



## DEGRADATION OF METHYLENE BLUE USING Fe-PILLARED BENTONITE CLAY

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(Received : 26.10.2014; Accepted : 12.11.2014)

### ABSTRACT

In the present work degradation of methylene blue by Fe-pillared bentonite clay in presence of light has been carried out. The progress of the reaction was monitored spectrophotometrically. The effect of some parameters affecting the rate of reaction, such as pH, dye concentration, amount of Fe-pillared clay, amount of iron concentration, H<sub>2</sub>O<sub>2</sub>, light intensity, etc. has been studied. Kinetic studies show that this reaction follows pseudo-first order kinetics. A tentative mechanism for photo-Fenton degradation of methylene blue has also been proposed.

**Key words:** Photo-Fenton degradation, Methylene blue, Fe-pillared bentonite clay.

### INTRODUCTION

Human activities have a large and important impact on the environment. In spite of many uses; agrochemicals, dyes and pesticides are toxic recalcitrant compounds, which may accumulate in the environment and improper disposal of their effluents is creating pollution in the environment. Waste water originating from agrochemicals, pesticides and dyes industries poses a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature.

Researchers have developed some methods for wastewater treatment like chemical oxidation, incineration, adsorbents, electrolyte decomposition, ion exchange method, biological methods etc. These treatment methods are not suitable at large scale due to high cost and therefore, some alternative methods are required, which are reliable as well as low cost and easy to handle. Photo-Fenton provides an eco-friendly pathway for degradation of many organic pollutants. This technique is considered as a promising technology for wastewater treatment.

A novel bentonite clay-based Fe-nanocomposite (Fe-Ben) was successfully developed by Feng et al.<sup>1</sup> and used as a heterogenous catalyst for photo-Fenton discolouration and mineralization of an azo-dye orange II.

Hydroxyl-Fe pillared bentonite (H-Fe-P-Ben) was successfully prepared by Chen and Zhu<sup>2</sup> and it was used as a solid catalyst for UV-Fenton process. Ji et al.<sup>3</sup> have used the heterogeneous photo-Fenton

process using  $\text{LiFe}(\text{WO}_4)_2$  as catalyst to degrade methylene blue (MB) dye in aqueous solution. The results indicated that  $\text{LiFe}(\text{WO}_4)_2$  could effectively catalyze the decolorization of MB in the presence of UV light and  $\text{H}_2\text{O}_2$ .

Kavitha and Palanivelu et al.<sup>4</sup> have examined the efficiency of different Fenton-related oxidative processes such as Fenton, solar-Fenton and UV-Fenton using phenol as a model compound in simulated and industrial wastewater. Giroto et al.<sup>5</sup> have carried out the degradation of polyvinyl alcohol (PVA) by the photo-Fenton process with aim of investigating the effect of process conditions on the polymer degradation rate.

Lucas and Peres et al.<sup>6</sup> have studied the oxidative decolorization of reactive Black 5 (RB5) in aqueous solution by using Fenton ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ) and photo-Fenton ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ ) processes while Hong et al.<sup>7</sup> have investigated the effect of temperature on the equilibrium adsorption of methylene blue dye from aqueous solution using bentonite.

Panizza et al.<sup>8</sup> have compared the direct and indirect electrochemical oxidation of a synthetic solution containing methylene blue whereas Rafatullah et al.<sup>9</sup> have investigated the use of low-cost adsorbents for the removal of methylene blue (MB) from solution.

Golder et al.<sup>10</sup> have studied electrocoagulation (EC) of aqueous dye solutions of two different industrial dyes of methylene blue and eosin yellowish. Ai and Jiang<sup>11</sup> reported the efficient removal of organic dye from aqueous solution with a self-assembled cylindrical graphene-carbon nanotube hybrid which can be directly fabricated by a simple one-step hydrothermal process.

Fatimah et al.<sup>12</sup> have carried out the synthesis of a ZnO/montmorillonite photocatalyst based on natural montmorillonite using a sol-gel intercalation in photocatalytic and photochemical degradation of methylene blue while Vaishnav et al.<sup>13</sup> studied effective decolorization and degradation of methylene blue dye by using photo-Fenton and sono-photo-Fenton processes.

## EXPERIMENTAL

### Preparation of bentonite supported photo-Fenton reagent

Solutions A, B, C, D and E were prepared separately in a beaker. 6.950 g, 13.90 g, 20.85 g, 27.80 g and 34.75 g of  $\text{FeSO}_4$  were taken, respectively and then in each 500 mL beaker of distilled water and 50 g bentonite clay and few drops of dilute  $\text{H}_2\text{SO}_4$  were added to it. Solutions A, B, C, D and E were separately stirred on magnetic stirrer for 5-6 hours. The product was filtered and washed with distilled water 6-7 times. It was dried in an oven at 100 °C for 4-5 hours.

Stock solution of methylene blue dye ( $1.0 \times 10^{-3}$  M) was prepared in doubly distilled water. It was further diluted as and when required. The photochemical degradation of methylene blue dye was studied after addition of 0.05 g of Fe-pillared clay in 50 mL dye solution ( $1.70 \times 10^{-5}$  M) and ( $0.15$  N  $\text{Fe}^{2+}$ ) was added to it. Then 0.2 mL amount of  $\text{H}_2\text{O}_2$  was added. The pH of the reaction mixture was adjusted to 3.0 and this solution was exposed to a 200 W tungsten lamp at  $50.0 \text{ mWcm}^{-2}$ . Irradiation was carried out in glass vessel (Pyrex. 100 mL). A solarimeter (Suryamapi CEL 201) was used for the measurement of light intensities.

Water filter was used to cut thermal effect. A digital pH meter (Systronic Model 335) was used to measure pH of the dye solutions. pH of the dye solutions were adjusted by addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solution. UV-Visible spectrometer (Systronic Model 106) was used to measure absorbance (A) of the dye solution at regular time intervals. Controlled

experiments were also carried out to confirm that the degradation of methylene blue by Fe-pillared bentonite clay and by using H<sub>2</sub>O<sub>2</sub> was photo-Fenton in nature.

## RESULTS AND DISCUSSION

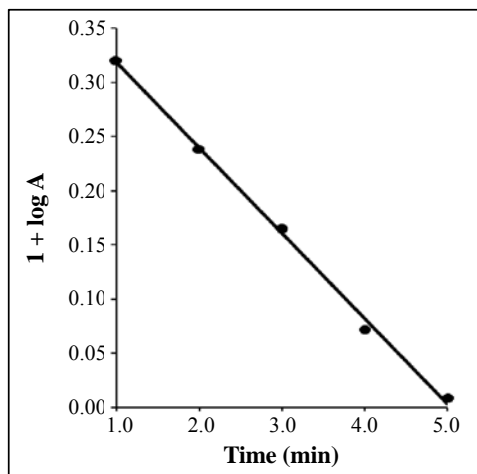
Degradation of methylene blue was observed at  $\lambda_{\max} = 665$  nm. A graph plotted between  $\log A$  v/s time was a straight line, which shows that photo-Fenton degradation of methylene blue follows pseudo-first order kinetics. The rate constant for degradation of dye was calculated by the following expression –

$$k = 2.303 \times \text{Slope} \quad \dots(1)$$

A typical run has been presented in Table 1 and graphically represented in Fig. 1.

**Table 1: A typical run**

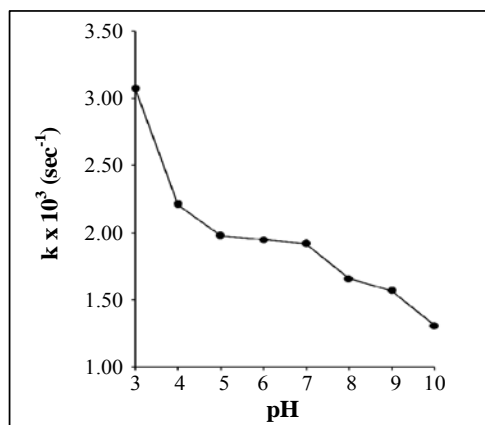
pH = 3.0	[Fe <sup>2+</sup> ] = 0.15 N	
[Methylene blue] = $1.70 \times 10^{-5}$ M	H <sub>2</sub> O <sub>2</sub> = 0.20 mL	
Amount of Clay = 0.05 g	Light intensity = 50.0 mWcm <sup>-2</sup>	
<b>Time (min.)</b>	<b>Absorbance (A)</b>	<b>1 + log A</b>
1.0	0.209	0.3201
2.0	0.173	0.2380
3.0	0.146	0.1644
4.0	0.118	0.0719
5.0	0.102	0.0086
Rate constant (k) = $3.07 \times 10^{-3}$ sec <sup>-1</sup>		



**Fig. 1: A typical run**

### Effect of pH

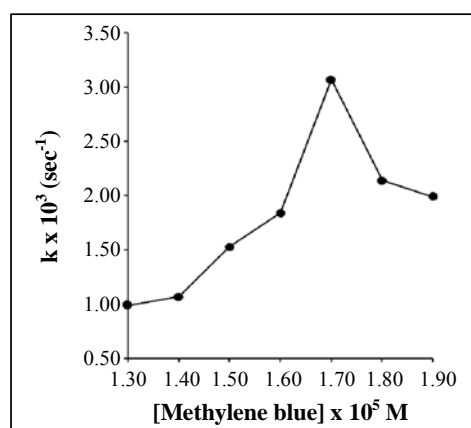
The effect of pH on the rate of degradation of methylene blue was investigated in the pH range 3.0 to 10.0. The results are graphically presented in Fig. 2. It is evident from the data that the photochemical degradation of methylene blue is very sensitive to pH of the reaction medium. The rate of reaction was found to optimum at pH = 3.0 and after that it decreases. It may be attributed to the fact that, at high pH, the generation of •OH radicals gets slowed down because of the formation of the ferric hydroxo complex.



**Fig. 2: Effect of pH**

### Effect of dye concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentrations of methylene blue solution. The results are graphically presented in Fig. 3. Effect of variation of dye concentration was also studied by taking different concentrations of dye i.e.  $1.3 \times 10^{-5}$  M to  $1.9 \times 10^{-5}$  M.

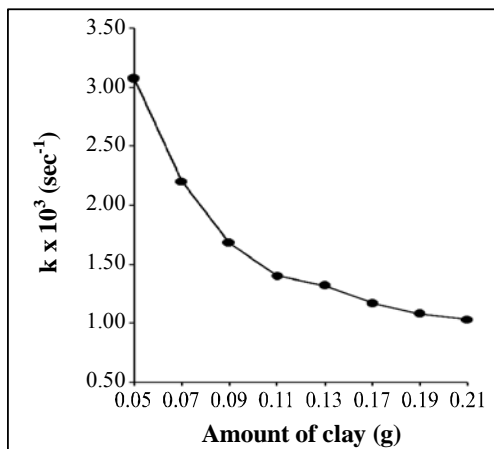


**Fig. 3: Effect of dye concentration**

The rate of photochemical degradation was found to increase with increasing concentration of methylene blue upto  $1.70 \times 10^{-5}$  M. Further increase in its concentration resulted in a sudden decrease in the rate of degradation. This may be explained on the basis that initially on increasing the concentration of methylene blue, more molecules of methylene blue were available for degradation. However, on increasing the concentration above  $1.70 \times 10^{-5}$  M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of methylene blue was increased above  $1.70 \times 10^{-5}$  M, it started acting like a filter for the incident light and therefore, its larger concentration will not permit the desired light intensity to reach the dye molecules in the bulk of the solution. Thus, a decrease in the rate of photochemical degradation of methylene blue was observed.

### Effect of amount of clay

The effect of amount of clay on the rate of photodegradation of methylene blue was observed by keeping all other factors identical. The amount of clay also affects the process of dye degradation. Different amounts of Fe-pillared clay were used (0.05 to 0.21 g). The results are graphically presented in Fig. 4.

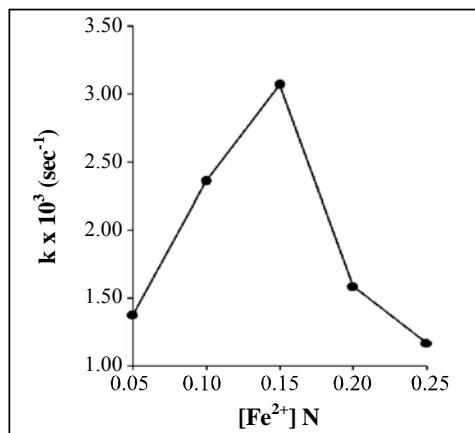


**Fig. 4: Effect of amount of clay**

There was a decreasing in the rate of reaction as increases the amount of Fe-pillared clay above 0.05 g. This may be due to the role of iron present in clay as a scavenger of  $\bullet\text{OH}$  radicals. As a result, the rate of photodegradation of the dye decreases.

#### **Effect of ferrous ion concentration**

The effect of concentration of  $\text{Fe}^{2+}$  ions on the rate of photodegradation of methylene blue was observed by keeping all other factors identical. Different iron concentration was used (0.05-0.25 N). The results are summarized in Fig. 5.

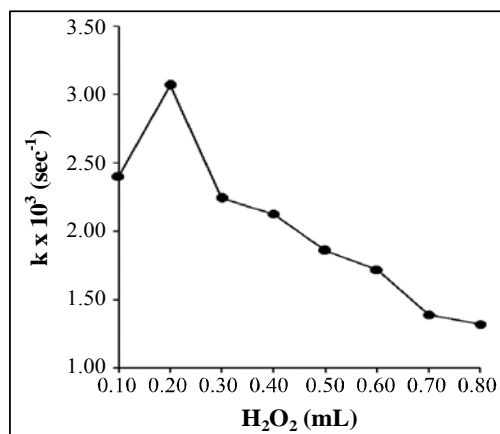


**Fig. 5: Effect of iron concentration**

It is clear from the data that the rate of photodegradation increases on increasing the concentration of  $\text{Fe}^{2+}$  ions upto 0.15 N, while a reverse trend was observed beyond this limit. This may be explained on the basis that increase in the  $\text{Fe}^{2+}$  ion concentration in the reaction mixture is accompanied by enhanced generation of  $\bullet\text{OH}$  radicals consequently increasing the rate of photodegradation. After the optimal  $\text{Fe}^{2+}$  ions addition, the higher concentration of  $\text{Fe}^{2+}$  resulted in a brown turbidity that causes the recombination of  $\bullet\text{OH}$  radicals.  $\text{Fe}^{2+}$  also reacts with  $\bullet\text{OH}$  as a scavenger and therefore, the rate decreases.

#### **Effect of amount of hydrogen peroxide**

The effect of amount of hydrogen peroxide on the photodegradation of methylene blue was also investigated. The amount of  $\text{H}_2\text{O}_2$  ranges from (0.1-0.8 mL). The results are graphically presented in Fig. 6.

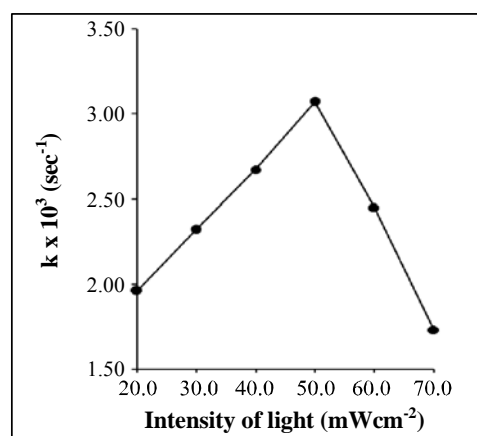


**Fig. 6: Amount of hydrogen peroxide**

It was observed that the rate of reaction increases on increasing the amount of H<sub>2</sub>O<sub>2</sub> upto 0.20 mL thereafter, a decrease in the rate of degradation was observed. This can be explained on the basis that at optimum concentration of H<sub>2</sub>O<sub>2</sub>, more hydroxyl radicals are produced by Fe<sup>2+</sup> ions, which degrade more dye molecules. On further increasing the amount of H<sub>2</sub>O<sub>2</sub>, the rate of reaction was found to decrease. It is because of the fact that as the amount of H<sub>2</sub>O<sub>2</sub> was increased along its optimum condition (0.20 mL), the rate of the reaction [Eq. 5 and 6 of mechanism] becomes fast and •OH radicals are consumed rapidly due to more availability of H<sub>2</sub>O<sub>2</sub> molecule. The peroxide radicals formed are utilized [Eq. 7 of mechanism] and H<sup>+</sup> ions were produced. The production of H<sup>+</sup> ions were confirmed by a slight decrease in pH of the reaction mixture at the end of reaction. As a consequence, the rate of photodegradation decreases.

### Effect of light intensity

The effect of light intensity on the photodegradation of methylene blue was also observed. The results are graphically presented in Fig. 6.



**Fig. 7: Effect of light intensity**

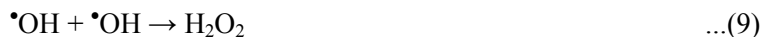
A linear plot was obtained between the rate constant and light intensity. It is evident from the data that an increase in the light intensity increases the rate of reaction because an increase in the intensity of light will increase the number of photons striking catalyst particles per unit time per square cm. As a result, more photons will react with Fe<sup>3+</sup> ions and generate more number of active species (hydroxyl radical) and hence, resulting in an increase in the rate of reaction.

## Mechanism

On the basis of the experimental observations and corroborating the existing literature, the mechanism of Fenton oxidation is based on the generation of  $\bullet\text{OH}$  radicals by the catalytic decomposition of  $\text{H}_2\text{O}_2$  in acidic media. In presence of  $\text{Fe}^{2+}$ , the peroxide breaks down to  $\bullet\text{OH}$  and  $\text{OH}^-$ , according to the following reaction.



Consumption of  $\bullet\text{OH}$  radicals



The ferrous ions decomposed  $\text{H}_2\text{O}_2$  into hydroxyl ions and hydroxyl radical, while ferrous ions undergo oxidation to ferric ions. The ferric ion generates  $\text{HO}_2\bullet$  radical due to dissociation of  $\text{H}_2\text{O}_2$  in presence of light. The aqueous solution of ferric ions on exposure to light dissociates water into a proton and  $\bullet\text{OH}$  radicals and ferric ions are reduced to ferrous ions. The incorporation of  $\bullet\text{OH}$  with  $\text{H}_2\text{O}_2$  also produces  $\text{HO}_2\bullet$  radicals. Ferric ions get reduced to ferrous ions by incorporation of  $\text{HO}_2\bullet$  radicals and producing  $\text{O}_2$  and  $\text{H}^+$  ions.  $\bullet\text{OOH}$  radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules.

## ACKNOWLEDGEMENT

Authors are thankful to Prof. Suresh C. Ameta, Dean, Faculty of Science, PAHER University, Udaipur for providing research facilities and for valuable guidance.

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