



Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology

M. Muruganandham, M. Swaminathan*

Department of Chemistry, Annamalai University, Annamalai Nagar 608002, India

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Abstract

The photochemical decolourisation of chlorotriazine reactive azo dye Reactive Orange 4 (RO4) has been carried out by Fenton and photo-Fenton processes. The effects of solution pH, applied H_2O_2 , Fe^{2+} dose, UV light intensity have been studied. The increase of initial dye concentration decrease the removal rate. Under optimum conditions the photo-Fenton process is found to be more efficient than Fenton process. About 2% of colour resurgens was observed at the end of the reaction.

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1. Introduction

Wastewaters from textile and dye industries are highly coloured with significant amount of auxiliary chemicals. The discharge of these wastewater introduced intensive colour and toxicity to aquatic environment causing serious environmental problem [1]. Reactive dyes are widely used in the textile industries because of its 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]. Hence, the

concentration remains constant in the environment. A number of physical and chemical techniques had been reported for the treatment of dye effluents. Among these, the advanced oxidation processes are more efficient as they are capable of mineralizing a wide range of organic pollutants. In our laboratory, we had reported the photocatalytic degradation of Reactive Orange 4 (RO4) using $\text{TiO}_2\text{P25}$ as catalyst [4,5] and H_2O_2 –UV process [6].

In recent years attention have been focused on photochemical advanced oxidation processes using Fenton reagent with UV light for the treatment of wastewater. Fenton reagent had been found to be effective in degrading the refractory organic contaminants such as chlorophenols [7,8], chlorobenzene [9], nitrophenols [10] and dye pollutants [11–14]. The oxidation power of Fenton reagent is due to the

* Corresponding author. Tel./fax: +914144-220572.

E-mail address: chemsam@yahoo.com (M. Swaminathan).

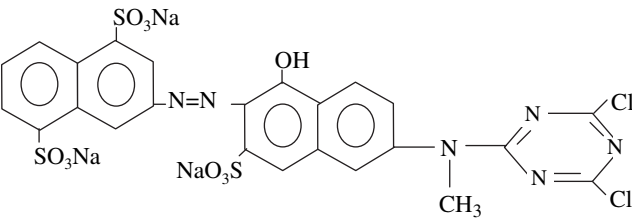
Name	Chemical Structure	λ_{\max} (nm)
Reactive Orange 4		489

Fig. 1. Chemical structure and absorption maxima of RO4.

generation of hydroxyl radical ($\cdot\text{OH}$) during the iron catalysed decomposition of hydrogen peroxide in acid medium. The hydroxyl radical with a high oxidation potential (2.8 eV) attacks and completely destroys the pollutants in Fenton process. The degradation of pollutants can be considerably improved by using UV-radiation. This is due to the generation of additional hydroxyl radicals. This photo-Fenton process had been effectively used to degrade the pollutants [15–18].

For economic colour removal of dye wastewater by Fenton and photo-Fenton processes, there is a need to determine the optimal conditions of experimental parameters. We have undertaken a reactive class mono azo dye Reactive Orange 4 and investigated the influence of various experimental parameters on the photooxidation.

The Reactive Orange 4 dye (C.I. 18260, M.wt. 769.21) is extensively used in dyeing the textile fabrics. The chemical structure and absorption maxima of RO4 are shown in Fig. 1.

2. Experimental

2.1. Material

Reactive Orange 4 dye obtained from Colour Chem, Pondicherry, was used as received. AnalaR H_2O_2 (30 w/w), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck) were used as received. The experimental solutions were prepared using double distilled water. The pH of the solution was adjusted using H_2SO_4 and NaOH.

2.2. Photoreactor

Heber multilamp photoreactor model HML-MP 88 (Fig. 2) 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 center. 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

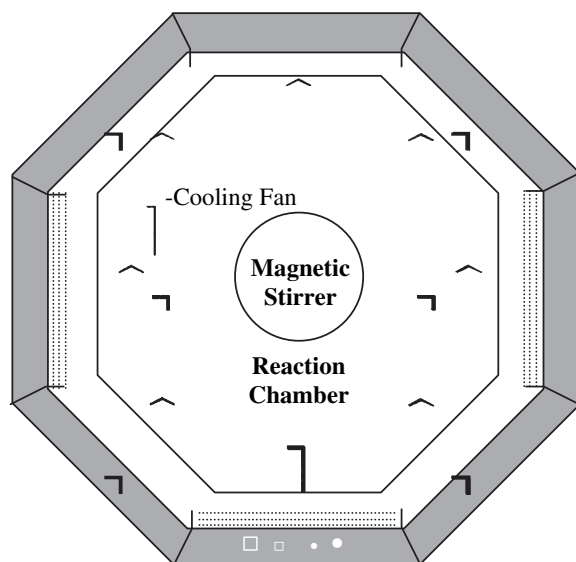


Fig. 2. Schematic diagram of photoreactor.

exposure length of 330 mm. The irradiation was carried out using four parallel medium pressure Mercury lamps.

2.3. Analysis

A desired molar ratio of dye/ Fe^{2+} / H_2O_2 solution was freshly prepared from FeSO_4 , H_2O_2 and the dye stock solution. The pH of the solutions was adjusted to 3.0. For Fenton process, the solution mixtures were kept in dark. In all cases, 50 ml of reaction mixture was irradiated. At specific time intervals 1–2 ml of the sample was withdrawn. NaOH solution was used to quench the oxidation by raising the pH to 7. At this pH further generation of hydroxyl radical is prevented. The sample (1 ml) was suitably diluted and its absorbance at 489 nm was measured. The absorbance at 489 nm is due to the colour of the dye solution ($n \rightarrow \pi^*$ transition in $\text{N}=\text{N}$ group) and it is used to monitor the decolourisation of 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

3.1. Photochemical degradability

Initially, the experiments were carried out under the following conditions: (i) dye + UV, (ii) dye + H_2O_2 + dark, (iii) dye + H_2O_2 + UV, (iv) dye + H_2O_2 + Fe^{2+} in dark (Fenton process), (v) dye + H_2O_2 + Fe^{2+} + UV (photo-Fenton process) and (vi) dye + Fe^{2+} + UV. The decolourisation results are shown in Fig. 3. From the results it is clear that the dye is resistant to (i) direct photolysis of UV light and (ii) irradiation in the presence of Fe^{2+} alone. For H_2O_2 with dye in dark 8.55% decolourisation was observed. But the combined action of UV and H_2O_2 caused 88.68% of decolourisation in 150 min. For Fenton process the colour removal was 56.2%, 79.89%, 91.4%, 97.28%, at 20, 40, 60, 120 min, respectively. In photo-Fenton process 57.81%, 95.5%, and 98.17% of decolourisation was observed at 20, 40, 60 min,

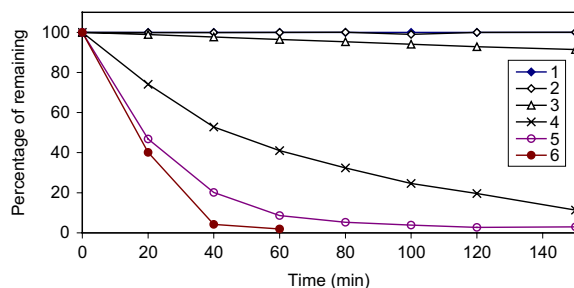
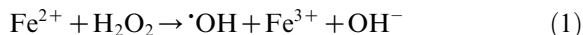


Fig. 3. Photochemical degradability of RO4 under different conditions. (1) Dye + UV, (2) dye + Fe^{2+} + UV, (3) dye + H_2O_2 + dark, (4) dye + H_2O_2 + UV, (5) dye + H_2O_2 + Fe^{2+} + dark (Fenton process), (6) dye + H_2O_2 + Fe^{2+} + UV (photo-Fenton process). $[\text{RO4}] = 5 \times 10^{-4}$ mol/l; $[\text{H}_2\text{O}_2] = 10$ mmol; $[\text{Fe}^{2+}] = 0.05$ mmol; pH = 3.

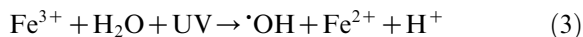
respectively. Initially, a large degree of removal was observed in both processes. This is due to fast reaction of Fe^{2+} and H_2O_2 producing hydroxyl radicals. At 40 min colour removal was 79.89% in Fenton and 95.5% in photo-Fenton process. Hence, photo-Fenton process is more efficient than Fenton process.

Decolourisation of dye is mainly due to hydroxyl radical generated by chemical and photochemical reactions of each process. Azo bonds are more active in these dyes. RO4 contain one azo bond and decolourisation of dye is due to the initial electrophilic cleavage of its chromophoric azo ($-\text{N}=\text{N}-$) bond attached to naphthalene ring.

The hydroxyl radical generated in Fenton process is due to iron catalysed decomposition of H_2O_2 (Eq. (1)) [19].



In photo-Fenton process in addition to the above reaction the formation of hydroxyl radical also occurs by the following reactions (Eqs. (2) and (3)):



The relative efficiencies of the above processes are in the following order: $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{UV} > \text{Fe}^{2+} + \text{H}_2\text{O}_2 > \text{H}_2\text{O}_2 + \text{UV} > \text{H}_2\text{O}_2 + \text{dark} > \text{dye} + \text{UV} = \text{dye} + \text{Fe}^{2+} + \text{UV}$.

The high efficiency of photo-Fenton process is due to the formation of more hydroxyl radical than the other processes. Iron catalysed decomposition of H_2O_2 is more than the UV catalysed decomposition of H_2O_2 . Hence, Fenton process is more efficient than H_2O_2 –UV process.

3.2. Effect of pH

The pH of the solution controls the production rate of hydroxyl radical and the concentration of Fe^{2+} . Hence, pH is an important parameter for Fenton and photo-Fenton processes. The effect of pH on the decolourisation of RO4 by Fenton and photo-Fenton processes is shown in Fig. 4. Increase of the pH of the solution from 1–3 increases the decolourisation sharply from 9.28 to 95.82% in photo-Fenton process and 4.71% to 79.8% in Fenton process at 40 min. Further increase of pH from 3–7 decreases the colour removal from 95.82% to 7.28% and 79.89 to 3.78% for photo-Fenton and Fenton processes, respectively. Hence, pH 3 is found to be the optimum pH for both processes. Our results are in good agreement with early reports [14,20,21]. In these processes the decrease in decolourisation at pH above 3 is due to the coagulation of hydroxo complex of Fe^{3+} formed during the reaction [14]. At low pH the removal rate is limited due to the hydroxyl radical scavenging effects of H^+ ion (Eq. (4)) [22].

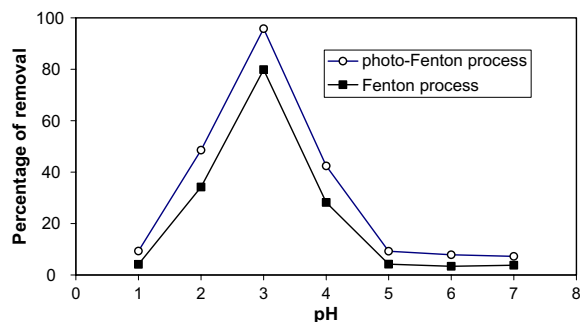
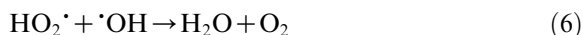
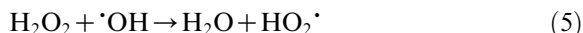


Fig. 4. Effect of pH on the decolourisation of RO4 by Fenton and photo-Fenton processes. $[\text{RO4}] = 5 \times 10^{-4}$ mol/l; $[\text{H}_2\text{O}_2] = 10$ mmol; $[\text{Fe}^{2+}] = 0.05$ mmol.

3.3. Effect of H_2O_2 dosage

Initial concentration of H_2O_2 plays an important role in the Fenton and photo-Fenton processes. The effect of addition of H_2O_2 (5–20 mmol for Fenton process and 5–25 mmol for photo-Fenton process) on the decolourisation of RO4 is shown in Figs. 5 and 6. In Fenton process, the addition of H_2O_2 from 5–15 mmol increases the decolourisation from 46.74% to 65.74% at 20 min. Further increase from 15–20 mmol causes no significant change in decolourisation. In photo-Fenton process, addition of 5–20 mmol increases decolourisation from 52.26% to 70.21% at 20 min. Further increase from 20–25 mmol increase the decolourisation slightly (70.21% to 71.33%). The increase in the decolourisation is due to the increase in hydroxyl radical concentration by the addition of H_2O_2 . But at high dosage of H_2O_2 the decrease in decolourisation is due to the hydroxyl radical scavenging effect of H_2O_2 (Eqs. (5) and (6)) and recombination of hydroxyl radicals (Eq. (7)) [23].



In Fenton and photo-Fenton processes the decolourisation efficiency is close to 97% for all H_2O_2 dosages at the end (Figs. 5 and 6). This implies that the overall removal efficiency can make no difference, in spite of the initial removal

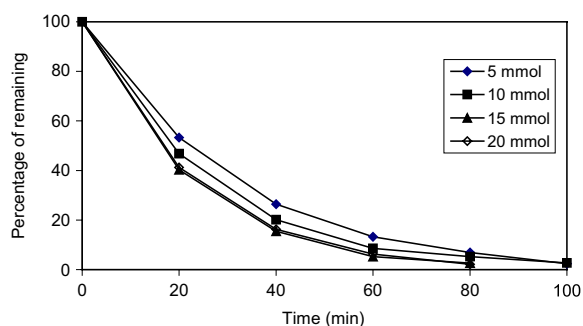


Fig. 5. Effect of addition of H_2O_2 on the decolourisation of RO4 by Fenton process. $[\text{RO4}] = 5 \times 10^{-4}$ mol/l; $[\text{Fe}^{2+}] = 0.05$ mmol; pH = 3.

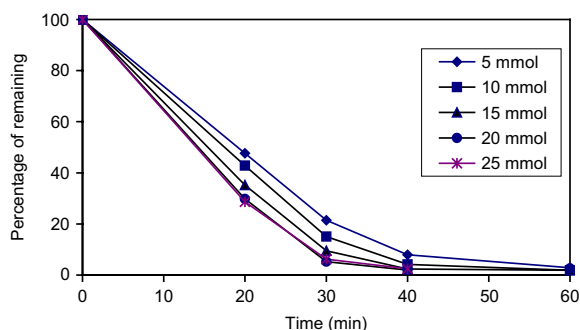


Fig. 6. Effect of addition of H_2O_2 on the decolourisation of RO4 by photo-Fenton process. $[\text{RO4}] = 5 \times 10^{-4} \text{ mol/l}$; $[\text{Fe}^{2+}] = 0.05 \text{ mmol}$; $\text{pH} = 3$.

being quite different from each other for all H_2O_2 dosages.

Hence, 15 mmol and 20 mmol of H_2O_2 appear as optimal dosages for Fenton and photo-Fenton processes, respectively.

3.4. Effect of ferrous dosage

Amount of ferrous ion is one of the main parameters to influence the Fenton and photo-Fenton processes. The effect of addition of Fe^{2+} ion (0.01 mmol to 0.1 mmol) on the decolourisation of RO4 has been studied. The results are shown in Figs. 7 and 8. In Fenton process addition of Fe^{2+} from 0.01 mmol to 0.1 mmol increases colour removal from 7.71% to 83.53% at 20 min and in photo-Fenton process the increase is from 24.68% to 97.85% for the same addition at 20 min.

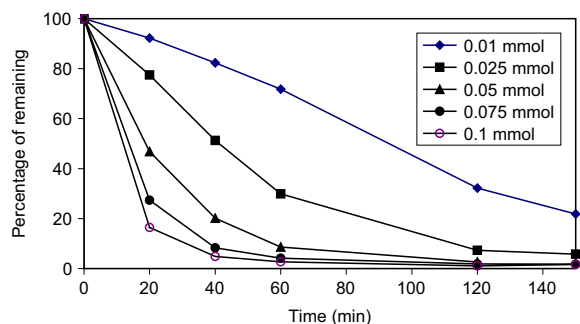


Fig. 7. Effect of addition of Fe^{2+} on the decolourisation of RO4 by Fenton process. $[\text{RO4}] = 5 \times 10^{-4} \text{ mol/l}$; $[\text{H}_2\text{O}_2] = 10 \text{ mmol}$; $\text{pH} = 3$.

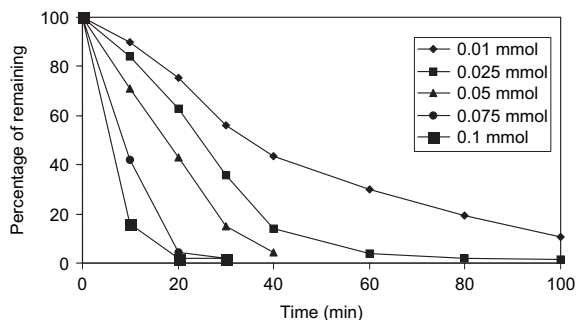


Fig. 8. Effect of addition of Fe^{2+} on the decolourisation of RO4 by photo-Fenton process. $[\text{RO4}] = 5 \times 10^{-4} \text{ mol/l}$; $[\text{H}_2\text{O}_2] = 10 \text{ mmol}$; $\text{pH} = 3$.

More hydroxyl radicals are produced with the increase in the concentration of Fe^{2+} . The decolourisation is faster in the early stage of the reaction than in the later stage. Yang et al. [24] reported that most of the H_2O_2 dosage was consumed in the early stage of the Fenton reaction. Since ferrous ion catalyses H_2O_2 to form hydroxyl radical quickly in the first stage of reaction, more decolourisation occurs in the early stage of reaction.

At low Fe^{2+} dosage (0.01 mmol and 0.025 mmol) a longer treatment time is required for complete decolourisation in both processes. 0.075 mmol of Fe^{2+} can be used as optimum dosage for both processes.

3.5. Effect of UV power

In photo-Fenton process, UV power is mainly used for (i) photolysis of H_2O_2 and (ii) photo reduction of ferric ion to ferrous ion. Hence, the influence of UV power on the decolourisation of RO4 has been investigated by varying the UV power from 16 W to 64 W. The results are shown in Fig. 9. Increase of UV power from 16 W to 64 W increases the decolourisation from 56.81% to 81.36% at 20 min. This increase in decolourisation is due to increased production of hydroxyl radical. At low UV power the rates of photolysis of H_2O_2 and photo reduction of Fe^{3+} are reduced. It is found that the UV power tested in our study lies in the linear range and all photons produced are effectively used. At 40 min the percentage of colour removal is nearly same for 32 W, 48 W and

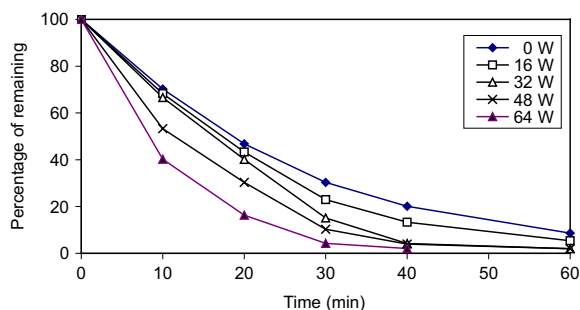


Fig. 9. Effect of UV power on the decolourisation of RO4 by photo-Fenton process. $[RO4] = 5 \times 10^{-4}$ mol/l; $[Fe^{2+}] = 0.05$ mmol; $[H_2O_2] = 10$ mmol; pH = 3.

64 W. Hence, the UV power of 32 W is sufficient for efficient colour removal.

3.6. Effect of dye concentration

The pollutant concentration is one of the important parameters in Fenton and photo-Fenton processes. The effect of initial dye concentration in these processes is shown in Figs. 10 and 11. The figures clearly reveal that the increase in dye concentration decreases the removal rate. Increase of dye concentration from 1 to 5×10^{-4} mol/l decrease the decolourisation from 89.49% to 53.2% for Fenton and from 94.79% to 59.84% for photo-Fenton process in 20 min. Hydroxyl radical is mainly responsible for dye decolourisation and its concentration remains constant for all dye concentrations. The increase in dye concentration

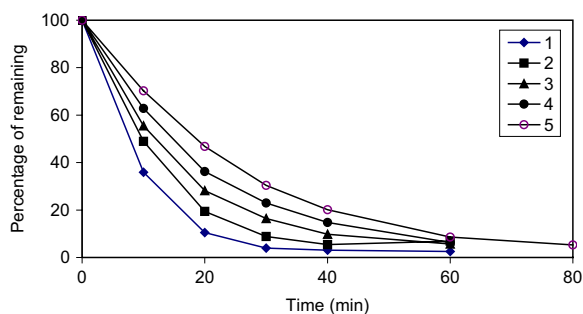


Fig. 10. Effect of dye concentration on the decolourisation of RO4 by Fenton process. (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 4×10^{-4} mol/l, (5) 5×10^{-4} mol/l. $[Fe^{2+}] = 0.05$ mmol; $[H_2O_2] = 10$ mmol; pH = 3.

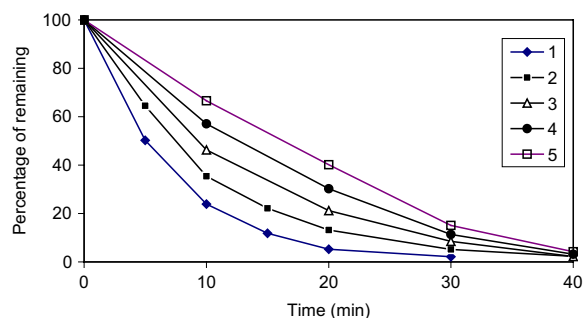


Fig. 11. Effect of dye concentration on the decolourisation of RO4 by photo-Fenton process. (1) 1×10^{-4} mol/l, (2) 2×10^{-4} mol/l, (3) 3×10^{-4} mol/l, (4) 4×10^{-4} mol/l, (5) 5×10^{-4} mol/l. $[Fe^{2+}] = 0.05$ mmol; $[H_2O_2] = 10$ mmol; pH = 3.

increases the number of dye molecules and not the OH radical concentration and so the removal rate decreases.

In photo-Fenton process at high dye concentration the penetration of photons entering into solution decreases thereby lowering the hydroxyl radical concentration.

3.7. Colour resurgens

In all the above photochemical processes, complete decolourisation was not observed. Only 98% colour removal occurred. This may be due to complexation of iron species with some of the non-degradable intermediates. Similar colour resurgens effect was reported [15]. In all cases, the colour resurgens did not exceed 2% at the end of the reaction.

4. Conclusions

Based on the results the following conclusions have been drawn. Though Fenton and photo-Fenton processes can be used for the decolourisation of RO4, the photo-Fenton process is more efficient. The photochemical oxidation is maximum at pH 3 in both processes. H_2O_2 concentrations of 15 mmol and 20 mmol appears as optimum dosages for Fenton and photo-Fenton processes, respectively. The decolourisation of dye increases by increasing the Fe^{2+} dosage from 0.01 mmol to 0.1 mmol. Increase in dye concentration decreases

the removal rate. About 2% of colour resurgens was observed at the end of the all reaction.

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