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Dyes and Pigments 73 (2007) 55–58

www.elsevier.com/locate/dyepig

The effect of sodium hydroxide in photolytic and photocatalytic degradation of Acid Blue 29 and Ethyl Violet

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Received 10 March 2005; received in revised form 11 July 2005; accepted 10 October 2005
Available online 1 December 2005

Abstract

The photodegradation of Acid Blue 29 and Ethyl Violet in the presence/absence of sodium hydroxide (NaOH) was investigated. The results show that the dyes degrade efficiently in the presence of 2 M NaOH. The addition of titanium dioxide as a catalyst and hydrogen peroxide as an oxidant, however, does not enhance the degradation rate of the dyes.

Keywords: Sodium hydroxide; Photodegradation; Acid Blue 29; Ethyl Violet

1. Introduction

Dyes are used to colour products, mainly in the textile industry. Many dyes are inert and non-toxic at the concentration discharged into the receiving waters; however, the colour they impart is very undesirable to the water user for aesthetic reasons. Some dyes discharged into rivers are harmful to the aquatic life [1,2] because some of these effluent streams contain mixtures of heavy metal ions (i.e. Cr, Al, Cu…) and other toxic organic pollutants including poly(vinyl alcohol), starches, various surfactants, pesticides, biocides and others, all of which have varying Biochemical Oxygen Demand (BOD) [3,4]. Also, the resulting wastewaters are highly toxic as some of them contain a large amount of metal complexing dyes [1]. Dyes often contain elements such as nitrogen, chlorine or sulphur. The oxidation products of these molecules may be more toxic than the parent molecule. Many of the dyes are, however, difficult to remove, as they are stable to light and heat and are biologically non-degradable.

Most of the methods that have been studied have focused on producing clean water suitable for recycling. There are many possible methods of degrading dyes, including adsorption [5–7], ozonation [8,9], Fenton's oxidation [10], electrochemical treatment [11,12], coagulation/flocculation [13], biological treatment [14] and photodegradation [15,16]. Colour removal from textile wastewaters, however, is difficult using a single conventional chemical or biological method [17]. Users of dyes employ various methods to reduce the impact of waste arising from the dyeing process.

This work describes the photodegradation of the dyes (Acid Blue 29 and Ethyl Violet in the presence/absence of NaOH). Model solutions of dyes were used in the study to mimic the industrial dye effluent. The aim of the work was also to optimise the photolytic and photocatalytic degradation of dyes in the presence/absence of sodium hydroxide.

2. Experimental

2.1. Apparatus and materials

A reaction vessel (Fig. 1) of 100 ml capacity (A) was placed within the UV-lamp coil (40 W, Philips) (B). The whole system was enclosed in an aluminium box (C) to minimise the loss of UV radiation. TiO_2 used as catalyst and hydrogen peroxide used as oxidant were supplied by BDH. Sodium

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doi:10.1016/j.dyepig.2005.10.008

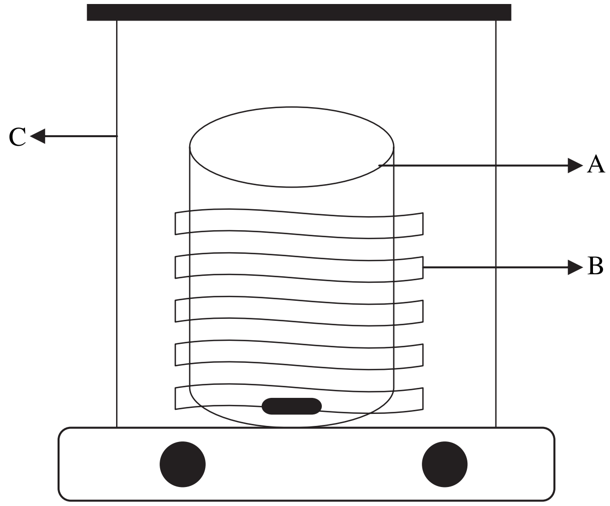

Fig. 1. Photodegradation reaction vessel.

hydroxide was supplied by BDH. Acid Blue 29 and Ethyl Violet were of laboratory reagent grade (BDH) which were used without further purification. Distilled water was also used throughout the work.

2.2. Photolysis experiments

Four different experimental conditions, (1) aqueous dye solution, (2) dye solution containing NaOH, (3) dye solution containing TiO_2, and (4) dye solution containing H_2O_2, were investigated. A solution of 100 ppm of the dye was prepared using distilled water. The reaction mixture was then stirred. Two sets of experiments were carried out to investigate (I) the effect of TiO_2 as a catalyst and (II) 30% H_2O_2 as an oxidant, on the degradation of dye solutions. TiO_2 as a catalyst was added to the dye solution in three different quantities, 0.1 g, 0.2 g, and 0.3 g. In the second set of experiments, 5 ml, 10 ml, and 15 ml of 30% H_2O_2, were added as an oxidant. The vessel was placed into the UV-lamp coil. In the case of TiO_2, the samples were centrifuged to remove the catalyst before the analyses. Samples were taken at hourly intervals for 6 h. Degradation of a solution containing 50 ppm Acid Blue 29 and 50 ppm of Ethyl Violet in 2 M NaOH was also investigated using a quantity of 0.1 g TiO_2 and 5 ml H_2O_2, respectively. All the experiments were carried out in duplicate. The degradation was monitored by UV–vis spectroscopy (Perkin Elmer, Model No. Lambda 9). The percentage of dye degradation was calculated from the UV spectroscopy peak height data.

3. Results and discussion

3.1. Photodegradation of Acid Blue 29

3.1.1. Effect of NaOH

Table 1
Effect of NaOH on degradation of Acid Blue 29

Time (h)	Degradation of Acid Blue 29 (%)	
	Absence of NaOH	Presence of NaOH
1	58	97
2	85	100
3	95	100
4	98	100
5	98	100
6	98	100

From Table 1, it can be seen that the presence of aluminium and sodium hydroxide can dramatically increase the degradation of Acid Blue 29. After photolysis for 1 h, 97% degradation of the Acid Blue 29 is achieved in the presence of sodium hydroxide, but only 58% of the dye degraded in the absence of sodium hydroxide. After 4 h, 98% degradation of the dye is achieved in the absence of sodium hydroxide. This shows that photolysis of the NaOH solution provides sufficient hydroxyl radicals to destroy Acid Blue 29. Kurbus reported that NaOH has a positive effect in a suitable concentration and can accelerate the degradation of the dye [17]. Additionally, at sufficiently high pH values the formation of oxidizing species such as the oxide radical anion $O^{-\bullet}$, which reacts in a different manner from $OH^{\bullet}$, can also be responsible for the rate enhancement of degradation [18].

3.1.2. Effect of TiO_2

The results in Table 2 reveal that the addition of TiO_2 increases the degradation of Acid Blue 29; however, increasing the amount of TiO_2 reduces the degradation of the dye. In the presence of 0.1 g of TiO_2, 96% degradation of the dye was achieved in 2 h whereas in the absence of TiO_2 only 85% of the dye was degraded. The addition of 0.2 g and 0.3 g of TiO_2, however, degraded 93% and 85% of the dye, respectively. The dye is virtually destroyed in the first hour in the presence of 0.1 g, 0.2 g and 0.3 g of TiO_2 (Table 2). The degradation of 97% is also achieved in the absence of TiO_2 in the first hour. Sodium hydroxide provides $OH^{\bullet}$ radicals to increase the degradation of the dye [17] and hence, complete degradation is achieved which shows that the presence of NaOH has significant effect.

3.1.3. Effect of H_2O_2

Increasing the concentration of H_2O_2 decreases the degradation as shown in Table 3. In the absence of H_2O_2, degradation of 98% is achieved after 4 h, while the corresponding

Table 2
Effect of TiO_2 on degradation of Acid Blue 29

Time (h)	Degradation of Acid Blue 29 (%)							
	Absence of NaOH				Presence of NaOH			
	Absence of TiO_2	Presence of TiO_2 (g)			Absence of TiO_2	Presence of TiO_2 (g)		
		0.1	0.2	0.3		0.1	0.2	0.3
1	58	79	77	77	97	100	100	100
2	85	96	93	85	100	100	100	100
3	95	98	97	97	100	100	100	100
4	98	–	–	–	100	–	–	–
5	98	–	–	–	100	–	–	–
6	98	–	–	–	100	–	–	–

Table 3
Effect of H_2O_2 on degradation of Acid Blue 29

Time (h)	Degradation of Acid Blue 29 (%)							
	Absence of NaOH				Presence of NaOH			
	Absence of H_2O_2	Presence of H_2O_2 (ml)			Absence of H_2O_2	Presence of H_2O_2 (ml)		
		5	10	15		5	10	15
1	58	32	28	25	97	70	45	70
2	85	53	42	36	100	88	76	85
3	95	69	53	45	100	93	91	94
4	98	81	61	52	100	96	95	98
5	98	89	69	61	100	97	95	100
6	98	94	74	68	100	97	97	100

Table 5
Effect of TiO_2 on degradation of Ethyl Violet

Time (h)	Degradation of Ethyl Violet (%)							
	Absence of NaOH				Presence of NaOH			
	Absence of TiO_2	Presence of TiO_2 (g)			Absence of TiO_2	Presence of TiO_2 (g)		
		0.1	0.2	0.3		0.1	0.2	0.3
1	11	32	28	11	98	100	100	100
2	11	45	30	27	–	–	–	–
3	32	90	85	80	–	–	–	–
4	85	99	87	82	–	–	–	–
5	91	99	97	96	–	–	–	–
6	91	99	99	99	–	–	–	–

values in the presence of H_2O_2 are 81% (5 ml), 61% (10 ml) and 52% (15 ml). This shows that the addition of H_2O_2 retards the degradation of dye [19]. In the absence of H_2O_2 there is 97% degradation in 1 h, but with the addition of 5 ml, 10 ml and 15 ml the degradation is 70%, 45% and 70%, respectively after 1 h (Table 3). This shows that although H_2O_2 can affect the degradation, NaOH can still play an important role in assisting dye destruction. Kurbus and coworkers reported that the presence of H_2O_2 and NaOH increases the photodegradation but the presence of excess NaOH decreases the speed of the reaction [17]. Higher concentrations of peroxide and NaOH can reduce the degradation of dyes because Na_2O_2 is produced and formation of $OH^\bullet$ is decreased as shown in Eq. (1) [18].

$$2NaOH + H_2O_2 + 6H_2O \rightarrow Na_2O_2 + 8H_2O \tag{1}$$

3.2. Photodegradation of Ethyl Violet

3.2.1. Effect of NaOH

The data in Table 4 show that the presence of NaOH increases the degradation of Ethyl Violet. On the other hand, in the absence of NaOH, only 91% degradation is achieved after 6 h which indicates that NaOH has positive effect on the rate of degradation.

3.2.2. Effect of TiO_2

The results in Table 5 show that although the addition of TiO_2 increases the degradation, increasing the quantities of TiO_2 decreases the degradation rate. After 4 h, a degradation of 99%, 87% and 82% is achieved in the presence of 0.1 g, 0.2 g and 0.3 g of TiO_2, respectively. The degradation is almost complete after 6 h but the absence of TiO_2 decreases the degradation to 91%. In the presence of TiO_2 and NaOH, the degradation of the Ethyl Violet can be completed in the first hour (Table 5). Degradation of 98% is achieved in the absence of TiO_2 in the first hour, which suggests that TiO_2 is not necessary as a catalyst in the degradation because the addition of NaOH provides hydroxyl radicals.

Table 4
Effect of NaOH on degradation of Ethyl Violet

Time (h)	Degradation of Ethyl Violet (%)	
	Absence of NaOH	Presence of NaOH
1	11	100
2	11	–
3	32	–
4	85	–
5	91	–
6	91	–

3.2.3. Effect of H_2O_2

Increasing the quantity of H_2O_2 from 5 ml to 15 ml in the dye solution increases the degradation as shown in Table 6. Almost complete degradation of the dye is achieved within 3 h but in the absence of H_2O_2, only 91% degradation is achieved after 5 h. The data indicate that H_2O_2 supplies $OH^\bullet$ radicals to degrade the Ethyl Violet. Complete degradation of dye is achieved within 1 h (Table 6) but increasing the quantity of H_2O_2 reduces the degradation because of the higher concentrations of peroxide and NaOH leading to the formation of Na_2O_2 as shown in Eq. (1). This result proves that the H_2O_2 is not essential as an oxidant for the decomposition of the Ethyl Violet in the presence of NaOH.

3.3. Photodegradation of a mixture of Acid Blue 29 and Ethyl Violet

3.3.1. Effect NaOH

The results in Table 7 indicate that the majority of the dye can be destroyed in 1 h in the presence 2 M NaOH.

Table 6
Effect of H_2O_2 on degradation of Ethyl Violet

Time (h)	Degradation of Ethyl Violet (%)							
	Absence of NaOH				Presence of NaOH			
	Absence of H_2O_2	Presence of H_2O_2 (ml)			Absence of H_2O_2	Presence of H_2O_2 (ml)		
		5	10	15		5	10	15
1	11	28	31	38	98	100	98	97
2	11	60	86	90	–	–	–	–
3	32	94	97	100	–	–	–	–
4	85	99	100	100	–	–	–	–
5	91	99	100	100	–	–	–	–
6	91	99	100	100	–	–	–	–

Table 7
Effect of NaOH on degradation of mixed dyes

Time (h)	Degradation of a mixture of 50 ppm Acid Blue 29 and 50 ppm Ethyl Violet (%)	
	Blank	2 M NaOH
1	31	96
2	58	97
3	78	100
4	89	100
5	95	100
6	98	100

Table 8
Effect of TiO_2 on degradation of mixed dyes

Time (h)	Degradation of a mixture of 50 ppm Acid Blue 29 and 50 ppm Ethyl Violet (%)	
	TiO_2	$NaOH + TiO_2$
1	70	99
2	88	99
3	99	99
4	99	99
5	99	99
6	99	99

Almost complete decomposition of the dye is achieved in 6 h in the absence of NaOH. Thus, these results confirm that it is the ease of free hydroxyl radical formation in the presence of NaOH which ultimately increases the degradation rate.

3.3.2. *Effect of TiO_2*

In the presence of NaOH and TiO_2 (Table 8), 99% degradation is achieved in the first hour. Whereas, 99% degradation is achieved in 3 h in the addition of TiO_2. This result reveals that the presence of NaOH increases the degradation of dye because it provides sufficient hydroxyl radicals to decompose the dyes.

3.3.3. *Effect of H_2O_2*

Degradation of 98% of the mixture of dyes is achieved within 5 h in the presence of $NaOH + H_2O_2$ as compared to 88% H_2O_2. As mentioned earlier sodium hydroxide increased the rate of degradation, however, the presence of excess H_2O_2 decreases the speed (Eq. (1)). There is decrease in the rate of degradation when the photolysis is carried out in the presence of H_2O_2 compared to when NaOH and H_2O_2 are used (Table 9).

Table 9
Effect of H_2O_2 on degradation of mixed dyes

Time (h)	Degradation of a mixture of 50 ppm Acid Blue 29 and 50 ppm Ethyl Violet (%)	
	H_2O_2	$NaOH + H_2O_2$
1	50	48
2	63	78
3	74	91
4	82	95
5	88	98
6	92	98

4. Conclusion

The results obtained using the photodegradation system show that Acid Blue 29 and Ethyl Violet can be degraded in the presence of sodium hydroxide. The addition of titanium dioxide as a catalyst and hydrogen peroxide as an oxidant in this system to enhance the degradation rate is not necessary. These results show that the developed method can be applied to an industrial sample without the need for any catalyst or oxidant.

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