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Dyes and Pigments 66 (2005) 129–134

DYES and PIGMENTS

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The effect of operational parameters on UV/H_2O_2 decolourisation of Acid Blue 74

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Received 25 June 2004; received in revised form 10 September 2004; accepted 23 September 2004
Available online 1 December 2004

Abstract

In the present study, advanced oxidation treatment, the UV/H_2O_2 process was applied to decolourisation of the indigoid dye C.I. Acid Blue 74 in aqueous solution. The UV radiation was carried out with a 15 W low-pressure mercury lamp. The rate of colour removal was studied by measuring of the absorbency at characteristic wavelength. The effects of H_2O_2 dosage, dye initial concentration and pH on decolourisation kinetics in the continuous circulation photoreactor were investigated. The highest decolourisation rates were observed at pH range between 3.5 and 5.5. The optimal levels of H_2O_2 needed for the process were examined. It appears that high levels of H_2O_2 could reduce decolourisation by scavenging the $^{\bullet}OH$. The colour degradation rate decreases as the dye concentration increases.

Keywords: C.I. Acid Blue 74; AOP; UV/H_2O_2; pH effects; Colour removal; Wastewater

1. Introduction

The textile industry consumes considerable amounts of water during the dyeing, printing and finishing operations. These effluent streams can be highly coloured and difficult to decolourise. Due to the large degree of aromatics present in these molecules and the stability of dyes, most conventional treatment methods are ineffective for decolourisation and degradation. Advanced Oxidation Processes (AOPs) have been successfully applied to the treatment of the various water pollutants [1–4]. Among the AOP methods, the use of ultraviolet radiation (UV) in the presence of hydrogen peroxide (H_2O_2) is a very promising technique. Mercury lamps emitting at 254 nm are the most commonly used in order to dissociate H_2O_2 into hydroxyl radicals which are very powerful oxidizing species. These reactive radicals can decompose and even mineralize the organic contaminates with high efficiency [5–7]. The main advantages of this process are that no additional disposal problems are generated after the completion of the above treatment and they are non-selective to a very broad range of chemicals.

The purpose of this study is to conduct experimental investigation concerning the decolourisation of C.I. Acid Blue 74 (AB74) dye commonly named "Indigo Carmine", in water in a continuous circulation photochemical reactor. AB74 was chosen, since it has been the topic of only a few articles and the nature of by-products remains a matter of conjecture. The effects of the key operating variables such as pH, hydrogen peroxide dosage, and dye concentration on the decolourisation kinetics were studied. The experiment was conducted by changing one variable at a time while keeping other parameters constant.

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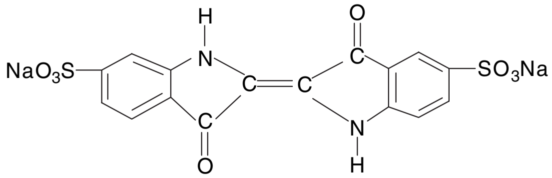
doi:10.1016/j.dyepig.2004.09.008

2. Materials and experimental methods

5,5′-Indigotindisulfonic acid disodium salt ($C_{16}H_8N_2Na_2O_8S_2$) named commercially C.I. Acid Blue 74 (85%) was purchased from Aldrich Chemical and used without further purification. The characteristics of the dye are as follows.

Colour index 73015, $M_w = 466\ \mathrm{g\,mol^{-1}}$, $\lambda_{max} = 610$ nm, $\varepsilon_{\lambda max} = 22.33 \times 10^3\ \mathrm{l\,mol^{-1}\,cm^{-1}}$ and structure:



Hydrogen peroxide (30% w/w) was obtained from Prolabo. The optical absorption spectrum of dye was recorded on a V-530 UV–VIS spectrophotometer. The reactor used in this study is a continuous column circulation photoreactor fitted with a 15 W electric power low-pressure mercury lamp (Philips emission at 253.7 nm). The radiant flux of this lamp was determined by means of the chemical actinometer hydrogen peroxide [8]. The incident photon flux was $6.1 \times 10^{-6}\ \mathrm{Einstein\,s^{-1}}$. This irradiation frequency was selected because a number of articles have reported the efficient degradation of chemicals in water using the same emission (253.7 nm) produced by mercury [9,10].

Absorption spectra of the dye solutions irradiated by UV light were recorded. The maximum absorption wavelength (λ_{max}) for C.I. Acid Blue 74 dye was determined to be 610 nm. This peak accounts for the blue colour of solutions and can be attributed to the n–π^* transition of the non-bonding nitrogen electrons to the anti-banding π^* group orbital of the double bond system [11] and it is used to monitor the decolourisation of dye. In the UV region, there is a second group of bonds, with an increasing absorbency towards lower wavelengths, characteristic of aromatic rings. We have observed that the position of the maximum absorption wavelengths varied, depending on the solution concentration. In addition, no new absorption peaks occurred near the original maximum. As a result, we can conclude that the absorption bands are not disturbed by intermediate oxidation products. Furthermore, the molar extinction (ε) of H_2O_2 varies between 15 and 25 ($\mathrm{l\,mol^{-1}\,cm^{-1}}$) for wavelengths ($\lambda$) between 450 and 650 nm. As a result, the measurement error that might be caused by H_2O_2 in the mixture is low. The photolysis of blank samples containing the same dose of H_2O_2 without dye was carried out, so that the interference due to H_2O_2 could be eliminated. The concentrations of dye solutions irradiated by UV could also be determined by spectrophotometry.

Each selected dye quantity (in the range 2×10^{-5}–$15 \times 10^{-5}\ \mathrm{mol\,l^{-1}}$) was dissolved in deionized water prior to use. A large excess of hydrogen peroxide in comparison to the dye was added to this solution (in the range 0.15×10^{-2}–$9 \times 10^{-2}\ \mathrm{mol\,l^{-1}}$), so that $[H_2O_2]$ could be considered as constant during the whole experiment. The pH of the solution was adjusted to the desired value by addition of sodium hydroxide or by hydrochloric acid and then it was measured by a Swott Gerate pH meter CG817T.

The unit for continuous circulation reactor used in the experiments was described in our previous study [12]. A total of 2500 ml of dye solution in the reservoir was used for the treatment while the liquid level in the radiation column was kept constant at 1600 ml. The liquid inside the column was exposed to a 15 W UV lamp. The treated wastewater was returned to the reservoir and then left to circulate back to the reactor column at a constant flow rate of $3.5\ \mathrm{l\,min^{-1}}$.

3. Results and discussion

At regular time intervals, samples were collected and analyzed by UV–VIS spectrophotometer to determine the decolourisation rate. Repeated operations were performed to examine the reproducibility of the results. Initial results demonstrate that neither H_2O_2 nor UV alone was able to appreciably decolourise C.I. Acid Blue 74. Combination of UV and H_2O_2 is necessary for production of OH radicals by photolysis of the hydrogen peroxide [3]. This radical is a non-selective and very powerful oxidiser with an oxidation potential of 2.8 V and can initiate the decolourisation reactions by reacting with the dye molecules. The result of this reaction is the destruction of colour according to the following reactions:

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \tag{1}$$

$$^{\bullet}OH + \mathrm{Dye} \rightarrow \mathrm{Oxidation\ product} \tag{2}$$

^{1}H NMR analysis reveals that the dye is first converted into isatinsulfonic acid, then into aliphatic acids.

When the kinetics of the photo catalytic decolourisation reactions was studied, it was found that the correlation between ln C/C_0 and the irradiation time was linear as shown in Fig. 1. This is a typical first-order reaction plot. The kinetic expression can be presented as follows:

$$\ln\frac{C}{C_0} = -kt \tag{3}$$

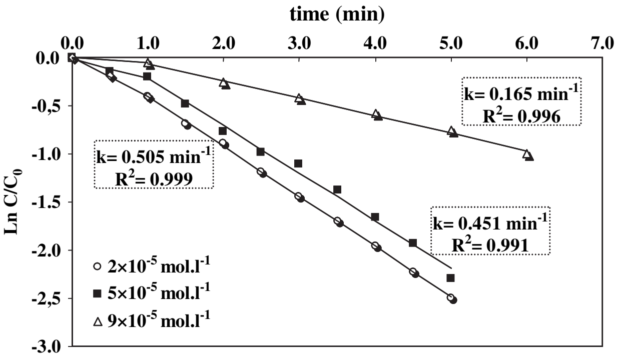


Fig. 1. Plot of ln C/C_0 versus irradiation time, $[H_2O_2] = 4.89 \times 10^{-2}$ mol l^{-1}.

where C: dye concentration at instant t (mol l^{-1}); C_0: dye concentration at $t = 0$; k: pseudo-first order rate constant (min^{-1}); t: time of reaction in minute.

The plot indicates a slow decolourisation rate at the first minute, followed by a higher variation. This observation is most likely due to the elapsed time between the start of the experiment and the warming up of the lamp [2].

The correlation coefficient that can explain the fitting extent of the function equation and the experimental data is presented by R^2. The values of these correlation coefficients confirm the goodness of the assumed kinetics. The slopes of the lines give the apparent rate constants (k).

3.1. The effect of pH

Since the dyes to be removed can be at different pHs in coloured effluents, we have studied the effect of pH on the rate of decolourisation reaction in the pH range between 2 and 11. Comparative irradiation experiments were performed following the evolution of the absorbency with time. The solutions of the dyes were adjusted to the desired pH by addition of HCl or NaOH. The different concentrations of acid or base have been chosen in order to add the minimum quantity of these species to avoid the volume change of the reaction mixture. The decolourisation rate constants of C.I. Acid Blue 74 as a function of the reaction pH are shown in Fig. 2. The decolourisation rate increases from pH 2 to 3.5 and then remains almost constant up to pH 5.5. After this value we have observed a decrease as the pH increases to 11.

These observations at different pH can be explained by taking into account the following parameters.

1) In the acidic pHs concomitant with acidification of the solution by HCl, increasing amounts of conjugated base were added to the solution. The anion Cl^- is able to react with hydroxyl radicals leading to inorganic radical ions (reaction 4).

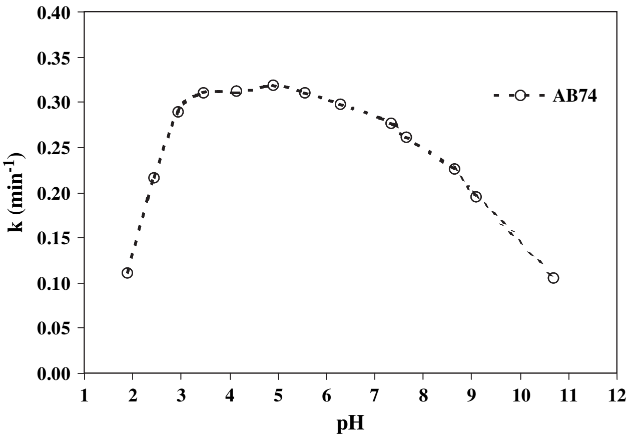


Fig. 2. Effect of pH on the rate of decolourisation of the AB74 solutions. $[H_2O_2]_0 = 4.98 \times 10^{-2}$ mol l^{-1}, $[AB74]_0 = 7 \times 10^{-5}$ mol l^{-1}.

$$Cl^- + {}^{\bullet}OH \rightarrow ClO^{\bullet -}H \quad k = 4.3 \times 10^{9}\ \mathrm{l\,mol^{-1}\,s^{-1}}\ [13] \tag{4}$$

These inorganic radical anions show a much lower reactivity than $^{\bullet}OH$, so that they do not take part in the dye decolourisation. There is also a drastic competition between the dye and the anions with respect to $^{\bullet}OH$. Similar results have already been reported [1,14].

2) At alkaline pH, the conjugate base of H_2O_2 increases (reaction 5).

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad pK_a = 11.6 \tag{5}$$

HO_2^- has a higher cross-section (240 mol cm^{-1}) at 254 nm than H_2O_2 (18.6 mol cm^{-1}), which favours the absorption of light by the reactive and should normally increase the $^{\bullet}OH$ production (reaction 6) [7,15].

$$HO_2^- + H^+ + h\nu \rightarrow 2\,{}^{\bullet}OH \tag{6}$$

But HO_2^- the conjugate anion of H_2O_2 reacts with a non-dissociated molecule of H_2O_2 according to reaction (7) which leads to dioxygen and water, instead of producing hydroxyl radicals under UV radiation. Therefore, the instantaneous concentration of $^{\bullet}OH$ is lower than expected.

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^- \tag{7}$$

Furthermore, the deactivation of $^{\bullet}OH$ is more important when the pH of the solution is high. The reaction of $^{\bullet}OH$ with HO_2^- is approximately 100 times faster than its reaction with H_2O_2.

$$^{\bullet}OH + HO_2^- \rightarrow H_2O + O_2^{\bullet -} \quad k = 7.5 \times 10^9\,\mathrm{l\,mol^{-1}\,s^{-1}} \tag{8}$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad k = 2.7 \times 10^7\,\mathrm{l\,mol^{-1}\,s^{-1}} \tag{9}$$

The reactivity of $O_2^{\bullet -}$ and $HO_2^{\bullet}$ with organic pollutants is very low [10].

3) The self-decomposition rate of hydrogen peroxide is strongly dependent on pH. In practice, H_2O_2 is supplied in slightly acid condition (pH = 5) because of its high self-decomposition rate at high pH. The first-order reaction rate constants of this self-decomposition were determined to be 2.29×10^{-2} and $7.40 \times 10^{-2}\,\mathrm{min^{-1}}$ at pH = 7 and 10.5, respectively [16].

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{10}$$

4) The decolourisation kinetic notably depends upon the basic molecular structure of the dyes. We have studied the evolution of the intensity of the maximum absorption band of the Acid Blue 74 at 610 nm as a function of the pH. As we can observe from Fig. 3 at pH of about 11, there is a drastic decrease of the absorbency. The spectrum change exhibiting a red shift of the maximum to 750 nm, indicates the predominance of other forms of the dye, probably conjugated base. However, the absorption at 610 nm is still important (Fig. 4).

In most cases, hydroxyl radicals react with dye through hydrogen abstraction mechanism (reaction 10) [7].

$$^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \tag{11}$$

In the deprotonated form, dye exhibits low reactivity due to the absence of a labile hydrogen atom. Indeed, in the molecule of C.I. Acid Blue 74, the nitrogen atom carries an H atom and this labile H atom makes the molecule of C.I. Acid Blue 74 especially vulnerable to attack by OH radicals [14]. The decrease of the colour removal rate at high basic solution (pH higher than 10.5) is probably due to the dissociation of the N–H bands.

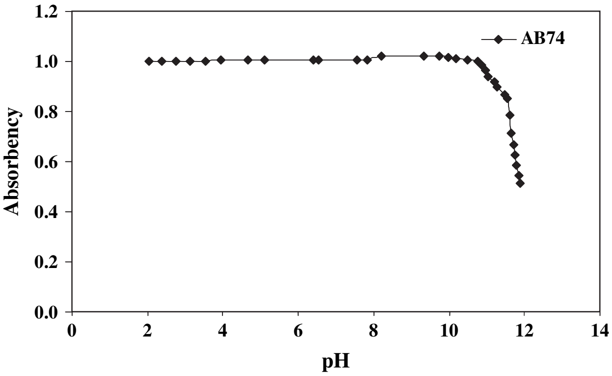


Fig. 3. Evolution of the intensity of the maximum absorption band of the dye at 610 nm as a function of the pH.

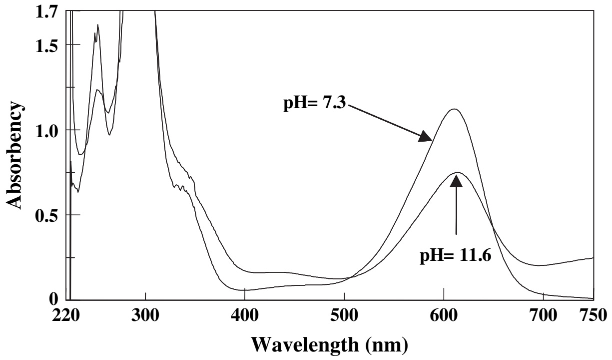


Fig. 4. Absorption spectra of AB74 solutions for two pH values.

3.2. The effect of initial hydrogen peroxide

Hydrogen peroxide concentration is an important parameter for the degradation of the colour in the UV/H_2O_2 photoreactor. Indeed, the OH free radicals produced upon photolysis of H_2O_2 can react with dye molecules, but also with an excess of H_2O_2. Excess of hydrogen peroxide and high OH radical concentration result in competitive reactions, producing an inhibitory effect on the decolourisation. OH radicals are prone to react or to recombine according to the following scheme [17]:

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{9}$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2 \tag{12}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{13}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{14}$$

Reactions (9) and (14) are $^{\bullet}OH$ consuming, so the probability of oxidation of substrate decreases. Therefore, an important step in the optimization of the method is the determination of the adequate amount of $[H_2O_2]$, to avoid an excess of reagent that can retard the decolourisation. The results of Fig. 5 point out the negative effect of a defect or excess of $[H_2O_2]$ on the reaction rate. We can observe an optimum value at about $0.05\,\mathrm{mol\,l^{-1}}$ for the hydrogen peroxide concentration.

The optimum value of the relative hydrogen peroxide concentration expressed as the molar ratio of the H_2O_2 concentration to that of the dye, has been reported to be

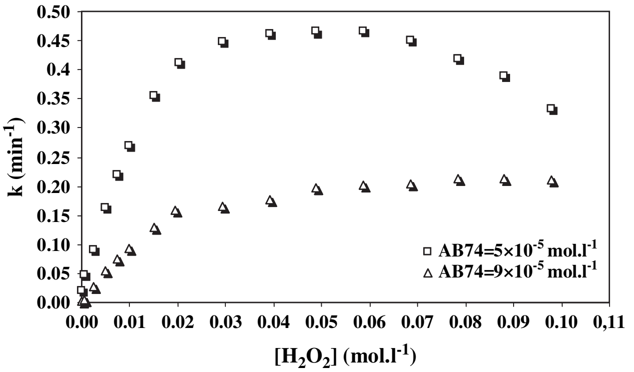


Fig. 5. Effect of the initial hydrogen peroxide concentration on the rate of decolourisation, pH ≅ 5.0.

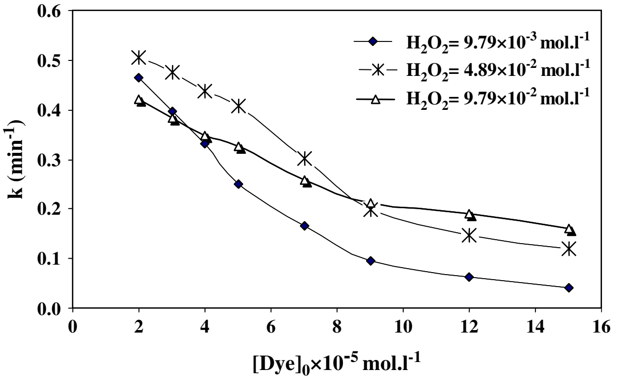


Fig. 6. Effect of initial concentration of dye on the kinetics of decolourisation, $[H_2O_2]_0 = 4.98 \times 10^{-2}$ mol l^{-1}, pH ≅ 6.0.

nearly equal to 1000 in our recent publication [18]. Galindo et al. [13] have studied the photocatalytic degradation of AB74 by UV/H_2O_2 process. Irradiation was performed in a batch photoreactor of 500 ml, fitted with a 15 W low-pressure mercury lamp. They have reported the optimum H_2O_2/AB74 molar ratio to be equal to 5000. In our study, the use of continuous circulation photoreactor has permitted to reduce this ratio five times. Therefore, application of this procedure can represent a lower cost.

At low H_2O_2 concentration, formation of $^{\bullet}OH$ is the kinetic determining step. H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate is logically slow. Further, most of the free radicals are directly consumed by the dye. In the presence of high concentration of H_2O_2, we could expect that more OH radicals would be produced. However, these radicals preferentially react with the excess of H_2O_2. This undesirable reaction competes with the degradation of the colour.

3.3. The effect of initial dyes concentration

In our study, the dye concentrations were chosen in the range of typical concentration in textile wastewater. The effect of initial dye concentration is shown in Fig. 6. The decrease of the decolourisation rate with the increase of the initial dye concentration has been observed. The difference in the resultant *k* shows that the reaction conditions were not comparable in the eight runs. It was due to the change of the C.I. Acid Blue 74 concentration, although the initial H_2O_2 concentration was the same. Recently, we have obtained similar results for Acid Orange 7, Acid Orange 8 and Methyl Orange dyes [19] in the same operating conditions. This can be explained by considering that both the aromatic dye and H_2O_2 absorb UV radiation in the range emitted by the lamp. However, the molar absorption coefficient of C.I. Acid Blue 74 at 254 nm is approximately 1000 times higher than that of H_2O_2, 22.04×10^3 versus 18.61 l mol^{-1} cm^{-1}, so that an increase in dye concentration induces a rise of the internal optical density and the solution becomes more and more impermeable to UV radiation. Then, hydrogen peroxide can only be irradiated by a smaller portion of UV light to form lower free radicals and the colour degradation rate decreases.

4. Conclusion

It can be concluded that the UV/H_2O_2 process using a continuous circulation reactor provides good performance in the decolourisation treatment of the C.I. Acid Blue 74 in water. The observations of these investigations clearly demonstrated the importance of choosing the optimum decolourisation parameters to obtain a high reaction rate. In the pH range between 3.5 and 5.5, the rate of decolourisation is improved. The rate of decolourisation increases by increasing the initial concentration of H_2O_2 up to 0.05 mol l^{-1}, at which it reaches a maximum and beyond which it is inhibited. Increasing the initial concentration of dye is in fact, like a filter absorbing more and more UV and decreasing the kinetics of removal.

Acknowledgements

The authors thank D. du Pac, lecturer in English at "Ecole Nationale Supérieure de Chimie de Mulhouse", for her corrections.

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