A Study of Adsorption Isotherms in Photo Degradation of Methyl Orange using Synthesized ZnO Nanoparticles

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Abstract

Adsorption of the dye over different adsorbents can be monitored through Langmuir and Freundlich adsorption isotherm models and feasibility of the process predicted in both cases. This study aimed at assessing the nature of adsorption isotherms resulting from photo degradation of methyl orange dye using ZnO nanoparticles. Precipitation technique was used to synthesize ZnO nanoparticles for two samples L_1 and L_2 and characterized using power X-ray diffraction (PXRD), fourier transform infra-Red (FTIR), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) methods of analysis. The EDX results showed elemental composition of ZnO nanoparticles which showed 54% Zn, 44.07% O and 1.93% Mn impurities for L_1 and 55.34% Zn, 42.3% O and 2.37% Mn impurities for L_2. The coefficients of correlation for ZnO nanoparticles for both sunlight and fluorescent irradiation for Langmuir expression (R^2) were all high. Thus the Langmiur expression provided better fit for the experimental data of photocatalytic degradation of methyl orange using ZnO nanoparticles than Freundlich expression implying surface monolayer mechanism. The values obtained for Lagergren second order plot of methyl orange adsorption under sunlight and fluorescent conditions were greater than those of first order. This suggests that the process followed the pseudo second order kinetics. Future studies should focus on the nature of adsorption isotherms in case where stabilizers are used to enhance the efficiency of nano ZnO in the removal of dyes from water waters.

Key Words: *Adsorption Isotherms, Photodegradation, nanoparticles, organic dyes*

I. INTRODUCTION

Photocatalytic degradation of organic dyes using photocatalysts is commonly expressed using two major adsorption isotherms: Langmuir and Freundlich (Romanchuk *et al.,* 2013). The Langmuir isotherm relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature (Choy *et al.,* 2000). The equation was developed by Irving Langmuir in 1916 (Langmuir & Hall, 2008).

Langmuir adsorption isotherm is the most commonly used due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent and each site can only accommodate one molecule.
2. The surface is energetically homogeneous and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

These four assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last (Kyzas *et al.,* 2013). The fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the BET isotherm for relatively flat (non-microporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics and thermodynamics (Senthamarai *et al.,* 2013).

The theory can be represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{b}Q_0 + \frac{C_e}{Q_0}$$

Where: Q_e is the amount of MeO adsorbed per unit mass of adsorbent (mg/g^{-1})

C_e is the equilibrium concentration of MeO

Q_o and b are Langmuir constants related to the capacity and energy of adsorption, respectively.

The Frendlich isotherm is not commonly used. The Freundlich adsorption isotherm is an empirical relation between the concentrations of a solute on the surface of an adsorbent to the concentration of the

solute in the liquid with which it is in contact (Umpleby *et al.*, 2001). In 1909, Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure (Ruthven, 1984). As this relationship is entirely empirical, in the case where adsorption behavior can be properly fitted by isotherms with a theoretical basis, it is usually appropriate to use such isotherms instead.

The empirical Freundlich isotherm equation is:

$$Q_e = K \times C_e^{(1/n)}$$

in logarithmic form (linear)

$$logQ_e = logKx\frac{1}{n}logC_e$$

Where k is related to adsorption capacity and n is related to intensity of adsorption

Q_e is the amount of MeO adsorbed per unit mass of adsorbent (mg/g^{-1})

C_e is the equilibrium concentration of MeO

II. MATERIALS AND METHODS

ZnO nanoparticles were synthesized using precipitation method. In this method, ZnO nanoparticles were prepared in two ways. In the first set, 100 ml of 1M $ZnSO_4$ solution was added to 100 ml of 2M NaOH solution in drops. When the addition was complete, the mixture was kept at room temperature under constant stirring using magnetic stirrer for a period of 2-4 hours.

The constant stirring using magnetic stirrer made the precipitation homogeneous and minimal particles which reduce the specific surface free energy of crystal nucleus which inhibit agglomeration and growth of the crystal nucleus so the particle size of the product is reduced (Zhang *et al*., 2010).

The resultant precipitate obtained was filtered then rinsed with distilled water. The formed white precipitate of $Zn(OH)_2$ was allowed to settle, filtered using filter paper of pore size 0.4 µm in a suction pump, washed with distilled water several times and dried in hot oven at 150^0C for 45 minutes. The synthesized ZnO nanoparticles were further irradiated at 180 W with microwave radiation in a microwave oven for 30 minutes and this was labeled sample L_1. The above procedure was followed to synthesize ZnO nanoparticles in different experimental conditions. $ZnSO_4$, NaOH and oxalic acid were used as stabilizing agents and thus one more sample L_2, was obtained.

The precipitation reaction was represented as

$$ZnSO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Zn(OH)_{2(s)} + Na_2SO_{4(aq)}$$

$$Zn(OH)_{2(s)} \xrightarrow{Heat} ZnO_{(s)} + H_2O_{(1)}$$

The resultant ZnO nanoparticles particles after irradiation were collected and stored in brown bottles.

The synthesized ZnO nanoparticles were subjected to (PXRD) and (FTIR)), in order to confirm the nanostructure.

A.Photo-catalytic degradation studies

Preparation of dye solution: The stock solution (1,000 ppm) was prepared and stored in a brown bottle. The stock solution was diluted to get different required several concentrations of the dye used. Dye concentration was determined using absorbance measured before and after the treatment using UV-VIS spectrometer.

The stock solution was diluted to different serial concentrations 10, 20, 30, 40 and 50 ppm for methyl orange in standard measuring flasks by making necessary dilutions with required volumes of distilled water. The optical density of each dye solution was measured using UV-VIS spectrophotometer (model – No-SL-150 Elico) at maximum wavelength value for MeO dye. A plot of optical density versus initial concentration was drawn and used as standard graph for estimation of dye by interpolation. The values of optical density for dye solutions before and after removal of dye were obtained by using UV-VIS spectrophotometer. Application of these optical densities the corresponding dye concentration was obtained from the graph.

Stock solution of MeO dye (1,000 ppm) was suitably diluted to get the required initial concentration from 15 – 45 ppm. A 10 ml of the dye solution of known initial concentration (C_1) was transferred to 50ml beaker. Required amount of the photo-catalyst (L_1 and L_2) was exactly weighed and then transferred to the dye solution with different C_1. The beaker was then exposed to fluorescent light and direct sunlight for a fixed period of contact time.

After bleaching, the optical density (OD) of these solutions was measured using UV-Vis spectrophotometer and the final concentrations (C_2) obtained from the standard graph. The extent of removal of the dye in terms of percentage removal was calculated using the following relationship.

$$\text{Percentage removal} = \frac{100(C_1 - C_2)}{C_1}$$

Where

C_1 = initial concentration of dye (ppm)

C_2 = final concentration of dye (ppm)

The effect of various experimental parameters on degradation of MeO dye in the aqueous suspension by ZnO nanoparticles were studied by varying the experimental conditions; concentration of the dye, amount of the sample (L_1 and L_2) and contact time.

III. RESULTS AND DISCUSSION

A. Powder X-Ray Diffraction (PXRD)

Figure 1 shows the XRD patterns of the synthesized ZnO nanoparticles.

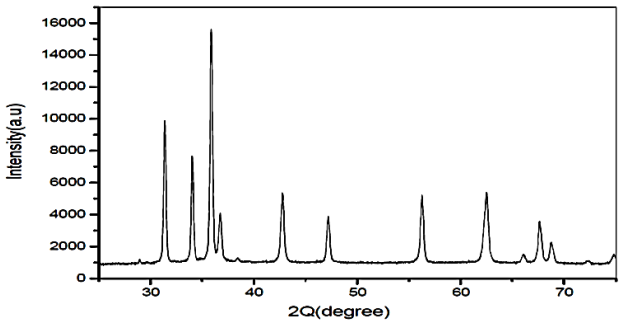

Figure 1: XRD patterns of the synthesized ZnO nanoparticles

The diffraction peaks at 31.7, 34.4, 36.2, 47.4, 56.4, 62.5, 67.6, and 68.7 can be indexed to ZnO as per the standard JCPDS file 80-0075. Powder diffraction patterns are characteristic of a particular substance. It is its "fingerprint" and can be used to identify a compound. Powder diffraction data from known compounds have been compiled into a database by the JCPDS. The synthesized sample can be confirmed to be ZnO nanoparticle. Clear crystallinity of the ZnO nanoparticles was observed. The samples had similar patterns. This suggests that the oxalic acid added as stabilizing agent had no effect on the Wurtzite structure of ZnO (Herrmann and Helmoltz, 2010).

Similar results were obtained by Gu *et al*. (2004) who obtained XRD peaks at scattering angles (2θ) of 31.3670, 34.0270, 35. 8596, 47.1635, 56.2572, 62.5384, 67.6356, and 68.7978, corresponding to reflection from 100, 002, 101, 102, 110, 103, 200 and 112 crystals. They indexed the XRD patterns to ZnO nanoparticles reference JCPDS file 80-0075 as well.

The average crystallite size of ZnO nanoparticles was estimated according to the diffraction reflection by Debye-Scherrer equation (Holzwarth & Gibson, 2011):

$$T = \frac{0.9\lambda}{\beta cos\theta}$$

Where

λ - the wavelength of incident X- ray ($1.5406A^0$)

β- the full width for half maximum (FWHM),

Θ - the Bragg's angle for the peak

β- can be calculated using the equation$\beta = (2\theta_2 - 2\theta_1)$, obtained to be 0.2755 radians.

The average crystallite sizes of synthesized ZnO nanoparticles were found to be around 26 nm.

Similar results were obtained by Shanthi and Kuzhalosai (2012), who characterized synthesized nano-ZnO using PXRD. For their three samples prepared. The sizes obtained were about18 nm, 16 nm and 12 nm.

B. FTIR analysis

Figure 2 shows the FTIR spectrum of the synthesized ZnO nanoparticles by precipitation method, which was acquired in the range of 400-4000 cm^{-1}. The red and black lines represent L_1 and L_2, respectively.

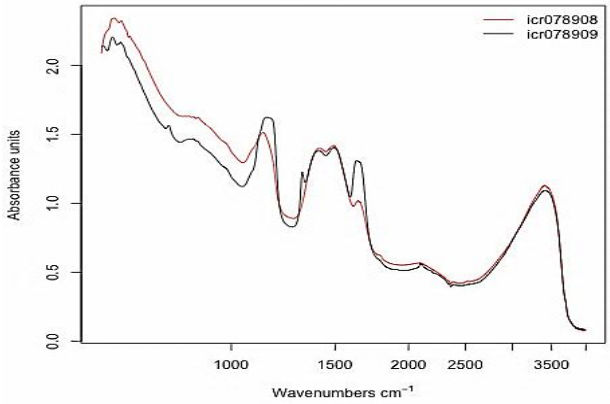

Figure 2: Observed FTIR pattern

FTIR of the ZnO nanocatalyst indicates the presence of water molecule adsorbed on the surface due to bands at around 3400 cm^{-1} which may be assigned to OH stretching vibration of adsorbed H_2O or due to residual $Zn(OH)_2$ present in the powder. The absorption band at 430 cm^{-1} correlated to metal oxide bond (Zn-O).

Kant and Kumar (2012) carried out similar study, FTIR spectra of ZnO obtained showed absorption band at 432.0 cm^{-1} which they attributed to (Zn-O) stretching frequency. Likewise peaks at 3401.3 cm^{-1} represent (OH) stretching mode. Shanthi and Kuzhalosai (2012) also carried out a similar study and their analysis showed a broad band between 419-430 cm^{-1}.Thespectra showed bands at (3250 and3500 cm^{-1}) which was assigned to OH^{--} stretching vibrationsdiagram for sample L_1 and L_2 at high magnification, respectively.

C. Photodegradation Studies

The optical density of each dye was measured using UV-Vis spectrophotometer at maximum wavelength of 480 nm. A plot of optical density versus initial concentration is shown in Figure 7.This plot was

used as standard graph for estimation of dye concentration by interpolation technique.

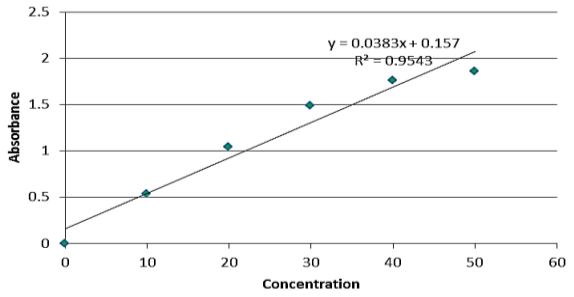

Figure 7: Standard curve for methyl orange dye

D. Equilibrium isotherm models for photo degradation of MeO dye using sunlight

Two isotherm models were tested in the present study and these are Langmuir and Freundlich. The applicability of the isotherm equation is compared by judging the correlation coefficient R_2 (Fytianos *et al.,* 2000). Langmuir theory was based on the assumption that adsorption was a type of chemical combination or process and the adsorption layer was unimolecular.

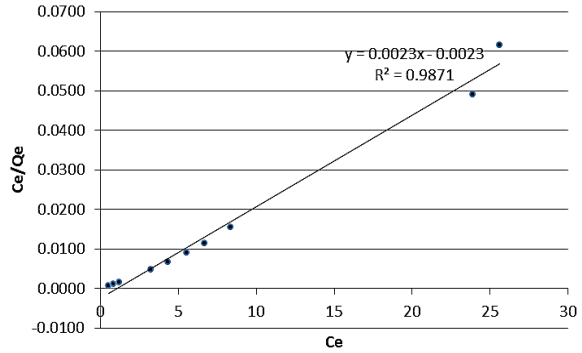

Figure 8: Langmuir adsorption isotherm of methyl orange adsorption

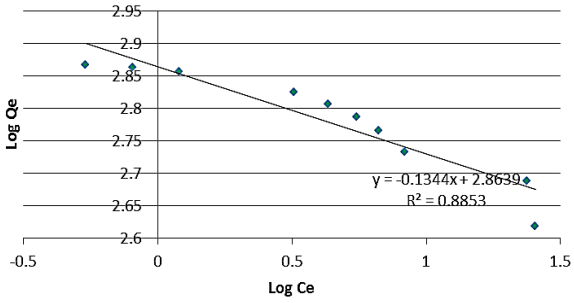

Figure 9: Freundlich adsorption isotherm of methyl orange adsorption

The coefficient of correlation for ZnO nanoparticles obtained from figure 8 for Langmuir expression (R^2= 0.9871) and ZnO coefficient of correlation obtained from figure 9 for Freundlich expression (R^2= (0.8853) indicated that Langmiur expression provided better fit for the experimental data of photocatalytic degradation of methyl orange using ZnO nanoparticles than Freundlich expression.

These findings are in agreement with those of a study conducted by Joshi and Shrivastava (2012) on degradation of alizarine red-s (a textiles dye) by photocatalysis using ZnO and TiO_2 as photo-catalyst. In their study, the good fit for the experimental data and the correlation coefficients R^2 higher than 0.9996 indicated the applicability and suitability of Langmuir isotherm model more than the Freundlich isotherm.

E. Equilibrium isotherm models for photo degradation of MeO dye using florescent

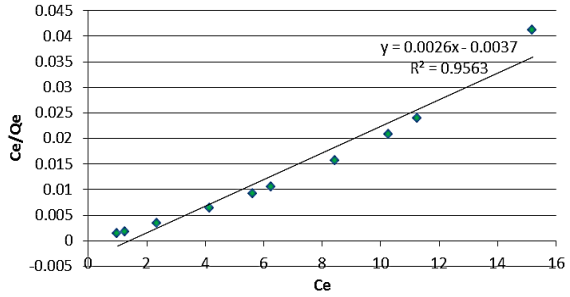

Figure 10: Langmuir Isotherm for photo degradation of MeO dye using florescent

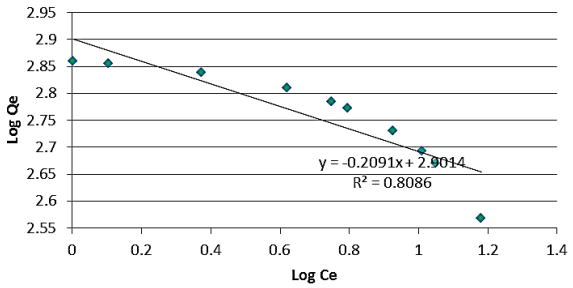

Figure 11: Freundlich Isotherm for photo degradation of MeO dye using fluorescent

The coefficient of correlation for ZnO nanoparticles obtained from figure 10 for Langmuir expression (R^2= 0.9563) and ZnO coefficient of correlation obtained from figure 11 for Freundlich expression (R^2= (0.8086) indicated that Langmiur expression provided better fit for the experimental data of photocatalytic degradation of methyl orange using ZnO nanoparticles under florescent than Freundlich expression.

These findings are in agreement with the findings of study conducted by Samarghandi *et al.* (2009), on two-parameter isotherms of methyl orange sorption using pinecone derived activated carbon. In their study, the good fit for the experimental data and the correlation coefficients R^2 higher than 0.9271 indicated the applicability and suitability of Langmuir isotherm model more than the Freundlich isotherm (0.5893).

IV. RECOMMENDATION

Future studies should focus on the nature of adsorption isotherms in case where stabilizers are used to enhance the efficiency of nano ZnO in the removal of dyes from water waters.

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