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Dyes and Pigments 68 (2006) 133–142
DYES and PIGMENTS
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Photocatalytic decolourisation and degradation of Reactive Orange 4 by TiO_2-UV process

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Received 2 June 2004; received in revised form 12 August 2004; accepted 3 January 2005
Available online 24 March 2005

Abstract

The photocatalytic decolourisation and degradation of an azo dye Reactive Orange 4 (RO4) in aqueous solution with TiO_2-P25 (Degussa) as photocatalyst in slurry form has been carried out using UV-A light (365 nm). There is a significant difference in adsorption of dye on TiO_2 surface with the change in the solution pH. The effect of various parameters such as catalyst loading, pH and initial concentration of the dye on decolourisation and degradation have been determined. The dye is decolourised in 80 min and completely degraded in 180 min under optimum conditions. The degradation was strongly enhanced in the presence of electron acceptors such as H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$. The photodecolourisation and degradation kinetics are discussed in terms of Langmuir–Hinshelwood kinetic model. The degradation intermediates were analysed by GC–MS technique.

Keywords: Photocatalysis; Photocatalytic degradation; Azodyes; Reactive Orange 4; Adsorption; TiO_2 + UV-light

1. Introduction

Dye wastewater pollutants are the major sources of environmental pollution [1]. Textile wastewater introduced intensive colour and toxicity to aquatic system. Reactive dyes are widely used in the textile industries because of its simple dyeing procedure and stability during washing process [2]. But, the main drawback of reactive dyes is low-fixation rate on the fabrics [3]. In order to overcome these difficulties electrolyte must be added to the dye bath. The added electrolyte is also discharged along with dye thus additionally polluting the water. Dyes possess complex aromatic structure. Hence, conventional biological treatment methods are ineffective for decolourisation and degradation [4]. Some physical and chemical techniques are currently available for the treatment of dye effluent [5]. But these processes have only limited success.

In recent years, attention have been focused on heterogeneous photocatalysis for the treatment of recalcitrant chemicals present in the waste water [6]. Due to the high photocatalytic activity and stability of Titanium dioxide, it is generally used as a photocatalyst for the removal of organic pollutants [7,8] and dye pollutants [9–12].

For practical application of dye wastewater treatment by TiO_2-UV process, there is a need to determine the optimal conditions of experimental parameters for economic removal of the dye. In the present investigation, we have undertaken a reactive class monoazo dye Reactive Orange 4 and examined the various parameters to find out the optimum conditions for removal of colour and aromatic part of the dye.

Reactive Orange 4 dye (C.I. No. 18260, M.F. = $C_{23}H_{13}N_6O_{10}S_3Cl_2Na_3$. Molecular weight = 769.21) is extensively used in dyeing the textile fabrics. The chemical structure and its absorption maxima are given in Table 1.

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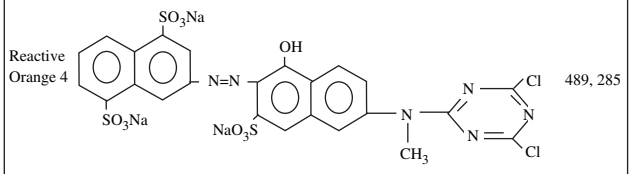
doi:10.1016/j.dyepig.2005.01.004

Table 1
Chemical structure and absorbance maxima of dye

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

2. Experimental

2.1. Material

Reactive Orange 4 dye, obtained from Colour Chem Pondicherry was used as received. A gift sample of TiO_2-P25 was received from Dugussa (Frankfurt, Germany). TiO_2-P25 contains mainly anatase 80% and rutile 20% with the mean particle size of 30 nm and a BET surface area of 50 m^2/g. AnalaR grade H_2O_2, $(NH_2)_2$ S_2O_8 and $KBrO_3$ (Merck) were used as such. The double distilled water was used to prepare experimental solutions. The natural pH of the aqueous dye solution is 4.8. The pH of the solutions were adjusted using H_2SO_4 and NaOH.

2.2. Apparatus

Heber multilamp photoreactor model HML-MP 88 (Fig. 1) was used for photoreaction. This model consists of eight medium pressure Mercury vapour lamps (8 W) 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.

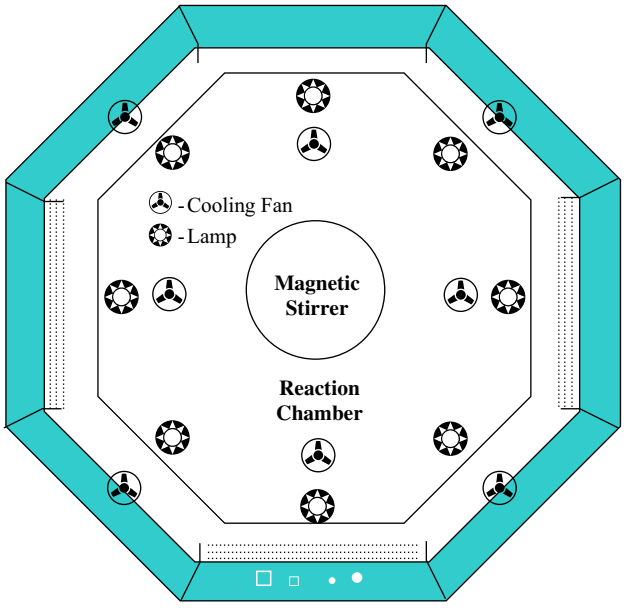


Fig. 1. Schematic diagram of photocatalytic reactor.

The irradiation was carried out using four parallel medium pressure Mercury lamps in open air condition. The solution with TiO_2 and dye was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution.

2.3. Procedure

In all cases 50 ml of the dye solution containing appropriate quantity of the TiO_2 suspensions were used. The suspension was stirred for 30 min in dark for the attainment of adsorption equilibrium. At specific time intervals 2 ml of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the centrifugate was diluted to 10 ml and its absorbance at 489 nm and 285 nm were measured. The absorbance at 489 nm is due to colour of the dye solution and it is used to monitor the decolourisation of dye. The absorbance at 285 nm represents the aromatic content of RO4 and the decrease of absorbance at 285 nm indicates the degradation of aromatic part of the dye.

2.4. Adsorption test

The adsorption experiments have been performed with the dye solutions at different concentrations and at different pH. Fifty milliliters of aqueous dye solution was made to contact with 200 mg of TiO_2 for overnight at 20 °C using mechanical shaker. In order to avoid the photoreaction of TiO_2, the samples were kept in dark for the entire period of the experiment. After adsorption the solutions were centrifuged to separate the catalyst. The concentration of the dye solution was determined from its absorbance at 489 nm. The amount of dye adsorbed on the catalyst was calculated by mass balance.

2.5. GC–MS analysis

For identification of intermediate products of RO4 photocatalytic degradation the sample taken after complete decolourisation was analysed. The sample for analysis was prepared by the following methods. The centrifugate obtained after irradiation was extracted 5 times with HPLC grade chloroform then it was dried over anhydrous sodiumsulphate to remove the water present in the solution. The solvent was removed by evaporation under reduced pressure. The final residual mass was taken for GC–MS analysis.

The GC (Perkin–Elmer Auto system) is equipped with a PE5 capillary column (30 × 250 μm) and 1 μm film thickness (Perkin Elmer elite series) and interfaced directly to the MS (Perkin Elmer turbo mass spectrophotometer). The GC column was operated at a temperature of 100 °C for 1 min then increased to 260 °C at the rate of 10 °C/min. The other experimental conditions are: EI impact ionisation 70 eV, Helium as carrier gas, injection temperature 260 °C, source temperature 180 °C.

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

3.1. Photodegradability of RO4

Initially the control experiments were carried out under the following conditions: (i) self photolysis of dye solution with UV-light; (ii) dye solution with catalyst in dark and (iii) under irradiation of UV-light with photocatalyst. The results are shown in Fig. 2. Dye is resistant to self photolysis as the energy of 365 nm is too low to degrade dye molecule. After 30 min of magnetic stirring without UV irradiation about 25% decrease in concentration was observed at 489 nm and 285 nm absorbance measurements. This is due to the adsorption of dye molecule on the surface of TiO_2. Simultaneous irradiation and aeration caused 95.1% of decolourisation and 63.88% of degradation after 60 min. Azo bonds are more active in these dyes and they are oxidised by positive hole, hydroxyl radical and reduced by electron in the conduction band [13]. RO4 contains one azo bond, and decolourisation of RO4 showed that the chromophoric azo bond of dye molecule is destroyed. Fig. 3 shows the changes in the optical densities of 489 nm and 285 nm of RO4 under different irradiation times. The complete decolourisation is achieved at 80 min of irradiation time while complete degradation occurs in 180 min. The fast decolourisation of dye is due to the initial electrophilic cleavage of its chromophoric azo (–N=N–) bonds attached to the naphthalene ring. The degradation of aromatic part of the dye molecule produced number of intermediate compounds and the removal of these intermediates took longer time.

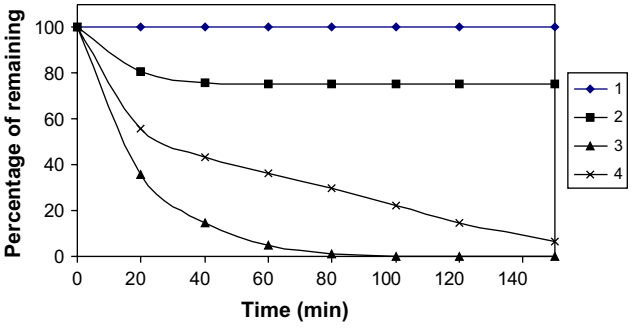


Fig. 2. Photodegradability of RO4. TiO_2 = 4 g/l, [RO4] = 5 × 10^{-4} mol/l, pH = 4.8. Dye solution irradiated with UV-light in the absence of TiO_2 (1), dye solution treated with TiO_2 in dark (2), dye solution irradiated with UV-light in the presence of TiO_2 (3 and 4), decolourisation (3), degradation (4).

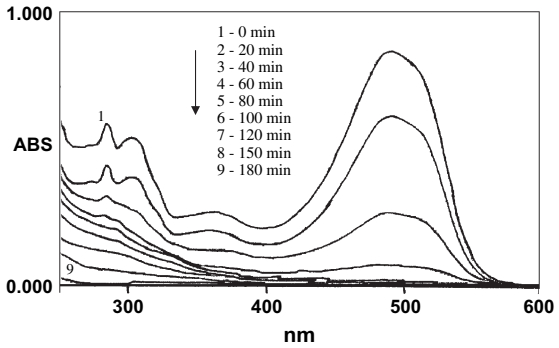


Fig. 3. The changes in UV–Visible spectrum on irradiation by means of UV-light of an aqueous suspension of TiO_2 containing RO4. TiO_2 = 4 g/l, [RO4] = 5 × 10^{-4} mol/l, pH = 4.8.

3.2. Adsorption isotherm

Adsorption of pollutants on the semiconductor surface is an important parameter in heterogeneous photocatalysis. The adsorption experiments have been carried out in order to evaluate the equilibrium constants of adsorption. The adsorption of RO4 dye on the TiO_2 surface at various pH is shown in Fig. 4. Adsorption isotherm expresses the relationship between the mass of dye adsorbed per unit weight of the TiO_2 and equilibrium concentration of the dye in solution. The extent of adsorption of dye on the TiO_2 surface under different pH is in the following order pH 5 > pH 3 > pH 7. The average value of the dye adsorbed per unit weight of the catalyst at pH 5, 3 and 7 are 6.23×10^{-4}, 2.18×10^{-4} and 1.56×10^{-4} mol/l, respectively. All isotherms showed (Fig. 4) a type of L-shape according to the classification of Giles et al. [14]. The L-shape isotherms mean that there is no strong competition between solvent and the dye to occupy the TiO_2 surface sites.

The data obtained from the adsorption experiments were fitted to the linear form of the rearranged Langmuir equation (Eq. (1)).

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (1)$$

C_e is the concentration of the dye in solution at equilibrium, q_e is the amount of dye adsorbed per unit

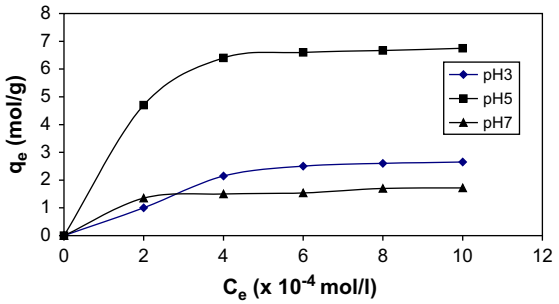


Fig. 4. Adsorption isotherm of RO4 on TiO_2 surface.

weight of the catalyst at equilibrium, b is the Langmuir adsorption constant and Q_o is the amount of dye adsorbed corresponding to monolayer coverage.

The dimensionless separation factor (R_L) (Eq. (2)) indicates the shape of the Langmuir isotherm to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

$$R_L = \frac{1}{1 + bC_o} \tag{2}$$

where, b is the Langmuir constant and C_o is the highest initial concentration.

Table 2 shows the Langmuir equilibrium constant and R_L factor. The adsorption of RO4 on TiO_2 at pH 5 was fairly good and it decreases on both sides.

The adsorption of dye on TiO_2 surface at different pH shows that increasing the pH from acidic to alkaline resulted in significant reduction in adsorption. The surface charge property of TiO_2-P25 changes with change in pH of the solution. The point of zero charge (Pzc) for TiO_2-P25 $\simeq$ 6.8 [15]. In acidic solution the pH is lower than (Pzc) and hence the TiO_2 surface is positively charged (Eq. (3)).

$$\text{When pH} < \text{Pzc}: \quad \text{TiOH} + \text{H}^+ \leftrightarrow \text{TiOH}_2^+ \tag{3}$$

In basic solution the surface is negatively charged as given in Eq. (4).

$$\text{When pH} > \text{Pzc}: \quad \text{TiOH} + \text{OH}^- \leftrightarrow \text{TiO}^- + \text{H}_2\text{O} \tag{4}$$

The RO4 dye in solution is negatively charged as the sulphonated group is hydrolysed. At pH < 6.8 the electrostatic attraction between positively charged TiO_2 surface and negatively charged sulfonic group leads to strong adsorption. At pH > 6.8 TiO_2 surface becomes negative and so it is electrostatically repulsive to the negatively charged dye molecules. Hence the adsorption of dye is less. In acidic pH range the adsorption of RO4 dye on TiO_2 surface is favourable nearer to Pzc. Lowering of the pH of the solution (pH 3 or below) creates the TiO_2 particles to aggregate and consequently reduces the adsorption capacity of the dye on to the TiO_2 surface.

Table 2
Langmuir equilibrium constants and R_L factor of RO4 adsorption on TiO_2 surface

pH	K_a (mol/l)	R_L
3	1.25	0.37
5	0.24	0.65
7	0.83	0.49

3.3. Effect of catalyst loading

For economic removal of dye effluent from wastewater, it is necessary to find the optimum amount of catalyst for efficient degradation. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process [16,17]. The effect of photocatalyst (TiO_2) concentration on the degradation of RO4 was investigated from 1 to 6 g/l. The effect of TiO_2 loading on the initial rate of removal for decolourisation and degradation is shown in Fig. 5. As the concentration of the catalyst increased from 1 to 4 g/l the initial rate of removal of dye increases sharply from 0.196 to 0.755 mol/min for decolourisation and 0.075 to 0.290 mol/min for degradation at 20 min irradiation time. This is due to increase in the number of TiO_2 particles, which increases the number of photons absorbed and also the number of the dye molecules adsorbed. Increase of the catalyst loading from 4 to 6 g/l the initial rate is almost constant. Increase of the catalyst loading beyond 4 g/l may cause light scattering and screening effects. These reduce the specific activity of the catalyst [18]. At high concentrations of catalysts, particle aggregation may also reduce the catalytic activity. The optimum amount of catalyst loading is found to be 4 g/l for the degradation and decolourisation of RO4. Hence 4 g/l was used as the catalyst dosage for the photocatalytic reactions.

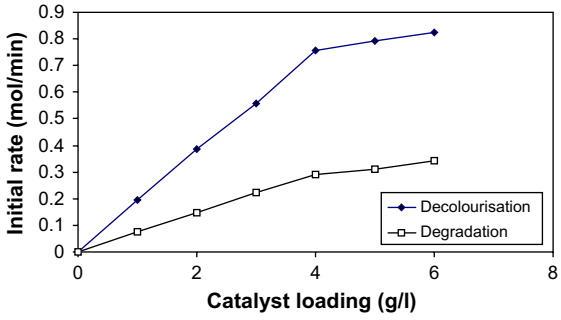


Fig. 5. Effect of catalyst loading on the photodecolourisation (20 min) and degradation (20 min) of RO4. [RO4] = 5×10^{-4} mol/l, pH = 4.8.

3.4. Effect of pH

As seen earlier the photocatalytic degradation efficiency is affected by surface charge property of TiO_2, charge of dye molecule, adsorption of dye on to TiO_2 surface and hydroxyl radical concentration. As these properties are pH dependent, pH plays an important role in the degradation of RO4. The effect of pH from 1 to 12 on the decolourisation and degradation are shown in Fig. 6. Increase of pH of the dye solution from 1 to 10 increases the decolourisation from 24.14 to 89.31% at the reaction time of 40 min and degradation from 13.25 to 86.59% at the time of 80 min. Further increase of pH from 10 to 12 decreases the efficiency of decolourisation from 89.31 to 81.20% and degradation from 86.59 to 77.35%. The photocatalytic removal of colour and degradation were observed to be fastest in slightly alkaline pH than in acidic pH range. Similar results were reported in literature for acidic dyes bearing sulfonate group [19–21]. At acidic pH range the removal efficiency is minimum. This is due to two reasons (i) at low pH value, TiO_2 particle agglomeration reduces the dye adsorption as well as photon absorption, (ii) in RO4 dye, the azo linkage (−N=N−) is particularly susceptible to electrophilic attack by hydroxyl radical. But at low pH the concentration of H^+ is in excess and H^+ ions interact with azo linkage decreasing the electron densities at azo group. Consequently, the reactivity of hydroxyl radical by electrophilic mechanism decreases.

Percentage removal of the dye increases with the increase in pH from 7 to 10, though RO4 adsorption on the Photocatalytic surface of TiO_2 decreases from pH 7 to 10. (The adsorption of dye on TiO_2 surface at different pH is discussed in Section 3.2.) This indicates that the effect of dye adsorption on photocatalytic activity is limited. Hence RO4 adsorption may not be the only determinative factor for the photocatalytic degradation.

The photocatalytic degradation of RO4 is mainly due to the hydroxyl radical attack on the dye molecule. The production of hydroxyl radical in acidic medium is different from basic medium.

$$H_2O + h_{VB^+} \rightarrow {}^{\bullet}OH + H^+ \quad (5)$$

$$OH^-_{surface} + h_{VB^+} \rightarrow {}^{\bullet}OH_{surface} \quad (6)$$

In acidic medium, photogenerated holes react with water molecule producing hydroxyl radical as given in Eq. (5). At alkaline pH the negative surface of the TiO_2 with OH^- ions act as efficient traps for the photogenerated holes and produce hydroxyl radicals (Eq. (6)) [22]. At pH > TiO_2 (Pzc) the hydroxyl radical and $O_2^{\bullet-}$ radical can easily diffuse from the negative surface of TiO_2 into the bulk of reaction solution. Hence hydroxyl radical is responsible for dye degradation. At high pH values (pH > 10), the hydroxyl radicals are rapidly scavenged and so the reaction of $^{\bullet}OH$ radical with dye decreases.

3.5. Effect of dye concentration

The pollutant concentration is a very important parameter in wastewater treatment. The effect of various initial dye concentrations on the photocatalytic decolourisation and degradation have been investigated from 1×10^{-4} to 11×10^{-4} mol/l. The results are shown in Figs. 7 and 8. It is found that the increase of the dye concentration decrease the removal rate. Similar results have been reported for the photocatalytic oxidation of other dyes [11,17,23]. Increase in the concentration of dye from 1×10^{-4} to 11×10^{-4} mol/l decrease the decolourisation from 99.48 to 25.6%, in 20 min and degradation from 98.79 to 23.91% in 60 min. When the dye concentration increases the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of TiO_2. The increase in dye concentration also decreases the path length of photon entering

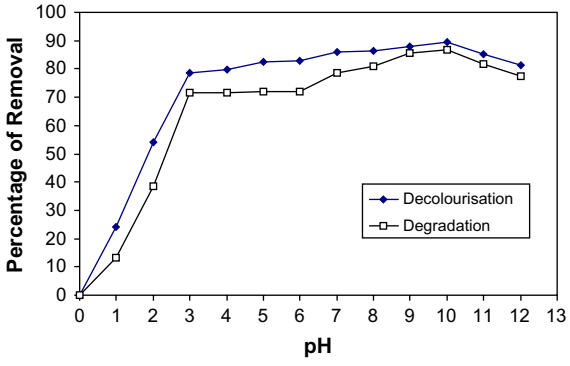


Fig. 6. Effect of pH on the decolourisation (40 min) and degradation (80 min) of RO4. TiO_2 = 4 g/l, [RO4] = 5×10^{-4} mol/l.

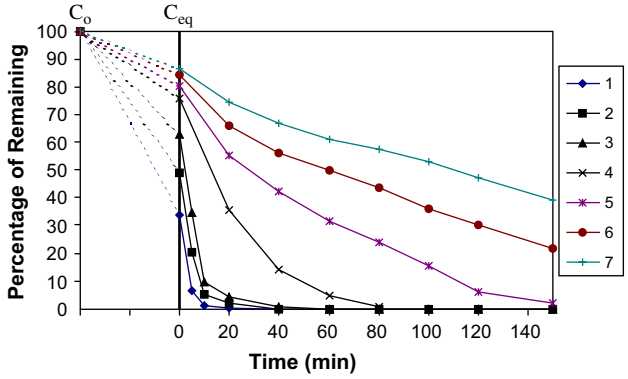


Fig. 7. Effect of various dye concentrations on the decolourisation of RO4. TiO_2 = 4 g/l, pH = 4.8. (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 5×10^{-4} mol/l, (5) 7×10^{-4} mol/l, (6) 9×10^{-4} mol/l, (7) 11×10^{-4} mol/l.

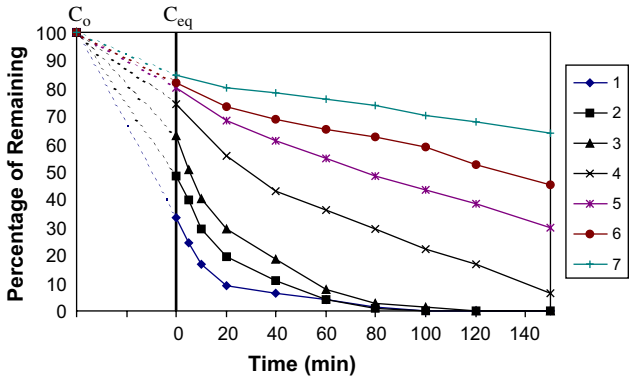


Fig. 8. Effect of various dye concentrations on the degradation of RO4. TiO_2 = 4 g/l, pH = 4.8. (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 5×10^{-4} mol/l, (5) 7×10^{-4} mol/l, (6) 9×10^{-4} mol/l, (7) 11×10^{-4} mol/l.

into the dye solution. At high dye concentration a significant amount of UV-light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency [24].

The photocatalytic decolourisation and degradation of RO4 dye containing TiO_2 obey apparently pseudo-first order kinetics at low initial dye concentration and the rate expression is given by Eq. (7).

$$\frac{-\mathrm{d}[C]}{\mathrm{d}t} = k'[C] \tag{7}$$

where k' is the pseudo-first order rate constant. The dye is adsorbed on to TiO_2 surface and the adsorption–desorption equilibrium is reached in 30 min. After adsorption the equilibrium concentration of dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integration of Eq. (7) (with the limit of $C = C_o$ at $t = 0$ with C_o being the equilibrium concentration of the bulk solution)

$$\ln\left[\frac{C_o}{C}\right] = k't \tag{8}$$

where C_o is the equilibrium concentration of dye, C is the concentration at time 't'.

Many authors [25–27] have used the Langmuir–Hinshelwood (L–H) kinetic expression to analyse the heterogeneous photocatalytic reaction successfully. The experimental data has been rationalised in terms of the modified form of L–H kinetic model to describe the solid–liquid reaction successfully [28]. The rate of oxidation of RO4 dye at surface reaction is proportional to the surface coverage of dye on the TiO_2 assuming that the dye is strongly adsorbed on the catalyst surface than the intermediate products [29]. The effect of dye concentration on the rate of degradation is given in the form of Eqs.(9) and (10) [28].

$$r = \frac{K_1 K_2 C}{1 + K_1 C} \tag{9}$$

$$\frac{1}{r} = \frac{1}{K_1 K_2 C} + \frac{1}{K_2} \tag{10}$$

C is the concentration of the dye at time 't', K_1 is the constant related to adsorption and K_2 is to the reaction properties of the dye. The applicability of L–H equation for the decolourisation and degradation has been confirmed by the linear plot obtained by plotting reciprocal of initial rate ($1/r$) against reciprocal of initial concentration ($1/C$) as shown in Fig. 9. The values K_1 and K_2 are found to be $0.215 \times 10^{-4}\ \mathrm{M}^{-1}$ and $0.388 \times 10^{-4}\ \mathrm{M}^{-1}$ for decolourisation and $0.43 \times 10^{-4}\ \mathrm{M}^{-1}$ and $0.5185 \times 10^{-4}\ \mathrm{M}^{-1}$ for degradation, respectively.

3.6. Effect of electron acceptors

In photocatalytic reaction of TiO_2 the major energy wasting step is the electron–hole recombination which leads to low quantum yield. Hence the prevention of electron–hole recombination becomes very important. This can be achieved by adding proper electron donor (or) acceptor to the system. Usually molecular oxygen is used as an electron acceptor in heterogeneous photocatalysed reaction. Besides the addition of molecular oxygen, the electron–hole recombination can be reduced by the addition of irreversible electron acceptors such as H_2O_2, $(NH_4)_2S_2O_8$, and $KBrO_3$. The addition of these electron acceptors enhanced the degradation rate by several ways (i) preventing the electron–hole recombination by accepting the conduction band electron (ii) increasing the hydroxyl radical concentration (iii) generating other oxidising species ($SO_4^{-\cdot}$) to accelerate the intermediate compound oxidation rate.

3.6.1. Effect of addition of H_2O_2

The effect of addition of H_2O_2 (5–20 mmol) on the photocatalytic oxidation has been investigated. The results are shown in Fig. 10. The addition of H_2O_2

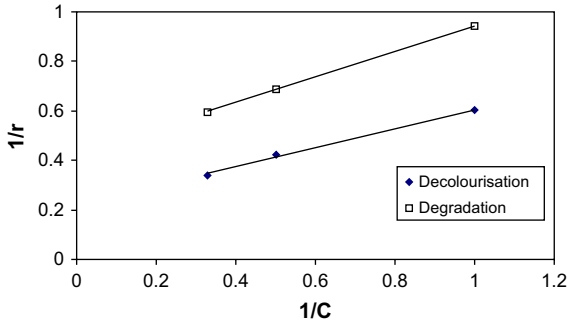


Fig. 9. Linearised reciprocal kinetic plot of the photodecolourisation and photodegradation of RO4. (Experimental conditions see Fig. 7).

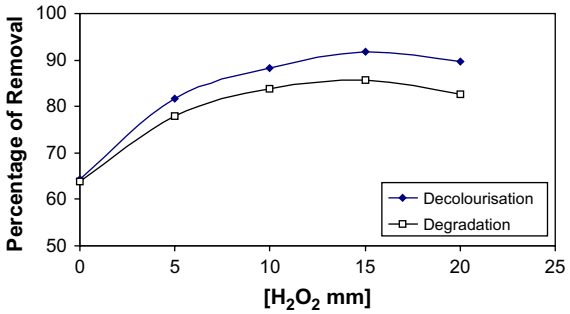


Fig. 10. Effect of addition of H_2O_2 on the decolourisation (20 min) and degradation (60 min) of RO4. TiO_2 = 4 g/l, [RO4] = 5×10^{-4} mol/l, pH = 4.8.

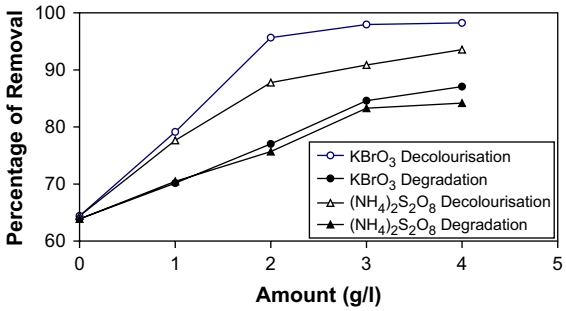


Fig. 11. Effect of addition of $(NH_4)_2S_2O_8$, $KBrO_3$ on the decolourisation (20 min) and degradation (60 min) of RO4. TiO_2 = 4 g/l, [RO4] = 5×10^{-4} mol/l, pH = 4.8.

(5–15 mmol) increases the decolourisation from 67.89 to 91.88% in 20 min and degradation from 70.41 to 94.77% in 80 min. Further increase of H_2O_2 concentration from 15 to 20 mmol decreases the decolourisation from 91.88 to 89.73% and degradation from 94.77 to 92.68%. Hence 15 mmol H_2O_2 concentration appears to be optimal for the degradation. Similar observation (an increase in H_2O_2 level enhanced the degradation rate upto optimal load beyond which inhibition occur) has been reported in dye degradation [11,12] and organic pollutant [30]. The enhancement of decolourisation and degradation by addition of H_2O_2 is due to increase in the hydroxyl radical concentration as shown by Eqs. (11) and (12).

$$TiO_2\ e^-_{(CB)} + H_2O_2 \rightarrow TiO_2 + {}^{\bullet}OH + OH^- \quad (11)$$

$$H_2O_2 \xrightarrow{h\nu} {}^{\bullet}OH + {}^{\bullet}OH \quad (12)$$

H_2O_2 also reacts with superoxide anion to form $^{\bullet}OH$ radical

$$H_2O_2 + O_2^{\bullet -} \rightarrow {}^{\bullet}OH + H^+ + O_2 \quad (13)$$

At high H_2O_2 dosage (20 mmol) the removal rate decreases due to its hydroxyl radical scavenging effect (Eqs. (14) and (15)).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (14)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (15)$$

3.6.2. Effect of $(NH_4)_2S_2O_8$

The effect of addition of $(NH_4)_2S_2O_8$ on the photocatalytic oxidation of RO4 has been investigated by varying the amount of $(NH_4)_2S_2O_8$ from 1 to 4 g/l. The results are shown in Fig. 11. Addition upto 3 g/l of $(NH_4)_2S_2O_8$ increases the decolourisation from 64.6 to 90.85% (20 min) and degradation from 70.41 to 91.4% (80 min). Our results are in good agreement with earlier results [17,31,32]. Further increase in the addition increases the decolourisation by 2.7% and degradation by 1.01%. The enhancement of reaction rate is due to the inhibition of electron–hole recombination and production of other oxidising species namely sulphate radical anion (Eq. (16)).

$$S_2O_8^{2-} + TiO_2\ e^-_{(CB)} \rightarrow SO_4^{-\bullet} + SO_4^{2-} \quad (16)$$

The sulphate radical anion may react with photogenerated electron and with water molecule producing hydroxyl radical (Eqs. (17) and (18)).

$$SO_4^{-\bullet} + e^-_{(CB)} \rightarrow SO_4^{2-} \quad (17)$$

$$SO_4^{-\bullet} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \quad (18)$$

The sulphate radical anion ($SO_4^{-\bullet}$) is a very strong oxidant (E^o = 2.6 eV) This radical anion also participates in the degradation process in the following way.

$$SO_4^{-\bullet} \nearrow \quad RO4 \longrightarrow SO_4^{2-} + \text{Dye intermediate}$$
$$SO_4^{-\bullet} \searrow \quad \text{Dye intermediate} \longrightarrow \text{degradation products.}$$

At high dosage of $S_2O_8^{2-}$ the inhibition of reaction occurs due to the increase in concentration of SO_4^{2-} ion (Eq. (16)). The excess of SO_4^{2-} ion is adsorbed on the TiO_2 surface and reduces the catalytic activity. The adsorbed SO_4^{2-} ion also reacts with the photogenerated holes (Eq. (19)) and with the hydroxyl radicals (Eq. (20)).

$$SO_4^{2-} + h^+ \rightarrow SO_4^{-\bullet} \quad (19)$$

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{-\bullet} + OH^- \quad (20)$$

Since $SO_4^{-\bullet}$ is less reactive than $^{\bullet}OH$ radical and h^+ the excess SO_4^{2-} reduces the photodegradation of the dye.

Without the photocatalyst, the persulphate alone causes 29.57% decolourisation and 15.87% of degradation after 150 min irradiation. This removal may be due to the excitation of dye molecule from S_0 to S_1 state by photon absorption followed by ionization and the degradation of the ionized dye by sulphate radical anion as given in Eqs. (21)–(23).

$$\text{Dye} \xrightarrow{h\nu} \text{dye}^* \tag{21}$$

$$\text{Dye}^* \rightarrow \text{dye}^+ + e^- \tag{22}$$

$$e^- + S_2O_8^{2-} \rightarrow SO_4^{2-\cdot} + SO_4^{2-} \tag{23}$$

3.6.3. Effect of $KBrO_3$

$KBrO_3$ is an efficient electron acceptor and used as an additive to enhance photocatalytic degradation rate [17,31,32]. The effect of addition of $KBrO_3$ (1–4 g/l) on the photocatalytic decolourisation and degradation are shown in Fig. 11. The addition of $KBrO_3$ from 1 to 3 g/l increases the decolourisation from 64.4 to 97.97% at the time of 20 min and increases the degradation from 63.88 to 89.47% at the time of 60 min. The enhancement of the removal rate is due to the reaction between BrO_3^- ion and conduction band electron (Eq. (24)) which reduces the recombination of electron–hole.

$$BrO_3^- + 6e^-_{(CB)} + 6H^+ \rightarrow Br^- + 3H_2O \tag{24}$$

On further increase of $KBrO_3$ addition only small enhancement was observed. This is due to adsorption effect of Br^- ion on TiO_2 surface which affects the catalytic activity of TiO_2.

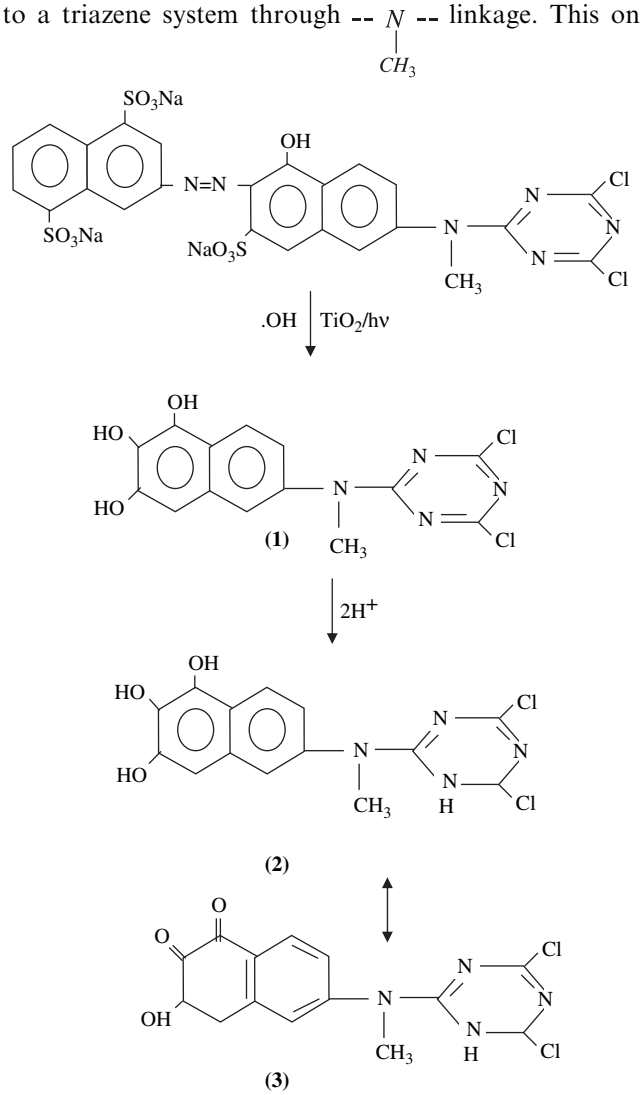
3.7. Photodegradation pathway

Based on the experimental results it is found that the hydroxyl radical is the primary oxidising species. This is also confirmed by the effect of isopropanol on the photocatalytic degradation. The addition of isopropanol, a known hydroxyl radical quencher, decreases the photodecolourisation and degradation efficiency.

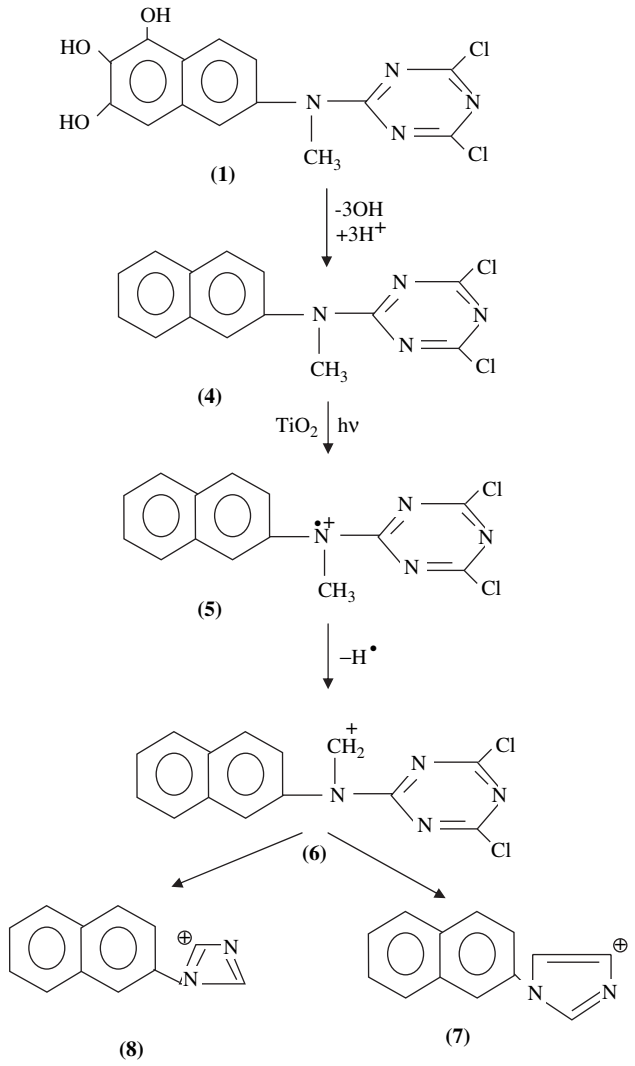
Since the oxidation of sulphonic groups to SO_4^{2-} takes place initially, a dual hole–radical mechanism can be proposed. According to this mechanism, direct h^+ oxidation of sulphonic groups takes place in combination with hydroxyl radical attack. As the decolourisation is very fast the attack of hydroxyl radical takes place first at the carbon atoms bearing the chromophoric azolinkage. Hence the fragments produced by the cleavage of the azo bond of the dye molecule must be the primary reaction intermediates. An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the dye after decolourisation through GC–MS analysis. The GC–MS analysis of the solution obtained after decolourisation showed the formation of the three main products with the retention times 11.314 min, 16.832 min and 21.727 min. These three products were identified based on their molecular ion and mass spectrometric fragmentation peaks and are given below.

Compound	Mass spectrum (m/z)
3	355,192,165,150,149,104,77,76,57,56
7	193,130,129,128,103,102,100,77,75,74,64,63,52
8	180,169,168,167,77,51

The formation of three compounds from the photoreaction of dye molecule is shown in Scheme 1. The attack of hydroxyl radical on the carbons bearing azolinkage and sulphonate groups leads to the formation of a trihydroxy compound **1**. The compound **1** on protonation forms **2** which isomerises to give compound **3**. The compound **1** on dehydroxylation and protonation gives **4** in which a naphthalene ring is linked to a triazene system through -- N -- linkage. This on



Scheme 1.



Scheme 1. (*continued*)

irradiation looses an electron from nitrogen atom forming a radical cation **5**. Compound **6** is formed from **5** by the loss of hydrogen atom. Compound **6** undergoes cyclisation giving rise to **7** and **8** with five and four membered ring systems, respectively.

4. Conclusions

The RO4 is easily degraded by TiO_2-P25 assisted photocatalysis in aqueous dispersion under irradiation by UV-A light. The dye is resistant to direct photolysis. The adsorption of RO4 on TiO_2 was found favourable by the Langmuir approach. The adsorption was maximum at pH 5. The optimum physico-chemical conditions for the degradation of 5×10^{-4} M solution at room temperature were determined to be: TiO_2-P25 concentration 4 g/l; initial pH range 7–10; initial H_2O_2 concentration 15 mm; initial $(NH_4)_2S_2O_8$ concentration 3 g/l; initial $KBrO_3$ concentration 3 g/l. The photocatalytic decolourisation and degradation obey pseudo-first order kinetics at low initial concentration. The initial decolourisation and degradation rates could be fitted to empirical Langmiur Hinshelwood equation up to 3×10^{-4} mol/l. The persulphate ions are found to oxidise the dye in the absence of catalyst. A dual hole–radical mechanism is proposed. Based on GC–MS analysis three products have been identified as intermediates of photocatalytic degradation.

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