

## Methylene Blue Dye Adsorption Using a Polymer Coated ZnO with Chitosan Nano-Catalyst

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**Abstract:** Polymer Coated ZnO with chitosan nanocatalyst was synthesized with a 0.2:0.2:0.4 molar ratios of polymer and chitosan to ZnO using microwave hydrothermal method. Using Polymer Coated ZnO with chitosan nanocatalyst as an adsorbent for the removal of methylene blue dye from synthetic waste water showed very good adsorption ability as compared to ordinary ZnO, individual polymer and polymer-ZnO samples. The decolorization adsorption efficiency was determined to reach 98.01% within 90 mins. In order to determine the maximum sorption capacity of the sample, various parameters such as pH, initial concentration and dosage of the catalyst used and time of contact. The adsorption process was found to follow the pseudo-second order reaction kinetics.

**Keywords:** Adsorption, Catalysis, Methylene blue and Kinetics

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### I. Introduction

The employment of organic, inorganic and semiconducting materials as nanocatalyst in the absorption of industrial waste water containing organic dyes has gained considerable interest in the recent years. Though various semiconductor nanoparticle materials have been used, ZnO nanomaterial has received much attention due to its chemical and thermal stability, non-toxicity, high catalytic efficiency and low cost. Generally, introducing inorganic materials such as metals into the matrix of semiconductor materials can result in some changes in the behavioural properties of the polymer such as; nanostructure, performance efficiency, improved moisture resistance and possession of multi-functional features beyond the normal semiconductor material exhibits. Although, TiO<sub>2</sub> is the most commonly used photo-catalyst for the degradation of organic pollutants such as dyes and phenolic contaminants, but at the same time ZnO is also a potential widely investigated photo-catalyst in the recent years. ZnO has some advantages over TiO<sub>2</sub> such as its ability to absorb over wide portion of the spectrophotometer and the visible region, hence it absorbs more light quanta compared to TiO<sub>2</sub> (Curri et al 2003; Chen et al 2008). Every photocatalytic reaction usually starts by irradiating photons from a semiconductor surface having the same or higher energy to its band gap, leading to generation of electrons and holes in the conduction and valence bands, respectively to the surface of the semiconductor. This electron thus becomes promoted to the conduction band (CB) hence leaving behind a positive hole in the valence band (VB). The recombination of electrons and holes easily occur in the excited-state and this result in the dissipation of the input energy as heat. However, reacting materials with either electron acceptors or donors with adsorbed compounds on the surface semiconductor can lead to their complete adsorption (Herrmann et al. 2007; Sánchez-Muñoz et al. 2013). For any adsorption process to occur the formation of radicals such as OH, O<sup>2-</sup> H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> is very important because they play a role in the formation of CO<sub>2</sub> and water from organic compound in a complete model adsorption reaction (Sánchez-Muñoz et al. 2013). This study aimed at measuring the organic dye absorption ability of the microwave prepared polymer coated ZnO with chitosan nanocatalyst under a closed reaction chamber equipped with visible light lamp.

### II. Methodology

11 grams of Zn(CH<sub>3</sub>OO)<sub>2</sub>.2H<sub>2</sub>O was dissolved in 100 mL deionised water and was agitated for 15 mins and then it was finally transferred into a Teflon reaction vessel where it was irradiated in the Microwave oven operating at 120°C and 240 Watt for 15 mins. The irradiated solution was then removed from the microwave and allowed to cool down naturally. After which two separate layers of condensate and water were formed and was separated by microfiltration, filtrate was washed several times with ethanol absolute and deionised water. The obtained crystallite sample was further dried in the oven for 6 hrs at temperature of 60°C.

### **Aqueous methyl blue dye adsorption procedure**

The MB dye adsorption was conducted under visible-light where 0.75g of the polymer coated ZnO with chitosan sample was suspended in 500 mL of a 50 ppm methyl blue (MB) solution. The light source was a visible LED lamp (4.5 W) in a closed photocatalytic chamber with under a magnetic stirrer where the suspensions were located for the experiments. Prior to irradiation, suspension with the photocatalyst was stirred for 45 mins to ensure that the surface of the photocatalyst was saturated with MB in order to attain adsorption-desorption equilibrium. The total exposition under UV-light of all experiments was 90 mins. The experiments were carried out in duplicate and the absorbance measures in triplicate as demonstrated in Fig. 1.

### **III. Results and Discussions**

Based on the results obtained from this study, the use of Polymer Coated ZnO with chitosan nanocatalyst showed an improved decolorization ability of methylene blue dye as compared with ZnO and chitosan coated samples from synthetic waste water.

#### **Effect of pH on Methylene blue dye adsorption**

One of the most important parameter to be considered during adsorption process is the pH of the solutions. The pH of any solution influences ionization level of the ions in the solution and thereby promoting the surface charge of the adsorbent (Akar, T et al. 2008). The Effect of pH on the adsorption of MB is shown in Fig. 2 where pH ranging from 3-8 was considered using  $100 \text{ mgL}^{-1}$  as the initial concentration of MB dye. Result obtained shows an increased MB adsorption from pH 3-5 and then decreased rapidly down from pH 6-8. For all the samples, the maximum MB adsorption was attained at pH 6 with efficiency 98.01, 40.35 and 43.19  $\text{mgg}^{-1}$  respectively for polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO only.

The observed lower adsorption at lower pH is as a result of higher acidic condition thus, causing the surface of the adsorbent more positively charged and the protonation at acidic conditions tends to reduce binding site for the sorption of the MB dye. Thereby causing a competitive adsorption between the  $\text{H}^+$  ion and the MB molecular ions present on the active adsorption site (Liu, Chen et al. 2010).

#### **Effect of catalyst initial concentration on MB adsorption**

The effect of catalyst concentration was studied by varying the concentration of the MB from 10, 20, 30, 40, 50, 70, 90 and 120 ppm. As observed from Fig. 3, the adsorption capacity all samples was found to increase with increase in concentration MB increases up to 50 ppm and then decreased then sharply decreased as the concentration was decreased further. Therefore, 50 ppm can be said to be the optimum concentration therefore it was considered throughout the analysis. The capacity of adsorption increased from 12.57 to 34.19, 15.41 to 40.35 and 38.2 to 98.01  $\text{mgg}^{-1}$  for ZnO, ZnO with chitosan and polymer coated ZnO with Chitosan respectively before decreasing. This observation could possibly be as a result of increased number of binding sites mainly due to the presence of more electrostatic interactions and interference from available solute (Akar et al. 2008).

#### **Effect of contact time on MB adsorption**

The decolorization capacity was determined as a function of time in order to evaluate the maximum time of contact during the adsorption process. As observed from Fig. 4, at first there was a gradual decolorization during the first 60 minutes, and then a suddenly increased very fast towards 90 mins but became saturated with MB ions after 15 mins. Therefore, the adsorption equilibrium time is assumed to be achieved between 75 – 90 minutes. This observation is similar in all the samples therefore 90 minutes were considered as the adsorption period for the study.

#### **Effect of catalyst dosage on MB dye adsorption**

The effect of catalyst dosage on decolorization efficiency of MB as illustrated in Fig. 5 by varying the catalyst dosage from 0.25 – 1.0 g in  $100 \text{ mgL}^{-1}$  of MB dye at pH 5. The decolorization of MB dye was found to increase as the catalyst dosage was increased from 0.25 to 0.5 g but decrease continuously as the dosage was increased from 0.5-1.0 g and this is observed in all the samples. The adsorption capacity decreases from 55.01 to 18.2, 9.56 to 2.10 and 4.47 to 0.95  $\text{mgg}^{-1}$ . This is because as the catalyst dose increases beyond the optimum load, there will be excess particles present in the solution which tends to shield the surface of the solute thus, causing a screening effect which lower sorption capacity utilization of the catalyst (Liu, Chen et al. 2010).

### Adsorption kinetic study

In order to study the adsorption process and the rate at which it occurs by evaluating the experimental data using most popular kinetic models which are pseudo-first order and pseudo-second order kinetic models and the process was observed to from the pseudo-second order kinetic model. The pseudo-second-order kinetics is based on the adsorption of solid phase capacity which is predicted over the entire data being the rate controlling step which is in agreement with chemisorptions process as given by ( Vijaya, Y et al. 2008 and Ho, McKay et al. 2000):

$$\frac{dq}{dt} = k_{2,ad} (q_e - q)^2 \quad (1)$$

Where  $k_{2,ad}$  is the rate constant for second-order-adsorption in (g/mg.min<sup>2</sup>) considering the same boundary conditions the integrated form of equation (1) can be expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

The initial adsorption rate,  $h$  (mg/g. min), at  $t = 0$  is given as

$$h = k_{2,ad} q_e^2 \quad (3)$$

Where  $k_{2,ad}$  and  $h$  are determined from the slope and intercept of the plots of  $t/q$  against  $t$  from Fig. 6

### IV. Conclusion

The adsorption of MB dye from synthetic wastewater was successfully reported using polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO as adsorbent. The effect of various experimental parameters influencing the adsorption ability of the adsorbent such as catalyst dosage, pH of the MB dye, initial concentration and time of contact were studied. The maximum methylene blue dye adsorption was observed to occur at pH 6 for all the samples. This occurred at very low dosage of 0.5 g for all samples at 90 mins. The optimum decolorization of MB dye was recorded as 98.01, 40.35 and 34.19 mgg<sup>-1</sup> polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO respectively. The kinetic studies shows the adsorption of MB dye by polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO follows the pseudo-second-order kinetics. The results obtained in this study show that polymer coated ZnO with chitosan has better ability to decolorize and adsorb MB dye as compared to ZnO with Chitosan and ZnO.

### V. Figures and Tables

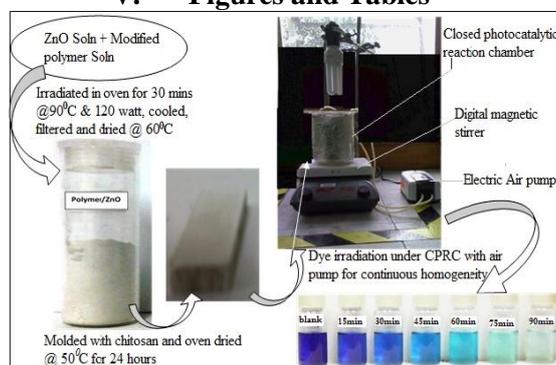


Figure 1: Illustration demonstration the formation of catalyst and its application in the adsorption of Methylene blue dye.

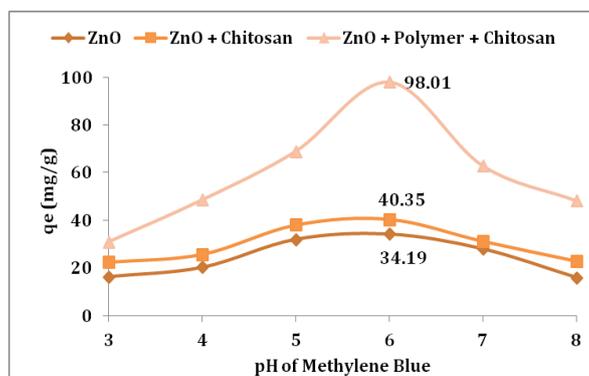
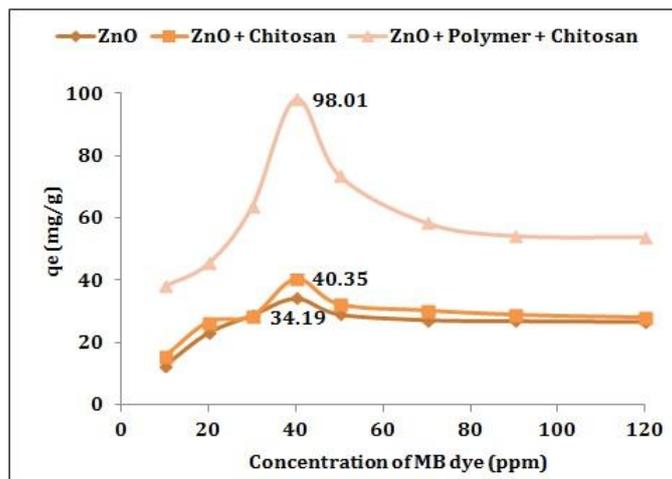
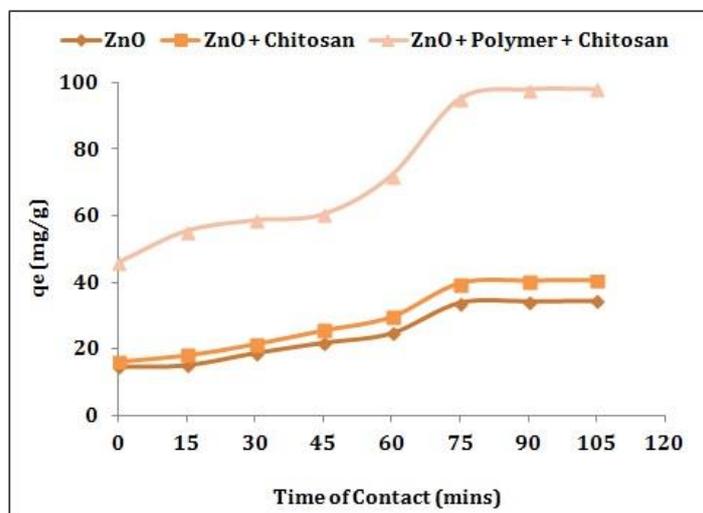


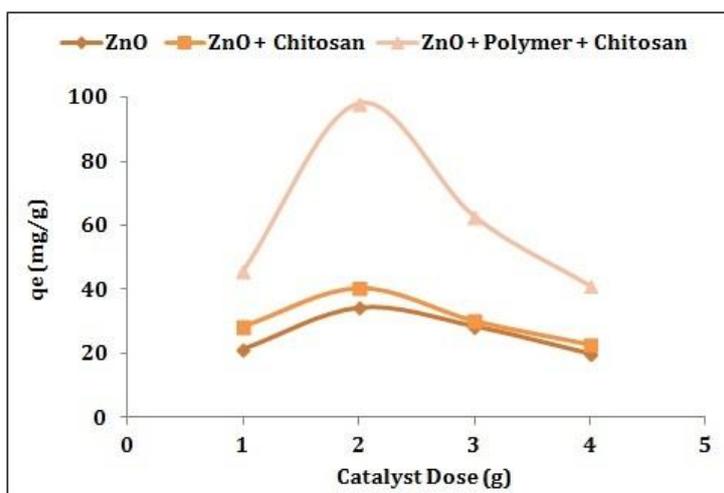
Figure 2: Effect of pH on adsorption ability of ZnO, ZnO with chitosan and polymer coated ZnO with Chitosan



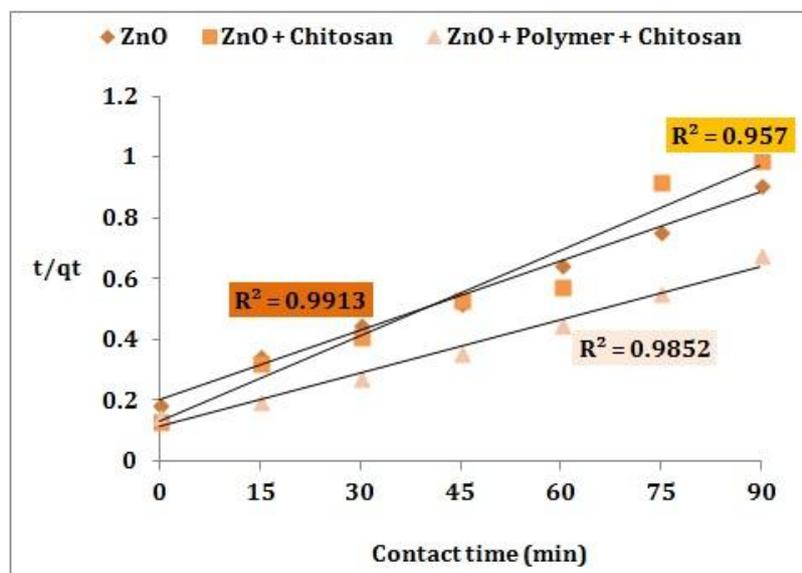
**Figure 3:** Effect of various catalyst concentrations on the adsorption of methylene blue. Experimental Condition: Mass of catalyst =0.5g, contact time 90 mins at pH 6.



**Figure 4:** Effect of contact time on the adsorption of methylene blue. Experimental Condition: Mass of catalyst =0.5g, contact time 0-105 mins at pH 6.



**Figure 5:** Effect of varying dosage on the adsorption of methylene blue. Experimental Condition: Mass of catalyst 0.25 - 1.0g, contact time 90 mins at pH 6.



**Figure 6:** Pseudo-second-order kinetics plot for MB dye onto polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO. Experimental Condition: MB dye concentration = 50 ppm, Mass of catalyst = 0.5 g, contact time = 90 mins at pH 6.

## VI. Conclusion

The adsorption of MB dye from synthetic wastewater was successfully reported using polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO as adsorbent. The effect of various experimental parameters influencing the adsorption ability of the adsorbent such as catalyst dosage, pH of the MB dye, initial concentration and time of contact were studied. The maximum methylene blue dye adsorption was observed to occur at pH 6 for all the samples. This occurred at very low dosage of 0.5 g for all samples at 90 mins. The optimum decolorization of MB dye was recorded as 98.01, 40.35 and 34.19  $\text{mgg}^{-1}$  polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO respectively. The kinetic studies shows the adsorption of MB dye by polymer coated ZnO with chitosan, ZnO with Chitosan and ZnO follows the pseudo-second-order kinetics. The results obtained in this study shows that polymer coated ZnO.

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