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Photochemical oxidation of reactive azo dye with UV–H_2O_2 process

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Abstract

The photooxidation of a chlorotriazine reactive azo dye Reactive Orange 4 has been carried out in the presence of H_2O_2 using UV-A light. The effects of reaction pH, applied H_2O_2 dose, UV light power have been studied. These parameters strongly influence the decolourisation and degradation. The increase of initial dye concentration decreases the removal rate. The kinetics of decolourisation and degradation follow pseudo-first order. The solar–H_2O_2 process is also able to oxidise the dye and its efficiency is comparable with UV–H_2O_2. The influence of dye assisting chemicals such as NaOH, NaCl and Na_2CO_3 on photodecolourisation has been investigated. Addition of these chemicals inhibit the removal rate. The optimum operating conditions of the method are reported.

Keywords: Photochemical oxidation; Reactive Orange 4; H_2O_2; UV-radiation; Solar light

1. Introduction

Synthetic dyes are the major industrial pollutants and water contaminants [1,2]. Textile water introduced intensive colour and toxicity to aquatic system. Reactive dyes are widely used in the textile industries because of its simple dyeing procedure and good stability during washing process [3]. Due to its complex structure most of the dyes are resistant to biodegradation [4]. Some physical and chemical techniques are currently available for the treatment of dye effluent. But these processes have only limited success.

Homogeneous advanced oxidation process (AOP) employing hydrogen peroxide with UV-light has been found to be very effective in the degradation of dye pollutants [5–8]. The complete decolourisation and mineralisation of dyes by UV radiation in the presence of H_2O_2 have been reported [9,10]. Galindo and Kalt [11] demonstrated that the UV–H_2O_2 process is able to destroy totally the chromophoric structure of azo dyes and the reaction rate of azo dyes depends on the basic structure and the nature of auxiliary groups attached to the aromatic nuclei of the dyes.

In UV–H_2O_2 process the photolysis of hydrogen peroxide generates effective oxidising species hydroxyl radical (.OH). The oxidation potential of hydroxy radical is 2.8 eV which can completely destroy the pollutants present in waste water. In

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addition, UV–H_2O_2 process has several advantages over other AOPs (i) There is no sludge formation during the treatment (ii) It can be carried out under ambient conditions (iii) The oxygen formed in this process is also useful for aerobic biological decay process [12].

Reactive dyes are poorly substantive to fibers, thus a substantial amount of electrolytes must be added in the dyeing process [13]. Sodium carbonate is applied as a pH buffer and dye fixation agent during the reactive dyeing process [14]. These reactive dye auxiliary chemicals discharged along with dye are additionally polluting the water. Hence the investigation of the effects of these chemicals on the UV–H_2O_2 process has practical importance.

For practical applications of dye waste water treatment by UV–H_2O_2 process, there is a need to determine the optimal conditions of experimental parameters. We have taken a reactive class mono azo dye Reactive Orange 4 and carried out the following (i) Analysis of various experimental parameters to find out the optimum conditions (ii) Comparison of the UV–H_2O_2 process with sunlight–H_2O_2 process (iii) The influence of dye auxiliary chemicals such as NaCl, NaOH and Na_2CO_3 on UV–H_2O_2 process. Reactive Orange 4 dye (C.I. No. 18260, M.Wt. 769.21) is extensively used in dyeing the textile fabrics. Its chemical structure and absorption maxima are shown in Fig. 1.

2. Experimental

2.1. Material

Reactive Orange 4 dye obtained from Colour Chem, Pondicherry was used as received. H_2O_2 (30% w/w) was obtained from Merck. AnalaR grade NaOH, Na_2CO_3, NaCl, were used as such. The double distilled water was used to prepare experimental solutions. The pH of the solutions were adjusted using H_2SO_4 and NaOH.

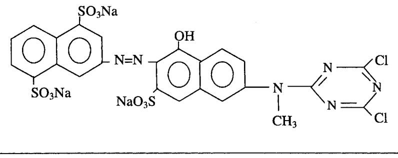
Name	Chemical Structure	λ_{max} (nm)
Reactive Orange 4		489, 285

Fig. 1. Chemical structure and absorbance maxima of RO4 dye.

2.2. Photoreactor

Heber multilamp photoreactor model HML-MP 88 was used for photoreaction. This model consists of eight medium pressure mercury vapour lamps (8W) set in parallel and emitting 365 nm wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminium and built in cooling fan at the bottom. It is provided with the magnetic stirrer at the centre. Open borosilicate glass tube of 50 ml capacity, 40 cm height and 20 mm diameter was used as a reaction vessel with the total light exposure length of 330 mm. The irradiation was carried out using four parallel medium pressure mercury lamps.

2.3. Procedure

A desired molar ratio of dye/H_2O_2 at pH 3 was prepared freshly before the experiments. In all cases 50 ml of reaction mixture was irradiated. At specific time intervals 1–2 ml of the sample was withdrawn. 1 ml of the sample was suitably diluted and its absorbances at 489 nm and 285 nm were measured immediately. The absorbance at 489 nm ($n \rightarrow \pi^*$ transition of N=N group) is due to the colour of the dye solution and it is used to monitor the decolourisation of dye. The absorbance at 285 nm ($\pi \rightarrow \pi^*$ transition in naphthalene group) represent the aromatic content of RO4 and the decrease of absorbance at 285 nm indicates the degradation of aromatic part of the dye.

UV spectral analysis was done using Hitachi U-2001 spectrophotometer.

The pH of the solution is measured by using HANNA phep (Model H 198107) digital pH meter.

3. Results and discussion

The primary analysis was carried out under the following conditions: (i) self photolysis of dye solution with UV-light, (ii) dye solution with H_2O_2 in dark, (iii) dye solution with H_2O_2 and UV-light. The results are shown in Fig. 2. Dye is resistant to direct UV-photolysis as the energy of 365 nm is too low to degrade dye molecule. For the dye solution with H_2O_2 in dark, 8.55% decolourisation and 3.0% degradation were observed. But the combined action of UV and H_2O_2 caused 88.68% decolourisation and 59.85% degradation at the time of 150 min. The degradation of the dye in UV–H_2O_2 process is by the reaction of hydroxyl radicals generated upon photolysis of hydrogen peroxide [Eq. (1)–(3)].

$$H_2O_2 \xrightarrow{h\nu} .OH + .OH \tag{1}$$

$$.OH + \text{dye} \longrightarrow \text{dye intermediate} \tag{2}$$

$$\begin{aligned} .OH + \text{dye intermediate} &\longrightarrow CO_2 \\ &+ H_2O + \text{mineralisation products} \end{aligned} \tag{3}$$

The hydroxyl radical is a very strong oxidising agent and it degrades the dye molecule. Fig. 3 shows the changes in the optical densities at 489 nm and 285 nm of RO4 under different irradiation times.

3.1. Effect of pH

The reactivity of hydrogen peroxide depends on the pH of the medium. The effect of pH on the decolourisation and degradation has been carried out in the pH range 1–8. The results are shown in Fig. 4. From the results, it is clear that the process is more efficient in acid medium (pH 2–4). Increase of pH from 1 to 3 increases the decolourisation from 10.32 to 88.68% and degradation from 0 to 59.85%. Further increase of pH from 3 to 8 decreases the decolourisation from 88.68 to 10.22% and degradation from 59.85 to 5.26% at the time of 150 min. The lowering of removal rate in this pH range is due to reduction of hydroxyl radical concentration. Under this condition H_2O_2 undergoes photodecomposition to water and oxygen rather than hydroxyl radical [Eq. (4)] [15].

$$2H_2O_2 \xrightarrow{h\nu} 2H_2O + O_2 \tag{4}$$

In alkaline medium the oxidising species hydroperoxy anion (HO_2^-) is also formed (HO_2^- anion is the conjugated base of H_2O_2). This HO_2^- anion reacts with .OH radical and residual H_2O_2 [Eqs. (5), (6)] consequently lowering the removal rate.

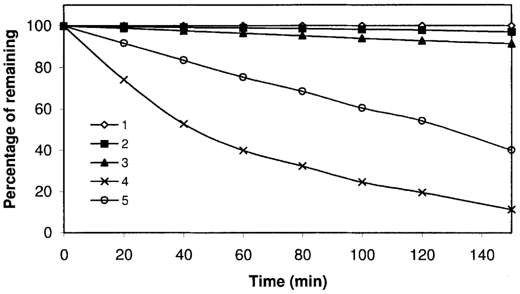


Fig. 2. Photochemical degradability of RO4.$[H_2O_2]$ = 10 mmol, [RO4] = 5 × 10^{-4} mol/l, pH = 3.0. Dye solution with UV light only (1). Dye solution with H_2O_2 in dark (2 & 3) 3. Decolourisation 2. Degradation. Dye solution with UV light and H_2O_2 (4&5) 4. Decolourisation 5. Degradation.

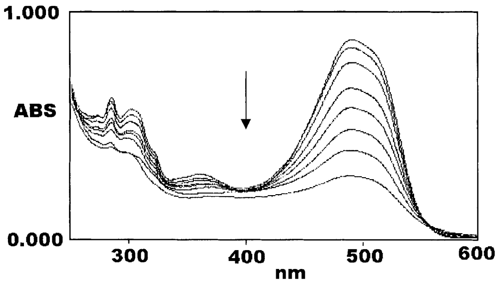


Fig. 3. The changes in UV–visible spectrum of RO4 on irradiation with UV-light and H_2O_2. $[H_2O_2]$ = 10 mmol, [RO4] = 5×10^{-4} mol/l, pH = 3.0.

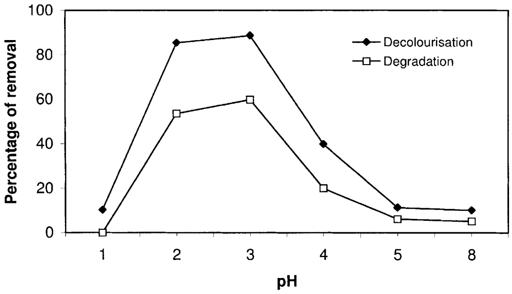


Fig. 4. Effect of pH on the decolourisation and degradation of RO4. $[H_2O_2]$ = 10 mmol, [RO4] = 5×10^{-4} mol/l, irradiation time = 150 min.

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + .OH \quad (5)$$

$$.OH + HO_2^- \rightarrow H_2O + O_2^- \quad (6)$$

3.2. Effect of addition of H_2O_2

The effect of addition of H_2O_2 (5–25 mmol) on the photochemical decolourisation and degradation has been investigated. The results are shown in Fig. 5. The figure shows the initial H_2O_2 concentration effects on the removal rate. The addition of 5 to 20 mmol increases the decolourisation from 83.6 to 98.3% and degradation from 50.12 to 75.6% at time of 150 min. Further increase of H_2O_2 from 20 to 25 mmol decreases the decolourisation from 98.3 to 94.3% and degradation from 75.62 to 68.83%. Hence 20 mmol H_2O_2 concentration appears to be optimal for the photo-oxidation. The enhancement of decolourisation and degradation by addition of H_2O_2 (5–20 mmol) is due to increase in the hydroxyl radical concentration. At low concentration H_2O_2 cannot generate enough hydroxyl radicals and the removal rate is limited. At high H_2O_2 concentration (25 mmol) H_2O_2 acts as a hydroxyl radical quencher [Eqs. (7), (8)] consequently lowering the hydroxyl radical concentration.

$$H_2O_2 + .OH \rightarrow HO_2^{\cdot} + H_2O \quad (7)$$

$$HO_2^{\cdot} + .OH \rightarrow H_2O + O_2 \quad (8)$$

3.3. Effect of UV-light power

The effect of UV-light power on the decolourisation and degradation of RO4 is shown in Fig. 6. The figure clearly shows that the removal rate steadily increased with increasing UV power with a linear relationship. The increase of light intensity from 16W to 62W increases the decolourisation from 50.69 to 79.86% and degradation from 18.66 to 45.69% at the time of 60 min.

The enhancement of removal rate is due to increase in hydroxyl radical concentration. The rate of photolysis of H_2O_2 depends directly on the incident power. At low UV power the photolysis of H_2O_2 is limited. At high UV power more hydroxyl radicals are produced upon the photodissociation of H_2O_2, hence removal rate increases. It appears that the UV power tested in our study lies within the linear range and hence all the photons provided were effectively used.

3.4. Effect of dye concentration

The effect of various initial dye concentrations on the photochemical decolourisation and degradation has been investigated from 1 to 5×10^{-4} mol/l. The results are shown in Figs. 7 and 8. Increase in the initial concentration of dye from 1 to 5×10^{-4} mol/l decreases the decolourisation from 93.47 to 60.97% and degradation from 62.9 to 24.62% at the time of 60 min. At high concentration the penetration of photons entering into the solution decreases, consequently lowering the hydroxyl radical concentration. Further quantita-

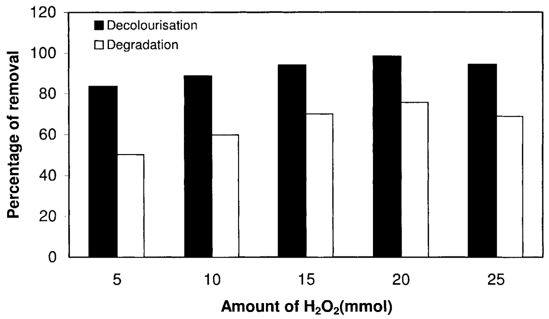


Fig. 5. Effect of addition of H_2O_2 on the decolourisation and degradation of RO4. H_2O_2 = 10 mmol, [RO4] = 5×10^{-4} mol/l, pH = 3.0, irradiation time = 150 min.

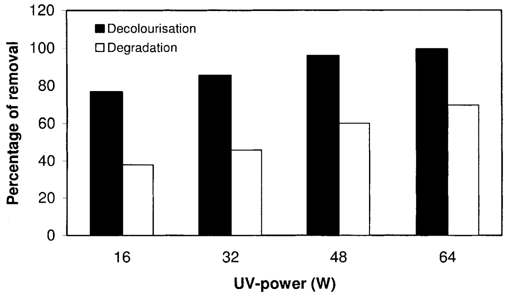


Fig. 6. Effect of UV-light power on the decolourisation and degradation of RO4. [H_2O_2] = 10 mmol, [RO4] = 5×10^{-4} mol/l, irradiation time = 60 min.

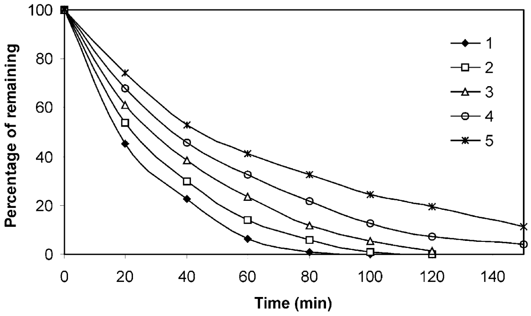


Fig. 7. Effect of initial dye concentrations on the decolourisation of RO4. $[H_2O_2]=10$ mmol, $pH=3.0$. $1=1\times10^{-4}$ mol/l, $2=2\times10^{-4}$ mol/l, $3=3\times10^{-4}$ mol/l, $4=4\times10^{-4}$ mol/l, $5=5\times10^{-4}$ mol/l,.

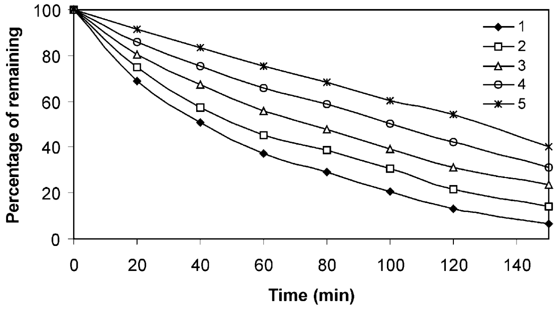


Fig. 8. Effect of initial dye concentrations on the degradation of RO4. $[H_2O_2]=10$ mmol, $pH=3.0$. $1=1\times10^{-4}$ mol/l, $2=2\times10^{-4}$ mol/l, $3=3\times10^{-4}$ mol/l, $4=4\times10^{-4}$ mol/l, $5=5\times10^{-4}$ mol/l.

tive interpretation of the results requires a kinetic model. Since concentration of H_2O_2 is in excess, the photodecolourisation and degradation reaction follow pseudo-first order kinetics with respect to azo dye concentration [Eq. (9)]

$$\frac{-\mathrm{d}C}{\mathrm{d}t}=kt \tag{9}$$

k is the pseudo-first order rate constant, t is the irradiation time, C is the dye concentration at a given time.

Integration of Eq. (9) with restriction of $C=Co$ at $t=0$ will lead to the relation [Eq. (10)]

$$\ln\left(\frac{Co}{C}\right)=-kt \tag{10}$$

The results are presented in Table 1. It is found that the increase in dye concentration decreases the pseudo-first order rate constant.

3.5. Solar experiments

For solar experiments the solution with H_2O_2 was taken in the same borosilicate glass tube and irradiated with solar light. The photodecolourisation and degradation of RO4 under solar irradiation with H_2O_2 ($1000-1100\times100$ lux) are shown in Fig. 9. Solar photooxidation with H_2O_2 produces 80.15% decolourisation and 50.91% degradation at the irradiation time of 150 min.

Fig. 10 shows the comparison of UV-light and sunlight processess on the decolourisation and degradation of RO4. At 150 min irradiation time 88.68% decolourisation and 59.85% of degradation were observed with UV–H_2O_2, whereas 80.15% decolourisation and 50.91% degradation were observed with sunlight–H_2O_2 process. Though UV light is more efficient than sunlight a considerable amount of photodegradation takes place in sunlight also. In tropical countries like India intense sunlight is available throughout the

Table 1
Pseudo- first order rate constants of RO4 decolourisation and degradation (150 min) $[H_2O_2]=10$ mmol, $pH=3.0$

Concentration of dye$\times10^{-4}$ mol/l	Decolourisation k (min^{-1})	Degradation k (min^{-1})
1	0.0454	0.0165
2	0.0327	0.0131
3	0.0241	0.0097
4	0.0186	0.0069
5	0.0156	0.0047

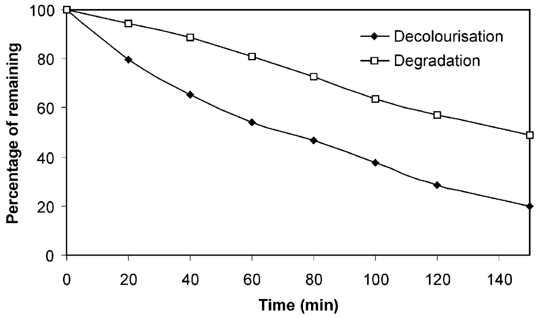


Fig. 9. Photochemical degradability of RO4 in solar–H_2O_2. $[H_2O_2]=10$ mmol, $[RO4]=5\times10^{-4}$ mol/l, $pH=3.0$.

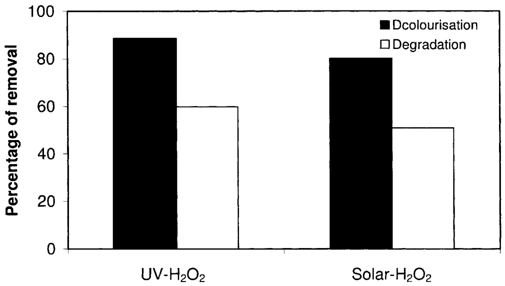


Fig. 10. Comparison of UV–H_2O_2 with solar–H_2O_2 on decolourisation and degradation of RO4. $[H_2O_2] = 10$ mmol, $[RO4] = 5 \times 10^{-4}$ mol/l, pH = 3.0. irradiation time = 150 min.

year and hence it could be effectively used instead of costly, hazardous UV-light.

3.6. Effect of dye assisting chemicals

The effects of addition of reactive dye auxiliary chemicals such as NaCl, NaOH, Na_2CO_3 (1g/l) on the photodecolourisation are shown in Fig. 11. Na_2CO_3 strongly retard the removal rate and only 3.58% of decolourisation was observed. The strong retardation effect is due to the .OH radical scavenging effect of carbonate and bicarbonate ions [Eqs. (11), (12)].

$$CO_3^{2-} + .OH \rightarrow OH^- + CO_3^{-\cdot} \qquad (11)$$

$$HCO_3^- + .OH \rightarrow H_2O + CO_3^{-\cdot} \qquad (12)$$

Addition of NaCl does not affect the removal rate significantly. The small decrease in the removal efficiency is due to the hydroxyl radical scavenging effect of chloride ion [16] [Eqs. (13), (14)]. Similar retardation by the addition of Na_2CO_3 and NaCl has been reported in UV–H_2O_2 process [17].

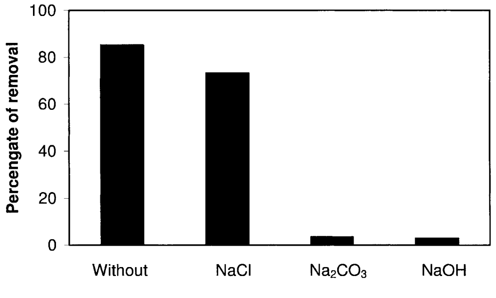


Fig. 11. Effect of dye assisting chemicals on the photodecolourisation of RO4. $[H_2O_2] = 10$ mmol, $[RO4] = 5 \times 10^{-4}$ mol/l pH = 3.0. irradiation time = 150 min.

$$Cl^- + .OH \rightarrow HOCl^-. \qquad (13)$$

$$HOCl^-. + H^+ \rightarrow Cl. + H_2O \qquad (14)$$

Like carbonate, addition of NaOH also strongly inhibit the removal rate. Only 2.79% decolourisation was observed at 150 min irradiation time. The strong inhibition of NaOH is due to the following reasons (i) The concentration of H_2O_2 decreases by the reaction of NaOH with H_2O_2 [Eq. (15)] (ii) Addition of NaOH makes the solution alkaline. As discussed earlier the alkaline medium reduces the photooxidation. Similar observation was reported in decolourisation of Reactive Red 120 by UV–H_2O_2 process [12].

$$2NaOH + H_2O_2 + 6H_2O \rightarrow Na_2O_2 + 8H_2O. \qquad (15)$$

4. Conclusions

The results show that the UV–H_2O_2 and solar–H_2O_2 processes can be efficiently used for the decolourisation and degradation of RO4. The photochemical oxidation by UV–H_2O_2 process is efficient at pH 3 and with 20 mmol H_2O_2. The decolourisation and degradation follow pseudo-first order kinetics. The dye assisting chemicals Na_2CO_3 and NaOH strongly inhibit the photooxidation.

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