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UV-induced decolourization of acid alizarine violet N by homogeneous advanced oxidation processes

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Abstract

The decolourization of an azo dye acid alizarine violet N by photoactivated hydrogen peroxide and sodium periodate (UV/H_2O_2 and UV/IO_4^-) has been studied in a small scale batch photoreactor. The wavelength of the UV source used was 254 nm. The treatment was carried out under different concentrations of peroxide (34–272 mg l^{-1}) and periodate (5.35–32.1 mg l^{-1}). The results obtained showed that increasing the concentration of peroxide or periodate resulted in a higher decolourization rate of the dye. The disappearance of the dye followed first-order kinetics. Reaction rate orders with respect to the oxidant species were 0.93 and 1.6 for respectively, peroxide and periodate. Kinetic parameters of the photodegradation process such as apparent rate constant (k_{app}), half life time ($t_{1/2}$) and initial reaction rate ($R_{initial}$) were calculated.

Keywords: Decolourization; Azo dye; Peroxide; Periodate; Kinetic parameters

1. Introduction

Synthetic textile dyes of the azo family represent an important part of the world production of synthetic dyes. They are degraded into potentially carcinogenic amines [1,2]. Moreover, their colour causes an aesthetic problem in receiving waters.

Conventional treatment of textile effluents such as air stripping, sorption, coagulation, neutralization, chemical precipitation and ion exchange are merely a form of pollution conversion in which the original polluting materials are transformed from one phase to another, leaving a problem of disposal of transferred materials [3,4].

Biodegradation by activated sludge is effectively used for remediation of normal organic pollutants. Many xenobiotic compounds, such as chlorophenols, herbicides, textile dyes and surfactants are, however, resistant to such treatment [5–7]. Thus, in recent years a series of new methods for water and wastewater purification, the so-called advanced oxidation processes (AOPS) have emerged. These processes leading to the generation of highly oxidative species such as hydroxyl radical ($^{\bullet}OH$) which are capable of converting the pollutants into harmless chemicals [8].

The use of hydrogen peroxide shows some advantages such as the complete miscibility of H_2O_2 with water, the stability and commercial availability of hydrogen peroxide, no phase transfer problems, no sludge formation, simplicity of operation and lower investment costs [9].

This work involves the decolourization of an azo dye, acid alizarine violet N, by homogeneous advanced oxidation processes. UV/H_2O_2 and UV/IO_4^- systems were used to oxidize the azo dye. The efficiency of photodegradation was evaluated by calculating the kinetic parameters of the degradation process such as k_{app}, $R_{initial}$ and $t_{1/2}$.

2. Materials and methods

2.1. Materials

Acid alizarine violet N (Fig. 1) and sodium periodate were purchased from the Aldrich Chemical Co. All other chemicals [hydrogen peroxide (30% w/v), acid and alkali for pH adjustment] were obtained from Fisher Scientific.

2.2. Methods

2.2.1. Photoreactor

The photoreactor (Fig. 2) comprised of a glass container and was operated with an initial working volume of 1000 ml. The

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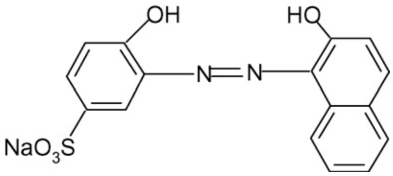

Fig. 1. Structure of acid alizarine violet N.

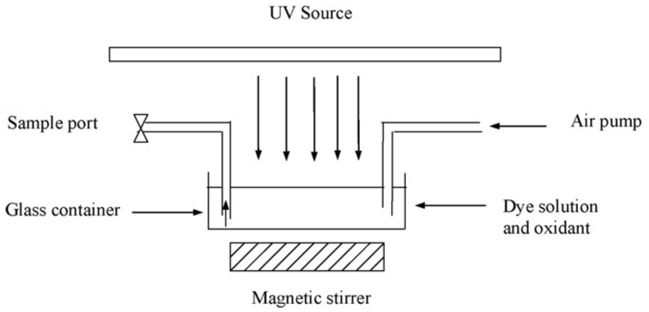

Fig. 2. Schematic diagram of the batch photoreactor.

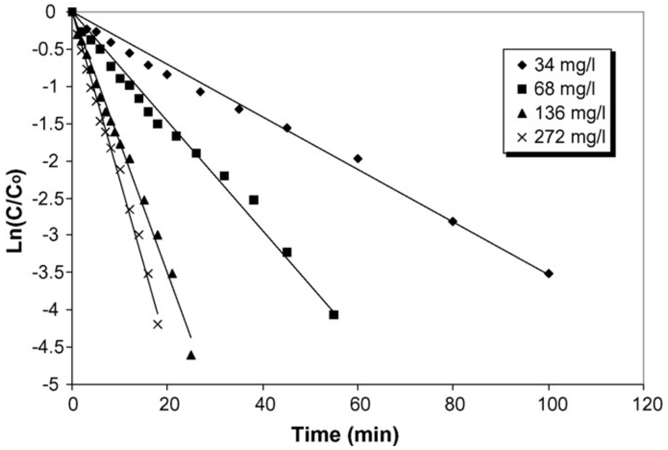

Fig. 3. First-order model for UV-induced decolourization of acid alizarine violet N in the presence of hydrogen peroxide.

contents of the container (the dye and the oxidant) were agitated by means of a magnetic stirrer. Dry air was fed into the solution via a glass sparger at a rate of 180 ml min^{-1} in order to aerate the dye solution. A tubular low pressure mercury vapour source (total rating 43 W, total UV output at 254 nm 13.4 W and length 0.40 m, Voltarc Tubes Inc., USA) was used to irradiate the solution which was located 0.10 m from the surface of the source. The UV intensity at the centre point of the solution was measured using a UV radiometer (Model UVX, UV Products Ltd, Cambridge) equipped with a sensor with peak sensitivity at 254 nm and was 40 W m^{-2}. Samples of dye solution (5 ml) were removed from the container via a sample port periodically for analysis. All experiments were performed with a dye solution of concentration 36.6 mg l^{-1}, at a pH of 6.1. This latter value was the natural pH of the dye solution at the concentration employed here in absence of hydrogen peroxide or periodate. All decolourization experiments were conducted at a temperature of 22 ± 2 °C.

2.2.2. Analytical procedures

The degradation of acid alizarine violet N was followed by measuring the decrease in absorbance at a wavelength of 501 nm (the peak absorptivity of the dye) using a UV-visible spectrophotometer (Model 1601 PC, Shimadzu, Japan). Samples were drawn periodically from the photoreactor and measured.

3. Results and discussion

UV/H_2O_2 and UV/IO_4^- technologies are a well known advanced oxidation processes for organic compounds degradation. The concentrations of oxidants used in this work were selected with reference to earlier studies and represent concentrations compatible with those previously shown to have aided degrading other targeted chemical species at reasonably high rates [10,11].

UV alone in the absence of oxidant species (H_2O_2 or IO_4^-) was found to have no measurable effect on the decolourization of acid alizarine violet N over the longest treatment time employed here. These results have been omitted from the figures presented here for the sake of clarity. The decolourization of acid alizarine violet N at different concentrations of peroxide (34, 68, 136 and 272 mg l^{-1}) under UV irradiation is shown in Fig. 3. The rate of decolourization increased with the concentration of peroxide. Fig. 3 shows the data plotted according to a first-order model for dye destruction. The data fits this form of kinetics quite closely and the apparent first-order rate constants (k_{app}) were obtained from the gradients of the lines of best fit. The constants ranged from 3.53×10^{-2} to 22.49×10^{-2} min^{-1} (Table 1).

The relationship between the apparent (k_{app}) and true rate constant (k) may be assumed to follow a power law relation which is dependent on the peroxide concentration [H_2O_2] thus:

$$k_{app} = k[H_2O_2]^n \tag{1}$$

The exponent, n, the order of reaction with respect to the oxidant species, was obtained by plotting the logarithm of k_{app} against the logarithm of the peroxide concentration (Fig. 4), which yielded a value for n of 0.93 (Table 1).

The principal output of the used UV source was at 254 nm, so that substantial photolysis of the hydrogen peroxide would have occurred producing hydroxyl radicals as shown below [12–21]:

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \tag{2}$$

Table 1
Apparent rate constants and reaction orders for degradation of acid alizarine violet N

Catalytic system	Oxidant concentration (mg l^{-1})	k_{app}(min^{-1})	Apparent reaction order(n)
UV/H_2O_2	34	3.53×10^{-2}	0.93
	68	7.32×10^{-2}	
	136	17.5×10^{-2}	
	272	22.49×10^{-2}	
UV/IO_4^-	5.35	3.11×10^{-2}	1.6
	10.7	35.22×10^{-2}	
	21.4	59.94×10^{-2}	
	32.1	158.01×10^{-2}	

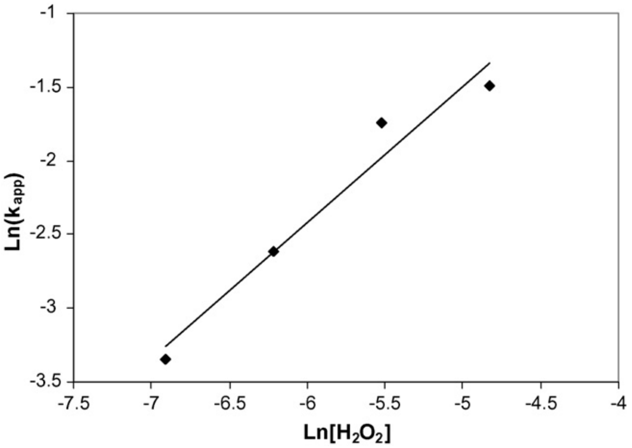

Fig. 4. The influence of hydrogen peroxide concentration on the apparent first-order rate constant.

Increasing peroxide concentration from 34 to 272 mg l^{-1} produces more hydroxyl radicals which oxidize the dye and leads to a higher rate of degradation [15,22,23].

The decolourization of acid alizarine violet N irradiated with UV at different concentrations of periodate (5.35, 10.7, 21.4 and 32.1 mg l^{-1}) is shown in Fig. 5. Photodegradation follows first-order kinetics. The apparent rate constants (3.11×10^{-2}–158.01×10^{-2} min^{-1}) were greater than those for peroxide (Table 1). The reaction rate order with respect to periodate, obtained from Fig. 6, was found to be 1.6, higher than for peroxide (Table 1).

The higher activity of periodate may be attributed to the formation of a number of highly reactive radicals and non-radical intermediates according to the following scheme [11,14,17,24]:

$$IO_4^- + h\nu \rightarrow IO_3^{\bullet} + O^{\bullet -} \quad (3)$$

$$O^{\bullet -} + H^+ \leftrightarrow {}^{\bullet}OH \quad (4)$$

$$^{\bullet}OH + IO_4^- \rightarrow {}^{-}OH + IO_4^{\bullet} \quad (5)$$

$$H_4IO_6^- + h\nu \rightarrow H_3IO_5^{\bullet -} + {}^{\bullet}OH \quad (6)$$

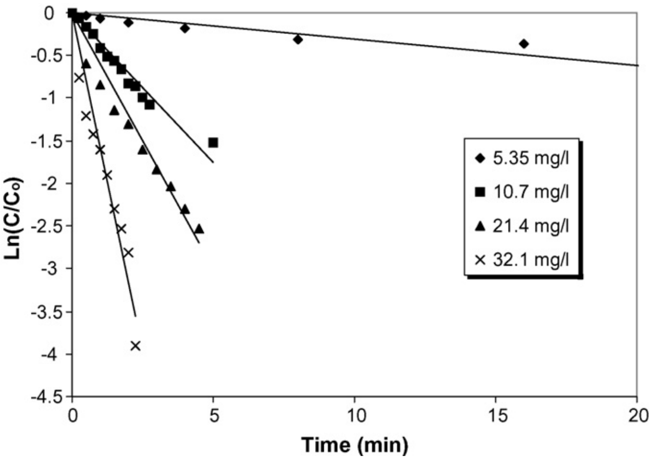

Fig. 5. First-order model for UV-induced decolourization of acid alizarine violet N in the presence of sodium periodate.

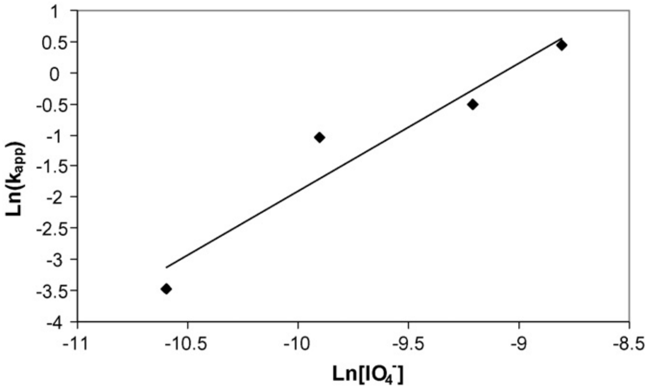

Fig. 6. The influence of sodium periodate concentration on the apparent first-order rate constant.

$$H_3IO_5^{\bullet -} \rightarrow IO_3^- + H_2O + {}^{\bullet}OH \quad (7)$$

These intermediates contribute to the dye degradation as follows: it is known that the colour of the azo dyes such as acid alizarine violet N is due to the presence of the azo bonds (–N=N–) [25]. The radical intermediates produced from photolysis of IO_4^- under UV (254 nm) attack the azo groups of the dye molecules causing oxidative cleavage due to their highly electrophilic character. Increasing the concentration of IO_4^- from 5.35 to 32.1 mg l^{-1} leads to an increase in the number of radicals formed, so greater decolourization of the dye produced in a short time. When all azo groups are degraded, complete decolourization of the dye occurs [26].

This study has shown that the two oxidants, peroxide and periodate, enhance the rate of UV-induced decolourization of the azo dye acid alizarine violet N. The rate of decolourization was greatest in the presence of periodate. The rate enhancing effects of these oxidants have been studied previously with reference to other organic pollutants. Wang and Hong [14] found a benefit in adding peroxide, persulfate or periodate to degrade 2-chlorobiphenyl solution irradiated with UV. The most effective oxidant was periodate. Similarly, Sadik and Shama [17] found that addition of peroxide, persulfate or periodate enhanced the rate of breakdown of azo dye acid black 24 when irradiated with UV. Periodate was found to be more effective than persulfate or peroxide. The degradation of Pb-EDTA in aqueous solution by a H_2O_2/UV process was studied by Jiraroj et al. [27]. They found that an increase in the initial concentration of H_2O_2 from 0.02 to 0.08 M leads to an increase in the degradation rate. Also, Weavers and his co-workers [11] reported enhanced rates of UV-induced degradation of triethanolamine in the presence of periodate. In accordance with our results presented here for acid alizarine violet N, all the work studied in literatures shows that the UV/IO_4^- had a greater effect than UV/H_2O_2 or UV only in photodegradation of dyes and other organic compounds. These results are in agreement with our results for photodecolourization of acid alizarine violet N.

The half life time ($t_{1/2}$) of the first-order reaction is the time required for the reactants to be degraded to half of their initial concentrations. The relationship between $t_{1/2}$ and k_{app} is given

Table 2
Half life time and initial reaction rate for degradation of acid alizarine violet N

Catalytic system	Oxidant concentration ($mg\,l^{-1}$)	$t_{1/2}$(min) = $0.693/k_{app}$	$R_{initial} = C_o\,k_{app}$ ($mg\,l^{-1}\,min^{-1}$)
UV/H_2O_2	34	19.63	1.29
	68	9.47	2.68
	136	3.96	6.41
	272	3.10	8.23
UV/IO_4^-	5.35	22.30	1.14
	10.70	1.97	12.90
	21.40	1.16	21.94
	32.10	0.44	57.83

by:

$$t_{1/2} = \frac{0.693}{k_{app}} \tag{8}$$

also the initial reaction rate for the first-order reaction ($R_{initial}$) is related to k_{app} by the following equation:

$$R_{initial} = C_o k_{app} \tag{9}$$

where C_o: is the initial dye concentration.

It was found that $t_{1/2}$ decreased with the concentration of peroxide or periodate, while $R_{initial}$ increased (Table 2).

4. Conclusions

Treatment of acid alizarine violet N with UV in the presence of hydrogen peroxide or sodium periodate led to complete decolourization. Periodate was the most effective oxidant, bringing about high rates of decolourization at low concentrations. The process of decolourization was adequately modeled using first-order kinetics and rate constants and reaction orders with respect to peroxide and periodate were obtained. Degradation parameters such as $t_{1/2}$, $R_{initial}$ were calculated and compared.

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