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Methylene Blue Adsorption Study Using Different Zno Types (Normal, Shaheed Factory, Nano)

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Abstract: ***The purpose of this research is to study the adsorption of methylene blue (M.B) on different types of ZnO (normal, shaheed factory copper and brass industry & nano) at 298K & different M.B concentration, then choose which one is the best for the removal of M.B dye, the adsorption process studies an independent of temperature. The adsorption kinetic was achieved and oby the first order model. The adsorption isotherm for (normal & shaheed) ZnO was fitting to Freundlich model while nano ZnO was fitting to Temkin isotherm. Its clear that, nano ZnO is the best then normal ZnO and shaheed ZnO is the latest for the removal of M.B depend on % Removal and particle size. The three types of ZnO were identify by AFM (Atomic Force Microscope) to measure the particle size and scan its morphology.***

Keyword: Nano ZnO, ZnO, AFM, Adsorption, methylene blue

1. Introduction

Environmental pollutant is the major cause for most of health illness. Water is the main source of contamination and pollution which effects health through biomagnification. Water gets pollutants from harmful chemicals, dyes, oils etc [1]. The types of water pollution were: (organic, inorganic, biological) pollutants [2]. Methylene blue was also the first synthetic compound ever used as an antiseptic in clinical therapy, and the first antiseptic dye to be used therapeutically. In fact, the use of methylene blue and its derivatives was widespread before the advent of sulfonamides and penicillin [3]. The molecular formula for Methylene blue is $C_{16}H_{18}ClN_3S$ and its structural is shown in the figure (1):

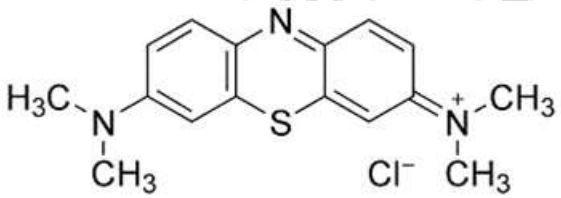

Figure 1: Chemical formula of methylene blue

The remove of pollution (i.e.: dyes) are available by current treatment technologies & can be used (physicochemical, biological) treatment techniques. The physicochemical processes involves (Biological methods [4], enzyme treatment [5], solvent extraction [6], adsorption [7], Advanced oxidation processes [8], electrochemical oxidation [9], catalytic oxidation [10], ion selective electrode [11]etc. Adsorption is the tendency for accumulation of a substance to take place at a surface or at an interface the accummence of adsorption is due to the atoms in any surface being subject to unbalanced forces of attraction perpendicular to the surface plane and therefore possessing certain unsaturation [12].

It is the contact of immiscible phases addition to adsorption, result in penetration of the bulk of one phase by the other [13].Adsorption has traditionally been divided into two kinds (weak physi-sorption, strong chemi-sorption), physic-sorption occurs when vapors near their saturation pressures adsorb to a dry surface in a process that resembles condensation. The Van der Waals forces and weak dipole interactions present here have heats of adsorption typically a few hundred cal/mol [14].

Chemical adsorption is a much stronger interaction than physical adsorption with heats of adsorption up to 800 kJ/ mole. But heat of adsorption values less than 80 kJ/mole do not necessarily rule out chemisorption. During the chemisorption process the adsorbing gas or vapor molecule splits into atoms, radicals, or ions that form a chemical bond with the adsorption site. This interaction involves the sharing of electrons between the gas and the solid surface and may be regarded as the formation of a surface compound [15]. There are many theories that describe the adsorption processes like (Langmuir, Freundlich, Temkin, etc) models. The Langmuir model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place [16]., Langmuir represented by the following equation [17]:

$$q_e = \frac{Q_0 K_L C_e}{1+K_L C_e} \quad (1)$$

Where: C_e = the equilibrium concentration of adsorbate (mg/L^{-1}), q_e= the amount of pollutant adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_0= maximum monolayer coverage capacity (mg/g), K_L = Langmuir isotherm constant (L/mg). The Freundlich model commonly used to describe the adsorption characteristics for the heterogeneous surface [18].These data often fit the empirical equation proposed by Freundlich [19]:

$$Q_e = K_f C_e^{1/n} \quad (2)$$

Where: K_f = Freundlich isotherm constant (mg/g), n = adsorption intensity; Ce = the equilibrium concentration of adsorbate (mg/L) Q_e = the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing Freundlich equation (2), can be written as:

$$\text{Log } Q_e = \text{Log } K_f + 1/n \text{ Log } C_e \quad (3)$$

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 [20].

The Tempkin is other contains a factor that explicitly taking i nto the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearity rather than logarithmic with coverage [21, 22].The Temkin model is given by the following equation [21]:

$$q_e = \frac{RT}{b}\ln(A_T C_e) \quad (4)$$

$$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b}\right)\ln C_e \quad (5)$$

$$B = \frac{RT}{b_T} \quad (6)$$

$$q_e = B \ln A_T + B \ln C_e \quad (7)$$

Where:

A_T =Temkin isotherm equilibrium binding constant (L/g), b_T = Temkin isotherm constant, R= universal gas constant (8.314J/$JK^{-1}mol^{-1}$), T= Temperature at 298K, B = Constant related to heat of sorption (J/mol).

Experimental part:

1- Determination of Maximum Absorption wave length (λ_{max}) for M.B:

Wavelength values utilize for estimation of quantity of compound are 664nm for Methylene blue as show in (Figure 2).

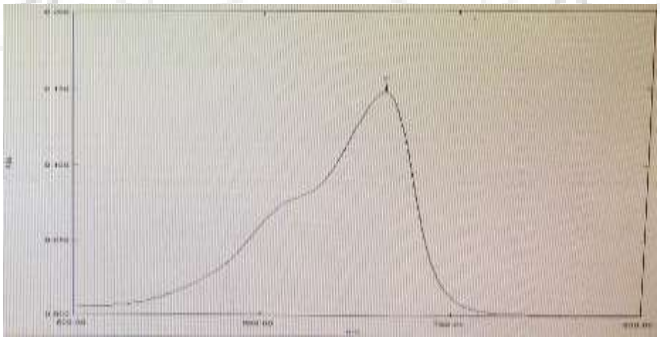

Figure 2: UV-Visible absorption spectrum for Methylene blue dye

2- Calibration Curve:

Figure 3 show the M.B calibration curve

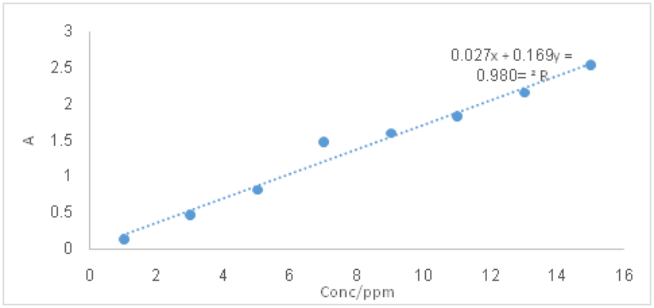

Figure 3: Calibration curve for methylene blue at λ_{max} = 664 nm, T=298K

3- Preparation of Methylene blue solutions:

Six concentrations of Methylene blue (10, 25, 50, 100, 150) ppm was prepared in 100 ml from stock solution of (1000 ppm M.B) to be used in Adsorption processes.

4- Calculation of $Q_e$and adsorption isotherm:

Q_e can be calculated from the following equation [23]:

$$C_e = \frac{A - Intercept}{Slope} \quad (8)$$

$$Q_e = \frac{C_o - C_e}{Wt} * V \quad (9)$$

Where: Q_e: Adsorption capacity of the adsorbent at equilibrium (mg/g), C_e: Equilibrium concentration of adsorbate after adsorption has occurred (mg/ml), C_o: Initial concentration of adsorbate (mg/ml), V: volume of solution (ml).

Adsorption of M.Bdye from an aqueous solution on different ZnOtypes surface were studied at different temperature, The plotted of Q_e versus equilibrium concentration (C_e) gives the type of adsorption isotherm.

5- Methylene blue % removal:

The % removal was calculated from the following equation [24]:

$$\%R = \frac{Co - Ce}{Co} * 100 \quad (10)$$

Where:

C_o: Initial concentration of M.B
C_e: concentration of M.B after adsorption process
%R: percentage removal

6- Thermodynamic parameters:

The standard free energy was determined using the following equation [25]:

$$\Delta G^{o}_{ads} = -RT \ln K \quad (11)$$

Where: ΔG^{o}_{ads}: The free energy kJ/mol, T: Absolute temperature in kelven, R: The gas constant (8.314 JK^{-1} mol^{-1}), K: The Langmuir constant, or Freundlish constant, or Tempkin constant, or the thermodynamic equilibrium constant obtained using the method of Khan & Singh.

The thermodynamic equilibrium constant (K) can be calculated also from the following equation [26]:

$$K = \frac{a_s}{a_e} = \frac{v_s Q_e}{v_e C_e} \quad (12)$$

Where: a_s: The activity of dye in solid phase, a_e: The activity of dye in solution at equilibrium, v_s: The activity coefficient of the absorbed dye, v_e: The activity coefficient of the dye in solution at equilibrium. The other thermodynamic parameters such as change in standard entropy ΔS^{o} & standared enthalpy ΔH^{o} were estimated from the following equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R}\frac{1}{T} \quad (13)$$

The value of change enthalpy ΔH^{o}& entropy ΔS^{o} were determined from the slope & intercept of the plot of lnKvs (1/T) respectively.

2. Result and Discussion

1- Characterization of ZnO:

The AFM analysis provides the measurements of average grain size (and the granularity cumulating distribution for normal ZnO, ZnO Shaheed factory and nanoZnO (Figure 4). The average diameter is 180.79 nm, 292.40 nm, and 80 nm for normal ZnO, shaheed factory ZnOand nanoZnO respectively.

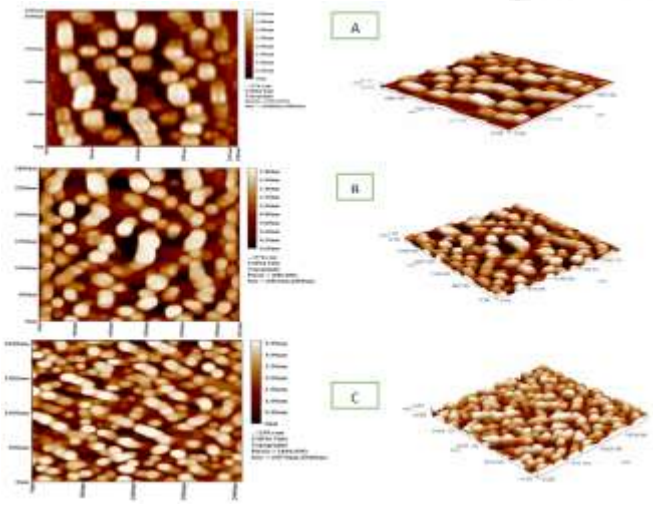

Figure 4: Atomic force microscope image for: A- normal ZnOB- Shaheed factory ZnO, C-nanoZnO

2- Adsorption isotherm models:

Table (1), Figure 5& Figure 6shows the variation of Q_e versus C_e& different concentration of M.B versus %R respectively using three types of ZnO (normal, shaheed, nano) at 298 K.

Table 1: Absorption amount of M.B by different types of ZnO at 298K

	Normal ZnO			ShaheedZnO			Nano ZnO		
C_o	C_e (mg/ml)	Q_e (mg/g)	% R	C_e (mg/ml)	Q_e (mg/g)	% R	C_e (mg/ml)	Q_e (mg/g)	% R
10	2.25	4.84	77.50	3.51	4.05	64.90	0.66	5.83	93.40
25	9.57	9.64	61.72	8.52	10.3	65.92	0.89	15.06	96.44
50	17.26	20.46	65.48	19.78	18.88	60.44	6.08	27.45	87.84
100	45.6	27.75	54.40	48.3	29.18	51.7	25.57	46.51	74.43
150	65	53.1	56.6	71.79	42.63	52.14	46.67	64.58	68.88

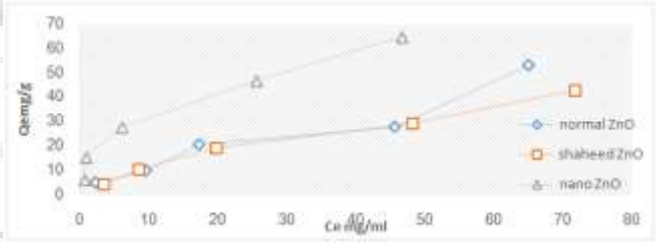

Figure 5: Adsorption isotherm of M.B on: (normal ZnO), (shaheed ZnO), & (nanoZnO) at 298K.

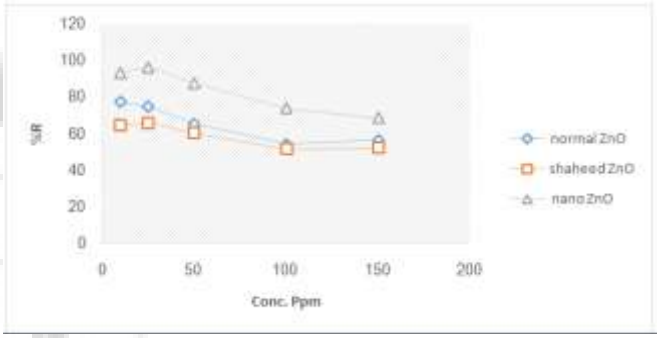

Figure 6: The %R of M.B on: (normal ZnO), (shaheed ZnO) & (nanoZnO) at 298K

It's clear that, the nanoZnO is the best for the removal of M.B than normal ZnO& the last compound is the best from shaheed factory ZnO dependent on particle sized that measured in AFM & % R.

Table 2 & Figure 7 show the adsorption parameters for different types of ZnO at 298K

Table 2: Absorption value of M.B on different types of ZnO surfaces for Langmuir application at 298K

	Normal ZnO		ShaheedZnO		Nano ZnO	
C_o	C_e/q_e (g/ml)	C_e (mg/ml)	C_e/q_e (g/ml)	C_e (mg/ml)	C_e/q_e (g/ml)	C_e (mg/ml)
10	0.46	2.25	0.86	3.51	0.11	0.66
25	0.99	9.57	0.82	8.52	0.05	0.89
50	0.84	17.26	1.04	19.78	0.22	6.08
100	1.64	45.6	1.65	48.3	0.54	25.57
150	1.22	65	1.68	71.79	0.72	46.67

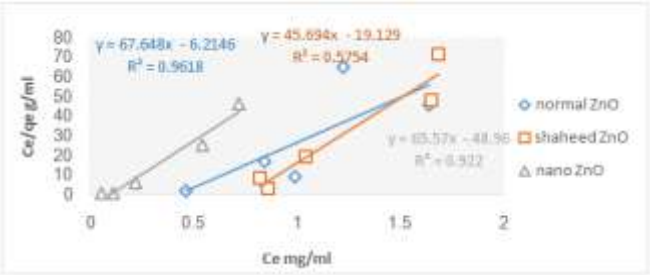

Figure 7: Linear Langmuir Adsorption of M.B dye on: (normal ZnO), (shaheedZnO) & (nanoZnO) at 298K

Table (3) & Figure (8) show the Freundlich applied of the adsorption isotherm for M.B on different ZnOtypes at 298K.

Table 3: Absorption value of M.B on different types of ZnO surfaces for Freundlich application at 298K

Normal ZnO			ShaheedZnO		Nano ZnO	
C_o	Log Q_e(mg/g)	Log C_e (mg/ml)	Log Q_e(mg/g)	Log C_e (mg/ml)	Log Q_e(mg/g)	Log C_e (mg/ml)
10	0.68	0.35	0.6	0.54	0.76	-0.18
25	0.98	0.98	1.01	0.93	1.17	-0.05
50	1.31	1.23	1.27	1.29	1.43	0.78
100	1.44	1.74	1.46	1.72	1.66	1.4
150	1.72	1.81	1.62	1.91	1.81	1.66

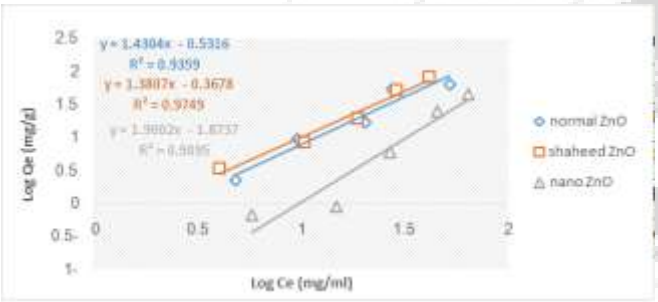

Figure 8: Freundlich Adsorption for M.B dyeon: (normal ZnO), (shaheed ZnO) & (nano ZnO) at 298K

Table (4) & Fig (9) shows the Temkin applied of the adsorption isotherm for M.B on different ZnO types at 298K

Table 4: Absorption value of M.B on different types of ZnO surfaces for Temkin application at 298K

Normal ZnO			ShaheedZnO		Nano ZnO	
C_o	q_e(mg/g)	Ln C_e (mg/ml)	q_e(mg/g)	Ln C_e (mg/ml)	q_e(mg/g)	lnC_e (mg/ml)
10	4.84	0.81	4.05	1.25	5.83	-0.41
25	9.64	2.25	10.3	2.14	13.06	-0.11
50	20.46	2.84	18.88	2.98	27.45	1.8
100	27.75	4.01	29.18	3.97	46.51	3.24
150	53.1	4.17	42.63	4.4	64.58	3.84

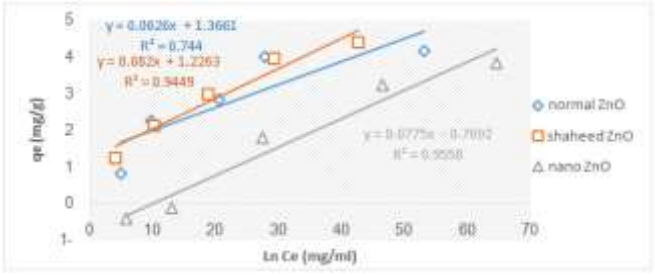

Figure 9: Temkin Adsorption for M.B dyeon: (normal ZnO), (shaheedZnO) & (nanoZnO) at 298K

Table (5) shows the empirical values & correlation factors for Langmuir, Freundlich & temkin constants.

Table 5: Empirical values & correlation factors for Langmuir, Freundlich & Temkin constants for the adsorption of M.B by different types ZnO at 298 K

Isotherm models	parameters	Normal ZnO at temperature	shaheedZnO at temperature	nanoZnO at temperature
Langmuir	q_m(mgg^{-1})	79.63	70.92	70.42
	K_L (Lmg^{-1})	0.0185	0.0180	0.1407
	R^2	0.5754	0.9220	0.9618
Freundlich	K_F (lmg^{-1})	2.669	2.332	74.765
	1/n	0.654	1.381	1.901
	R^2	0.9395	0.9749	0.9095
Temkin	A_T (L/g)	2.380	3.650	2.415
	B(J/mol)	11.883	11.529	12.328
	R^2	0.7440	0.9449	0.9558

The normal ZnO & shaheed ZnO were fitting to Freundlich equation. The best fit of equilibrium data that on the (Freundlich isotherm) given a heterogeneous surface with nonuniform distribution of heat of adsorption over the surface. The value of 1/n for (normal &nano) ZnO referred to physisorption while the adsorption on shaheed ZnO (chemisorption) & correlation coefficient (R^2) indicated that the M.B sorption process was favorable to Freundlich model [27], the value of 1/n (0.1< 1/n < 1) referred to favorable adsorption of M.B dye at experimental condition while the adsorption data for M.B with nanoZnO was fitting to Temkinisotherm model dependent on the R^2 value that referred to the M.B adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy[28].

3- Thermodynamic parameters:

Thermodynamic parameters derived from equation (12) for M.B adsorption (25 ppm on different ZnO types is shown in the table (8).

Table 8: Comparison of thermodynamic parameters for adsorption of 25 ppm M.B dye on different types of ZnO

T(K)	1/T (K^{-1})	$K_{ZnO\ normal}$	Ln K	ΔG^okJ/mol	ΔH^o kJ/mol	ΔS^oJ/mol. K
293	0.0034	4.470	1.497	-3.64	-11.09	-25.38
298	0.00335	1.612	1.284	-1.18		
303	0.0033	3.424	1.231	-3.1		
308	0.0032	3.307	1.196	-3.06		
T(K)	1/T (K^{-1})	$K_{ZnOshaheed}$	Ln K	ΔG^okJ/mol	ΔH^o kJ/mol	ΔS^oJ/mol. K
293	0.0034	1.312	0.272	-0.66	14.28	51.96
298	0.00335	1.934	0.659	-1.63		
303	0.0033	1.834	0.606	-1.52		
308	0.0032	2.011	0.698	-1.78		
T(K)	1/T (K^{-1})	$K_{ZnOnano}$	Ln K	ΔG^okJ/mol	ΔH^o kJ/mol	ΔS^oJ/mol. K
293	0.0034	40.05	3.69	-8.98	-36.71	-93.25
298	0.00335	27.08	3.299	-8.17		
303	0.0033	53.94	3.987	-10.04		
308	0.0032	14.42	2.668	-6.83		

It clear that, the adsorption of M.B on different ZnO types negative value ΔG^o indicated to the adsorption process was spontaneously and thermodynamic favorable. The negative value of free energy with increase temperature indicated to the driving force at adsorption process. The adsorption process with (nano & normal) ZnO were exothermic dependent on the value of ΔH^o (negative), while the ΔH^o values of M.B adsorption on shaheed ZnO have positive sign reflecting on endothermic process. The value of ΔS^o with (nano & normal) ZnO were negative which referred to decrease disorder at the solid/liquid interface during M.B sorption while the ΔS^o for shaheed ZnO was positive which referred to increase disorder at the solid/liquid interface during M.B sorption [29].

3. Conclusion

1. Methylene blue dye have an aromatic structure, substituted with ionic part (Cl^-), this part can be connected with ZnO surface by sorption process. Therefore, can be remove the M.B dye.
2. The sorption of M.B dye on (normal, shaheed) ZnO was of Freundlich type, & this indicates that multi-layer has formed.
3. The sorption of M.B dye on nano ZnO was of Temkin process & this indicates that decrease linearity.
4. When the average diameter was decrease, the adsorption for M.B increase.
5. The negative value of ΔH indicates that the adsorption process is dominating rather than M.B may also inter inside the ZnO surface.

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