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Degradation of Congo red Using Fe-Loaded Montmorillonite Clay as a Heterogeneous Photo-Fenton Catalyst

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Abstract: Heterogeneous photo-Fenton degradation of Congo red over Fe-loaded montmorillonite in the presence of light has been carried out. The progress of reaction was monitored spectrophotometrically. The effect of some parameters such as pH, dye concentration, amount of Fe-loaded montmorillonite, light intensity etc. has been studied. Kinetic studies shows that this reaction follows pseudo-first order kinetics. A tentative mechanism for heterogeneous photo-Fenton degradation of Congo red has also been proposed.

Keywords: Heterogeneous photo-Fenton, Congo red, Fe-loaded montmorillonite.

INTRODUCTION

Effluents from various industries like textile, pulp, paper, dyeing, and printing industries contain pollutants like acid, detergent, soap, pesticides etc. are the major source of water pollution, this organic pollutants are very hazardous for human health[1,2].For environmental protection, there are a number of methods (chemical, physical, and biological) for treating discolored azo dye effluents from various industries. Biological and physical treatment methods are not satisfactory because they simply transfer the pollutants from one phase to another, and the equipment involved in these processes is expensive. In

recent years, treatments using advanced oxidation processes, i.e., chemical methods, have attracted much attention. Advanced oxidation processes such as homogeneous photo-Fenton reactions can produce hydroxyl radicals, which are powerful oxidants for organic degradation[3-6].

The Fenton reaction was discovered by H. J. Fenton in 1894, Fenton et al.[7], carried out oxidation of polycarboxylic acid with H_2O_2 and noted that there was a powerful promotion within the presence of metal ions (Fe^{2+}). A.Y. Sychev and V.G. Isak [8]carried out homogeneous catalysis via iron compounds true activation of O_2 and H_2O_2 and of their oxidation of organic substances. Formations of various intermediate species and of their role in these processes are analysed. B.G. Kwon et al.[9] carried out characteristics of the Fenton oxidation of p-chlorophenol Fenton's reagent. Various parameters such as the effects of pH, Fe^{2+} and hydrogen peroxide levels, *p*-chlorophenol concentration and chloride level. The decomposition proceeded rapidly only within a limited pH range of 2–4. Y.W. Kang and K.Y. Hwang[10] studied Fenton's oxidation process with quantitative analysis of the amount of the organic substances removed by oxidation and coagulation in treatment of the non-biodegradable landfill leachate by Fenton's reagents.

MATERIALS AND METHOD

Montmorillonite K10 clay was obtained from Aldrich. Congo red used as model pollutant in present investigation was obtained from SD fine chemicals, H_2O_2, ferrous sulphate, H_2SO_4 and NaOH (Qualigens) were of analytical grade. All the solutions were prepared with doubly distilled water. Ferrous sulphate aqueous solutions of different concentrations (0.05 N, 1.0 N, 1.5 N, 2.0 N and 2.5 N) were prepared in 500 ml doubly distilled water. Montmorillonite K-10 (50 g) was mixed with appropriate concentration of ferrous sulphate solution and the mixed suspension was stirred for 4-5 h at 25-30 °C. The Preparation of Fe-montmorillonite catalyst product was centrifuged and washed with water several times and finally dried in vacuum oven at 100 °C for 6-8h. The Fe-Montmorillonite catalyst was obtained as fine powder. This prepared semiconductor was used for the degradation of Congo red dye.

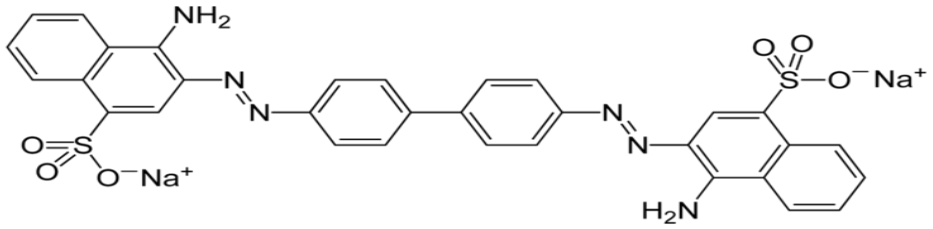

Figure: **Structure of Congo red dye**

Photo degradation methods and analysis: Stock solution of Congo red dye (1 x 10^{-3} M) was prepared in doubly distilled water. It was further diluted as and when required. The total volume of the reaction mixture was 50 mL. The heterogeneous photo-Fenton catalytic degradation of 50 ml of Congo red dye solution (1 X 10^{-5} M) was studied with appropriate quantity of Fe-loaded montmorillonite and H_2O_2 suspension was stirred for half an hour in dark and then a 200W tungsten lamp was used for irradiation (50.0 mW cm^{-2} light intensity). 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. The progress of reaction was observed at regular time intervals by measuring optical density using UV-Visible spectrometer (Systronic Model 106) at λ max 625 nm. The rate of dye degradation with the time was monitored continuously.

RESULTS AND DISCUSSION

Montmorillonite Characterization: The morphology of montmorillonite and Fe-loaded montmorillonite was studied with the help of JSM 5610 card, Zeiss scanning electron microscope. The SEM of this two systems are given in Figures A and B respectively. The SEM of pure Montmorillonite sample seem to have smooth particles while SEM of Fe-loaded montmorillonite showed some roughness in particles, which may be due to iron loading. The particle size of pure montmorillonite ranges between 15-45 µm. While the partical size of Fe-loaded Montmorillonite was slightly on the lower side i.e. 10-20 µm. It indicates that loading of iron on Montmorillonite not only make surface of the particle rough and irregular but also reduces its size. Thus corresponding increase the surface area.

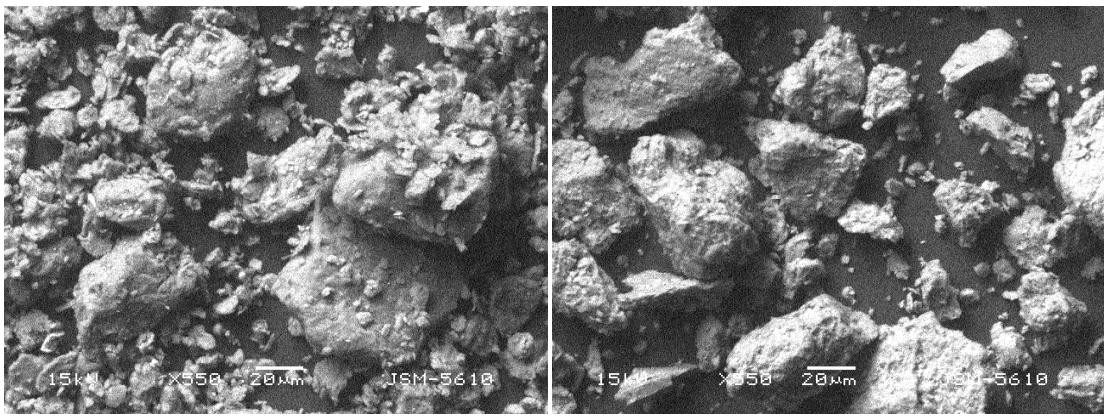

Figure A: SEM of pure montmorillonite clay Figure B: SEM of Fe-loaded montmorillonite clay

EXPERIMENTAL

Degradation of Fast green FCF was observed at λ = 625 nm. A graph plotted between logAbsorbance v/s time was a straight line, which shows that heterogeneous photo-fenton degradation of Fast green FCF follows pseudo-first order kinetics. The rate constant for degradation of dye was calculated by the following
Expression –

$$k = 2.303 \times \text{slope} \quad \ldots (4)$$

Table 1: Typical run

pH = 3.0 Fe-loaded montmorillonite = 0.17 g
[Congo red] = 4.0×10^{-5} M Light Intensity = 60.0 $mWcm^{-2}$
Amount of H_2O_2 = 0.4 mL

Time (min.)	Absorbance (A)	1 + log A.
8.00	0.478	0.6794
16.0	0.452	0.6551
24.0	0.417	0.6201
32.0	0.383	0.5831
40.0	0.351	0.5453
48.0	0.323	0.5092
56.0	0.303	0.4814
64.0	0.284	0.4533
72.0	0.253	0.4031
80.0	0.225	0.3521

Rate constant (k) = 1.73×10^{-4} sec^{-1}

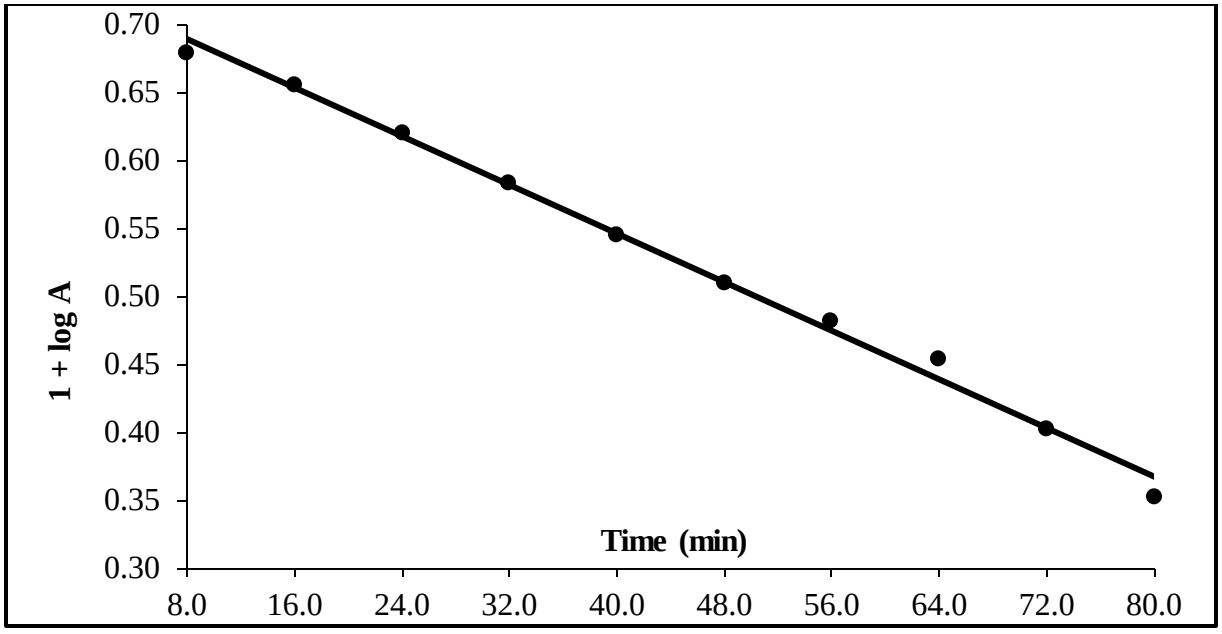

Fig. 1: Typical Run

Effect of pH: The effect of pH on photo-Fenton degradation was investigated at different pH and the results are given in Figure 2. The reaction rates were determined in the pH range 3.0–8.0 and the photo-Fenton degradation of Congo red was found maximum at pH 3.

[Congo red]= 4.0×10^{-5} M Light Intensity = 60.0 $mWcm^{-2}$

Fe-loaded montmorillonite = 0.17 g Amount of H_2O_2 = 0.4 mL

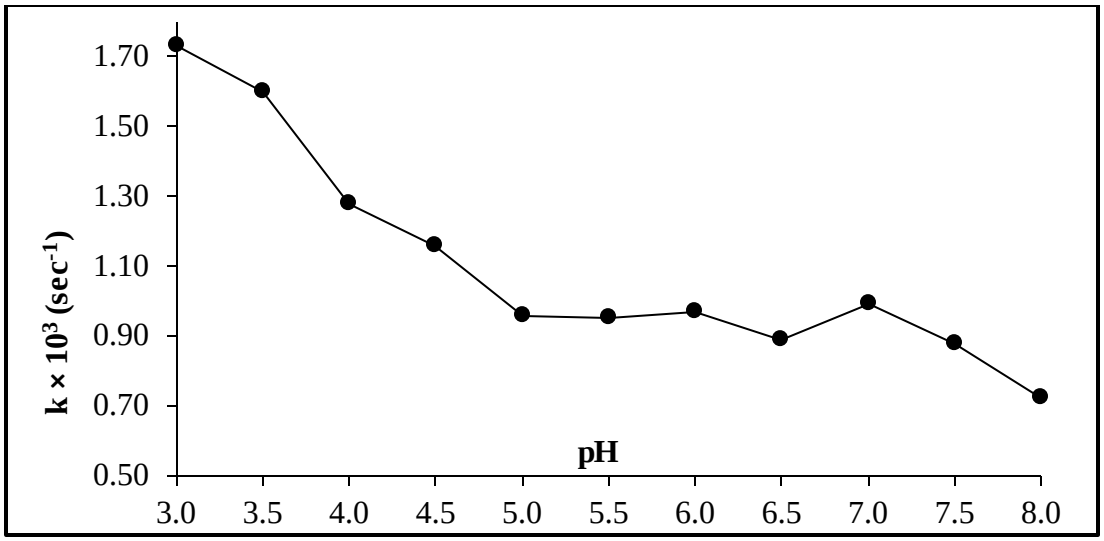

Fig. 2: Effect of pH

It has been observed that the rate of heterogeneous photo-Fenton degradation of Congo red decreased as the pH of medium was increased. It attained optimum value at pH 3.0. There is a greater probability for the formation of oxygen anion radicals ($O_2^{-\bullet}$) by reaction of dissolved oxygen with electron released by ferrous ions on exposure to light. This anion radical will react with H^+(at lower pH) to form $HO_2^{\bullet}$radical, which is an oxidizing species. Above pH 3.0, a decrease in the rate of photo-Fenton degradation of the dye was observed, which may be due to the fact that anionic form of Congo red is converted to its neutral form, which faces no attraction towards the negatively or positively charged semiconductor surface due to adsorption of ^-OH or H^+ ions

Effect of Congo red concentration: Effect of variation of dye concentration on rate of reaction was also studied by taking different concentrations of Congo red solution. The results are given in Fig, 3.The rate of heterogeneous photo-Fenton degradation of dye was found to increase on increasing the concentration of Congo red up to 4.0×10^{-5} M. It may be due to the fact that as the concentration of the dye was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of degradation of the dye was observed. A decrease in rate was observed on increasing the concentration of dye above 4.0×10^{-5} M; because now, dye will start acting as an internal filter and it will not permit the desired light intensity to reach the surface of the semiconductor present at the bottom of reaction vessel.

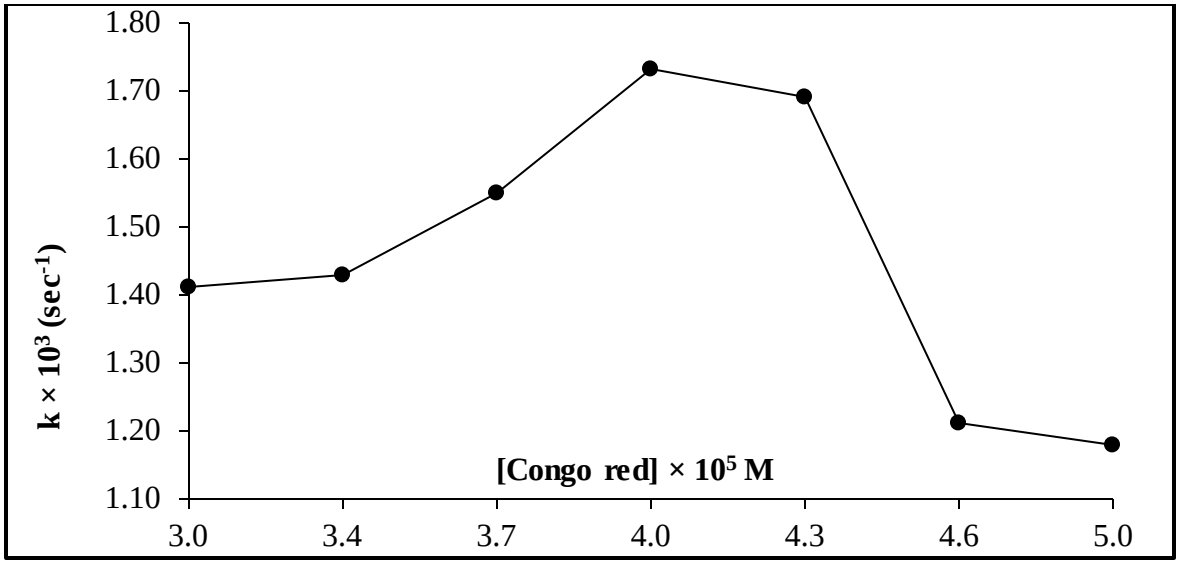

Fig. 3: Effect of Congo red concentration

Effect of amount of Fe-loaded montmorillonite: The effect of variation in the amount of catalyst on photo- Fenton degradation of Congo red was investigated in the range of 0.11 to 0.20 g. The results are presented in Fig. 4.

It was observed that the rate of reaction increases with increase in the amount of Fe-loaded montmorillonite. The rate of degradation was optimum at 0.17 g of it. Beyond 0.17 g, the rate of reaction become virtually constant. This may be due to fact that as the amount of Fe-loaded montmorillonite was increased, it exposed surface area was also increased. However, after this limiting value (0.17 g), an increase in its amount only increases the thickness of the layer and not the exposed surface area.

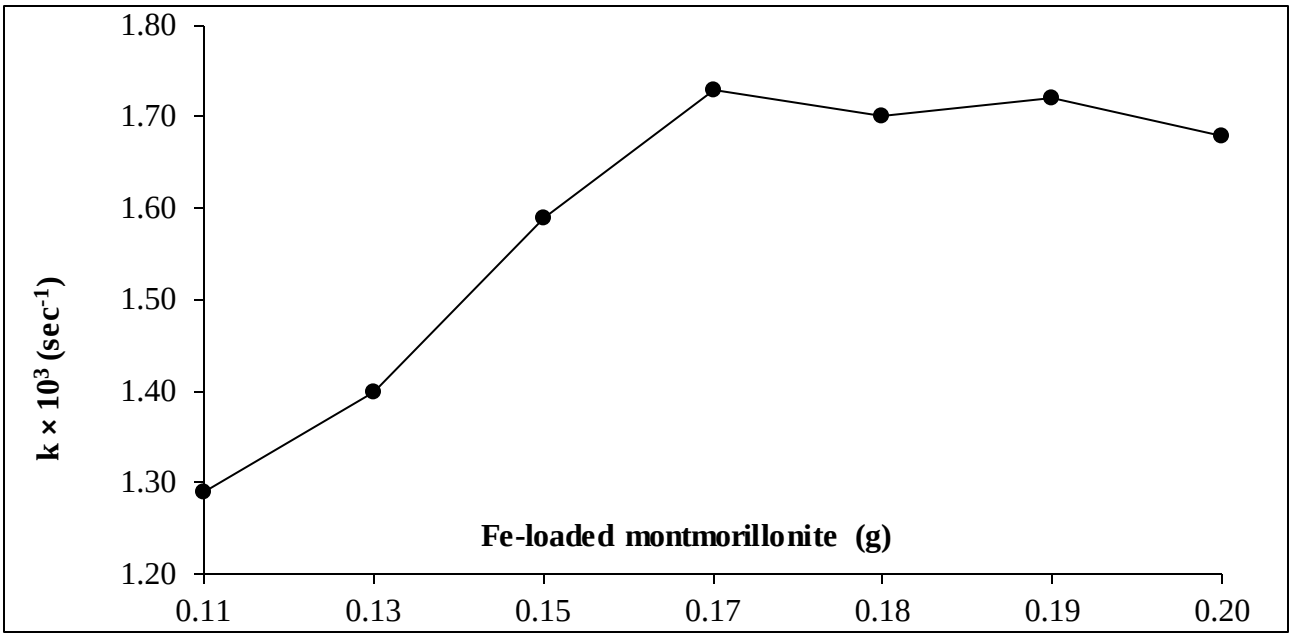

Fig. 4: Effect of amount of Fe-loaded montmorillonite

This was also confirmed by using reaction vessels of different dimensions.It was observed that the point of saturation was shifted to a higher value for vessels of larger capacities while it was shifted to lower value for vessels of smaller capacities.

Effect of iron-loading: The effect of concentration of Fe^{3+} ions on the rate of photo-Fenton degradation of Congo red was observed by keeping all other factors constant. The results are presented in Fig. 5.It was observed that the rate of reaction increases with increase in the Fe-loading. The rate of degradation of Congo red increases because number of Fe^{2+} ions increases with higher iron-loading the results were obtained for 0.15 N Fe-loaded montmorillonite because the reaction become so fast that degradation could not be monitored.

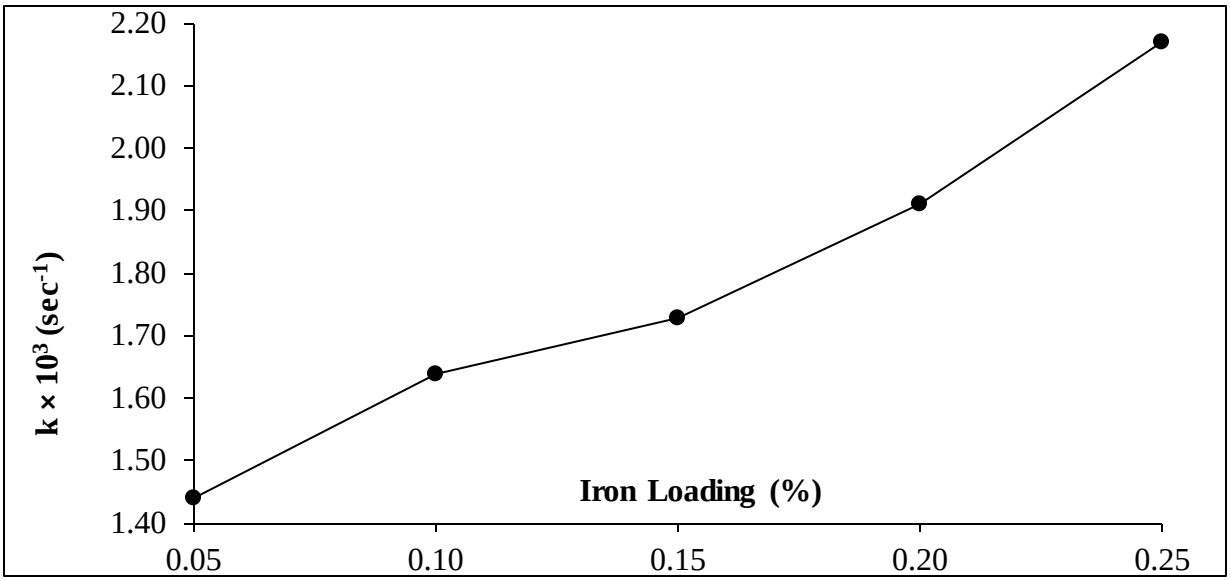

Fig. 5: Effect of iron-loading

Effect of hydrogen peroxide: The effect of amount of hydrogen peroxide on photo-Fenton oxidation of Congo red was also reported. The results obtained are given in Fig. 6

It was observed that the rate of reaction increases with increase in the amount of H_2O_2. Reaction rate increases with increase in the amount of H_2O_2 as it generates more OH ions in presence of light and Fe^{2+}-Mont, which in turn donates it electron to dissolved oxygen generating more oxygen anion radicals ad consequently more $HO_2^{\bullet}$ radical, the active oxidizing species.

Effect of light intensity: The effect of light intensity on the photo-Fenton degradation of Congo red was also observed. The results obtained are given in Fig. 7.

The results indicate that photo-Fenton degradation of Congo red was accelerated as the intensity of light was increased, because an increase in the light intensity will increase the number of photons striking per unit area of Fe-loaded montmorillonite surface per unit time. On further increasing the intensity of light above 50.0 $mWcm^{-2}$, there was a slight decrease in the rate of reaction. This may be due to some side reactions or thermal effect.

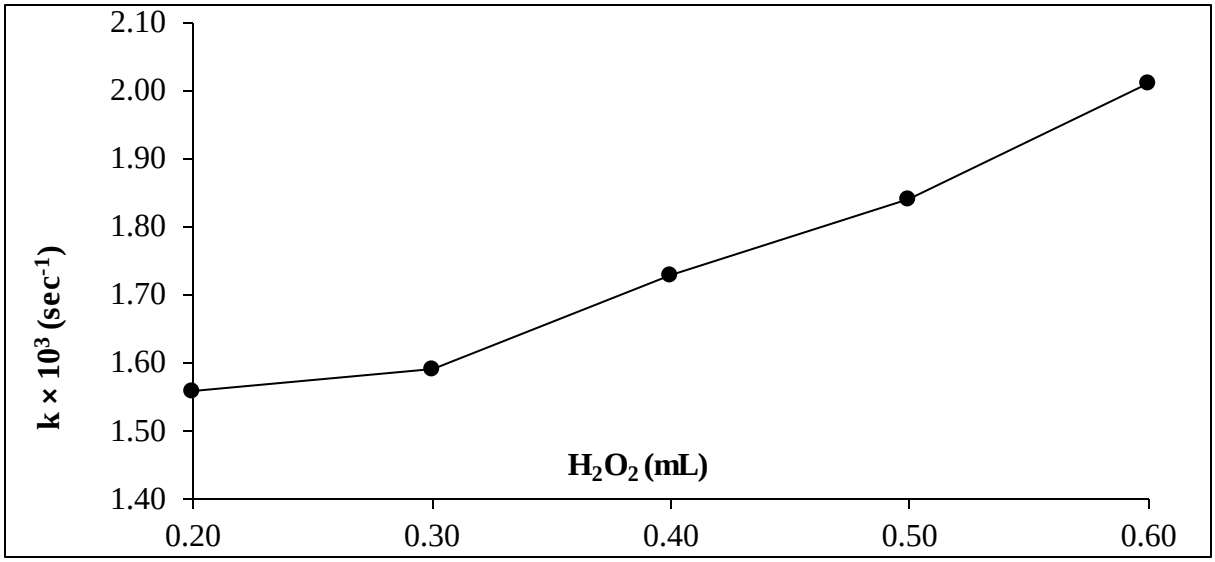

Fig. 6: Effect of Hydrogen peroxide amount

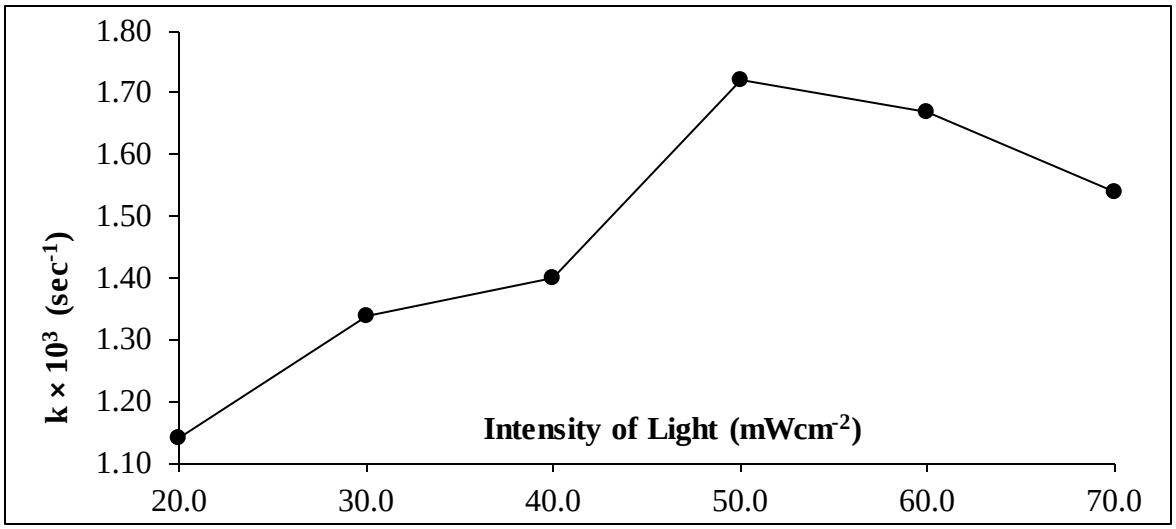

Fig. 7: Effect of Light Intensity

MECHANISM

On the basis of these observations, a tentative mechanism for photo-Fenton degradation of Congo red dye is proposed as follows:

$$^{1}CR_{0} \xrightarrow{h\nu} {}^{1}CR_{1} \quad \text{.... (1.1)}$$

$$^{1}CR_{1} \xrightarrow{ISC} {}^{3}CR_{1} \quad \text{.... (1.2)}$$

$$Fe^{2+} - Mont + H_2O_2 \xrightarrow{h\nu} Fe^{3+} - Mont + {}^{\bullet}OH + {}^{-}OH \quad \text{.... (1.3)}$$

$${}^{-}OH + O_2 \longrightarrow O_2^{-\bullet} + {}^{\bullet}OH \quad \text{.... (1.4)}$$

$$H^{+} + O_2^{-\bullet} \longrightarrow HO_2^{\bullet} \quad \text{.... (1.5)}$$

$$HO_2^{\bullet} + 3CR_1 \longrightarrow \text{Leuco CR} \quad \text{.... (1.6)}$$

$$Fe^{3+} \text{-} Mont + H_2O \xrightarrow{h\nu} Fe^{2+} - Mont + H^{+} + {}^{\bullet}OH \quad \text{.... (1.7)}$$

$${}^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \quad \text{.... (1.8)}$$

$$\text{Leuco CR} \longrightarrow \text{Products} \quad \text{.... (1.9)}$$

Congo red absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the Fe-loaded montmorillonite (Fe-Mont) react with H_2O_2 and is converted into Fe^{3+}- loaded montmorillonite, hydroxyl radical and hydroxide ion. An electron from ^{-}OH ion will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will react with proton (H^{+}) and will generate hydroperoxyl radical ($HO_2^{\bullet}$). This $HO_2^{\bullet}$willoxidize the dye Congo red to its leuco form,which may ultimately degrade to products. Fe^{3+}-Mont is reverted back to Fe^{2+}mont in presence of both light and water. Hydroxyl radicals may dimerize to regenerate hydrogen peroxide. Here, $^{\bullet}OH$ radical does not participate as an active oxidizing species in this degradation. It was also confirmed that this degradation proceeds through oxidation by $HO_2^{\bullet}$radicals as the rate of degradation was not affected appreciably in presence of hydroxyl radical scavenger (2-propanol).

CONCLUSION

Heterogeneous phot-Fenton process is capable of oxidizing dye like Congo red into colorless degradation product. The present's works open an eco-friendly method by using heterogeneous photo-Fenton system to carry out waste water treatment. The treated waste water may be used for cooking, cleaning, irrigation, etc. which is not possible otherwise by colored water.

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