

# Catalytic degradation of methylene blue by Fenton like system: model to the environmental reaction

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**Abstract:** To develop more efficient chemical methods for the demineralization of organic pollutants from water bodies, which one was also mimic to the nature, a degradation of methylene blue by Fe(III) and H<sub>2</sub>O<sub>2</sub> in the absence of light instead of Fe(II) and H<sub>2</sub>O<sub>2</sub> was studied. Results showed that use of Fe(III) is more promising than Fe(II). The present study reflects that Fenton reaction is more efficient, in the presence of a small amount of salicylic acid is added which is a one of the priority pollutant.

**Keywords:** advanced oxidation technology; Fenton reaction; iron(III); catalytic degradation; environmental application

## Introduction

A variety of physical, chemical and biological methods are presently available for the treatment of polluted water. Biological treatment is a good and promising as well as cost effective technology but it has a number of disadvantages. Physical methods such as liquid-liquid extraction, ion exchange, GAC adsorption, air stripping etc. are ineffective for pollutants which are not adsorbable or volatile similarly these technologies only transfer the pollutant from one phase to another phase. In the light of limitations of these methods, the chemical oxidation methods are capable to almost complete mineralisation of organic pollutants and effective to the wider range of pollutants.

Among the chemical oxidation methods, oxidation by Fenton's reagent is popular method. Advantages of Fenton's reagent over other oxidizing treatment are numerous, including simplicity, suitability to treat a wide range of substance, no special equipment is needed etc. (Arnold, 1995). Generally in the Fenton's process ferrous ion is commonly used with the H<sub>2</sub>O<sub>2</sub> as a source of OH<sup>-</sup> radical in presence or absence of light. At the end of chemical reaction, use of Fe<sup>2+</sup> leads to the formation of sludge of Fe<sup>3+</sup> which affects the economy of the process (Bull, 1992).

Recent investigations showed that addition of small amount of *p*-hydroxy benzoic acid enhanced the degradation of pollutant. This is because Fe(III) forms a complex with *p*-hydroxy benzoic acid, which enhanced the decomposition of H<sub>2</sub>O<sub>2</sub> (Sun, 1992; Walling, 1973; Rivas, 2001). *p*-hydroxy benzoic acid is one of the water pollutants. If this is the fact, then technically this method is more promising. Fe(III) is a dominant species of iron occur in the natural ecosystem, hence it is well if in the chemical treatment method we use a Fe(III) instead of Fe(II) which directly reflect the role of natural ecosystem in environmental demineralization. Also number of investigation showed that there is the presence of H<sub>2</sub>O<sub>2</sub> (Gunz, 1990; Sakugawa, 1990) in the water bodies. Hence in the present study we use Fe(III)/H<sub>2</sub>O<sub>2</sub> system instead of Fe(II)/H<sub>2</sub>O<sub>2</sub> which directly reflect the possibility of natural demineralization and possibility of use of *p*-hydroxy benzoic acid as a Co-catalyst for the further degradation help to understand the more insight in to the environment. Methylene blue has been selected a refractory model compound in this oxidation process. Methylene blue is a basic dye extensively used for dyeing and

printing cotton, silk, etc. It is also used as a medicinal dye because of its antiseptic properties (Venkataraman, 1952). Detail investigation regarding to its application are present here. Also we search the possibility of degradation of two pollutants by single technology with advanced feature.

## 1 Experimental

### 1.1 Materials

All chemicals used in this experiment are A. R. grade and used as received. Ferric nitrate and methylene blue from Qualigens, India. NaOH, H<sub>2</sub>SO<sub>4</sub>, 1, 10-phenanthroline, H<sub>2</sub>O<sub>2</sub> (6% w/v), salicylic acid are from E. Merck. All solution are prepared in the double distilled water.

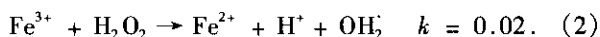
### 1.2 Method

Glass beaker (Borosil, Capacity-500 ml) containing 100 cm<sup>3</sup> aqueous dye solution placed in the thermostat to keep the temperature constant and use an external stirrer for constant stirring. All the experiment carried out at 27 ± 0.3 °C. The required amount of Fe(III) and H<sub>2</sub>O<sub>2</sub> were added in the dye solution simultaneously. The concentration of dye was determined spectrophotometrically using Shimadzu 160A UV-Visible Spectrophotometer (Graphicord) at 665 nm. 0.5 ml dye solution is removed for the analysis time to time. The pH of the solution was measured by digital pH-Meter (Model LI, 120, Elico, India). pH-sensitive combine glass electrode is immersed in the solution continuously to measure the pH of the solution during the course of reaction time. The Fe<sup>2+</sup> was analyzed at 510 nm ( $\epsilon = 1.11 \times 10^4$ ) via its complex with 1, 10-phenanthroline and the interference from the undegraded dye was subtracted by the absorbance at 510 nm measured before the addition of the phenanthroline ligand. All the samples were analyzed immediately to avoid any further reaction. H<sub>2</sub>O<sub>2</sub> concentration determined by the standard potassium permanganate method. COD is determining by standard method (APHA-AWWA-CPWF, 1995).

## 2 Results and discussion

Fenton's chemistry is very well known and it is one of the high potential oxidation technologies because it produces a highly reactive species {OH<sup>-</sup>} (Fenton, 1894; Haber, 1934). In most of the study Fe(II) is use as an inorganic species instead of Fe(III), this may be due to the following reaction





From the above equation it is clear that rate constant of Reaction (1) is more than that Reaction (2). So the rate of oxidation of pollutant is also more in case of (1) than (2). Hence we studying the degradation of methylene blue as a representative of dye system in presence both Fe(III) and Fe(II) with all other conditions are identical. Degradation of methylene blue in presence of Fe(III) and Fe(II) are shown in Fig. 1.

From Fig. 1, it is clear that degradation of methylene blue is not follow only these reaction but other reaction are also play an important role in the degradation. The complete degradation of methylene blue in presence of Fe(III) occur within 90 min while in presence of Fe(II) occur within 2 h. In presence of Fe(II), within 10 min 89% of dye was decayed while rest of reaction took place in 2 h, while in case of Fe(III) the degradation of dye was gradual means the oxidant species ( $\text{OH}^-$ ) which was responsible for the degradation are generated continuously. It is also observed that at the end of degradation reaction in presence of Fe(III), no precipitation of iron hydroxide occur, while in case of Fe(II), the precipitation of iron hydroxide obtained. In case of Fe(III) more chemistry is involved than the Fe(II) during the degradation.

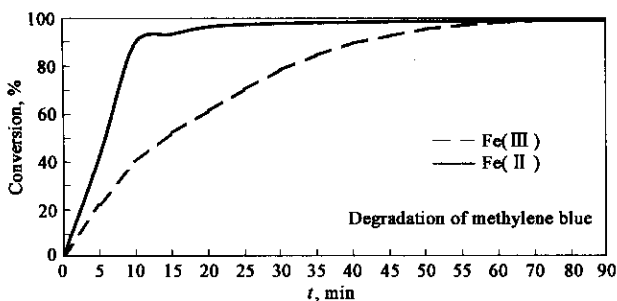
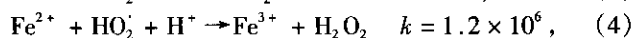
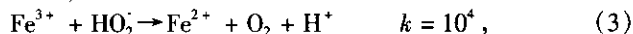


Fig. 1 Degradation of methylene blue by Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(III)/H<sub>2</sub>O<sub>2</sub> concentration of Fe(III)/H<sub>2</sub>O<sub>2</sub> (solution pH = 1.78) and Fe(II)/H<sub>2</sub>O<sub>2</sub> (solution pH = 3.2) is 1:1 molar ratio Initial concentration of methylene blue is  $1 \times 10^{-5}$  mol/L

To understanding the more chemistry, we monitor the analysis of Fe(II) by 1,10-phenanthroline method and H<sub>2</sub>O<sub>2</sub> decomposition by potassium permanganate method. The decomposition of H<sub>2</sub>O<sub>2</sub> is shown in Fig. 2. In the case of decomposition of dye in presence of Fe(III), the formation of Fe(II) is varied time to time and no precipitation of Fe(III) as an iron hydroxide while in case of decomposition of dye in presence of Fe(II), almost 45% Fe(II) is converted in to Fe(III) at the end of the reaction. According to Fig. 2, decomposition of H<sub>2</sub>O<sub>2</sub> is very rapid when decomposition reaction starts with Fe(II) while decomposition of H<sub>2</sub>O<sub>2</sub> is gradual when decomposition reaction starts with Fe(III). So according to above observation, we assume that when decomposition of dye start with Fe(II), the Fenton's Reaction (1) is more dominating, while the decomposition of dye start with Fe(III), the Fenton's Reactions (1), (2) and other reaction may be involved during the decomposition reaction, which are shown below



All the results reported here so far based on analysis of the dye solutions spectrophotometrically. So it is important to

measure the COD of the dye solutions after the degradation in order to verify whether the dye actually degraded by Fenton-like reactions or the disappearance of color was due to some other effect. To determine the reduction of COD of the dye solution, initial COD and COD at different time intervals was measured in both cases which shown in Fig. 3.

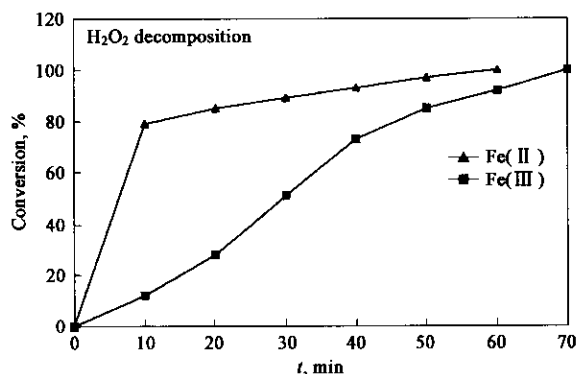


Fig. 2 Destruction of H<sub>2</sub>O<sub>2</sub> during Fenton like reaction Concentration of Fe(II)/H<sub>2</sub>O<sub>2</sub> (solution pH = 3.2) and Fe(III)/H<sub>2</sub>O<sub>2</sub> (solution pH = 1.78) is 1:1 molar ratio

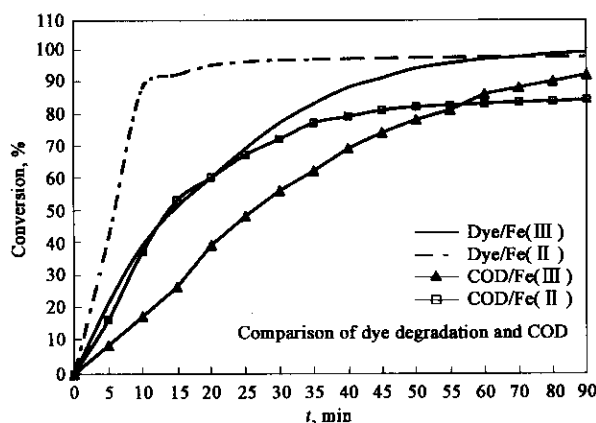


Fig. 3 Comparison of dye degradation and COD removal in presence of Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(III)/H<sub>2</sub>O<sub>2</sub> Concentration of Fe(III)/H<sub>2</sub>O<sub>2</sub> (solution pH = 1.78) and Fe(II)/H<sub>2</sub>O<sub>2</sub> (solution pH = 3.2) is 1:1 molar ratio. Initial concentration of methylene blue is  $1 \times 10^{-5}$  mol/L

According to Fig. 3, it is clear that the Fenton like oxidative degradation was followed degradation of dye and not by others. When reaction starts with Fe(II), at 90 min; 98% degradation of dye was occurred while 85% COD reduction observed. When reaction starts with Fe(III), within 90 min, 100% degradation of dye was observed while 93% reduction of COD observed. From the above it is clear that some reaction intermediate which was colorless are form during the reaction and take more time to degrade. This type of difference is also reported earlier for the degradation of phenol by UV/H<sub>2</sub>O<sub>2</sub> (De, 1997). When reaction start with Fe(III), complete demineralization was observed within 2 and half hour.

In the case of Fe(II), at the end of the reaction iron precipitate out while in the case of Fe(III) such precipitation was not observed. To study this observation we monitor the pH change during the reaction course, which is shown in Fig. 4. It is observed that in the case of Fe(III) the initial pH of the solution is 1.78, after few minutes it was dropped at 1.62 and subsequently the change in pH was negligible.

While in the case of  $\text{Fe}(\text{II})$  the initial pH of the solution is 3.2, after few minutes it was dropped at 2.4, subsequently the change in pH was negligible and at the end of the reaction again the pH of the solution was slightly increases. The drastic drop in the pH of the solution is probably due to the formation of some acidic reaction intermediates, which could not be characterized. Similar results are reported in the earlier study. Earlier reports and our present observation concluded that in the case of  $\text{Fe}(\text{III})$  the pH of the solution was more acidic and hence no precipitation was observed as well as complete degradation of methylene blue take place. While in case of  $\text{Fe}(\text{II})$  the pH of the solution was acidic but which was not sufficient to prevent the precipitation of iron and as a result the complete degradation was also not observed.

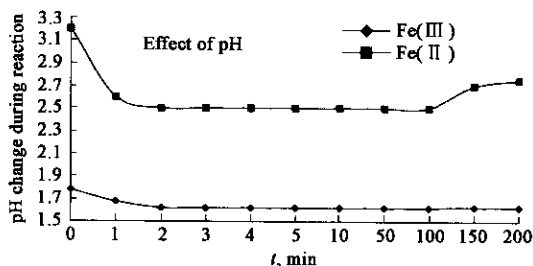


Fig.4 Change of pH during the degradation of methylene blue by  $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$  and  $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ . Concentration of  $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$  (solution pH = 1.78) and  $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$  (solution pH = 3.2) is 1:1 molar ratio. Initial concentration of methylene blue is  $1 \times 10^{-5}$  mol/L.

Very recently Rivas F. J. *et al.* reported that in presence of  $\text{Fe}(\text{III})$ ,  $\text{H}_2\text{O}_2$  and *p*-hydroxy benzoic acid, enhanced the degradation of atrazine, a representative of pesticide (Rivas, 2001). We studied the same reaction for the degradation of methylene blue as a representative of dye solution. Degradation dye by  $\text{Fe}(\text{III})$ ,  $\text{H}_2\text{O}_2$  and salicylic acid is shown in Fig. 5. It is observed that, discolorations of dye solution took place within a 10 min of time that was quite less than the  $\text{Fe}(\text{III})$  and  $\text{H}_2\text{O}_2$ . This is happen may be due to the catalytic decomposition of  $\text{H}_2\text{O}_2$  is very fast and hence the degradation of dye take place within a very short time. The degradation of dye in presence of salicylic acid,  $\text{Fe}(\text{III})$ ,  $\text{H}_2\text{O}_2$  and reaction with  $\text{Fe}(\text{II})$ ,  $\text{H}_2\text{O}_2$  is quite similar. More insight in presence of salicylic acid, which is one of the priority pollutants, is under vision.

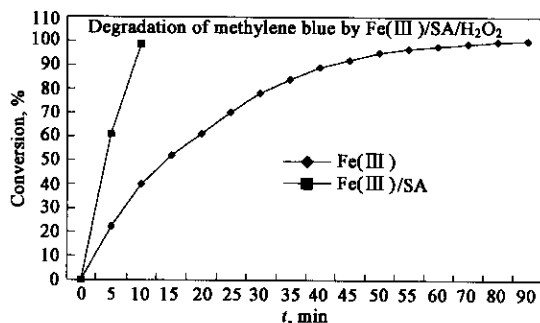


Fig.5 Dye degradation in presence of salicylic acid and absence of salicylic acid by mixture  $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ . Concentration of  $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$  (solution pH = 1.78) is 1:1 molar ratio concentration of salicylic acid is 0.001 mol/L (5 mol/L added in a reaction). Initial concentration of methylene blue is  $1 \times 10^{-5}$  mol/L.

According to Faust and Hoigne (Faust, 1987), it is well known that the hydroxy complexes of  $\text{Fe}(\text{III})$  are able to form  $\text{OH}^\cdot$ . Taking considering of this fact we monitor the degradation of dye in presence of  $\text{Fe}(\text{III})$  without  $\text{H}_2\text{O}_2$  in absence of light. It is observed that no degradation of dye for a long time (72 h) in absence of light and  $\text{H}_2\text{O}_2$ . This observation concluded that for the degradation of dye  $\text{H}_2\text{O}_2$  is necessary which is a source of  $\text{OH}^\cdot$  radical,  $\text{Fe}(\text{III})$  alone in dark is not sufficient.

### 3 Conclusions

From the above observation, we can say that the degradation of dye start with  $\text{Fe}(\text{III})$  rather than  $\text{Fe}(\text{II})$  is more promising. When reaction starts with  $\text{Fe}(\text{II})$  the 89% degradation of dye take place within 10 min but for the complete degradation it took more time while when reaction starts with  $\text{Fe}(\text{III})$ , the degradation is gradual but complete degradation take place within 90 min. The pH study showed that the pH of the reaction solution plays an important role during the degradation reaction. It is also observed that, when a small amount of salicylic acid enhanced the degradation of dye that was technically more promising because it took very less time. Present study concluded that  $\text{Fe}(\text{III})$  in a dark is not sufficient for the degradation of dye. Above study reflect that there is a possibility of environmental remediation that was more efficient and also work in absence of light also. More vigorous study was under vision for both fundamental understanding as well as technical application.

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