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ADSORPTION KINETICS FOR REMOVAL OF METHYL ORANGE DYE USING SYNTHESIZED ZnO NANOPARTICLES

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ABSTRACT

Nano-sized crystals of zinc oxide (ZnO) were synthesized, with a size of 26 nm. The products have been subjected to thorough characterization with Fourier Transform Infra Red spectroscopic techniques as well as X-ray diffraction analysis. These investigations confirm the formation of zinc oxide nanoparticles. The nano-particles showed remarkable adsorption efficiency in removal of methylorange dye. For the evaluating the adsorption kinetics of methyl orange on ZnO nanoparticles, the data was treated with Lagergren first order model. Thusthis studyaimed at assessing the nature of adsorption kinetics resulting from photo degradation of methylorange dye using ZnO nanoparticles. Precipitation technique was used to synthesize ZnO nanoparticles. The values obtained for Lagergren second order plot of methyl orange adsorption under sunlight and fluorescent conditions were higher than those of Lagergren 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 nanoZnO in the removal of dyes from water waters.

KEYWORDS: Adsorption Kinetics, Photodegradation, ZnO Nanoparticles, dyes.

INTRODUCTION

For the evaluating the adsorption kinetics of methyl orange on ZnO nanoparticles, the data was treated with Lagergren first order model expressed as:

$$\log(Q_e - Q_t) = \log Q_e - \left(K_1/2.303\right)t$$

The first order rate constant k_1 is obtained from the slope of the plot log (q_e-q_t) versus time, Adsorption kinetics were also explained by the pseudo second order model

$$\frac{t}{Q_t} = \frac{1}{K_2} x\ (Q_e)^2 + \frac{t}{Q_e}$$

where K_2 is the second order rate constant (g $mg^{-1}min^{-1}$). The value of K_2 is different initial dye concentration for all adsorbents which were calculated from the slope of the respective linear plot of t/qt vs t.

MATERIALS AND METHODS

ZnO nanoparticles were synthesized using precipitation method. In this method, ZnO nanoparticles were prepared in two ways. In the first set, 100ml of 1M $ZnSO_4$ solution was added to 100ml 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.*, 2008).

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 0.4µm 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. This was named as 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 agent. Thus one more sample was obtained and referred to as L_2.

The precipitation reaction was represented as

$$ZnSO4(aq) + 2NaOH\ (aq) \longrightarrow Zn\ (OH)2(s) + Na2SO4(aq)$$

$$Zn(OH)2(s) \xrightarrow{Heat} ZnO(s) + H2O(1)$$

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

The synthesized ZnO nanoparticles were subjected to (PXRD), (FTIR), at ICRAF Nairobi, (SEM) and (EDX), at The University of western Cape (South Africa) in order to confirm the nanostructure.

Photo-catalytic degradation studies

Preparation of dye solution: The stock solution (1,000ppm) was prepared and stored in brown bottles. The stock solution was diluted to get different required initial concentrations of the dye used. Dye concentration was determined by using absorbance measured before and after the treatment using UVVISspectrometer.

Measurement of concentration of dye solution: The stock solution was diluted to different initial concentrations10, 20, 30, 40 and 50 ppm for methyl orange in standard measuring flasks by making necessary dilutions with required volume 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. This plot was used as standard graph for estimation of dye by interpolation technique. The values of optical density for dye solutions before and after removal of dye were obtained by using UV-VIS spectrophotometer. Using these optical densities the corresponding dye concentration was obtained from the graph.

Determination of extent of removal of the dye: Stock solution of MeO dye (1,000ppm) was suitably diluted to get the required initial concentration from 15 – 45ppm. A 10ml of the dye solution of known initial concentration (C_1) wastransferredto 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 wasthen 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)

Factors that govern degradation process: 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.For evaluating the adsorption kinetics of methyl orange on nanoparticles,the data was treated with lagergren model.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction (PXRD)

Figure 1 below show the XRD patterns of the synthesized Zinc oxide nanoparticles.

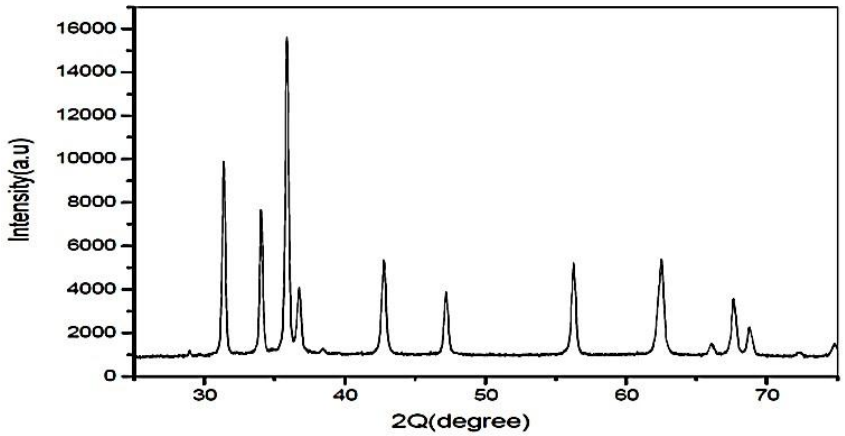


Figure 1: XRD patterns of the synthesized Zinc oxide nanoparticles.

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 wurzite 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 using Debye-Scherrer equation (Holzwarth& Gibson, 2011):

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

Where

λ -is the wavelength of incident X- ray (1.5406A^0) β- Is the full width for half maximum (FWHM),

Θ -is 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 also by Shanthi and Kuzhalosai (2012), who characterized synthesized nano-ZnO using PXRD. For their three samples prepared. The sizes obtained were about18nm, 16nm and 12nm.

The 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.

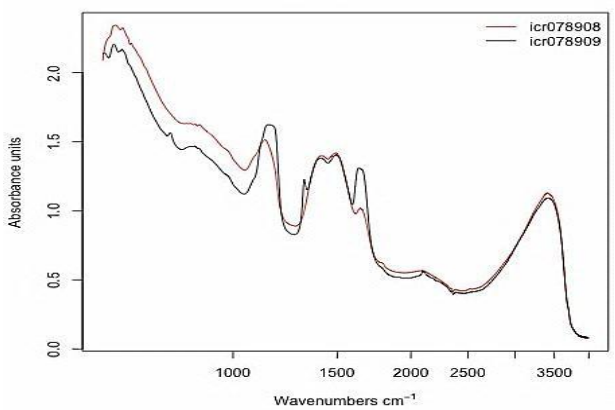


Figure 2: Observed FTIR pattern.

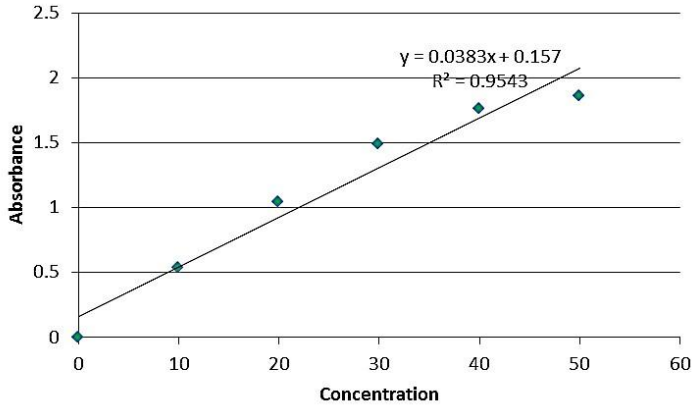
FTIR of the ZnO nanocatalyst indicates the presence of water molecule adsorbed on the surface due to bands at around 3400 which may be assigned to OH stretching vibration of adsorbed H_2O or due to residual $Zn(OH)_2$ present in the powder. The absorption band at 430cm^{-1} correlated to metal oxide 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 419-430cm^{-1}.The

spectra showed bands at (3250 and3500cm^{-1}) which was assigned to OH stretching vibrations.

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.



Adsorption kineticsfor photo degradation of MeO dye using sunlight

For the evaluating the adsorption kinetics of methyl orange on ZnO nanoparticles, the data was treatedwith Lagergren first order model expressed as

$$log(Q_e - Q_t) = logQ_e - \left({}^{K_1}/_{2.303}\right)t$$

The first order rate constant k_1 is obtained from the slope of the plot log (qe-qt) versus time,

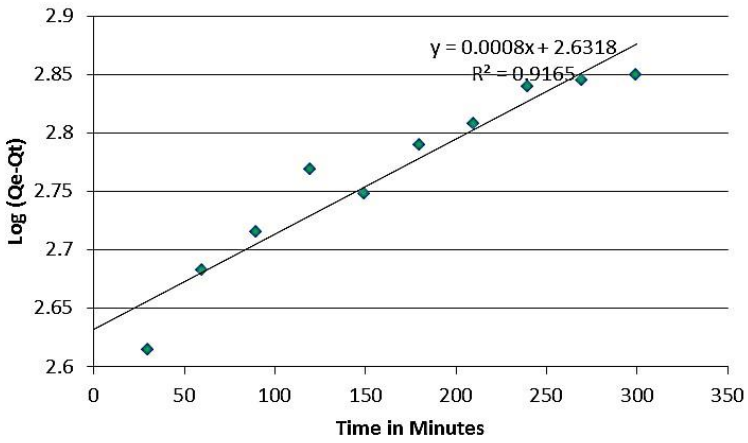


Figure 12: Lagergren first order plot of methyl orange adsorption under sunlight.

Adsorption kinetics were also explained by the pseudo second order model

$$\frac{t}{Q_t} = \frac{1}{K_2} x\,(Q_e)^2 + \frac{t}{Q_e}$$

where K_2 is the second order rate constant ($mg^{-1}min^{-1}$). The value of K_2 is different initial dye concentration for all adsorbents were calculated from the slope of the respective linear plot of t/qtvs t.

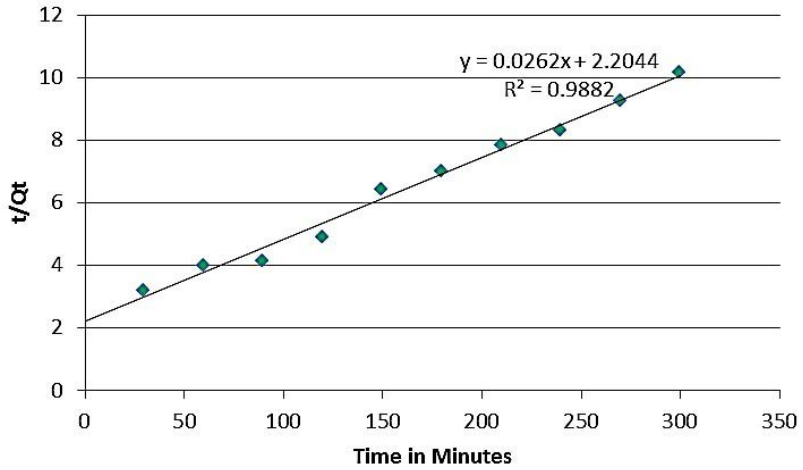


Figure 13: Lagergren second order plot of methyl orange adsorption under sunlight.

The correlation coefficients from figures 4.15 and 4.16for these two tests ranged from 0.9165 for the first order kinetics to 0.9882 for the second order kinetics. This suggests that there existed a strong relationship between the parameters and also that the process followed the pseudo second order kinetics. This shows that the adsorption process of methyl orange onZnO nanoparticles followed pseudo second order kinetics.

These findings are in agreement with those of Joshi &Shrivastava (2012) who conducted a study on the degradation of alizarine red-S (a textiles dye) by photocatalysis using ZnO and TiO_2 as photocatalyst. For their study, the correlation coefficients were 0.9946 and 0.9998 for first order and second order, respectively suggesting a strong relationship between the parameters and also explaining that the process followed the pseudo second order kinetics.

The findings also correlate with the findings of Sampa and Biney (2004) who conducted a study on photo-catalytic degradation of modern textile dyes in waste water using ZnOnanocatalyst. For their study, the correlation coefficients were 0.9849 and 0.9988 for first order and second order, respectively, suggesting a strong relationship between the parameters and also explaining that the process followed the pseudo second olrder kinetics.

Adsorption kinetics for photo degradation of MeO dye using florescent

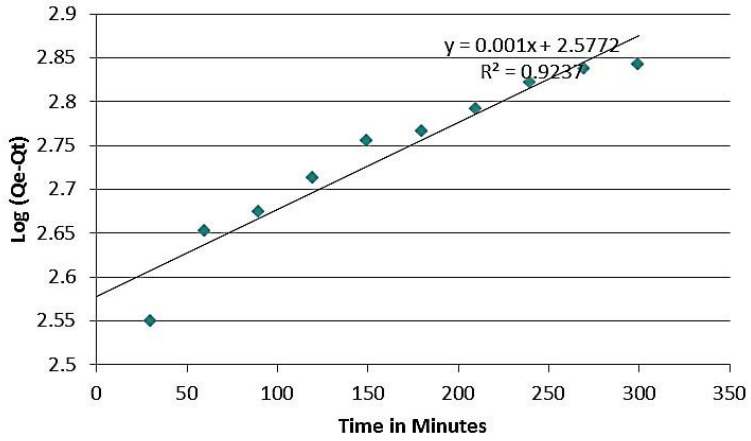


Figure 14: Lagergren first order plot of methyl orange adsorption under fluorescent.

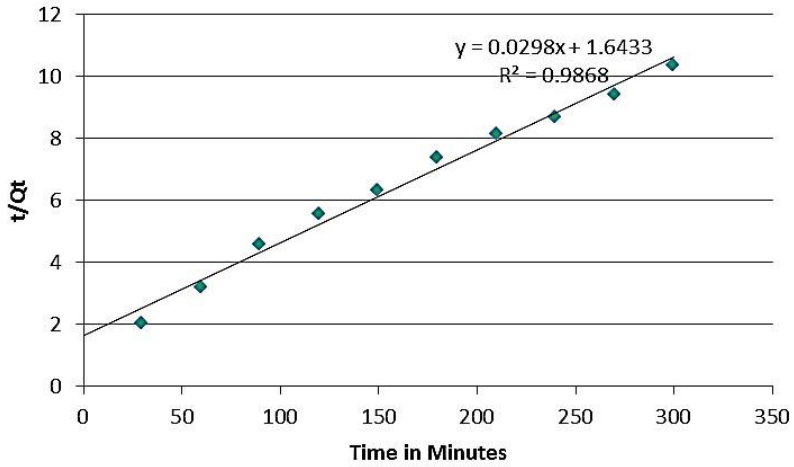


Figure 15: Lagergren second order plot of methyl orange adsorption under fluorescent.

The correlation coefficients from figures 14 and 15 for these two tests ranged from 0.9237 for the first order kinetics to 0.9868 for the second order kinetics. This suggests that there existed a strong relationship between the parameters and the process followed the pseudo second order kinetics. This shows that the adsorption process of methyl orange on ZnO nanoparticles under florescent follows pseudo second order kinetics.

These findings are in line with those of Jalil*et al.* (2010) who conducted a study on the adsorption of methyl orange from aqueous solution onto calcinedLapindo volcanic mud under flourescent conditions. For their study, the correlation coefficients were 0.9643 and 0.9898 for first order and second order respectively, suggesting a strong relationship between the parameters and also explaining that the process followed the pseudo Second order kinetics.

CONCLUSION

The values obtained for Lagergren second order plot of methyl orange adsorption were higher than those of Lagergren first order. This suggests that the process followed the pseudo second order kinetics. This shows that the adsorption process of methyl orange on ZnO nanoparticles follows pseudo second order kinetics.

RECOMMENDATION

Future studies should focus on the nature of adsorption kinetics of adsorbent grafted with natural materials like plant or animal materials. In case where this stabilizers are used the efficiency of nano ZnO in the removal of dyes from water waters is investigated.

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