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Optimization of solar photocatalytic degradation conditions of Reactive Yellow 14 azo dye in aqueous TiO_2

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Abstract

The photocatalytic decolourisation and degradation of an azo dye Reactive Yellow 14 (RY14) in aqueous solution with TiO_2-P25 (Degussa) as photocatalyst in slurry form have been investigated using solar light. The study on the effect of various photocatalysts on the decolourisation and degradation reveals the following order of reactivity: ZnO > TiO_2-P25 > TiO_2 (anatase). CdS, Fe_2O_3 and SnO_2 have negligible activity on RY14 decolourisation and degradation. The effects of various parameters such as catalyst loading and initial dye concentration on decolourisation and degradation have been investigated to find out optimum conditions. The decolourisation and degradation kinetics have been analysed. Both follow Langmuir kinetic model. A study on the effect of electron acceptors on photooxidation reveals that both decolourisation and degradation increase in the presence of H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$ to certain dosage beyond which the enhancement effect is negligible. Addition of dye assisting chemicals such as CO_3^{2-} and Cl^- inhibits the dye removal rate.

Keywords: AOPs; Solar energy; Reactive Yellow 14; TiO_2; Electron acceptors

1. Introduction

Synthetic dyes are the major industrial pollutants and water contaminants [1]. Textile wastewater introduced intensive colour and toxicity to the aquatic system. Reactive dyes are widely used in the textile industries because of their simple dyeing procedure and good stability during washing process [2]. Due to the complex aromatic structure and stability of these dyes, conventional biological treatment methods are ineffective for degradation [3–6]. Some physical and chemical techniques are currently available for the treatment of dye effluent. But these processes have only limited success.

In recent years attention has been focused on heterogeneous photocatalysis for the treatment of recalcitrant chemicals present in the wastewater [7]. Due to the high photocatalytic activity and stability of titanium dioxide, it is generally used as a photocatalyst for the removal of organic pollutants [8–13]. The main problem of heterogeneous photocatalysis is the separation of photogenerated electron–hole pair. These could be achieved by using either electron acceptors or hole scavengers.

Photodegradation of pollutants using TiO_2 with solar light can make it economically viable process since solar energy is an abundant natural energy source. This solar energy can be used instead of artificial light sources. The artificial light sources need high electrical power, which is costly and hazardous. Solar energy has been successfully used for photocatalytic degradation of pollutants [14–23]. Nogueira and Jardim [24] demonstrated how the photobleaching of some dye could be achieved by solar light irradiation using TiO_2 as photocatalyst. In our earlier work we have reported the photocatalytic degradation of Reactive Orange 4 azo dye in TiO_2 suspension using solar light [25].

For the practical application of TiO_2–sunlight process to dye wastewater, there is a need to determine the optimal conditions of experimental parameters. In the present investigation we have undertaken a photocatalytic degradation of mono azo dye Reactive Yellow 14 (RY14) and examined the various parameters to find out the optimum conditions for removal of colour and aromatic part of the dye. The chemical structure and its absorption maxima are given in Table 1.

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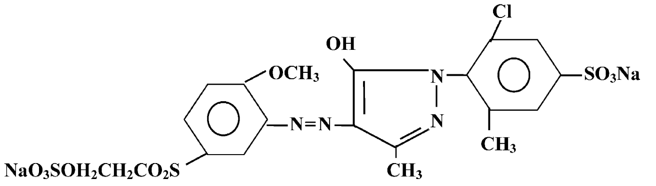
Table 1
Chemical structure of Reactive Yellow 14



2. Experimental

2.1. Material

The commercial azo dye Reactive Yellow 14 obtained from colour Chem Pondicherry was used as such. A gift sample of TiO_2-P25 was obtained from Degussa (Germany). It has an average particle size of 30 nm and a BET specific surface area of 55 m^2/g. ZnO has a particle size of 0.1–4 μm and a surface area of 10 m^2/g. TiO_2 (anatase) received from Aldrich Chemical Company has a medium particle size of approximately 1 μm with a specific surface area of 8.9 m^2/g. The other photocatalysts CdS, Fe_2O_3 and SnO_2 (S.D. Fine Chemicals) and analytical grade H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$ (Merck) were used as received. The double distilled water was used to prepare experimental solutions. The natural pH of the aqueous dye solution is 5.5. The pH of the solutions was adjusted using H_2SO_4 or NaOH.

2.2. Irradiation experiments

All photocatalytic experiments have been carried out under similar conditions on sunny days of April–May between 11 a.m. and 2 p.m. An open borosilicate glass tube of 50 ml capacity, 40 cm height and 20 mm diameter was used as a reaction vessel. The suspensions were magnetically stirred in dark for 30 min to attain adsorption–desorption equilibrium between dye and TiO_2. Irradiation was done in the open-air condition. Fifty milliliters of dye solution with TiO_2 was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution. During the illumination time no volatility of the solvent was observed.

2.3. Procedure

After dark adsorption the first sample was taken. 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 absorbances at 410 and 254 nm were measured. The absorbance at 410 nm is due to colour of the dye solution and it is used to monitor the decolourisation of the dye. The absorbance at 254 nm represents the aromatic content of RY14 and the decrease of absorbance at 254 nm indicates the degradation of aromatic part of the dye.

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

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

2.4. Solar light intensity measurements

Solar light intensity was measured for every 30 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set in the position of maximum intensity. The intensity of solar light was measured using a LT Lutron LX-10/A Digital Lux meter and the intensity was 1250 × 1000 lx. The intensity was nearly constant during the experiments.

3. Results and discussion

3.1. Photodegradability

The photocatalytic degradability experiments were carried out under the following conditions: (i) dye solution with the solar light in the absence of TiO_2; (ii) dye solution with TiO_2 in dark; (iii) dye solution under irradiation of solar light with TiO_2. The results are shown in Fig. 1. The dye is resistant to self-photolysis in solar light. After 30 min of magnetic stirring in the presence of photocatalyst without solar irradiation, about 22% decrease in concentration was observed from absorbance measurements. This is due to the adsorption of dye molecule on the surface of TiO_2. No degradation was observed for the dye solution with TiO_2 in solar light without purging air (data not given). These results indicate that the degradation is only due to band gap excitation of photocatalysts and not to sensitized degradation. The irradiation with the catalysts caused 100% of decolourisation and 73.5% of degradation after 80 min. This shows that the dye could be effectively decolourised and degraded by solar light using TiO_2. The decolourisation of the dye is faster than its degradation. The fast decolourisation of the dye is due to the initial electrophilic cleavage of its chromophoric azo (–N=N–) bond. Azo bonds are most active in these dyes and they are oxidised by positive hole and hydroxyl radical and reduced by electron in the conduction band [26]. RY14 contains one azo bond and decolourisation of RY14 shows

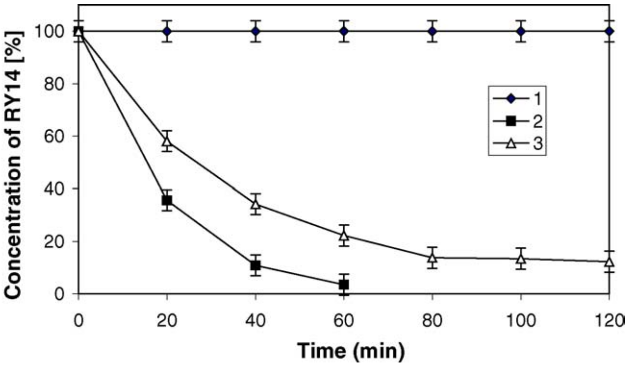


Fig. 1. Effect of solar irradiation of RY14 by solar/TiO_2-P25. TiO_2-P25 = 4 g/l, [RY14] = 5×10^{-4} mol/l, pH 5.5 ± 0.1. Dye solution irradiated with solar light in the: (1) absence of TiO_2-P25 and (2 and 3) presence of TiO_2-P25. (2) Decolourisation and (3) degradation.

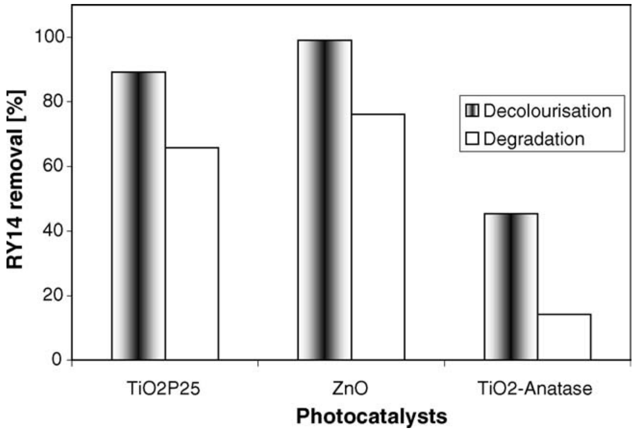


Fig. 2. Effect of various photocatalysts on decolourisation and degradation of RY14. [RY14] = 5 × 10^{-4}, pH 5.5 ± 0.1, irradiation time = 40 min.

that the chromophoric azo bond of dye molecule is destroyed. The degradation of aromatic part of the dye molecule produced a number of intermediate compounds and removal of these intermediates took longer time. The degradation of aromatic part of the dye molecule was not complete. Only 90% of the dye was removed even after 15 h of irradiation. This shows that some of the intermediates produced are resistant to photocatalytic oxidation reaction.

3.2. *Effect of various photocatalysts*

The photooxidation by other photocatalysts such as TiO_2-P25, TiO_2 anatase, ZnO, SnO_2, CdS and Fe_2O_3 has been investigated (Fig. 2). SnO_2, Fe_2O_3 and CdS have negligible activity on RY14 decolourisation and degradation and hence they are not shown in Fig. 2. TiO_2-P25 and ZnO are found to be more efficient when compared to TiO_2 anatase. The decolourisation efficiencies of TiO_2-P25, ZnO and TiO_2 anatase are 89.1, 99.0, and 45.2%, respectively, at the time of 40 min. At the same time the degradation efficiencies of these catalysts are 65.7, 76.0 and 14.2%. Generally, semiconductors having large band gap have strong photocatalytic activities. TiO_2 and ZnO have a band gap 3.2 eV and show strong photocatalytic activities. The order of activities of the photocatalysts is ZnO > TiO_2-P25 > TiO_2 anatase in both processes. ZnO is found to be more efficient than TiO_2-P25 and TiO_2 anatase. Kormann et al. [33] stated that the quantum yield of H_2O_2 production in illuminated aqueous suspensions of ZnO was found to be one order of magnitude higher than the corresponding value for TiO_2-P25. Poulious and Tsachpinis [34] found that ZnO is more efficient than TiO_2-P25 in the mineralisation of Reactive Black 5 dyes in UV light. Govea et al. [28] found that ZnO is more efficient than TiO_2 anatase in reactive dye degradation. But ZnO has the disadvantage of undergoing photocorrosion under acidic condition on illumination. In the case of TiO_2 anatase the decolourisation and degradation proceed with lower efficiencies compared with TiO_2-P25. The photocatalytic activity of semiconductors is also dependent on the crystallinity, particle size, surface area and concentration of the impurities in the catalysts. The high photoreactivity of TiO_2-P25 compared to TiO_2 anatase is due to the slow recombination of electron–hole pair and large surface area. The surface area of TiO_2-P25 is six times as high as that of TiO_2 anatase [35]. Since band gap of SnO_2 is 3.87 eV, solar light energy is not sufficient to activate the catalyst. CdS and Fe_2O_3 have smaller band gap (2.4 and 2.3 eV) which permits rapid recombination of hole and electron and so conduction band electron in these semiconductors cannot move into the electron acceptors in the solution rapidly. Hence, a negligible photocatalytic activity for decolourisation and degradation is observed in these catalysts. In the present study TiO_2-P25 was chosen because of its high photocatalytic activity, high surface area, resistance to photocorrosion, biological immunity and low cost.

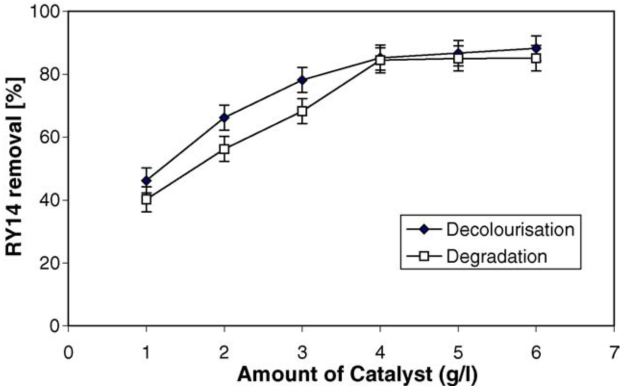


Fig. 3. Effect of catalyst loading on the decolourisation and degradation of RY14. [RY14] = 5 × 10^{-4} mol/l, pH 5.5 ± 0.1. Irradiation time: decolourisation = 40 min and degradation = 60 min.

3.3. *Effect of catalyst loading*

In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for the efficient removal of dye. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process [27–29]. The effect of catalyst weight (TiO_2-P25) on the percentage removal of RY14 was investigated in the range of 1–6 g/l of the catalyst, at 5 × 10^{-4} mol/l dye concentration and at pH 5.5. The results are shown in Fig. 3. The results clearly show that the increase in catalyst weight from 1 to 4 g/l increases the dye decolourisation sharply from 46.2 to 85.2% at the time of 40 min and degradation from 40.2 to 84.4% at 60 min. The enhancement of removal rate is due to: (i) the increase in the amount of catalyst weight which increases the number of dye molecule adsorbed and (ii) the increase in the density of particles in the area of illumination. But at concentrations in the range of 4–6 g/l the decolourisation and degradation efficiencies are almost constant. This may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration. The optimum concentration of the catalyst for efficient solar photodecolourisation and degradation is found to be 4 g/l. Bekoblet and Ozkosemen [30] found that 4 g/l of TiO_2 was the optimum catalyst loading for efficient degradation and stated that above this concentration the suspended particles of TiO_2 block the UV-light passage and reduce the formation of electron–hole pairs and active sites. Garcia and Takashima [31] found that 8 g/l of TiO_2 loading were

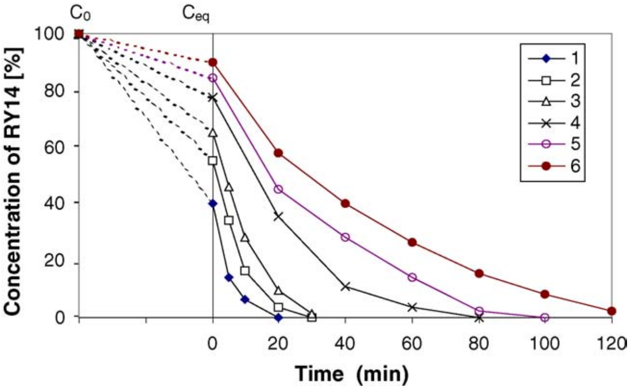


Fig. 4. Effect of initial dye concentrations on the decolourisation of RY14. $TiO_2 = 4$ g/l, pH 5.5 ± 0.1. (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 5×10^{-4} mol/l, (5) 7×10^{-4} mol/l and (6) 9×10^{-4} mol/l.

most efficient in degradation and mineralisation of imazaquin in UV light. Alhakimi et al. [32] reported that a catalyst loading of 3 g/l was found to be optimum for potassium hydrogen phthalate degradation using TiO_2 and sunlight. From these results it is clear that the optimum catalyst loading is not common for all photocatalytic reactions and it is dependent on various experimental parameters. Hence, the optimum concentration of 4 g/l was used as the catalyst dosage for all photocatalytic reactions.

3.4. *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 has been investigated in the range of 1×10^{-4} to 9×10^{-4} mol/l. The results are shown in Figs. 4 and 5. It is found that the increase in the dye concentration decreases the removal rate (Table 2). Similar results have been reported for the photocatalytic oxidation of other dyes [27,36,37]. Increase in the dye concentration from 1 to 9×10^{-4} mol/l results in the decrease of the decolourisation from 100 to 41.8% and degradation from 90.7 to 27.5% in 20 min, respectively. When the dye concentration increases, the amount of the dye adsorbed on the catalytic surface increases. This affects the catalytic activity of TiO_2. The increase in the dye concentration also decreases the path length of photon entering into the dye solution. At high dye concentration the dye molecules may absorb a significant amount of solar light rather than the catalyst and this may also reduce the catalytic efficiency [38].

Table 2
Rate constants of RY14 decolourisation and degradation by solar O_2-P25 process

Initial concentration ($\times 10^{-4}$ mol/l)	Decolourisation, k' (min^{-1})	Degradation, k' (min^{-1})
1	0.214	0.083
2	0.136	0.058
3	0.096	0.045
5	0.019	0.019
7	0.011	0.016
9	0.008	0.013

The photocatalytic decolourisation and degradation of RY14 dye containing TiO_2 obey pseudo-first-order kinetics. At low initial dye concentrations the rate expression is given in Eq. (1)

$$\frac{-\mathrm{d}\,[C]}{\mathrm{d}t} = k'[C] \tag{1}$$

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 taken as the initial dye concentration for kinetic analysis. Integration of Eq. (1) (with the limit of $C = C_o$ at $t = 0$ with C_o being the equilibrium concentration of the bulk solution) gives (2)

$$\ln\left[\frac{C_o}{C}\right] = k't \tag{2}$$

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

A plot of $\ln C_o/C$ versus t for photodecolourisation and degradation is shown in Figs. 6 and 7. A linear relation between dye concentration and irradiation time has been observed.

Many authors [39–42] have used the Langmuir kinetic expression to analyse the heterogeneous photocatalytic reaction successfully. The experimental data have been rationalized in terms of the Langmuir kinetic model to describe the solid–liquid reaction. The rate of oxidation of RY14 dye at surface is propor-

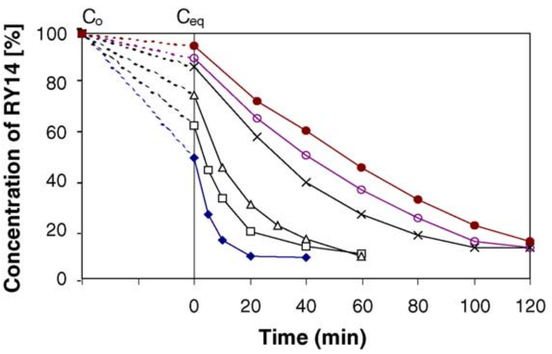


Fig. 5. Effect of initial dye concentrations on the degradation of RY14. $TiO_2 = 4$ g/l, pH 5.5 ± 0.1. (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 5×10^{-4} mol/l, (5) 7×10^{-4} mol/l and (6) 9×10^{-4} mol/l.

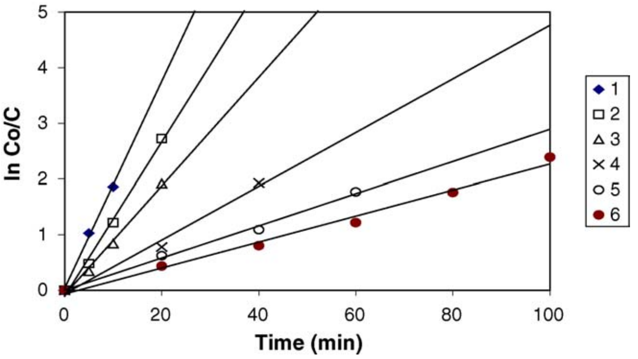


Fig. 6. Kinetics of RY14 dye decolourisation for different initial concentrations (experimental conditions, see Fig. 4): (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 5×10^{-4} mol/l, (5) 7×10^{-4} mol/l and (6) 9×10^{-4} mol/l.

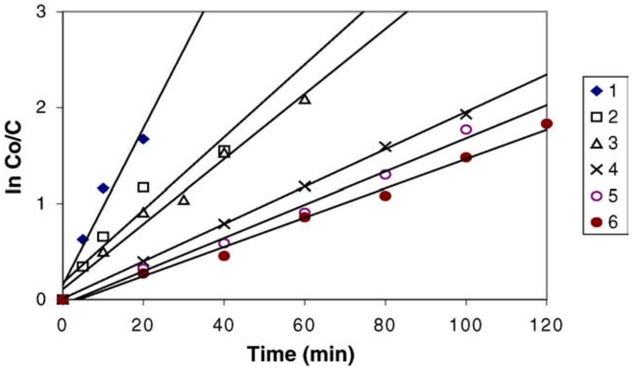


Fig. 7. Kinetics of RY14 dye degradation for different initial concentrations (experimental conditions, see Fig. 5): (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 5×10^{-4} mol/l, (5) 7×10^{-4} mol/l and (6) 9×10^{-4} mol/l.

tional to the surface coverage of the dye on the TiO_2 assuming that the dye is strongly adsorbed on the catalyst surface than the intermediate products [43]. The effect of dye concentration on the rate of degradation is given in the form of Eqs. (3) and (4) [44].

$$r = \frac{K_1 k C}{1 + K_1 C} \tag{3}$$

$$\frac{1}{r} = \frac{1}{K_1 k C} + \frac{1}{k} \tag{4}$$

where C is the concentration of the dye at time 't', K_1 the constant related to adsorption and k is to the reaction properties of the dye. The applicability of Langmuir equation to the decolourisation and degradation has been confirmed by the linear plot obtained by plotting reciprocal of the initial rate ($1/r$) against reciprocal of the initial concentration ($1/C$) as shown in Fig. 8. The values K_1 and k are found to be 0.26×10^{-4} M and 0.35×10^{-4} M min^{-1} for decolourisation and 0.33×10^{-4} M and 0.50×10^{-4} M min^{-1} for degradation, respectively.

3.5. *Effect of addition of H_2O_2*

In order to keep the efficiency of the added H_2O_2, it is necessary to choose the optimum concentration of H_2O_2 according to the type and concentration of the pollutants. The effect of addition of H_2O_2 (5–25 mmol) on the photocatalytic oxidation has been investigated. The results are shown in Fig. 9. The addition of H_2O_2 in the range of 5–20 mmol increases the decolourisation from 78.1 to 89.2% in 20 min and degradation from 70.1 to 82.3% in 40 min. Further increase in the H_2O_2 concentration from 20 to 25 mmol limits the removal rate. Hence, 20 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 up to the optimal load beyond which inhibition occurred) had been reported in dye degradation [45] and organic pollutant degradation [46]. The enhancement of decolourisation and degradation by addition of H_2O_2 is due to increase in the hydroxyl radical concentration by the following ways:

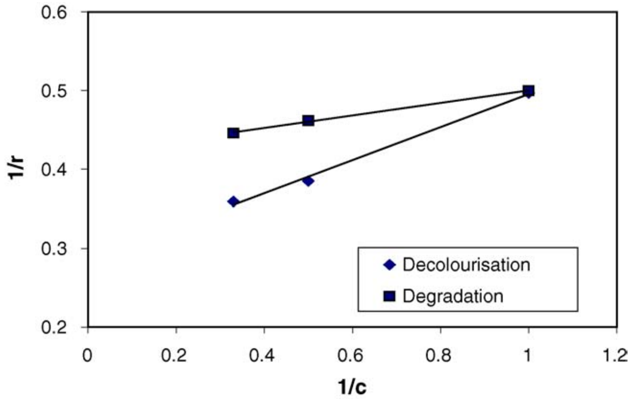


Fig. 8. Linearised reciprocal kinetic plot of the photodecolourisation and photodegradation of RY14 (experimental conditions, see Fig. 6).

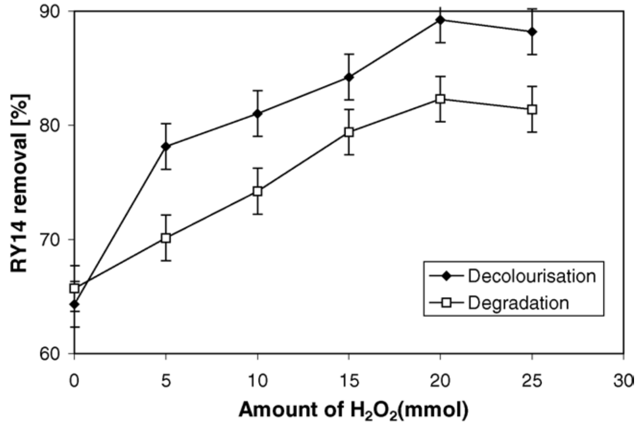


Fig. 9. Effect of addition of H_2O_2 on the decolourisation and degradation of RY14. TiO_2 = 4 g/l, [RY14] = 5×10^{-4} mol/l, pH 5.5 ± 0.1. Irradiation time: decolourisation = 20 min and degradation = 40 min.

(i) According to Okamoto et al. [47], oxygen is the primary acceptor of the conduction band electron with formation of superoxide radical anion (Eq. (5)). H_2O_2 can compensate for the O_2 lack and play a role as an external electron scavenger according to Eq. (6). It can trap the photogenerated conduction band electron, thus inhibiting the electron–hole recombination and producing hydroxyl radicals as shown by the equations:

$$TiO_2 e_{(CB)}{}^- + O_2 \rightarrow O_2{}^{\bullet -} \tag{5}$$

$$e_{(CB)}{}^- + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- \tag{6}$$

(ii) H_2O_2 may also be photolysed to produce hydroxyl radicals directly (Eq. (7))

$$H_2O_2 \xrightarrow{h\nu} 2{}^{\bullet}OH \tag{7}$$

H_2O_2 has extremely low absorption of solar light. Hence, the oxidation of the dye by photolytic H_2O_2 (Eq. (7)) will be insignificant.

(iii) H_2O_2 also reacts with superoxide anion to form ${}^{\bullet}OH$ radical (Eq. (8)).

$$H_2O_2 + O_2{}^{\bullet -} \rightarrow {}^{\bullet}OH + H^+ + O_2 \tag{8}$$

At high H_2O_2 dosage (20 mmol) the removal rate decreases due to:

(i) Hydroxyl radical scavenging effect of H_2O_2. The reaction between excess hydrogen peroxide and hydroxyl radical (${}^{\bullet}OH$) forms hydroperoxy radical. These hydroperoxy radicals are much less reactive and do not contribute to oxidative degradation of the dye (Eqs. (9) and (10)).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (9)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (10)$$

(ii) H_2O_2 is also a powerful hole scavenger [48]. In excess it may react with holes to produce oxygen and proton. In photocatalytic degradation, hole directly oxidises the dye and with water produces hydroxyl radical. Hence, the removal of holes decreases the dye removal rate (Eq. (11)).

$$H_2O_2 + 2h_{VB}^{+} \rightarrow O_2 + 2H^{+} \quad (11)$$

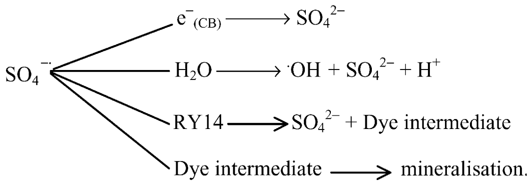
3.6. *Effect of $S_2O_8^{2-}$*

The effect of addition of $S_2O_8^{2-}$ on the photocatalytic oxidation of RY14 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. 10. Addition of 1–3 g/l of $(NH_4)_2S_2O_8$ increases the decolourisation from 88.0 to 98.0% in 20 min and degradation from 74.3 to 79.1% in 40 min. Further increase in the addition (4 g/l) decreases the decolourisation. Similar enhancement was reported for the addition of $S_2O_8^{2-}$ [49–51]. Further increase in the addition above 4g/l increases the decolourisation by 1.39% and degradation by 0.91%. Addition of persulphate to photocatalytic processes enhances the decolourisation rate by the following three ways:

(i) Persulphate ion scavenges the conduction band electron and promotes the charge separation and production of other oxidising species namely sulphate radical anion (Eq. (12)).

$$S_2O_8^{2-} + TiO_2e_{(CB)}^{-} \rightarrow SO_4^{\bullet -} + SO_4^{2-} \quad (12)$$

(ii) $S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet -}$) both thermally and photolytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes by the following ways:



(iii) 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. (12)). 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 photogenerated holes (Eq. (15)) and with hydroxyl radicals (Eq. (16)).

$$SO_4^{\bullet -} + h^{+} \rightarrow SO_4^{\bullet -} \quad (15)$$

$$SO_4^{2-} + OH \rightarrow SO_4^{\bullet -} + OH^{-} \quad (16)$$

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

3.7. *Effect of BrO_3^{-}*

BrO_3^{-} is an efficient electron acceptor and used as an additive to enhance photocatalytic degradation rates [27,34,52,53]. The effect of addition of BrO_3^{-} on the photocatalytic decolourisation and degradation is shown in Fig. 11. The addition of $KBrO_3$ from 1 to 4 g/l increases the decolourisation from 69.2 to 78.2% by the time of 20 min and the degradation from 70.7 to 81.4% by the time of 40 min. On further increase in $KBrO_3$ addition there is no increase in the removal rate. The enhancement of the removal rate is due to its electron scavenging effect by the reaction between BrO_3^{-} ion and conduction band electron (Eq. (17)). Martin et al. [54] reported that BrO_3^{-} scavenges conduc-

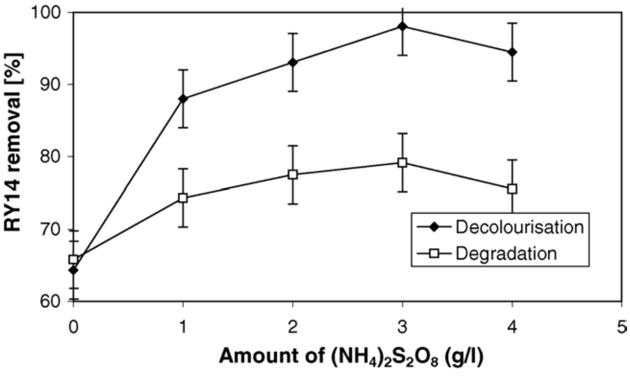


Fig. 10. Effect of addition of $(NH_4)_2S_2O_8$ on the decolourisation and degradation of RY14. TiO_2 = 4 g/l, [RY14] = 5×10^{-4} mol/l, pH 5.5 ± 0.1. Irradiation time: decolourisation = 20 min and degradation = 40 min.

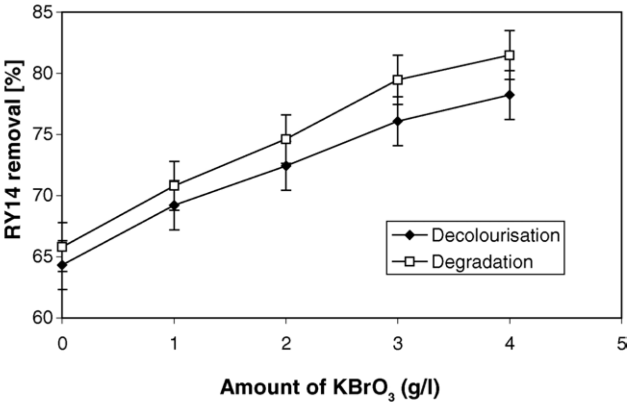


Fig. 11. Effect of addition of $KBrO_3$ on the decolourisation and degradation of RY14. TiO_2 = 4g/l, [RY14] = 5×10^{-4} mol/l, pH 5.5 ± 0.1. Irradiation time: decolourisation = 20 min and degradation = 40 min.

tion band electron more efficiently than oxygen.

$$BrO_3^- + 6e_{(CB)}^- + 6H^+ \rightarrow [BrO_2^-, HOBr] \rightarrow Br^- + 3H_2O \qquad (17)$$

Further increase of $KBrO_3$ from 3 to 4 g/l increases the decolourisation by 0.55% and degradation by 2%. This is due to the adsorption effect of Br^- ion on TiO_2 surface, which affects the catalytic activity of TiO_2.

3.8. *Effect of CO_3^{2-} and Cl^-*

The other auxiliary chemicals such as Na_2CO_3 and NaCl are used in the dyeing process. Na_2CO_3 is added to adjust the pH of the dye bath, which is important in fixing the dye on the fabrics and in the fastness of colour. Sodium chloride is mainly used in the dyeing process for the transfer of dyestuff to fabric [55]. Therefore, the dye industry wastewater contains a considerable amount of carbonate and chloride ions. Hence, it is important to study the influence of CO_3^{2-} and Cl^- ions in the photocatalytic degradation.

The effect of addition of Na_2CO_3 on the photocatalytic oxidation of RY14 is shown in Fig. 12. Addition of 1–4 g/l Na_2CO_3 decreases the removal from 62.3 to 56.4% for decolourisation by the time of 20 min and degradation from 59.2 to 48.2% by the time of 40 min. Similar observations have been reported earlier in literature [56,57]. The decrease in degradation efficiency of the dye is due to hydroxyl radical scavenging property of carbonate ion as shown in the following equations ((18) and (19)):

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow OH^- + CO_3^{\bullet -} \qquad (18)$$

$$HCO_3^- + {}^{\bullet}OH \rightarrow H_2O + CO_3^{\bullet -} \qquad (19)$$

Thus, the primary oxidant hydroxyl radical decreases gradually with the increase in carbonate ion and consequently there is a significant decrease in photocatalytic degradation.

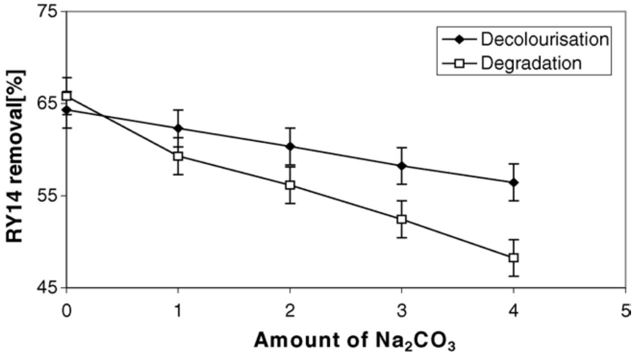


Fig. 12. Effect of addition of Na_2CO_3 on the decolourisation and degradation of RY14. TiO_2 = 4 g/l, [RY14] = 5×10^{-4} mol/l, pH 5.5 ± 0.1. Irradiation time: decolourisation = 20 min and degradation = 40 min.

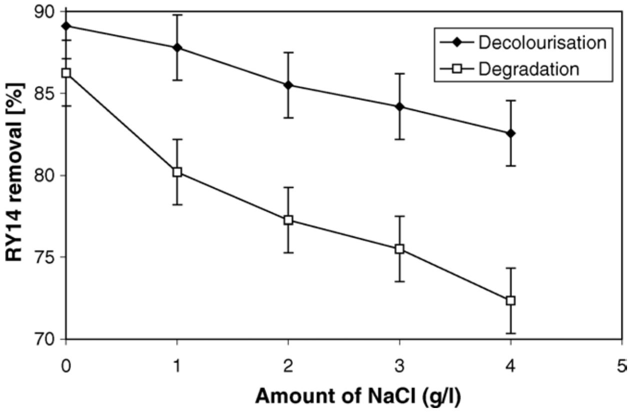


Fig. 13. Effect of addition of NaCl on the decolourisation and degradation of RY14. TiO_2 = 4 g/l, [RY14] = 5×10^{-4} mol/l, pH 5.5 ± 0.1. Irradiation time: decolourisation = 40 min and degradation = 80 min.

The influence of Cl^- on the photocatalytic oxidation of RY14 has been studied using NaCl. The results are shown in Fig. 13. Increase in the addition of Cl^- ion from 1 to 4 g/l to the reaction solution decreases the decolourisation from 87.7 to 82.5% by the time of 40 min and degradation from 80.1 to 72.3% by the time of 80 min. Similar observation was reported in the organic pollutant degradation [39]. The decrease in degradation efficiency in the presence of chloride ion is due to the hole scavenging and hydroxyl radical scavenging properties of chloride ion [58,59] (Eqs. (20) and (21)).

$$Cl^- + h_{VB}^+ \rightarrow Cl^{\bullet} \qquad (20)$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet -} \qquad (21)$$

The reaction of dye molecule with the hole has to compete with this reaction (Eq. (20)). The chloride radical anions formed can also block the reactive sites of the catalyst surface. The inhibitory effect of chloride and phosphate ion on the photocatalytic degradation has been reported [60]. The inhibiting effect of CO_3^{2-} ion is greater than the inhibiting effect of Cl^- ion.

4. Conclusions

The RY14 is successfully degraded by TiO_2-P25 assisted photocatalysis in aqueous dispersion under irradiation by solar light. The dye is resistant to direct photolysis. The optimum physico-chemical conditions for the decolourisation and degradation of 5×10^{-4} mol/l solution at room temperature were as follows: TiO_2-P25 concentration 4 g/l; initial H_2O_2 concentration 20 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 concentrations. The initial decolourisation and degradation rates could be fitted to Langmuir equation up to 3×10^{-4} mol/l. The persulphate ions are found to oxidise the dye in the absence of catalyst. The presence of auxiliary chemicals such as Na_2CO_3 and NaCl decreases the photocatalytic decolourisation and degradation.

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