

Iron Activated Persulphate based Advanced Oxidation and Mineralization of an azo dye

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Abstract— In this study, the possibility of removal of the azo dye reactive magenta MB by persulphate based advanced oxidation process has been evaluated. The process effectiveness in treating real field wastewater also studied. Persulphate based advanced oxidation was found to be very effective for the degradation of the dye Magenta MB. Fe(II) catalyst was used for activating persulphate to produce Sulphate radical ($SO_4^{\cdot-}$). Also study was conducted in presence and absence of UV light in process. The effect of operational parameters such as persulphate dosage, catalyst dosage, pH and initial dye concentration were studied. The optimal operating conditions for activation of persulphate by Fe(II) in the absence of UV were persulphate dosage of 100mg/L, pH 3, Fe(II) dosage of 60mg/L for 100mg/L of the dye solution. The optimum reaction time observed was 30 minutes. At these conditions, a colour removal efficiency of 95.8% and TOC removal efficiency of 55.67% were observed. The optimal operating conditions for the activation of persulphate by Fe(II) in the presence of UV were, persulphate dosage of 100mg/L, pH 3, Fe(II) dosage of 60mg/L for 100mg/L of the dye solution. The optimum reaction time observed was 30 minutes. At these conditions, a colour removal efficiency of 96.11% and TOC removal efficiency of 57.13% were observed. There was no significant increase in the colour and TOC removal efficiencies with the application of UV radiation. So, by considering the economy and effectiveness, usage of Fe (II) in the absence of UV alone will be sufficient. A TOC removal of 55.67% within 30 minutes indicates the good mineralization of the compound. Degradation of textile dye by iron activated persulphate based advanced oxidation was found effective. Optimum value of pH, Fe (II) dosage, persulphate dosage were 3, 100mg/L and 500mg/L. Optimum reaction time was 60 minutes. Under optimum conditions a maximum colour and TOC removal efficiencies of 84.12% and 51.11% were obtained in 60 minutes.

Keywords— Persulphate; $SO_4^{\cdot-}$, homogeneous process, inorganic ions; UV light; TOC.

I. INTRODUCTION

Dyes are widely used in many industries such as textile, rubber, paper, plastic, cosmetic, food, pharmaceuticals etc. Among them, textile industries are the largest consumers of the dye stuffs (Zonoozi *et al.*, 2008). Textile industry consumes a large amount of process water approximately 21-377m³ per tones of textile and discharge large volume of waste water to the water bodies (Abdul aziz *et al.*, 2014). Reactive azo dyes are the most commonly used textile dyes because of their advantages of bright colour, excellent colourfastness, and ease of application. But reactive dyes hydrolyze easily, resulting in 20-30% of unfixed or hydrolyzed dyes (Kusic *et al.*, 2011). The problems caused by dyeing wastewater includes aesthetically displeasing effect, decreasing light penetration, retarding photosynthetic activity in aquatic system and inhibiting the growth of biota, bio accumulation ((Das *et al.*, 2007; Hassemer *et al.*, 2008). Some dyes are also toxic and carcinogenic. The dye compounds are specifically designed to be recalcitrant with poor biodegradability. Recalcitrant or refractory compounds are not biodegraded by organisms normally present in biological treatment system within the hydraulic retention times. So effective dye waste water treatment before discharge into the effluents is needed.

The commonly adopted methods for the treatment of textile wastewater like biological treatment (biodegradation), chemical precipitation, membrane technology, activated carbon adsorption, evaporation, specific coagulation chemical flocculation (Badani *et al.*, 2005) etc. Most of the dyes are only adsorbed on the sludge and are not degraded in biological treatments. Physical methods are ineffective for volatile pollutants, and they simply transfer the pollutants to another phase rather than destroying them (Das *et al.*, 2006). Some of these methods (reverse osmosis, nano- filtration, and multiple effect evaporators) are found to be effective but quite expensive (Chacko *et al.*, 2008; Hassemer *et al.*, 2008). Due to these disadvantages, there is an active search for highly effective and environmental friendly method to degrade the dyes. Recently, the usage of advanced oxidation process for the treatment of such recalcitrant pollutants has found wider attention.

The major attraction of an advanced oxidation process is that it is able to chemically destruct molecular structures of target pollutants, and transform them into less toxic forms. Most of the advanced oxidation processes do not generate sludge (Shabiimam *et al.*, 2012). Advanced oxidation processes (AOP's)

are based on the use of highly reactive oxidizing radicals to oxidize organic contaminants. The oxygen bearing radicals (e.g.: OH^\cdot , SO_4^\cdot , O_2^\cdot) formed are the principle reactant species in most of the Advanced oxidation processes (Romero *et al.*, 2010; Hassemer *et al.*, 2011).

Particularly, persulphate ($\text{S}_2\text{O}_8^{2-}$) based AOPs have recently emerged as an alternative for decomposition of organic pollutants in contaminated soil and water (Rodriguez *et al.*, 2012). Persulphate itself is an oxidizing agent with oxidation potential of 2.2V. The activation of persulphate by appropriate methods, results in the formation of more active sulphate radicals (Liang *et al.*, 2009).

Persulphate have several advantages over the other chemicals used for oxidation, which include high solubility, high stability at ambient temperature, relatively low cost, harmless end products. So persulphate reductions are considered to be environmental friendly. Moreover the rate of consumption of SO_4^\cdot is less, enabling contact with more reacting species, it is more selective in oxidation than OH^\cdot . (Romero *et al.*, 2013; Abdul aziz *et al.*, 2014)

II. MATERIALS AND METHODS

Chemicals

The $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8$, NaOH , MnCl_2 , Na_2CO_3 , NaCl , NaF , Na_2SO_4 , NaNO_3 and H_2SO_4 . Ethanol (99.9%). In this study, Magenta MB which is a reactive azo dye has been selected as a model pollutant.

Preparation of the Stock Solution

A stock solution of Magenta MB of 1000mg/L concentration was prepared by dissolving one gram of dye salt in one liter ultra-pure water and was subsequently diluted to the required concentration. These solutions were used for batch study.

Dye Removal Study

Initial dye concentration of 100mg/L was used throughout the study. Entire study was conducted at room temperature. Experiments were conducted in batch mode in 500mL borosil beaker with dye solution of volume 250mL. Initially the pH was adjusted Then predetermined amount of persulphate and catalyst were added. The working volume was subjected to constant stirring by means of a magnetic stirrer to ensure homogeneity and good reaction. Samples were withdrawn at predetermined time intervals. The sample removed was analyzed immediately in UV/ Vis spectrophotometer for dye concentration. The mineralization study was also conducted by measuring TOC.

Experimental procedure for treating waste water

Collection of samples: Wastewater samples were collected from a plant manufacturing both cotton and synthetic fabrics and transferred to laboratory for analysis and treatment. The tests were performed with raw effluent. The dyes in use at the time of the study were reactive, acid and disperse types.

Analysis of samples: An initial analysis was performed on the effluents under study, and their main characteristics were summarized.

The study consisted of batch tests. The volume of sample in reactor for each test was 2L. The reactor was installed above a magnetic stirrer, to keep the sample under constant agitation. The test was conducted in triplicate and samples were removed for pre determined intervals. Dye removal study conducted in the same manner as mentioned in the case of aquas solution of dye Magenta MB.

III. RESULTS AND DISCUSSION

Dye degradation study

The dye degradation study was carried out with persulphate activated by Fe(II) catalyst. The effect of presence of UV light was also studied. The results obtained from the studies are given below.

Effect of Catalyst Dosage

The effect of catalyst dosage was investigated by varying the dosage of Fe(II) in activation of persulphate. Fig 1 and Fig 2 illustrates the removal efficiency of Magenta MB as a function of time at varying catalyst dosage in the absence and presence of UV light in the process. In the absence of UV light, a removal efficiency of 95.80% was obtained in 30 minutes and it increased to 96.70% in 60 minutes. In the presence of UV light, the removal efficiency was 96.11% and 97.8% in 30 minutes and 60 minutes respectively. This rapid degradation of Magenta MB will be due to the formation of SO_4^\cdot . The reason for the positive effect of irradiation on the degradation rate include the photo-reduction of Fe^{3+} to Fe^{2+} ions and the photo dissociation of persulphate. But when the Fe(II) dosage was increased further, in the both systems, the removal efficiency was found to decrease. It will be because of the scavenging effect of excess Fe(II) on SO_4^\cdot .

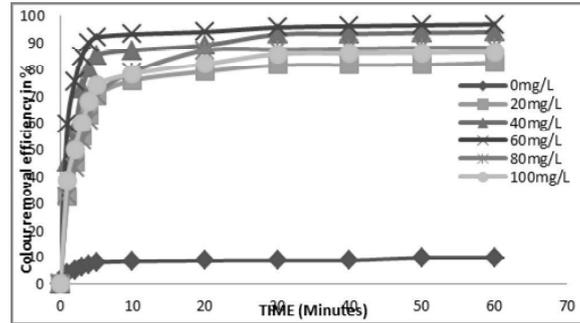


Fig.1 Effect of catalyst dosage on the decolorization in Fe (II) Based Activation. (Reaction conditions: MagentaMB= 100mg/L, PS =100mg/L, pH3)

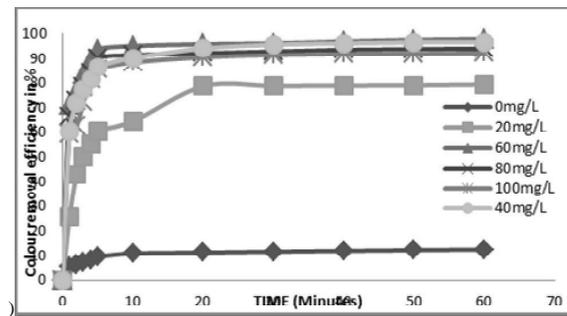
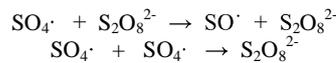


Fig.2 Effect of catalyst dosage on the decolorization in Fe (II)/UV Based Activation. (Reaction conditions: MagentaMB= 100mg/L, PS =100mg/L, pH 3)

Effect of Initial Persulphate Concentration

Study was conducted by varying the persulphate dosage and quantifying the degradation acquired with time. The results are shown in Fig.3 and Fig.4. In the absence of UV radiation, the optimum persulphate concentration was 100mg/L. In that condition, a removal efficiency of 96.03% was obtained in 30 minutes and it increased to 96.82% in 60 minutes. In the case of Fe (II)/UV mode of activation, the optimum persulphate concentration was 100mg/L. At this condition colour removal efficiency of 97.12% and 97.5% were obtained in 30 minutes and 60 minutes of reaction time respectively. When the dosage was increased further, the colour removal efficiency was found decreasing. This may be due to the inhibition effect of excess $SO_4^{\cdot -}$ present in the system on the $SO_4^{\cdot -}$.

Also, at higher persulphate concentration, consumption of $SO_4^{\cdot -}$ by $S_2O_8^{2-}$ may also occur as shown in Eq. and also if $SO_4^{\cdot -}$ is excess in the system, it will combine among themselves Eq. to form persulphate ions.



In addition to that annihilation of photo decay in excess persulphate concentration may be another reason in the case of UV based activation.

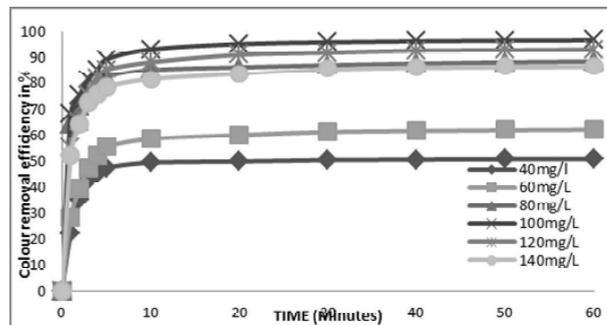


Fig.3 Effect of persulphate dosage on the decolonization in Fe (II) Based Activation. (Reaction conditions: MagentaMB= 100mg/L, Fe(II) =60mg/L, pH 3)

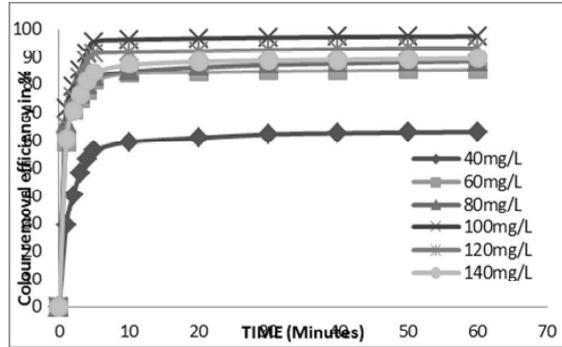


Fig.4 Effect of persulphate dosage on the decolonization in Fe (II)/UV Based Activation. (Reaction conditions: MagentaMB= 100mg/L, Fe(II) =60mg/L, pH 3)

Effect of pH

The effect of pH was studied in both Fe (II) based and Fe(II)/UV based activation result shown in fig.5 and fig.6 In both modes, the removal rate was less at pH 2. pH 3 was chosen as the optimum. When the pH was increased from 2 to 3, there was a rapid increase in the reaction rate. This will be due to the formation of $SO_4^{\cdot -}$ in pH range 3 to 5. In this pH, the dye removal observed was 92.1% and 91.2% in 30 minutes and 60 minutes respectively for Fe (II) assisted activation.

In Fe (II)/UV based activation, the dye removal efficiencies were 95.33% and 96.69% in 30 minutes and 60 minutes respectively.

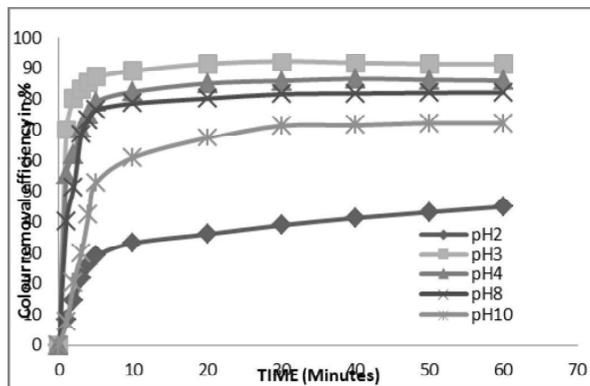


Fig.5 Effect of pH on the decolonization in Fe (II)Based Activation. (Reaction conditions: MagentaMB= 100mg/L, Fe(II) =60mg/L, PS=100mg/L)

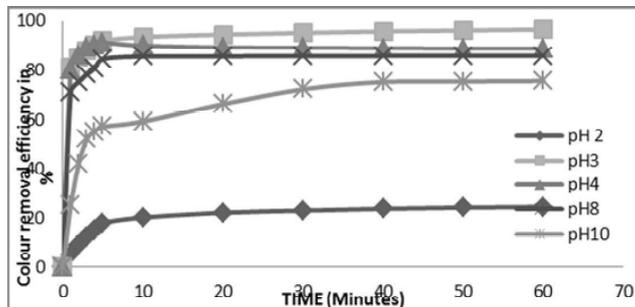


Fig. 6 Effect of pH on the decolonization in Fe (II)/UV Based Activation. (Reaction conditions: MagentaMB= 100mg/L, Fe(II) =60mg/L, PS=100mg/L)

Effect of Initial Dye Concentration

The colour removal efficiency was greater for 50mg/L of initial dye concentration, later the removal rate was very less. With the increase in initial concentration of the dye, more dye molecules were adsorbed onto the surface of catalyst. Thus, there action between the catalyst and the persulphate was inhibited, there by decreased the degradation efficiency. Also, the reactant species produced during the process (SO_4^- , Fe(II)) will not be sufficient to degrade the excess dye molecules .

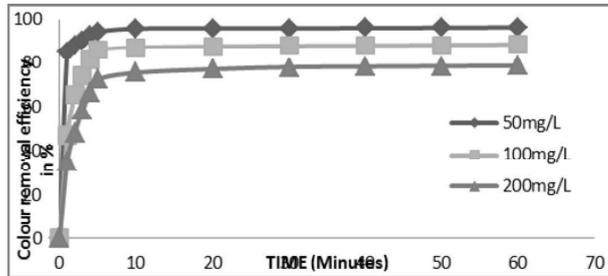


Fig. 7 Effect of initial dye concentration on the decolonization in Fe (II) Based Activation. (Reaction conditions: pH=3, Fe(II) =60mg/L, PS=100mg/l

Mineralization Study

It is necessary understand the mineralization degree of the Magenta MB dye to evaluate the degradation and to ensure the intermediate compounds formed are also getting degraded. Fig. 8 and Fig 9 shows the colour and TOC removal efficiency observed at 30 minutes and 60 minutes observed for Fe(II) and Fe(II)/UV based activation of persulphate. The initial TOC of 100mg/L of the dye was 23mg/L. At 30 and 60 minutes, the TOC removal efficiency was 55.67% and 61.82%. Whereas the colour removal efficiency was 95.8and 96.7% at 30 and 60 minutes.. In the presence of UV radiation The TOC removal efficiency obtained were 57.13% and 61.93% in 30 minutes and 60minutes respectively. The colour removal efficiencies were 96.11% and 97.8% in 30minutes and 60 minutes respectively.

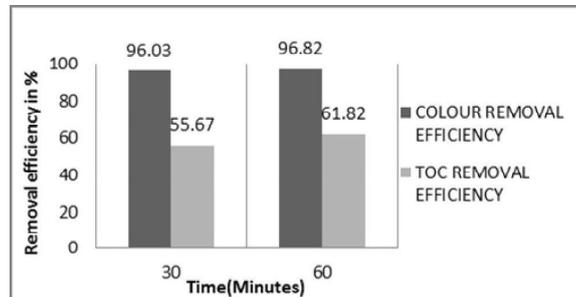


Fig. 8 Colour and TOC Removal in Fe (II) Based Activation. (Reaction conditions: pH=3, Fe(II) =60mg/L, PS=100mg/l, Magenta MB=100mg/L)

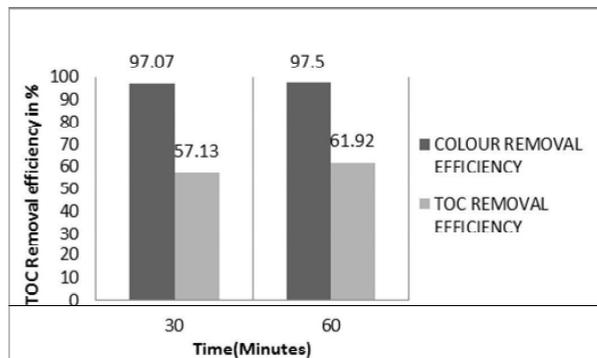


Fig. 9 Colour and TOC Removal in Fe (II) /UV Based Activation. (Reaction conditions: pH=3, Fe(II) =60mg/L, PS=100mg/l, Magenta MB=100mg/L)

Effect of Presence of Inorganic Ions on Decolourization

In the real wastewater, several chemical compounds will be present. This includes Cl⁻, SO₄²⁻, F⁻ etc. The performance of the oxidation process may be affected by the background impurities present in wastewater. So, in order to study the effect of inorganic ions on the persulphate based advanced oxidation process, ions like Cl⁻, SO₄²⁻, F⁻ were supplemented in the form of NaF, NaCl and Na₂SO₄. The result obtained is shown in Fig10. The process was found very well affected by the presence of inorganic ions. Especially with the presence of F⁻. When 20, 40 and 60mg/L of F⁻ was present in the treated solution, the colour removal efficiency decreased from 96.33% to 69.98%, 45.93% and 37.16%. The reduction in the colour removal efficiency due to the presence of Cl⁻, SO₄²⁻ were relatively very less. Inhibition by these species may be due to precipitation of iron, scavenging of SO₄^{•-} or coordination to dissolved Fe (III) to form a less reactive compounds.

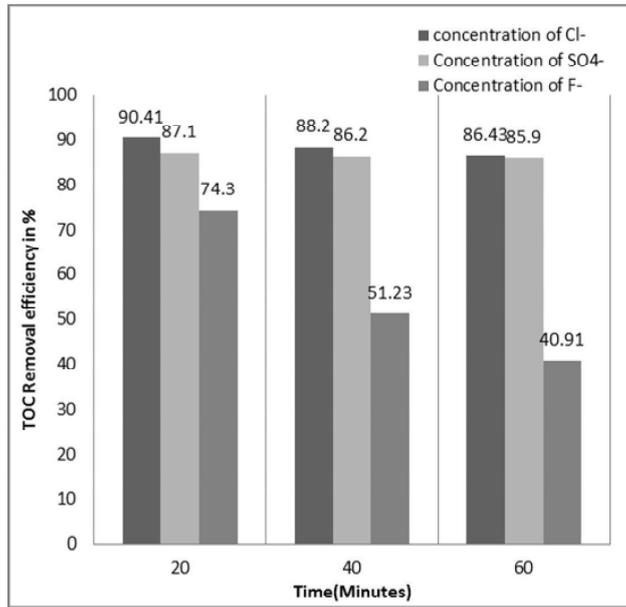


Fig 10 Effect of Presence of Inorganic Ions on Decolourization

STUDY OF PROCESS EFFECTIVENESS IN REAL FIELD WASTEWATER

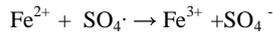
An initial analysis was performed on the effluents under stud, and their main characteristics are summarized in Table 1.

Parameter	Raw effluent
pH	10 ± 0.46
Turbidity	50 ± 11
Alkalinity	714 ± 0.48
Conductivity	4.54 ± 0.88
TOC	170 ± 66
TSS	96 ± 12
COD	712 ± 26
BOD ₅	238 ± 12
Chlorides	1512 ± 62
Sulphates	682 ± 29
Absorbance λ _{max} : 511	0.280 ± 0.03
λ _{max} : 620	0.294 ± 0.05

Table 1 Characteristics of raw effluent

Effect of catalyst dosage

The effect of catalyst dosage was investigated by varying the dosage of Fe(II) in activation of persulphate. It was decided to adopt a pH of 3, persulphate concentration of 500mg/L as initial condition. Waste water volume 2L. Fig 10 illustrates the colour removal efficiency of waste water as a function of time at varying catalyst dosage. The experiment was started with 0mg/L ie., with no Fe(II). The removal rate was very less in that condition. The Fe(II) dosage was gradually increased in each run. The removal efficiency increased considerably with increase in the catalyst dosage till 100mg/L. Under this condition, removal efficiency of 85.82% was obtained in 60 minutes and it increased to 86.61% in 105 minutes.. This rapid colour removal with the addition of Fe(II) catalyst will be due to the formation of $SO_4^{\cdot -}$. But when the Fe(II) dosage was increased further, the removal efficiency was found to decrease. It will be because of the scavenging effect of excess Fe(II) on $SO_4^{\cdot -}$ shown in



Therefore in dosage of catalyst Fe(II) of 100mg/L was giving maximum efficiency .

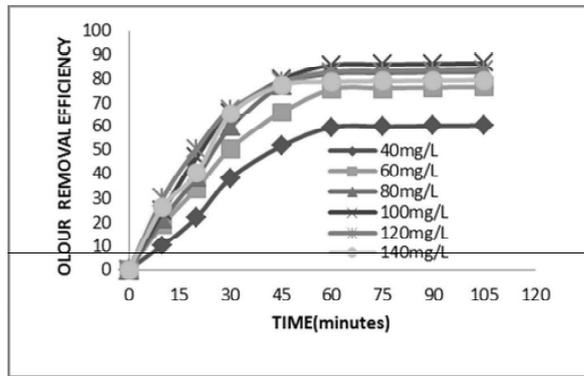


Fig.11 Effect of catalyst dosage on the decolorization in Fe (II) Based Activation. (Reaction conditions: PS =500mg/L, pH 3)

Effect of Initial Persulphate Concentration

To find the effect of persulphate dosage the persulphate concentration was varied from 150mg/L to 1000mg/L. The results are shown in Fig.11. The removal efficiency was found to considerably increase with increase in persulphate dosage till 500mg/L. In that condition, a removal efficiency of 84.12% was obtained in 60 minutes and it increased to 84.91% in 105 minutes. When the dosage was increased further, the colour removal efficiency was found decreasing. This may be due to the inhibition effect of excess $SO_4^{\cdot -}$ present in the system on the $SO_4^{\cdot -}$.

Also, at higher persulphate concentration, consumption of $SO_4^{\cdot -}$ by $S_2O_8^{2-}$ may also occur as shown in Eq And also if $SO^{\cdot -}$ is excess in the system, it will combine among themselves Eq. to form persulphate ions.

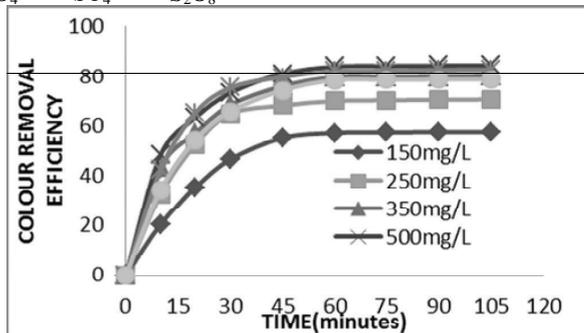


Fig 12 Effect of persulphate dosage on the decolonization in Fe (II) Based Activation. (Reaction conditions:, Fe(II) =1000mg/L, pH 3)

Effect of pH

The effect of pH was studied. The results are shown in fig. 13. The removal rate was less at pH 2. When the pH was increased from 2 to 3, there was a rapid increase in the reaction rate. This will be due to the formation of $SO_4^{\cdot-}$ in pH range 3 to 5. Optimum pH was selected as 3. In this pH, the dye removal observed was 80.21% and 80.48% in 60 minutes and 105 minutes respectively.

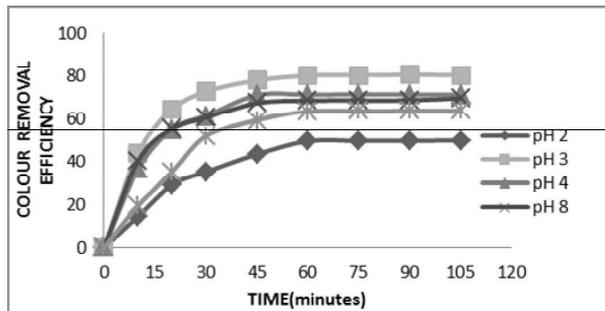
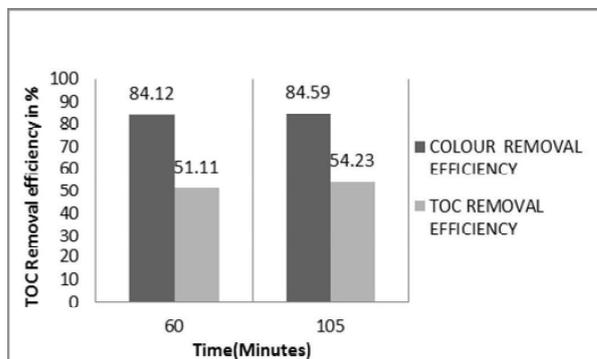


Fig.13 Effect of pH on the decolonization in Fe (II)Based Activation. (Reaction conditions: Fe(II) =1000mg/L, PS=500mg/L)

Mineralization Study

It is necessary understand the mineralization degree of the dyes to evaluate the degradation and to ensure the intermediate compounds formed are also getting degraded. Fig. 13 shows the colour and TOC removal efficiency observed at 60 minutes and 105 minutes observed for Fe(II) based activation of persulphate. The initial TOC of the waste water was 170 ± 66 mg/L. At 60minutes, the TOC removal efficiency was 51.11%. In 105 minutes, it increased to 54.23%. Whereas the colour removal efficiency was 84.12% in 60 minutes and 84.59% at 105 minutes.



FFig. 14 Colour and TOC Removal in Fe (II) Based Activation. (Reaction conditions: pH=3, Fe(II) =100mg/L, PS=500mg/l)

IV. CONCLUSIONS

Iron activated persulphate based advanced oxidation was found to be very effective for the degradation of the dye Magenta MB. The optimum conditions obtained were almost same in both presence and absence of UV light. Optimum value of pH, Fe (II) dosage, persulphate dosage and optimum reaction time were 3, 60mg/L and 100mg/L and 30minutes in both the presence and absence of UV radiation. At that time maximum colour and TOC removal efficiencies of 95.8% and 55.67% were in the absence of UV radiation. 96.11% and 57.13% were in presence of UV radiation. There was no significant increase in the colour and TOC removal efficiencies with the application of UV radiation. So, by considering the economy and effectiveness, usage of Fe (II) in the absence of UV alone will be sufficient. A TOC removal of 55.67% within 30 minutes indicates the good mineralization of the compound.

Degradation of textile dye by iron activated persulphate based advanced oxidation was found effective. Optimum value of pH, Fe (II) dosage, persulphate dosage were 3, 100mg/L and 500mg/L. Optimum reaction

time was 60 minutes. Under optimum conditions a maximum colour and TOC removal efficiencies of 84.12% and 51.11% were obtained in 60 minutes.

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