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Kinetic Study of Degradation of Methylene Blue Dye using Fenton Catalyst

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Introduction

Manufactured colors are generally utilized for the production of material, mash and paper, plastic, nourishment etc. With large scaled production of colors, release of manufactured color containing wastewater has been increased. This imposes potential threat for the environment, as degradation of dyes are relatively difficult due to their complex and stable structure. Moreover, there are severe effects has already been reported on human and aquatic life due to increased production of dye and dye containing wastewater [1, 2]. So economically viable treatment of dye containing wastewater has gained consideration. Heterogeneous Fenton type catalyst can be answer to this problem. In this study, we have focused on kinetics of degradation of methylene blue dye. Kinetics of said reaction may be useful for design of wastewater treatment plant.

Preparation of Fenton catalyst:

Catalyst with 5 wt.% Fe loading was prepared by wet impregnation method [3]. Image of prepared catalyst is shown in Figure 1.Detailed steps are outlined below.

1. **Solution Preparation:** The solution was prepared by dissolving required weight of metal precursor salt into a required quantity of distilled water. $FeSO_4$**.** $7H_2O$ was selected as metal salt precursor.
2. **Impregnation:** An aqueous solution was taken in burrete and added in to a flask which already contained support γ-Al_2O_3. Solution was stirred for 12 hr for the impregnation of metal salt on support.
3. **Drying:** The slurry form solution was kept for overnight (12hr) for drying in the hot air oven at 110 °C for removal of moisture.
4. **Calcination:** In the calcination process, dried catalyst was kept in the open air mu□e furnace at 500 °C for 4hr with rise of 14 °C/6.86 min from room temperature.

Figure 1. Image of 5 wt.% Fe catalyst.

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Experimentation:

All experiments were performed in a conical flask (250 mL) placed on magnetic stirrer with 280 rpm rotation speed. Reaction suspension has containing methylene blue dye concentration is in ppm and 0.25 gm (5 wt.%) Fe/γ-Al_2O_3 catalyst was prepared, and its initial pH was adjusted to 3 by diluted 1N HCl. The experiments were initiated by adding the desired amount of 6% W/V H_2O_2 to the reaction mixture. Samples were collected at pre-determined time intervals during the reaction, and then 1 N NaOH was immediately added to the sample as reaction inhibitor. Dye concentration before and after reaction were analyzed by UV-vis spectroscopy techniques. For the same, calibration curve (Figure 2.) was prepared by preparing solutions of known concentration of methylene blue dye.

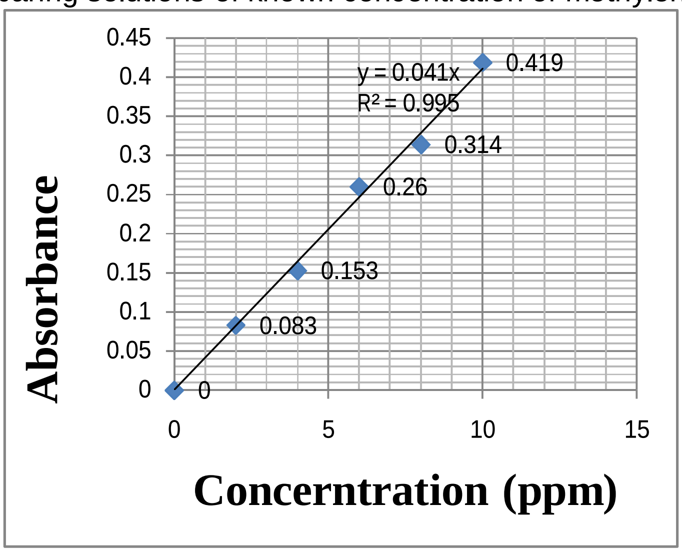

Figure 2. Absorbance versus methylene blue dye concentration

Kinetic study:

Kinetics of dye degradation reaction was analyzed by integral method of analysis. Analysis were carried out by assuming zero, half, first and second order kinetics with respect to dye concentration. Following equations were considered and plotted against time in order to estimate actual order of reaction [4]. Where, C_t is dye concentration at time t and C_0 is initial dye concentration. While k_0, $k_{0.5}$, k_1 and k_2 are rate constant for zero, half, first and second order reactions respectively.

For zero order reaction

$$C_t = C_0 - k_0 t$$

For half order reaction

$$\sqrt{C_t} = \sqrt{C_0} - \frac{k_{0.5}}{2} t$$

For first order reaction

$$lnC_t = lnC_0 - k_1 t$$

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For second order reaction

$$\frac{1}{C_t} = \frac{1}{C_0} + kt$$

Left hand side term of above equations were plotted against time t in Figure 3, 4, 5 and 6.

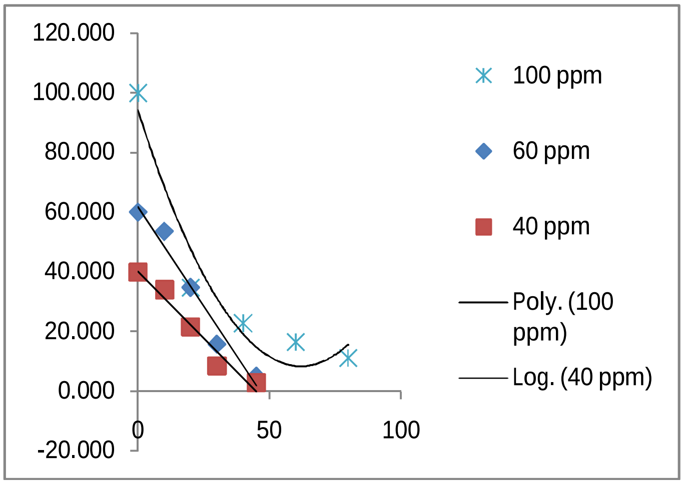

Figure 3. For zero order reaction, Ct versus time t relation.

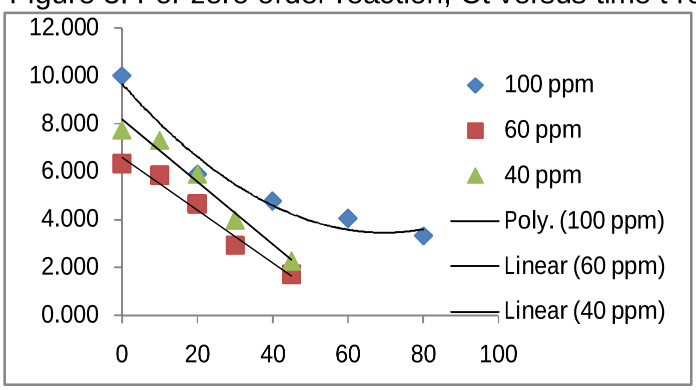

Figure 4. For zero order reaction, $\sqrt{C_t}$ versus time t relation.

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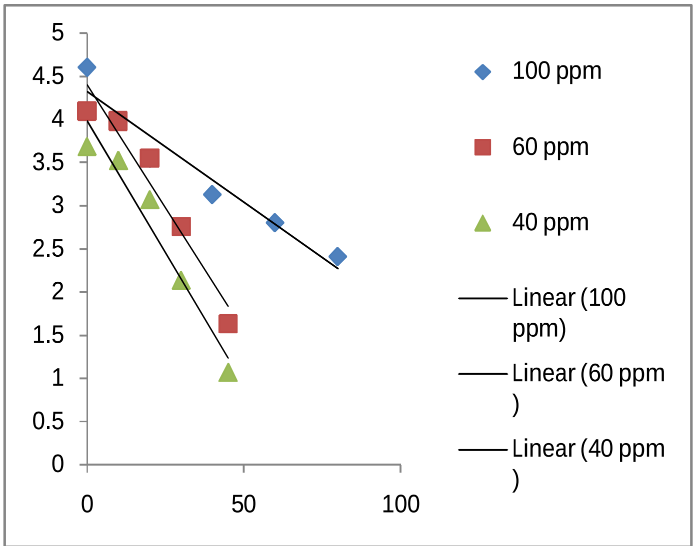

Figure 5. For first order reaction, ln C_t versus time t relation.

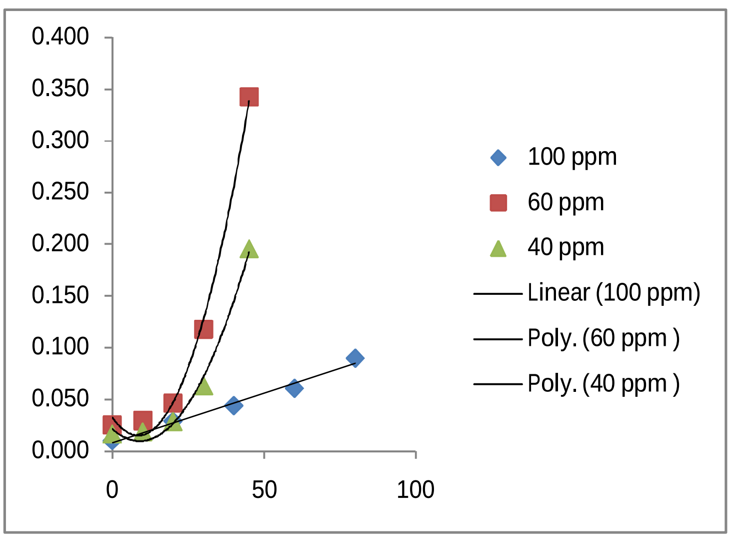

Figure 6. For second order reaction, $1/C_t$ versus time t relation.

After careful examination of above curves, it was found that dye degradation closely follow first order kinetics. Because graph for ln Ct versus t was almost straight line for 100, 60 and 40 ppm initial dye concentration samples

Conclusion:

In this study kinetics of methylene blue dye degradation were studied and it was observed that it follows first order reaction with respect to dye concentration. This study further can be extended to encounter effect of temperature, pH and catalyst loading. Collectively all these information can provide detailed kinetics of reaction. This study can be stepping stone in further research in this area.

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