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Removal of reactive magenta-MB from aqueous solution by persulphate-based advanced oxidation process

K. Sarath, R. Gandhimathi*, S.T. Ramesh, P.V. Nidheesh

Department of Civil Engineering, National Institute of Technology, Tiruchirappalli 620 015, Tamil Nadu, India, Tel. +91 9496360359; email: sarath_janardhanan@yahoo.com (K. Sarath), Tel. +91 431 250 3171; Fax: +91 431 250 0133; email: rgmathii@nitt.edu (R. Gandhimathi), Tel. +91 431 250 3166; Fax: +91 431 250 0133; email: stramesh@nitt.edu (S.T. Ramesh), Tel. +91 9745648455; email: nidheeshpv129@gmail.com (P.V. Nidheesh)

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ABSTRACT

In this study, the possibility of removing magenta-MB by persulphate (PS)-based advanced oxidation process has been evaluated. PS was activated by chemical means with the use of ferrous ion to produce sulphate radical ($SO^{\bullet}_4$). Experiments were conducted in batch mode. The effect of operational parameters such as PS dosage (varied from 40 to 140 mg/L), ferrous ion dosage (varied from 0 to 100 mg/L), pH (both acidic and basic) and contact time were studied. For an initial dye concentration of 100 mg/L, maximum decolourization efficiency of 96.33% was obtained within 30 min with a PS dosage of 100 mg/L and ferrous ion dosage of 60 mg/L. At the optimum conditions, TOC removal efficiencies of 55.23 and 61.2% were obtained in 30 and 60 min, respectively. The effect of inorganic ions (Cl^-, F^- and SO_4^{2-}) on the treatment efficiency was also evaluated. It was found that the inhibiting effect due to the presence of inorganic ions followed the order as: $F^- >> Cl^- > SO_4^{2-}$. Very good removal efficiency obtained with very low chemical dosage (PS and Fe^{2+}) makes iron-activated PS a good alternative for the removal of dye from aqueous solution.

Keywords: Persulphate; $SO^{\bullet}_4$; Magenta MB; Mineralization; Dye removal

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1. Introduction

Dyes are widely used in many industries such as textile, rubber, paper, plastic, cosmetic, food, pharmaceuticals, etc. [1,2]. Among them, textile industries are the largest consumers of dye stuffs. A portion of the dye used is usually let out to the water bodies as wastewater. The problem caused by dying waste water includes aesthetically displeasing effects, impeding light penetration, retarding photosynthetic activity and inhibiting the growth of biota [3,4]. Some dyes are also toxic and carcinogenic. Since dye compounds are specifically designed to be recalcitrant with poor biodegradability, they are very stable and difficult to degrade [4,5].

The advanced oxidation process (AOP) can be a good alternative for the removal of these compounds. AOPs are based on the use of highly reactive oxidizing radicals to oxidize organic contaminants [6–9]. The oxygen bearing radicals (e.g. $OH^{\bullet}_4$, $SO^{\bullet}_4$, $HO^{\bullet}_2$ and $O_2^{-\bullet}$) formed are the principle reactant species in most of the AOPs. The major attraction of AOP is that it is able to chemically destruct molecular structures of target pollutants, and transform them into less toxic

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*Corresponding author.

forms [10]. Most of the AOPs do not generate sludge. Almost complete mineralization of organic compounds to CO_2 occurs during the course of reaction [4,11,12]. Particularly, persulphate (PS) ($S_2O_8^{2-}$)-based AOPs have recently emerged as an alternative for the decomposition of organic pollutants in contaminated soil and water [11,13–16]. PS itself is an oxidizing agent with an oxidation potential of 2.2 V. The activation of PS by appropriate methods results in the formation of more active sulphate radicals [11,14,17]. Sulphate radicals, similar to hydroxyl radicals ($OH^{\bullet}$), have an extremely high redox potential ranging from 2.5 to 3.1 V [18–20]. The activation of PS results in the formation of $SO_4^{\bullet}$ by cleavage of $S_2O_8^{2-}$ bonds (Eq. (1)), which is generally achieved by means of heat, ultrasound, UV, etc. or by chemical means by the usage of metals such as Fe(II) (Eq. (2)), Co(II) and Mn(II) [11,13,16,17,21–24].

$$S_2O_8^{2-} \rightarrow SO_4^{\bullet} + SO_4^{-} \tag{1}$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{-} + SO_4^{\bullet} \tag{2}$$

PS has several advantages over the other chemicals used for oxidation, which include high aqueous solubility, high stability at room temperature, relatively low cost and harmless end products [10,25,26]. Also sulphate radical is relatively more stable in water than the hydroxyl radical ($OH^{\bullet}$), thus greater detention time can be obtained [27]. Moreover, the rate of consumption of $SO_4^{\bullet}$ is less, enabling contact with more reacting species [11,14]. The higher oxidation potential of PS has been used for the treatment of various pollutants such as stabilized leachate [28], dyes [19,21,22,29,30], tetrabromobisphenol A [31], atrazine [20], tetracycline [24], trichloroethylene [17], p-chloroaniline [15], diuron [11,25], phenol [26,32], antipyrine [16] and sulfamonomethoxine [23].

In the present work, treatment of magenta MB (MMB) dye using ferrous ion-activated PS has been studied. The effectiveness of the process was evaluated in terms of decolourization and TOC removal percentages. Effect of various parameters affecting the dye removal efficiency of the process has been studied.

2. Materials and methods

2.1. Materials

Commercially available MMB dye was used throughout the experiments. A stock solution of the dye was prepared by dissolving 1,000-mg dye stuff in 1-L deionized water. $FeSO_4 \cdot 7H_2O$, NaOH, NaCl, NaF, $CaSO_4$, EDTA and H_2SO_4 were purchased from Merck. $K_2S_2O_8$ was purchased from Ranbaxy. Ultra pure water from Siemens LaboStar TWF (UV) 7 was used for the preparation of all reagents and standard solutions in this study.

2.2. Experimental procedure

An initial dye concentration of 100 mg/L was used throughout the study, unless otherwise specified. Experiments were conducted in batch mode in 500-mL borosil beaker with dye solution of volume 250 mL. Initially, the pH was adjusted to the desired value using H_2SO_4 and NaOH before the addition of the reactant species. pH measurements were done with Eutech PC 510 pH/conductivity/TDS/℃/℉ m. It was ensured that only negligible volume of acid or base is added compared to the volume of dye solution. A glass rod dipped in the acid or base solution was dipped in the dye solution and stirred and pH was monitored till the desired value was reached. Then, predetermined amount of PS and Fe(II) ions were added. The working volume was subjected to a constant stirring by means of a magnetic stirrer to ensure homogeneity during the reaction. Sample was withdrawn at predetermined time intervals. A reaction time of one hour was adopted during the study as it was observed that the removal rate was very much less later on. The sample removed was analysed immediately in UV–vis spectrophotometer (Lambda 25, Perkin Elmer, USA) for dye concentration. The mineralization study was performed with Shimadzu TOC analyzer TOC-L CPH/CPN PC controlled model, Japan. Direct measurement of TOC by non-purgeable organic carbon method was carried out. TOC analysis was performed for the optimum conditions of dye removal. Ethanol was added to the sample collected for TOC analysis to quench further reactions. The entire study was conducted at room temperature. Experiments in which optimum conditions arrived were repeated twice or thrice to ensure reproducibility of the result.

3. Results and discussion

3.1. Effect of Fe(II) dosage

As in the Fenton process, Fe(II) reacts with the PS ion ($S_2O_8^{2-}$) via one electron transfer mechanism, leading to the production of $SO_4^{\bullet}$ (Eq. (2)). Finding out an optimum Fe(II) dosage required for the activation of PS is an important factor to be considered in PS-based AOP because the presence of excess Fe(II) in the system has a scavenging effect on $SO_4^{\bullet}$ [33], as shown in Eq. (3).

$$\mathrm{Fe}^{2+} + \mathrm{SO}_4^{\cdot} \rightarrow \mathrm{Fe}^{3+} + \mathrm{SO}_4^{-} \tag{3}$$

Therefore, in order to find the effect of Fe(II) concentration on the dye degradation reaction and to find an optimum dosage, experiments were carried out with various ferrous ion concentrations ranging from 0 to 100 mg/L. For this study, in each run, a PS concentration of 100 mg/L and pH of 3 was adopted. The effect of ferrous ion dosage on the dye removal efficiency of PS oxidation is depicted in Fig. 1. From the figure, insignificant dye removal efficiency of PS in the absence of ferrous ion is observed, indicating the need of activation of PS for the efficient abatement of organic pollutants. With the increase in ferrous ion dosage, a significant improvement in the colour removal efficiency was observed and is mainly due to the formation $\mathrm{SO}_4^{\cdot}$ in the system. The increase in dye removal efficiency of PS increased up to a ferrous ion concentration of 60 mg/L and further increase in ferrous ion concentration decreased the dye removal efficiency. The observed colour removal efficiencies at 60-mg/L ferrous ion dosage were 96.33% at 30 min and 96.42% at 60 min. The reduction in dye removal efficiency of the PS for ferrous ion concentration greater that 60 mg/L is mainly due to the scavenging reaction occurring between ferrous ion and sulphate radical (Eq. (3)) as in Fenton processes [34–36].

3.2. *Effect of solution pH*

One of the parameter which was given major importance in this study was the pH. The conclusion by many authors showed some discrepancy in the optimum pH values observed. Venny et al. [37] observed the pH-independent behaviour of PS oxidation. In some studies, the formation of $\mathrm{OH}^{\cdot}$ (Eqs. (4) and (5)) in basic pH was found in PS oxidation [11,17,28], and maximum efficiency was observed in basic pH.

$$\mathrm{SO}_4^{\cdot} + \mathrm{H_2O} \rightarrow \mathrm{OH}^{\cdot} + \mathrm{HSO}_4^{-} \tag{4}$$

$$\mathrm{SO}_4^{\cdot} + \mathrm{OH}^{-} \rightarrow \mathrm{OH}^{\cdot} + \mathrm{SO}_4^{2-} \tag{5}$$

Some studies reported neutral pH as optimum for effective PS reaction [29], even though majority of the articles report acidic conditions as optimal [11,38,39]. At acidic conditions, the sulphate radical formation from PS ions occurs by its decomposition in the presence of protons as in Eqs. (6) and (7) [11].

$$\mathrm{S_2O_8^{2-}} + \mathrm{H}^{+} \rightarrow \mathrm{HS_2O_8^{-}} \tag{6}$$

$$\mathrm{HS_2O_8^{-}} \rightarrow \mathrm{H}^{+} + \mathrm{SO}_4^{\cdot} + \mathrm{SO}_4^{2-} \tag{7}$$

In the current study, pH of 2, 3, 4, 6, 7, 8.5, 9.5 and 10.5 were adopted to study the pH dependence of PS oxidation (Fig. 2). From the figure, it can be seen that increase in solution pH from 2 increased the dye removal efficiency of ferrous-activated PS oxidation. The less removal efficiency at pH 2 is may be due to the insufficient amount of protons required for the decomposition of PS. At lower pH values, the protons are in the form of $\mathrm{H_3O^+}$ and the quantity of this ion

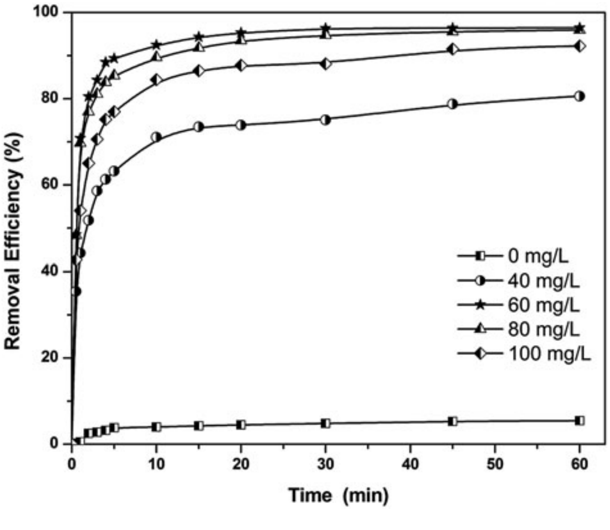

Fig. 1. Effect of Fe(II) dosage on the removal of MMB. (Reaction conditions: MMB = 100 mg/L, PS = 100 mg/L and pH 3.)

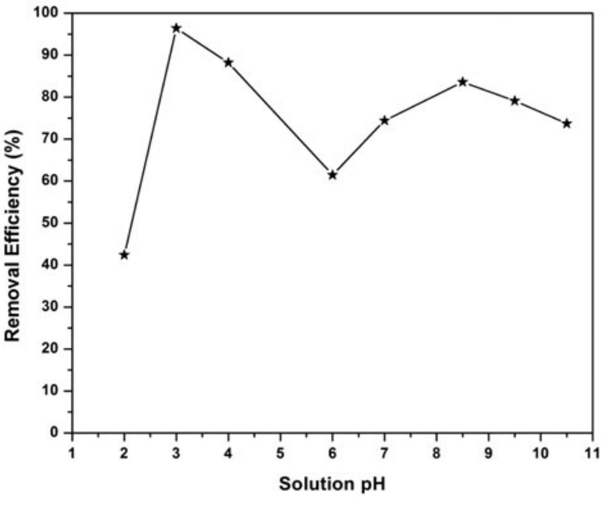

Fig. 2. Effect of solution pH on the removal of MMB. (Reaction conditions: MMB = 100 mg/L, Fe(II) = 60 mg/L, PS = 100 mg/L and oxidation time = 60 min.)

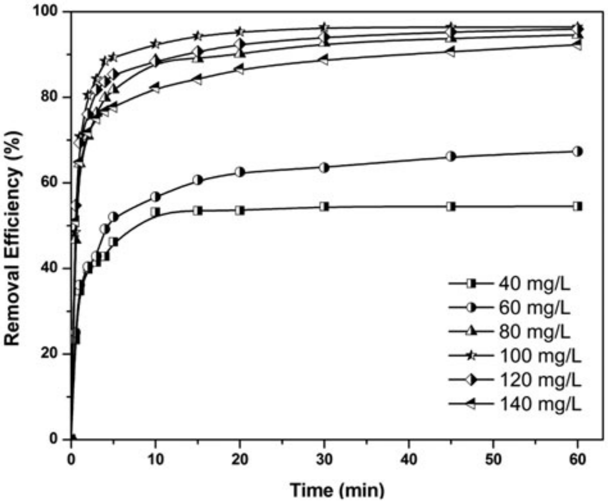

Fig. 3. Effect of PS dosage on the MMB removal. (Reaction conditions: MMB = 100 mg/L, Fe(II) = 60 mg/L and pH 3.)

increases with decrease in solution pH. Therefore, the concentration of H_3O^+ at pH 2 is higher than that at pH 3. This decreases the effective decomposition of PS ions (as in Eq. (6)) at pH 2. Further increase in solution pH from 3 decreased the dye removal efficiency, following the same trends of Fenton reactions [40–43]. The concentration of ferrous ions is very high at pH near to 3 [44,45]. The increase in solution pH from 3 results in hydrolysis of ferrous ions and forms insoluble hydroxyl complexes such as $Fe(H_2O)_5(OH)^+, Fe_2(H_2O)_4(OH)_2$ [46]. These complexes cannot activate PS as ferrous ions can. Also, ferric ions resulting from the activation reaction form ferric hydroxyl complexes such as $[Fe(H_2O)_8(OH)_2]^{4+}$, $[Fe_2(H_2O)_7(OH)_3]^{3+}, [Fe_2(H_2O)_7(OH)_4]^{5+}$ [47] and finally get transformed into $Fe(OH)_3$. These insoluble precipitates are gelatinous in nature and cause coagulation of pollutants [42]. This indicates that the removal efficiency observed at alkaline pH is not due to the ferrous activation and is mainly by the formation of hydroxyl radicals as in Eqs. (4) and (5).

3.3. Effect of initial PS concentration

To find the effect of PS dosage on MMB removal and to find the required optimum dosage, studies were conducted by varying the PS dosage and quantifying the degradation acquired with time. For this, the PS concentration was varied from 40 to 140 mg/L. The results are shown in Fig. 3. Initially, the removal efficiency increased with increase in PS dosage till 100 mg/L. In that condition, a removal efficiency of 96.33% was obtained at 30 min and it increased to 96.42% at 60 min. Further increase in PS dosage, decreased the dye removal efficiency of the system. This may be due to the inhibition effect of excess SO_4^- present in the system on the $SO_4^{\bullet}$ [17].

Also, at higher PS concentration, consumption of $SO_4^{\bullet}$ by $S_2O_8^{2-}$ may also occur as given in Eq. (8) and also if $SO_4^{\bullet}$ is excess in the system, they will combine among themselves (Eq. (9)) to form PS ions [48].

$$SO_4^{\bullet} + S_2O_8^{2-} \rightarrow SO_4^- + S_2O_8^{2-} \tag{8}$$

$$SO_4^{\bullet} + SO_4^{\bullet} \rightarrow S_2O_8^{2-} \tag{9}$$

3.4. Effect of inorganic ions

In the real field, the dying wastewater contains inorganic ions, which may affect the treatment processes. In order to study the effect of inorganic ions on the dye removal efficiency of the PS system, experiments were carried out in the presence of inorganic salts such as NaCl, NaF and $CaSO_4$ (Fig. 4). As seen in Fig. 4, F^- had a significant effect on the dye degradation. Presence of 60-mg/L F^- reduced the efficiency from 96.33 to 37.16%. Inhibition by these species may be due to the scavenging of $SO_4^{\bullet}$ by inorganic ions present or coordination to dissolved Fe(III) to form a less reactive complex [49]. The adverse effect of salts on dye removal was in the order $F^- >> Cl^- > SO_4^{2-}$. The dye removal efficiency of PS oxidation is severely affected by fluoride ions' addition. Similar result has been observed by Xavier et al. [43] for the degradation of dye by Fenton oxidation. With the addition of 40-mg/L NaF during the Fenton oxidation, the efficiency of the Fenton process reduced by 58%. Insignificant reduction in dye removal efficiency in the presence of sulphate and chloride ions was observed. Therefore, pretreatment of dye wastewater containing fluoride ions is required for the effective degradation of dye.

3.5. Mineralization study

It is known that reaction intermediates can be formed during the oxidation of azo dyes and some of them could be long lived and even more toxic than the parent compounds [13,15]. Therefore, TOC analysis was carried out to find the mineralization achieved. TOC measurement is time-consuming, therefore in order to avoid further chemical reaction, 0.5-mL ethanol was added to the collected sample to quench the reaction [23,31]. Initial TOC of 100-mg/L MMB was found to be 22.9 mg/L. TOC removal efficiencies of 55.23 and 61.2% were obtained after 30 and 60 min,

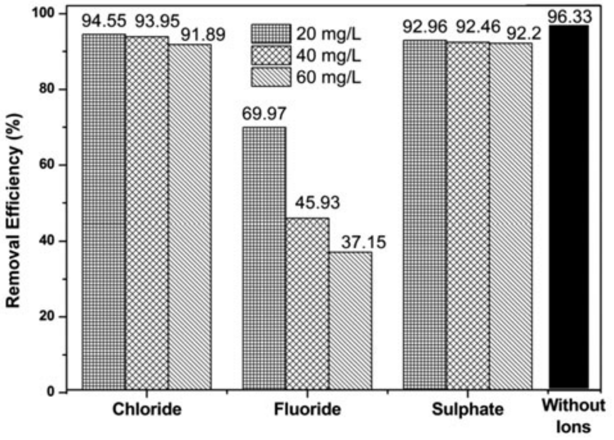

Fig. 4. Effect of inorganic ions on PS oxidation of dye. (Reaction conditions: MMB = 100 mg/L, Fe(II) = 60 mg/L and pH 3.)

respectively. This indicates that the complete degradation of dye is well below its removal.

3.6. Effect of initial dye concentration

Dye concentrations of 50, 100, 200 and 300 mg/L were opted for studying the effect of initial dye concentration. The removal rate was rapid in the case of 50-mg/L (Fig. 5) dye initially. But, after 5 min, the rate was very less. By the end of 30 min, the dye removal efficiencies observed for 50- and 100-mg/L MMB were almost equal. The lesser removal efficiency observed in later stage in the case of 50 mg/L can be attributed to either one of the following facts. At lesser concentration, the frequency of collisions between reactants molecules decreases and the frequency of effective collisions that causes a reaction to occur will also be low [35,36]. Also, when less dye molecules are present, the Fe(II) in the system may be surplus leading to scavenging reaction. With the increase in MMB concentration from 100 mg/L, the dye removal efficiency of the system is decreased. This may be due to the insufficient production of reactive species required for the effective degradation of dyes at higher concentrations [24].

Even though the dye removal efficiency of the system decreased with increase in initial MMB concentration, the absolute dye removal increased with increase in dye concentration. For example, the dye removed after 60 min for 50- and 300-mg/L MMB solution was 48.9 and 188.63 mg/L, respectively. Similar trend has been observed by various researchers [35,36] and is mainly due to the increased effective collision between dye molecules and oxidation species.

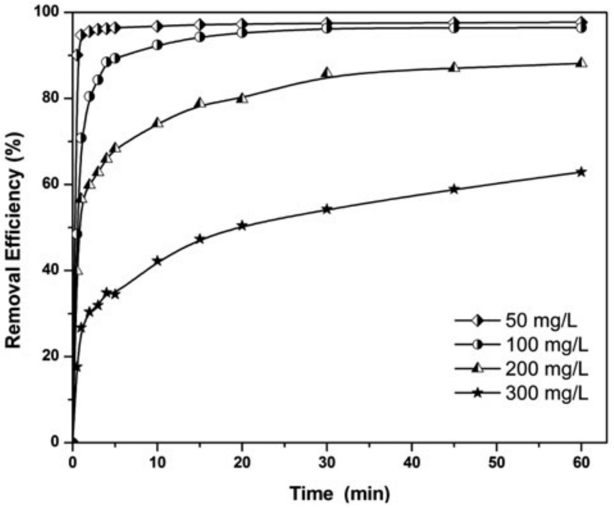

Fig. 5. Colour removal in various initial dye concentrations. (Reaction conditions: PS = 100 mg/L, Fe(II) = 60 mg/L and pH 3.)

3.7. Comparison with Fenton process

Our previous work [43] reported 90.9% removal efficiency for the Fenton system at optimal conditions of catalyst concentration of 400 mg/L, H_2O_2 dosage of 0.38 M, initial pH 3 and dye concentration of 50 mg/L. In the present study, the optimal conditions are Fe(II) dosage of 60 mg/L, PS dosage of 100 mg/L and pH of 3 with a removal efficiency of 96.3% from 100 mg/L MMB dye. In both the cases, the optimal solution pH is 3. This is mainly due to the existence of ferric and ferrous ions in its ionic forms other than complex forms at pH 3. The removal efficiency of PS oxidation is very much higher than that of the Fenton process. At the optimal conditions, 42-mg/L dye was removed from an initial MMB concentration of 50 mg/L via the Fenton process, while that of PS oxidation were 93 mg/L from initial MMB concentration of 100 and 48.95 mg/L from 50 mg/L of MMB solution. The concentration of catalyst required is also very high in the Fenton process.

4. Conclusion

PS was found very efficient in removing reactive MMB from aqueous solution. With very less dosage of PS (100 mg/L), 96.33% of the dye (with initial concentration 100 mg/L) was removed within 30 min. In this study, Fe(II) dosage of 60 mg/L, PS dosage of 100 mg/L and pH of 3 were found optimum. TOC removals of 55.23% obtained at 30 min and 61.2% at 60 min indicate good mineralization of the compound. Among the inorganic ions added, F^- showed significant inhibiting effect on dye removal. The adverse effect was of the following order $F^- >> Cl^- > SO_4^{2-}$.

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