bleached dye solutions are non-toxic and harmless. Secondly, the dye containing coloured water is almost of no use, but if this coloured solution is bleached to give colourless water, it may be used for washing, cooling, irrigation and cleaning purposes. Thus sonochemical degradation will provide a low cost method to solve the problem of water pollution. Degradation by ultrasound is considered as ecofriendly pathway because it is of low cost and less time consuming. Moreover it generates substances which are not hazardous for the environment.

Vinodgopal et al.[1] investigated degradation of reactive remazol black dye in oxygen saturated aqueous solution using high frequency ultrasonic generator. Sivakumar and Pandit[2,3] studied degradation of cationic dye rhodamine-B by hydrodynamic cavitations and cavitations generated by ultrasound. The rate of ultrasound assisted degradation of aryl-azonaphthol dye was investigated by different workers[4-6]. The degradation of azo dye acid orange-8 in aqueous suspension was carried out under sonolysis by Selli[7].

Results and discussion

The sonolytic bleaching of brilliant cresyl blue has been observed at λ_{max} 620 nm. The results for a typical run are graphically represented in Fig. 1.

It is noted that the color of dye fades on exposure to ultrasound. A graph between 2 + log A and time is plotted. Some curve like behavior with two straight lines intersecting at a point is obtained. It indicates that the
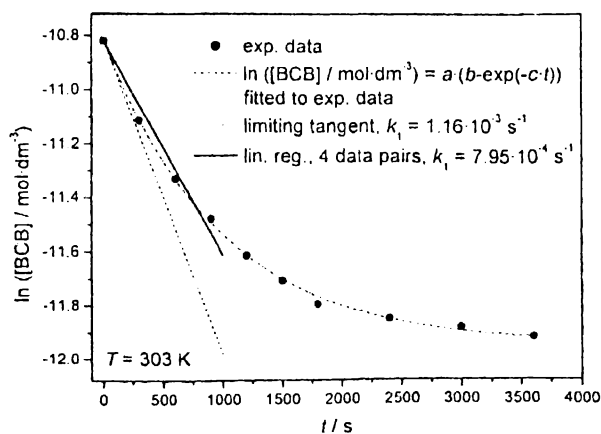

Fig. 1. A typical run; first order kinetics.

reaction proceeds in two stages. It is observed that the first stage is rapid which is followed by a slower one. Both these stages follow pseudo first order kinetics. The rate constants are determined by the following expression :

Rate constant = 2.303 × slope

As the major part of the reaction is over in the first stage (approximately 80%), only k_1 has been reported for all the other variations.

Effect of pH :

The pH of the solution is likely to affect the bleaching of the brilliant cresyl blue. The effect of pH on the rate of bleaching of brilliant cresyl blue solution has been investigated in the range 4.0–6.5 and the results are reported in Fig. 2.

It has been observed that the rate of sonolytic bleaching of the dye first increases and then decreases within acidic range as the pH is increased. The sonochemical degradation passes through a maximum at pH ≈5.0; higher or lower acidic media affect the rate of degradation adversely.

Degradation of the dye proceeds more smoothly, at pH ≈5.0, it may be assumed, more protonated form of dye at pH < 5.0 does not degrade easily.

Effect of solvent composition :

The composition of the solvent ethanol-water mixture affects the rate of the reaction. Different ratios of volumes of ethanol to water were used. The results obtained are shown in Fig. 2.
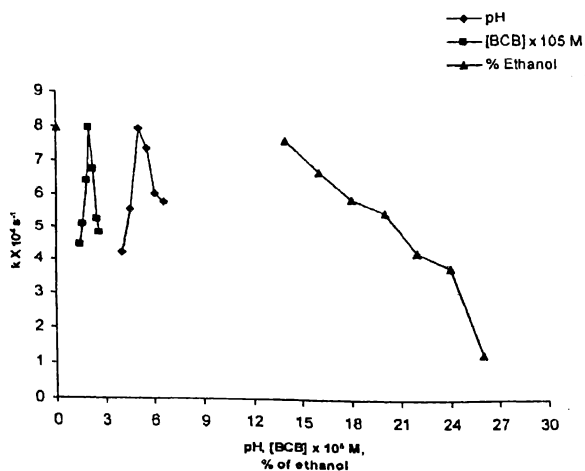
It is observed that as the polarity of the medium is decreased (ε_{water} = 78.65 and $\varepsilon_{ethanol}$ = 24.55), the rate of degradation of dye also decreases. The observed data. suggests that the sonochemical degradation of the dye proceeds much faster in more polar medium. This may be attributed to the charged dye molecules (cationic in the present case). It also suggests the involvement of some charged intermediates during this degradation.

Effect of brilliant cresyl blue concentration :

The concentration of the dye may affect the rate of the reaction. It is examined with the dye concentration varied from 1.4×10^{-5} to 2.6×10^{-5} M. The results are reported in Fig. 2. It has been observed that the rate of sonochemical degradation is increased with an increase in the concentration of the dye upto 2.0×10^{-5} M, but above this concentration, the rate decreases on further increase in concentration of the dye. This may be attributed to the fact that as the concentration of the dye is increased, more dye molecules were available to interact with ultrasound and hence, an increase in the rate has been observed. The rate of sonolytic degradation is found to decrease with further increase in the concentration of dye beyond 2.0×10^{-5} M. This may be explained on the basis that higher concentration of the dye molecules will not permit the ultrasound to interact with the dye molecules present in interior of the bulk solution.

Effect of nature and concentration of surfactant :

The effect of the nature and concentration of surfactant (anionic, cationic and non-ionic) on the rate of sonochemical bleaching of brilliant cresyl blue has also been observed and the results are given in Table 1.

Fig. 2. Effect of different parameters.

Table 1. Effect of the nature and concentration of surfactant

[Brilliant Cresyl Blue] = 2.00×10^{-5} M, Temp. = 303 K, pH = 5.0, Intensity = 4 MHz

[Surfactant] × 10^5 M	Rate constant $k \times 10^4$ (s^{-1})		
	SLS	CPC	Brij-35
0.00	7.95	7.95	7.95
0.25	8.33	7.31	7.72
0.50	8.76	7.21	7.53
1.00	9.58	6.60	7.10
2.50	9.19	6.02	7.05
5.00	8.79	5.38	6.84
10.00	6.12	4.15	6.53
25.00	5.50	3.93	6.33
50.00	4.87	3.72	6.14
100.0	3.62	3.29	5.74

It is observed that the cationic surfactant cetyl pyridinium chloride (CPC) retards the rate of reaction. This may be attributed to the fact that the dye is also of cationic nature and therefore, cationic surfactant will hinder its bleaching due to coulombic repulsion between the dye and the surfactant, while non-ionic surfactant (Brij-35) keeps the rate virtually unaffected. This may be due to steric hindrance offered by the surfactant molecules. However, in the case with the anionic surfactant like sodium lauryl sulphate (SLS), the rate first increases on increasing its concentration (up to $\approx 1 \times 10^{-5} M$) but decreases after that. This may be due to the fact that the dye is of cationic nature and the surfactant is anionic. The anionic surfactant (SLS) will support its degradation due to columbic attraction between the dye and the surfactant which causes a binding between the two species. But after a particular concentration of the surfactant, sonochemical degradation of dye decreases due to formation of micelles, which may hinder the approach of the ultrasound to the dye molecules due to their larger size.

Effect of temperature :

The effect of temperature has been studied in range 303 K to 323 K under ultrasonic irradiation. The results are shown in Fig. 3.
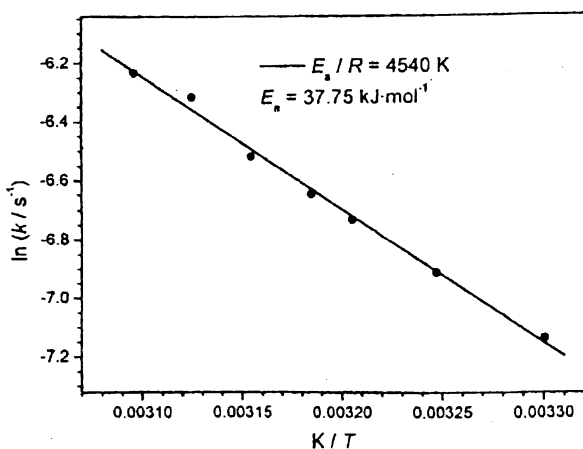

Fig. 3. Effect of temperature.

A straight line is obtained for the plot $4 + \log k$ vs $1/T$, with a negative slope, and the activation energy has been computed to be $\Delta E_a = 37.75$ kJ mol^{-1}. The activation energy for brilliant cresyl blue is seen to be smaller compared to those for ordinary chemical reactions. Thus, it may be concluded that the energy barrier of a sonochemical pathway is lower than that for an ordinary chemical reaction.

Experimental

Brilliant cresyl blue dye (Loba-Chimie) has been used in the present investigation. A stock dye solution ($1.00 \times 10^{-3} M$) has been prepared in doubly distilled water. For generating ultrasound, an ultrasonic interferometer of frequency 4 MHz (Mittal Enterprizes, Delhi) has been used. The pH of the solution has been measured by a digital pH meter (Hanna Instrument ISO 9001). The desired pH of the solution has been adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solution. A UV-visible spectrophotometer (Systronics Model 106) has been used for measuring absorption maximum and absorbance (A) at different time intervals.

Brilliant cresyl blue

$\lambda_{max} = 620$ nm   F.W. = 385.96
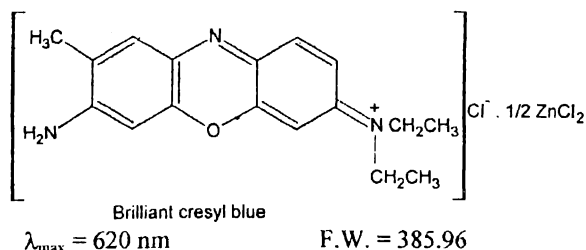
One liter effluent containing brilliant cresyl blue from printing industries was collected and diluted to a concentration around $2.0 \times 10^{-5} M$ and the total volume of effluent was made to 500 liters. This solution was exposed to ultrasonic radiation in batches of 2.0, 2.5 liter in ultrasonic bath. The dilute solution of effluent is bleached within 3 to 4 h.

Mechanism :

The rate of sonochemical bleaching of the dye has been found to be drastically reduced in the presence of some hydroxyl radical scavengers i.e. branched chain alcohols like isopropanol and *t*-butanol etc., which suggests that the hydroxyl radicals act as reactive species in the degradation of the dye. Thus, a tentative mechanism for the sonochemical bleaching of dye may be proposed as

$$H_2O \xrightarrow{\;\;\bullet))))\;\;} {}^\bullet H + {}^\bullet OH$$

$$Dye + {}^\bullet OH \xrightarrow{\hspace{2cm}} \text{Oxidized products}$$
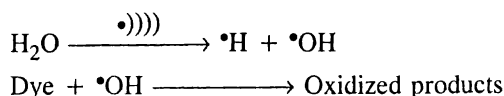
The products CO_2 and NH_4^+ has been detected as the final products by their usual chemical tests.

Acknowledgement

References

1. K. Vinodgopal, J. Peller, O. Makogon and P. V. Kamat, *Water Research*, 1998, **32**, 3646.

2. M. Sivakumar and A. B. Pandit, *Ultrason. Sonochem.*, 2002, **9**, 123.

3. M. Sivakumar and A. B. Pandit, *Ultrason. Sonochem.*, 2001, **8**, 233.

4. N. H. Ince and G. Tezcanli-Guyer, *Ultrasonics*, 2004, **42**, 591.

5. I. Gultekin and N. H. Ince, *Ultrason. Sonochem.*, 2006, **13**, 208.

6. I. H. Nilsunh and G. Tezcanli-Guyer, *Ultrasonics*, 2003, **42**, 591.

7. E. Selli, *Phys. Chem. Chem. Phys.*, 2002, **4**, 6123.