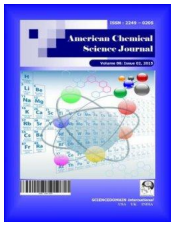

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Adsorption, Thermodynamics and Kinetics of Methylene Blue on Nano Structured ZnO Crystals

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Authors' contributions

This work was carried out in collaboration between both authors. Author IKAK designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author MSM managed the analyses of the study and the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

This investigation was concern to study the removal of methylene blue pollutants from aqueous solution using nano ZnO synthesized from raw materials of zinc oxide. The equilibrium adsorption data were analyzed using adsorption models of Langmuir, Freundlich and Temkin. The thermodynamic and kinetics parameters were calculated using adsorption process on nano ZnO for the methylene blue solution at different temperatures. It was found that a ZnO at nano level has a very significant adsorption for methylene blue compared to that of raw materials. The results showed that the model isotherms are fitting very well with the experimental data. The specific adsorption percentage of methylene blue was highly affected by addition of nano ZnO and decreasing with temperature compared to that of control sample. It has been found that the adsorption capacity was increased by increasing the methylene blue concentrations, and these values indicated that the methylene blue adsorption onto nano ZnO was spontaneous and endothermic in nature. All values of Gibbs functions were negative with values of -15 and -17 $kJmol^{-1}$ for temperatures of 293 to 323K, while values of enthalpy and entropy about -33 $kJmol^{-1}$ and 72 JK^{-1} mol^{-1} for nano ZnO respectively. These results indicated that the adsorption process was feasible, spontaneous and exothermic. Kinetic Study showed that the value of the rate constant is 0.338 min^{-1}.

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1. INTRODUCTION

Metal oxide nano particles showed photo catalytic activities with special availability of high surface area. Higher surface area caused more adsorption of the target molecules and higher will be the efficiency of the photo catalytic reactions [1]. ZnO, with a high surface reactivity owing to large number of active sites, has emerged to be an efficient photo catalyst as compared to TiO_2. ZnO is an attractive material for water treatment as it can be tailored to absorb visible light and is capable of ushering in the area of solar photo catalysis. It has an edge over other metal oxides like TiO_2 in water purification and other environmental remediation processes as it is soluble in water [2] and ends up as metallic zinc in the ecosystem. TiO_2 is however insoluble in water and the nano particles can persist in the environment ending up as potential environmental contaminants [3]. Further, ZnO can be synthesized under mild conditions and the asymmetry in the crystal structure allows anisotropic growth that can provide large surface to volume ratios [4,5].

Nano particles of metal oxides are efficient photo catalysts and can degrade both chemical and biological contaminants. The biggest limitation in the use of nano particles for practical applications is the difficulty of removing the particles after the treatment. It is necessary to granulate the photo catalyst nano particles into micron-sized particles (hundreds of microns) or load them onto highly porous substrates, which could be used in various flow-through water treatment facilities to avoid the dispersion of these nano particles into the environment and its possible consequences on the environment. The removal of these particles requires expensive post purification through nano filtration usually together with flocculation and there is serious concern that these particles may ultimately affect the ecosystem. The possible harmful effects of nano particles on human health and the eco-system are not yet properly understood. This has necessitated the use of photo catalyst supports, which can be regenerated and can be conveniently removed. It is important to understand how engineered nano materials migrate, behave, and interact with living organisms and the a biotic components of the environment, and take proactive steps towards the long-term goal of safer design and disposal of products containing these nano particles [6]. For example, the problem related to the removal of ZnO nano particles from purified water was addressed by growing ZnO nano rods on various substrates [4,7-9]. Nano wires consist of a large number of low coordination number atoms at the edge and corner sites of the crystal lattice providing numerous catalytically active sites. Considerable scientific interest is seen for the removal of harmful effects of chemical contaminants from groundwater mainly through photo catalysis using nano particles of metal oxide like TiO_2 and ZnO [10,11].

The role of oxygen in the photo destruction of organics on catalyst surfaces has been investigated as early as in 1991 [12]. Kinetics models were developed to predict the electron uptake by oxygen. The adsorption of oxygen on illuminated photo catalyst surfaces depends on the number of hydroxyl groups of the surface [13]. It has also been studied that the dependence of degradation rate constants of organics on the dissolved oxygen concentration can be well described by the Langmuir–Hinshelwood (L–H) equation [1,14].

2. MATERIALS AND METHODS

Methylene blue chloride (MB) was selected as a source of dye because it is chemically stable and difficult to be removed from wastewater [15]. Meanwhile, MB was selected as a model compound for evaluating the potential of ZnO to remove dye from aqueous solution. A stock solution of methylene blue (MB) was prepared and various concentrations (0.5-22 mg/l) were generated for the calibration curve and adsorption processes using the wave length of 664 nm.

2.1 Optimum Conditions of Adsorption

2.1.1 Effect of initial concentration and contact time

The influence of contact time on the efficiency of MB adsorption has been studied by adding 100 mg of nano ZnO to 50 ml MB solution (8 mg/l) in 100 ml flask for adsorbent. The adsorption process was conducted at 298 K at thermostatic shaker bath until equilibrium. The initial time was recorded and after each 15 minutes, 5 ml of sample was taken. The absorbance of these samples was measured by using UV-visible spectrophotometer at the wave length of 664 nm.

The process was repeated until equilibrium reached.

2.1.2 The effect of concentration

The experiment was carried out to observe the effect of different amount of adsorbents for methylene blue adsorption at constant contact time. The experiment was conducted for 8 mg/l concentration of dye solution with different amounts of adsorbent at constant temperature with agitation speed of 200 rpm for shaking.

2.2 Adsorption Isotherms

Nano particles of metal oxides as adsorbent for adsorption process was synthesized by sonicated raw materials of zinc oxide as described in previous work [16].

2.2.1 Methylene blue adsorption

Adsorption measurements of methylene blue dye on prepared nano- ZnO were carried out by mixing 100 mg of nano particles ZnO at different initial concentrations (8-22 mg/l) with 50 ml of MB aqueous solution and placed in conical flasks. The samples were shacked for 60 min at 200 rpm and temperature of 298 K and then filtered. Equilibrated concentrations of methylene blue were determined by measuring the absorbance using UV-visible spectrophotometer at wavelength of 664 nm.

The quantity of adsorbate was calculated by using the following formula [17].

$$Q_e = V_{Sol} (C_o - C_e)/ M$$

Where:

Q_e = Quantity of adsorbate (mg/g).
V_{Sol} = Total volume of adsorbate solution (L)
C_o = Initial concentration of adsorbate solution (mg/L)
C_e = Concentration of adsorbate solution at equilibrium (mg/L)
M = Weight of adsorbate (g)

While, adsorption percentage Q% was calculated by using following formula.

$$\% \text{ Adsorption Percentage} = (C_o - C_e)/ C_o \times 100$$

Isotherms of Langmuir, Freundlich, Temkin, and Brunauer, Emmet, and Teller (BET) were applied to calculate some adsorption data.

2.2.2 The effect of temperature

The effect of temperature on the amount adsorbed was investigated in the temperature range of 293-323 K in a thermostatic shaker bath. Nano ZnO (100 mg) were added to 50 ml of MB (8-22 mg/l) of aqueous solutions for different equilibrium time then the adsorbed amounts were calculated by the determination of concentrations using UV-Visible spectrometer by measuring absorbance at maximal characteristic wavelength 664 nm.

2.3 Kinetics Studies

The kinetic study for MB adsorption was performed by mixing 100 mg of Nano ZnO of 16 mg/l MB aqueous solution immersed in the thermostatic shaker bath at the temperature range of 293-323 K and at various time intervals. The concentration of solution was determined by measuring the absorbance of maximal characteristic wavelength of 664 nm.

3. RESULTS AND DISCUSSION

3.1 The Effect of Adsorbent Dose of Nano ZnO on MB Adsorption

The effect of adsorbent dose on the adsorption of MB was carried out with adsorbent levels of 1, 3, 6, 9, 30, 60, 90, 100, and 130 mg/ 50 ml using initial dye concentration of 16 mg /l, contact time of 90 minutes and temperature of 293 K. A dramatic decrease in concentration were observed with adsorbent quantity of nano scale, meanwhile there was high significant increase in adsorption percentage (Table 1). No significant changes in equilibrated concentration and adsorption percentage were occurred at raw materials.

3.2 The Effect of Contact Time on MB Adsorption

The effect of contact time on the percentage of MB removal was investigated. Table 2 showed a significant variation of Qe with the contact time. There was a little amount of adsorption observed at 15 minutes and thereafter a gradual increase in adsorption with increasing contact time. Therefore, the time of 90 minutes is an optimum contact time which considered for adsorption processes through the experiment.

Table 1. Equilibrated concentration and Qe% at different quantity of adsorbent

Parameter	Quantity of adsorbent, mg								
	1	3	6	9	30	60	90	100	130
Ceq (mg/l)of nano	15.7	15.2	14.5	13.4	8.36	1.33	0.21	0.31	0.82
Ceq(mg/l) 0f raw	15.8	15.7	15.7	15.6	15.6	15.5	15.5	15.5	15.5
Q% of nano	2.18	4.81	9.20	22.9	47.7	91.7	98.7	98.1	94.9
Q% of raw	1.37	2.12	2.18	2.50	2.75	2.93	3.25	3.31	3.31

It is clear that the adsorption of MB shows two phases : (i) an initial rapid adsorption that sharply increased within the first 15 min due to the rapid surface adsorption (external surface adsorption) and (ii) a slower increasing to the total dye adsorption (internal surface adsorption). It may also be observed from Fig. (1) that more than 90% of MB adsorption taking place within the contact time of 60 min and increases gradually thereafter [18]. Also, it was found that a rising amounts of adsorbent lead to enhance in removal percentage which probably attributed to increase in the number of active sites of the adsorbent (Fig. 1).

Table 2. Qe and Ce values at different time for 16 mg/l of MB with nano ZnO at 298 k

Time (min)	Ce (mg/l)	Qe (mg/g)
15	2.29	6.86
30	1.46	7.23
45	1.00	7.50
60	0.78	7.61
75	0.75	7.62
90	0.68	7.66
105	0.67	7.68
120	0.66	7.67

3.3 The Effect of Temperature

The effect of temperature on the adsorption for different concentration of MB onto 0.09 g of nano ZnO was studied using (8, 12, 14, 16 mg/L) of MB. The results showed that the adsorption capacity increased with increasing temperature from 293 to 323 K, which indicated that the process was endothermic (Fig. 2). The temperature has either two major effects on the adsorption process [19]. The first one when the temperature increase might be led to increase in the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores diffusion of the adsorbent particle, it is caused to the decrease in the viscosity of the solution. While the second effect is concern a temperature change that will conduct a change in the equilibrium capacity of the adsorbent for a particular adsorbate [20].

3.4 Effect of Initial MB Concentration

The initial concentration of MB solution was changed and the amount of MB removal by nano ZnO was estimated and followed up. The adsorption was decreased with increasing initial MB concentration. At a lower dye concentration, there was an increase in color removal which occurred due to high ratio of adsorbent sites to dye molecule. While at higher concentration of MB, a removal percentage was decreased significantly due to the saturation of adsorbent surface (Fig. 3). However, it was found that actual amount of adsorbed dye has reverse correlation with removal percentage and at higher initial concentration more magnitude of MB was removed on the same value of adsorbent. The initial concentration provides an important driving force to overcome all mass transfer resistances between the aqueous and solid phases [19,20].

3.5 Adsorption Isotherms

3.5.1 Langmuir isotherm model

The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems [21]. Langmuir Isotherm model is a good representative of chemisorption, it is depends on the assumption that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent [22]. The isotherm of the methylene blue dye adsorption by synthetic cellulose nanocrystal was represented by applying the Langmuir adsorption model, and it was found that the adsorption process on the synthetic nano ZnO fit very well with isotherm model (Table 3).

The Langmuir equation is

$$Q_e = (Q_o C_e)/(K_L + C_e) \quad (1)$$

Where Q_o is the maximum amount of adsorption corresponding to complete monolayer coverage

and K_L is the Langmuir constant. The fitting of adsorption data to Langmuir isotherm equation was investigated by plotting Ce/Qe versus Ce.

Equation 1 is rearranged and gives a straight line as shown in equation 2.

$$C_e/Q_e = (1/K_L\ Q_o) + (1/Q_o)\ C_e \quad (2)$$

All Langmuir factors, adsorption data and relations were shown in Table 3 and it is clear that the Langmuir isotherm model fits the analyzed data with its correlation coefficient (R^2).

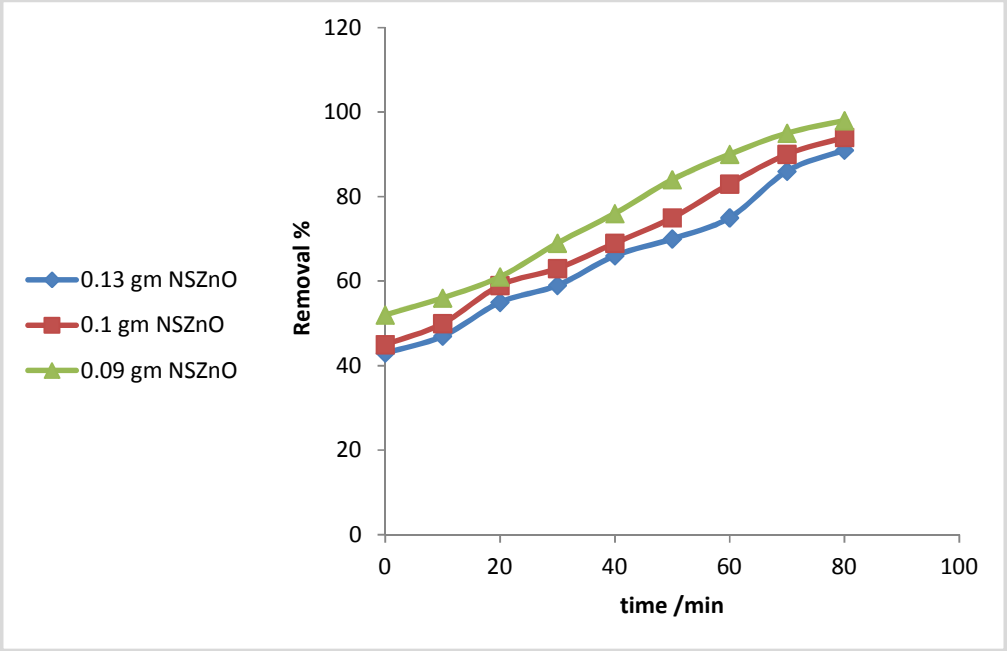

Fig. 1. Effect of contact time on the removal of MB onto nano ZnO

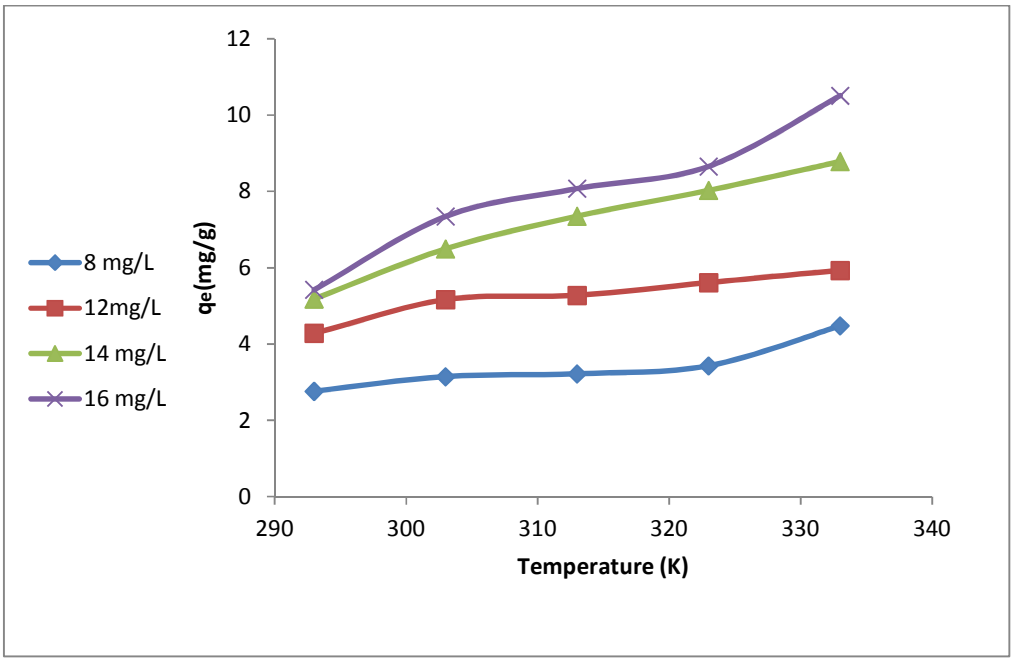

Fig. 2. Effect of temperature on the adsorption capacity for different concentration of MB on nano ZnO

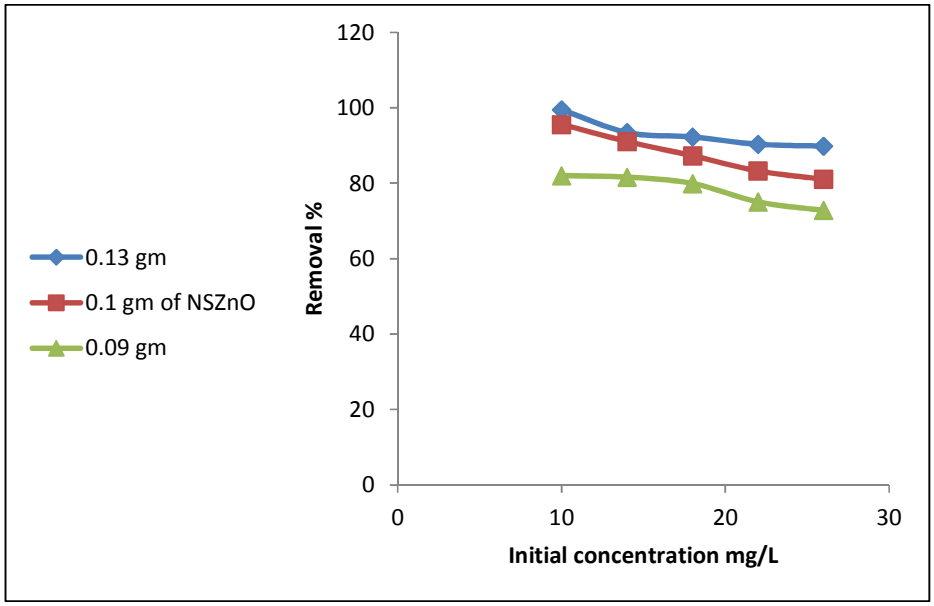

Fig. 3. Effect of initial dye concentration on the removal of MB on nano ZnO

Table 3. Constant values of methylene blue dye adsorption on nano ZnO at different temperatures

T(K)	Langmuir parameters			Freundlich parameters			Temkin parameters		
	Q^omg/l	K_L l/mg	R^2	n	K_f mg/l	R^2	B	k_T	R^2
293	0.58	4.46	0.977	1.63	1.82	0.965	1.40	9.06	0.961
303	0.57	5.29	0.982	1.58	2.84	0.982	1.88	6.79	0.974
313	0.90	8.55	0.986	2.20	2.85	0.985	2.81	4.04	0.975
323	0. 54	1.23	0.882	2.65	4.23	0.980	5.84	0.38	0.980

3.5.2 Freundlich isotherm model

The Freundlich equation is as following:

$$Q_e = K_f C_e^{1/n} \quad (3)$$

Where,

K_f is Freundlich isotherm constant {mg/g]
n is adsorption intensity

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. This isotherm is usually used in special cases for heterogeneous surface energy and it is characterized by the heterogeneity factor 1/n. Q_e is the equilibrium value of methylene blue dye adsorbed per unit weight of synthetic nano ZnO, i.e. a liquid-phase sorbate concentration occurred at equilibrium, K_f as the Freundlich constant and 1/n is the heterogeneity factor. On average, a favorable adsorption tends to have Freundlich constant (*n*) between 1 and 10. Larger value of *n* (smaller value of 1/*n*) implies stronger interaction between the adsorbent and the adsorbate and positive cooperatively in binding and a heterogeneous nature of adsorption.

However, Table 3 showed that (*n*) values were between 1 and 10 emphasizing favorable adsorption of methylene blue dye onto the nano ZnO.

The Freundlich equation was linear zed by taking logarithms on each side of the equation and gives a straight line as shown in equation 4.

$$\text{Log } Q_e = \log K_f + 1/n \log C_e \quad (4)$$

All Freundlich factors, adsorption data and relations were shown in table 3, and it is clear that the Freundlich isotherm model fits the analyzed data with its correlation coefficient (R^2).

The Freundlich model assumes that the uptake of any adsorbate occurs on a heterogeneous

surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with increasing the concentration. From these assumptions it can be concluded that synthetic nano ZnO takes up methylene blue dye on a heterogeneous surface by multilayer adsorption.

3.5.3 Temkin isotherm model

The linear from of Temkin isotherm is expressed as,

$$q_e = B \ln A + B \ln C_e \quad (5)$$

The adsorption data were analyzed according to eq. (5) and a plot of q_e versus ln C_e enables the determinations of the isotherm constants A and B. The isothermal model of Temkin is based on vapor pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid [23,24]. Therefore, the adsorption enthalpy changes linearly with pressure [23,25]. Table 3 shows the Temkin factors and relations and it is clear that the Freundlich isotherm model fits the analyzed data with its correlation coefficient (R^2).

The rate adsorption of the dye increased with increasing of methylene blue dye concentration and the adsorption percentage of methylene blue dye decrease as temperature increase, whereas the adsorption process is an exothermic process (Tables 1 and 2). It can be seen that adsorption capacity increases until an equilibrium concentration is obtained. This confirms a favorable adsorption system. There was a decrease in % adsorption efficiency with added adsorbate with slight increase in temperature. Hence it is clearly proved that methylene blue dye adsorption by synthetic nano ZnO agrees fair enough with all three model isotherms. The correlation coefficient was very high throughout the experimental range of methylene blue dye concentrations studied.

3.6 Thermodynamics Analysis

The thermodynamic parameters ΔG^0, ΔS^0, and $\Delta H^0$for these adsorption processes are determined by using following equation (19).

$$\Delta G^0 = -RT \ln K \quad (6)$$

Where, K is the thermodynamic equilibrium constant. The effect of temperature on thermodynamic constant is determined by:

$$d \ln K/dt = \Delta H^0/RT^2 \quad (7)$$

$$\text{Log } K = \Delta S^0 / 2.303\ R - \Delta H^0/2.303\ RT \quad (8)$$

Gibbs free energy ΔG^0 is given by:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

Where ΔG^0 is the free energy change (KJ/mol); R is the universal constant (8.314 J/mol K) and T the absolute temperature (K); ΔH^0change in enthalpy; ΔS^0 is the change in entropy.

The ΔH^0 and ΔS^0 values were calculated from slope and intercept of the linear plot, of ln K vs. 1/T as shown in Fig. 4. The corresponding values of thermodynamic parameters are presented in Table 4. The negative values of ΔG^0 indicate that the methylene blue adsorption process is spontaneous and feasible. The decrease in negative value of ΔG^o with an increase in temperature indicated that the adsorption process of MB on nano ZnO becomes more favorable at higher temperatures. The positive values of (ΔH^o) indicated that the adsorption reaction was exothermic. The results showed that all values of (ΔH^o) almost are smaller than 40KJ/mol, which means that the adsorption of MB onto nano ZnO is a physisorption process [26]. The positive value of (ΔS^o) suggested that some structural changes will occur on the adsorbents and the randomness at the solid / liquid interface in the adsorption system increases during the adsorption processes.

3.7 Kinetic Studies

The adsorption kinetic behavior of methylene blue (16 mg/l) onto nano ZnO at 298K was fitted through kinetic model of pseudo-second order:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where, q_e and q_t are the amounts of methylene blue adsorbed on the surface of the adsorbent at equilibrium and at any time respectively and k_1 is the rate constant min^{-1}.The value of the rate constant is 0.338 min^{-1}, which reflecting the intra-particle and extra particle diffusion.

Table 4. Thermodynamic parameters of nano ZnO/MB adsorption system

Samples	T(K)	$\Delta H^{o} * 10^{-3}$ kJ.mol^{-1}	ΔS^{o} J.mol^{-1}.k^{-1}	ΔG^{o} kJ.mol^{-1}
Nano ZnO	293	-33.148	72.256	-15.410
	303			-16.132
	313			-16.854
	323			-17.576

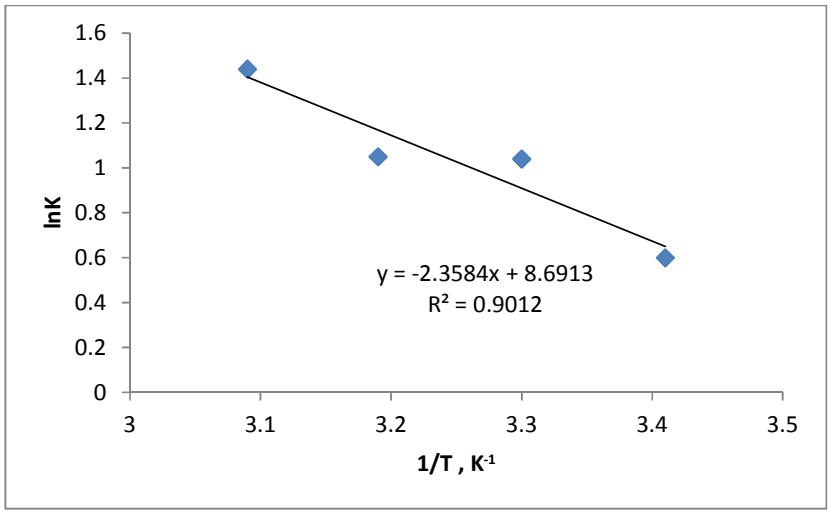

Fig. 4. The relation between lnK vs. 1/T

4. CONCLUSION

There was a dramatic reduction in a methylene blue concentration by using a synthetic nano ZnO as an absorbent, compared to that of bulk ZnO. A high reduction in equilibrium concentration of methylene blue was obtained using 0.1 gm of synthetic nano ZnO for 50 ml of methylene blue by using different concentrations. The process of adsorption on nano ZnO fits all isotherm equilibrium adsorption models along with very high correlation coefficients. The adsorption process was feasible, spontaneous and exothermic. Nanoparticles synthesized using ZnO processed has to be further investigated for other pollutants. Kinetically the model of pseudo-first order is the most suitable formula.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Chen D, Sivakumar M, Ray AK. Heterogeneous photocatalysis in environmental remediation. Chem. Eng. Mineral Process. 2000;8:505-550.
2. Han J, Qiu W, Gao W. Potential dissolution and photo dissolution of ZnO thin films. J. Hazard. Mater. 2010;178:115-122.
3. Baruah S, Dutta J. Nanotechnology applications in pollution sensing and degradation in agriculture. Environ. Chem. Lett. 2009;7:191-204.
4. Baruah S, Dutta J. Hydrothermal growth of ZnO nanostructures. Science and Technology of Advanced Materials. 2009;10:013001.
5. Baruah S, Mahmood MA, Myint MTZ, Bora T, Dutta J. Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods. Beilstein J. Nanotechnol. 2010;1:14-20.
6. Alvarez PJJ, Colvin V, Lead J, Stone VAN. Research priorities to advance eco-responsible nanotechnology. ACS Nano. 2009;3:1616-1619.
7. Baruah S, Dutta J. pH-dependent growth of zinc oxide nanorods. J. Cryst. Growth. 2009;311:2549-2554.
8. Baruah S, Dutta J. Effect of seeded substrates on hydrothermally grown ZnO

nanorods. J. Sol-Gel Sci. Technol. 2009;50:456-464.
9. Sugunan A, Warad HC, Boman M, Dutta J. Zinc oxide nanowires in chemical bath on seeded substrates: Role of hexamine. J. Sol-Gel Sci. Technol. 2006;39:49-56.
10. Bianco-Prevot A, Fabbri D, Pramauro E, Morales-Rubio A, De la Guardia M. Continuous monitoring of photocatalytic treatments by flow injection. Degradation of dicamba in aqueous TiO2 dispersions. Chemosphere. 2001;44:249-255.
11. Herrmann JM, Guillard C. Photocatalytic degradation of pesticides in agricultural used waters. Comptes Rendus de l'Academie des Sciences - Series IIc: Chemistry. 2000;3:417-422.
12. Gerischer H, Heller J. The role of oxygen in photo oxidation of organic molecules on semiconductor particles. J. Phys. Chem. 1991;95:5261-5267.
13. Bickley RI, Stone FS. Photo adsorption and photocatalysis at rutile surfaces: I. Photo adsorption of oxygen. J. Catal. 1973;31:389-397.
14. Matos J, Laine J, Hermann JM. Effect of the type of activated carbons on the photocatalytic degradation of aqueous organic pollutants by uv-irradiated titania. Appl. Catal. B. 1998;18:281-291.
15. Niya MM, Unes S, Afshin M, Bagher H, Farhood N. Synthesis of cationic polymeric adsorbent and dye removal isotherm, kinetic and thermodynamic. J. Envir. Sci. 2013;139:1368-1374.
16. Al-Khateeb IK, Muna SM. Synthesis and identification of nanostructured ZnO crystals using ultrasonic technique. (Under Publication).
17. Al-Khateeb IK, Mohammed AM, Haider AJ, Al-Douri Y. Removal of benzene from aqueous solution using carbon nanotube synthesized from fuel oil waste. Adv. Mat. Res. 2014;925:105-109.
18. Meena S, Ashok KS, Jagieet SY. Adsorptive removal of methylene blue dye from an aqueous solution using water hyacinth root powder as a low cost adsorbent. Inter. J. Chem. Sci. Appl. 2012;3:338-345.
19. Barka N, Qourzal S, Assabbance A, Nounah A. Alt-Ichou Y. Adsorption of Disperse Blue SBL dye by synthesized poorly crystalline hydroxyapatite. J. Enviro. Sci. 2008;20:1268-1272.
20. Lei G, Wei S, Lingying K. Adsorption of methylene blue by NaOH-modified dead leads of plane trees. Comput. Water, Energy, and Enviro. Eng. 2013;2:13-19.
21. Thomans WJ, Crittenden B. Adsorption technology and design. Butter Worth Hiene- mann; 1988.
22. Langmuir I. The adsorption of gases on plane surface of glass, mica and platinum. J. Amer. chem. Soc. 1918;40:1316-1403.
23. Atkins P. Physical chemistry. 9th Ed., University of Oxford, Oxford, UK; 2010.
24. Shahryari Z, Goharrizi A, Azadi M. Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. Int. J. Water Reso. Environ. Eng. 2010;2:016-028.
25. Time B. Hygroscopic moisture transport in wood. Ph.D. Thesis, Norwegian University of Science and Technology, Department of Building and Construction Engineering; 1998.
26. Karaca S, Gurses A, Acikyildiz M, Dong Ping L. Adsorption of cationic dye from aqueous solutions by activated carbon. Korucu. Microporous Mesoporous Mater. 2008;115:376-382.

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