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Equilibrium and Kinetic Studies on Adsorption of Methylene Blue Dye by ZnO Nanoparticles Synthesized by Hydrothermal Method

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ABSTRACT:

Metal oxides play significant role in many fields of nanotechnology including nanocatalysis, sensing, supermagnetic properties, fuel cells, nanoenergy storage and conservation. Dyes are synthetic compounds which have wide range of application in textiles, paints etc., and the dye effluents from the dyeing industries cause water pollution**.** In this present study, ZnO photocatalyst have been synthesized by hydrothermal method and were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and UV-VIS techniques. The XRD data revealed the hexagonal Wurtzite structure. The surface morphology of the synthesized ZnO photocatalyst was in the range of 50 -70nm in size which was obtained by SEM analysis. Degradation of methylene blue dye was studied using the synthesized ZnO photocatalyst. The process of degradation relies due to oxidation by highly reactive hydroxyl radicals. The factors such as ZnO dosage, pH and concentration of methylene blue dye were examined. Equilibrium and kinetic datum were derived from adsorption isotherms such as Freundlich and Langmuir models.

KEYWORDS: *Hydrothermal method, ZnO photocatalyst, Methylene blue, Freundlich Isotherm, Langmuir Isotherm*

1. INTRODUCTION

ZnO has the Wurtzite hexagonal crystal structure which is the most stable. [1]. ZnO nanoparticles have been extensively used in many industrial areas such as solar cells [2], UV- light emitting devices, gas sensors, photocatalysts [3] and cosmetic industries[4]. ZnO nanoparticle is non-toxic and it is a strong antibacterial agent [5].The dyes are extensively used in textile, printing, cosmetics food processing etc. in recent years, environmental pollution caused by the release of toxic chemicals from industries. The toxic effluents causes various environmental and health hazards [6]. To overcome this major issue various removal techniques were established such as biodegradation [7], adsorption [8], evaporation, reverse osmosis and advanced oxidation process (AOP) [9].

ZnO nanoparticles are synthesized by various methods such as microwave assisted synthesis [10], sol-gel method, hydrothermal synthesis [11], precipitation method [12] and green synthesis [13]. In this present study, ZnO photocatalyst was synthesized by hydrothermal method. ZnO is a better semiconductor and effectively degrade dyes in both acidic and basic medium. Hence, ZnO photocatalyst is used for the removal of methylene blue, a basic dye.

2. EXPERIMENTAL METHODS

2.1 Preparation of ZnO Photocatalyst by Hydrothermal Method

Zinc acetate (6g) is dissolved in 30ml of distilled water, added 15% starch solution as stabilizing agent and stirred. To the above mixture added 0.1N NaOH in drops along the sides of the flask and stirred for 2 hours. The recovered ZnO dried at 100°C.

2.2 Preparation of stock dye solution

The stock solution of methylene blue dye was prepared by dissolving 0.5g of methylene blue dye in 100ml of double distilled water in 100ml standard flask.

2.3 Characterization

UV-VIS analysis was carried out using ELICO SL-159 UV-VIS spectrophotometer to determine the λ_{max} of ZnO and dye solution. FT-IR analysis carried out to determine the functional groups. XRD studies were carried out to determine the structure of ZnO and SEM analysis for surface morphology of ZnO nanoparticles.

2.4 Variation of dosage with time

The aqueous dye solution was treated with ZnO nanoparticles of different dosages (0.25-0.75g) and stirred for 30min in magnetic stirrer. The solution was centrifuged and absorbance was measured at the wavelength of 610nm. The dye solution was treated with 0.5g of ZnO and stirred for 120 min and absorbance was recorded at the time interval of 10min at the wavelength of 610nm.

2.5 Variation of initial dye concentration of dye and pH

The different concentrations of dye solution (3-7 mg/L) were prepared and 0.5g of ZnO nanoparticles were added and stirred for 30min in magnetic stirrer. The solution was centrifuged and absorbance was measured at the wavelength of 610nm.

The different pH (2-12) were adjusted using pH meter by adding 0.1N HCl and 0.1N NaOH. The solutions were treated with 0.5g of ZnO and stirred for 30min in magnetic stirrer. The solution was centrifuged and absorbance was measured at the wavelength of 610nm.

2.6 Adsorption isotherms

Adsorption isotherm models of Langmuir and Freundlich were applied to determine the extent of adsorption feasibility of the reaction.

2.7 Comparison of the rate of degradation of dye

The rate of degradation of dye was compared with and without the addition of photocatalyst.

3. RESULTS AND DISCUSSION

3.1 Determination of maximum absorption of methylene blue dye

The absorbance of the methylene blue dye was recorded as a function of wavelength. The value of λ_{max} was found to be at 610nm (figure 1) and standardized (figure 2).

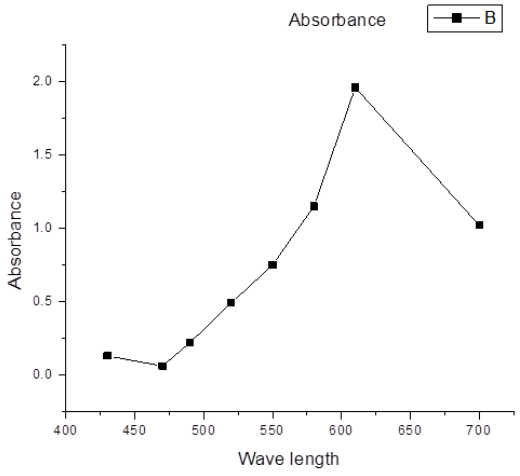

Figure 1

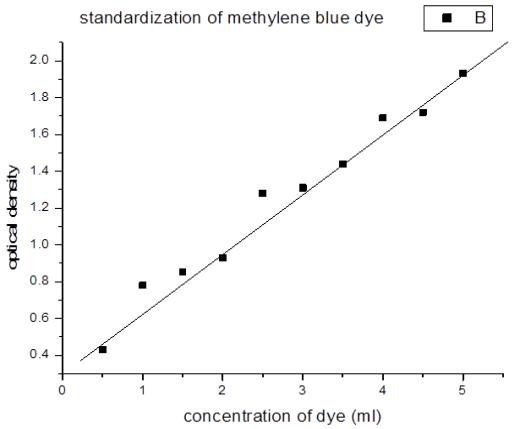

Figure 2

3.2 UV-VIS analysis of ZnO

The intense peak at the wavelength of 351nm in UV region confirmed the presence of ZnO photocatalyst (figure 3).

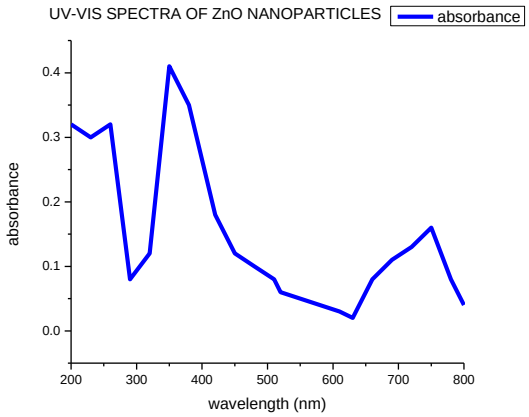

Figure 3

3.3 FTIR Spectral Analysis of ZnO Photocatalyst

The characteristic broad peak at 3200 cm^{-1} indicates the –OH stretching, 1448 cm^{-1} shown fundamental overtone of –OH stretching frequency. The peaks at 888-704 cm^{-1} shows the fingerprint region of Zn-O stretching frequency.

3.4 SEM Analysis

The scanning electron micrograph clearly revealed the surface morphology of the biosorbent. It was evident from the micrographs that the synthesized photocatalyst was found to be in the range of 70 nm in size (figure 5).

3.5 XRD spectral analysis

The XRD pattern of ZnO synthesized by hydrothermal method is shown in fig -5. The major diffraction peaks observed at 2ɵ values are 31.02°, 31.6°, 36.8°, 47.48°, 56.7°, 62.37°, 68.8° correspond to (103), (110), (106), (103), (110), (201), (112) reflection planes respectively. These results are accordance with the reported literature (JCPDS 36-1541) which implies the hexagonal Wurtzite structure of ZnO.

The mean crystalline sizes of ZnO nanostructure was calculated using Scherrar's formula,

$$D = 0.9\,\lambda / \beta \cos\theta \qquad (1)$$

Where, λ is the wavelength of X-rays (1.540 for CuKα), ɵ is the Bragg's angle, β is the full width at half maximum. The calculated mean crystalline sizes of ZnO nanostructures are 34.12, 34.32, 34.5, 53.83, 37.32, 38.52, and 39.42 nm respectively.

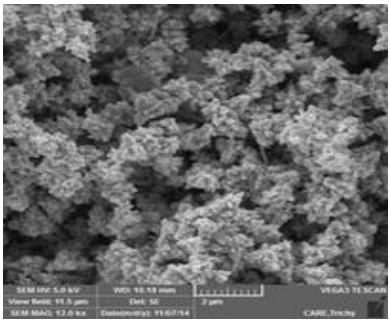

Figure 5

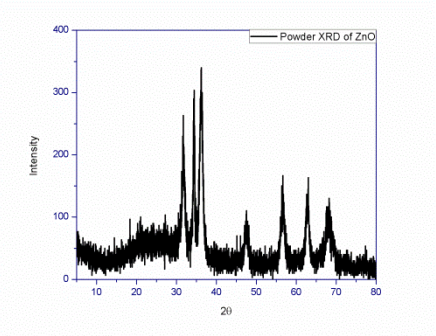

Figure 6

3.6 Variation of Dosage With Time

The effect of adsorption increases with increase in ZnO dosage up to dosage 0.5mg/L and then attains the stability. Hence the effective dosage 0.5mg/L was found to be optimum (figure 7).

The effect of adsorption was found to be maximum at 70min and then the absorbance shows quite increase which shows that the solution attained the state of equilibrium (figure 8)

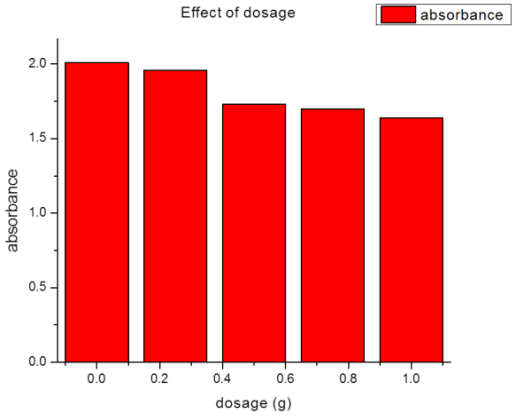

Figure 7

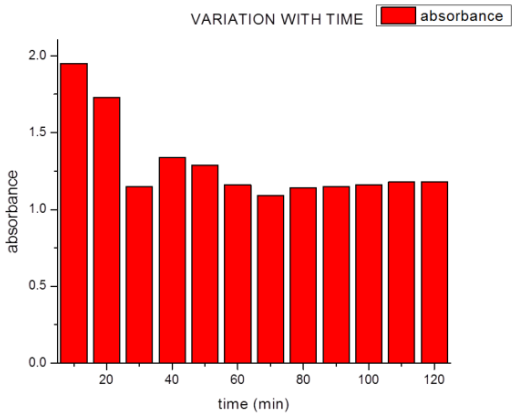

Figure 8

3.7 Variations with Initial Dye Concentration and pH

The effect of initial dye concentration increases with increase in dye concentration (figure 9)

The effect of pH was found to increase with increase in pH (figure 10). High pH favors the higher efficiency of adsorption of dye.

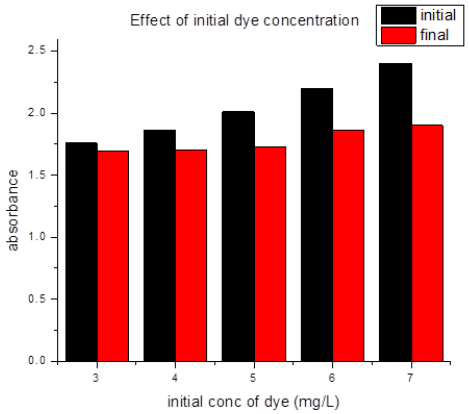

Figure 9

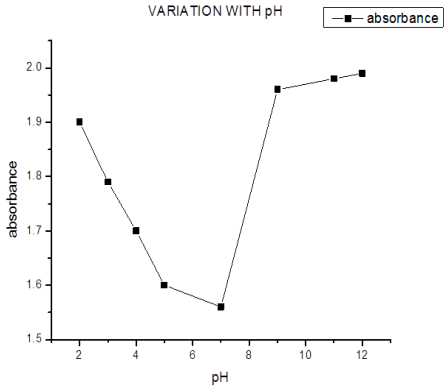

Figure 10

3.8 Adsorption isotherms

Freundlich isotherm of sorption of methylene blue dye at different initial concentration using the sorbent dosage of 0.5g/L and at the temperature 30˚C was shown in figure 11.

The Freundlich adsorption isotherm was calculated using the following equation

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad (2)$$

Where,K_f and n indicates the adsorption capacity and adsorption intensity where the values are obtained by plotting $\ln q_e$ versus C_e.

Figure 12 shows the equilibrium data fitted with Langmuir isotherm for the sorption of methylene blue at different initial concentrations with the sorbent dosage of 0.1g/L and temperature of 30˚C.

Langmuir adsorption isotherm can be defined as par the following equation,

$$C_e / q_e = (1+bC_e) / Q_0 b \qquad (3)$$

Where q_e is the quantity of dye absorbed per unit weight of biosorbent at equilibrium. Q_0 is the maximum possible amount of dye that can be adsorbed per unit weight of biosorbent to form a complete monolayer on the surface, b is the empirical constant, indicating the affinity of sorbent towards the sorbate. The plot C_e / q_e versus C_e found to be linear.

Adsorption capacity Q_0 = 0.3428 and adsorption / desorption energy constant b = 0.0291 the isotherm can be expressed by an equilibrium parameter,

$$R_L = 1 / (1+bC_i) \quad (4)$$

The R_L value is found to be less than 1. Hence the process is favorable, spontaneous process.

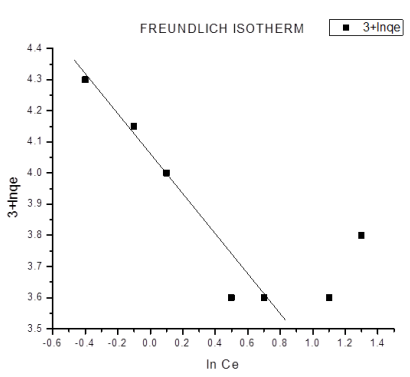

Figure 11

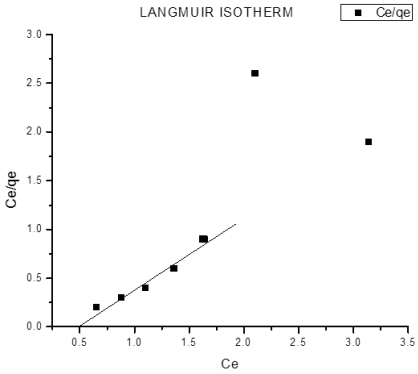

Figure 12

3.9 Comparison of Dye Degradation with and Without Zno Photocatalyst

Adsorption was found to be more for in the presence of photocatalyst than in absence (Figure 13).

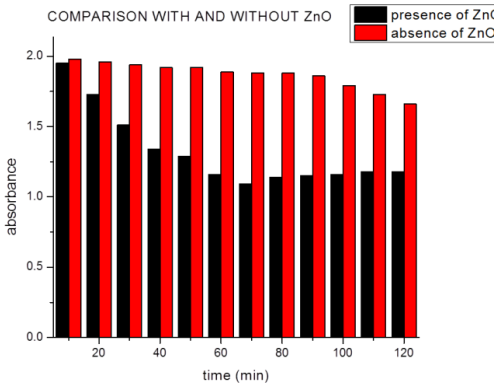

Figure 13

4. CONCLUSION

ZnO photo catalyst synthesized by hydrothermal method shows an efficient degradation activity with methylene blue dye. It possesses Wurtzite hexagonal structure. The equilibrium data were best fitted with Langmuir and Freundlich isotherm models. The reaction was found to be spontaneous and favorable one.

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