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Ability of different adsorbent for removal of Rhodamine B from aqueous solution

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Abstract

Adsorption of Rhodamine B dye on powdered TiO_2, zinc oxide (ZnO) and natural Bentonoit clay from aqueous solutions have been studied .The potential for the adsorption of Rhoamine dye at a fixed initial concentration of 5 ppm. The experiments were carried out in a batch system to optimize operation variables initial concentration, effect of time adsorption isotherms.

The langmuir and frendlish isotherm equations were applied to the data and values of parameters of these results suggest that the adsorption of (RB) dye on ZnO observed more fit to Freundlich model it means the Rhodamine B adsorbed weakly to the surfaces of ZnO, physical adsorption is achieved between the adsorbed and adsorbent, but the adsorption on TiO_2 and bentonite better fit to Langmuir model. Kinetics study was made using lagergreen equation the results show the sorption of Rhodamine B dye uptake on ZnO fitted to first order reaction. And the sorption of RB on TiO_2, and Bentonite fitted with second order. The partition coefficient k_d for the sorption of RB on TiO_2, ZnO and bentonite also determined and shows the value of Kd increases with time until equilibrium and becomes constant. we can conclude that the proportion of RB dye on each adsorbent increase which means that the large number of adsorption sites available with the rate slowing with time as sites fill up. The enthalpy of adsorption of rhodamine B on TiO_2, + 4.09 kJ/mol, on ZnO +15.25 kJ/mol and on bentonite +4.01 kJ/mol indicates that the process is endothermic. The thermodynamic quantities $\Delta G°$, $\Delta H°$, and $\Delta S°$, for the adsorption of rhodamine B dye on the surfaces of TiO_2, ZnO and bentonite have been calculated. The result shows that the value of $\Delta G°$ decrease with an increase in temperature indicates that the adsorption process is more favorable at high temperature. Whereas the positive value of $\Delta S°$ as a result of rhodamine B adsorption due to an increased degree of freedom in the system and indicates high affinity of the adsorbent for Rhodamine molecules.

Introduction

The rapid growing world population and rapidly advancing industrialization is causing more demand than ever for the decreasing supply of water, which makes it costly in many countries [1]. A growing many of contaminants are entering water supplies from industrialization and human activity such as heavy metals, dyes, pharmaceuticals, pesticides, fluoride, phenols, insecticides, pesticides and detergents leads to generation a large amount of waste water containing toxic pollutants [2]. Many water pollutants remain to be addressed, due to rapid industrialization new chemical compounds are sustainably being developed and brought to the market will appear into the aquatic systems [3]. Dye is one of that contaminants it might be recognized in a wastewater because a very small amount of synthetic dyes in water are highly visible, affecting the aesthetic quality, transparency and gas solubility of water bodies [4]. Dye and dye intermediates industries which are the main raw materials used for the manufacturing dyestuff such as, textile, leather,

cosmetic, paper, plastic and paint industries [5]. A number of physical, chemical and biological treatment techniques and methods have been developed for the removal of the pollutants in water and wastewater [6]. Although several of these operations and processes are combined in most treatment systems, they are usually considered separately [7].

These include: physical methods such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis) and sorption techniques, chemical methods such as coagulation or flocculation combined with flotation and filtration, precipitation [8-11].

Among these processes the adsorption process considered as one of the most efficient technique for the treatment and removal of organic pollutants in waste water treatment [12] and13]. Dyes are considered is one of that common contaminants it might be recognized in a wastewater because a very small amount of synthetic dyes in water are highly visible, affecting the aesthetic quality, transparency and gas solubility of water bodies [14]. Among many dyes Rhodamine B removal has been studied in this work. Rhodamine B is a xanthene dye, its highly soluble in water and most common non-polar solvents, making it easily mixed with most bait materials [15]. It has been widely used as fluorescent probes owing to their high absorption coefficient and broad fluorescence in the visible region of electromagnetic spectrum, high fluorescence also applied as laser dyes [16], photosensitizers [17], and as chemo sensors used either in vitro as in vivo in detection of heavy metals [18].

Many researchers have been working for the preparation of low-cost adsorbents. Exploration of good low-cost adsorbent may contribute to the sustainability of the environment and offer promising benefits for the commercial purpose in future. The nature of adsorbent is more effective factor in adsorption progress for removal of pollutants [19]. The purpose this research is based on searching for economical, available starting raw materials and low-cost adsorbent for removal of Rhodamine B dye. The comparison ability of different adsorbents for Rhodamine B removal from aqueous solution it's the other aim of this study.

Experimental

Materials

The rhodamine B dye was purchased from Merck (Germany). The adsorbents TiO2 and ZnO were purchased from Sigma-Aldrich (USA) and the bentonite clay was collected in depth (1 m) from Garmian region of Kurdistan. The bentonite sample was washed with distill water then dried at 80 ^{o}C for 4 hours. The residue was dried, crushed and sieved through a 35 mesh sieve. The sample was sent to State company of geological survey and mining in Iraq for analyzing.

Adsorption studies

A stock solution of Rhodamine B (1000 mg/ L) was prepared by dissolving 1 gm of Rhodamine B dye in one liter of distilled water and suitably diluted to the required initial dye concentrations. The calibration curve of initial concentrations C_i of Rhodamine B was obtained by measuring the absorbance of known concentration (C_i range: 0.5 – 10 mg/L) at λ_{max} =552 nm using UV/Vis – spectroscopy. The adsorption experiments were carried out at room temperature in batch mode. Exactly 25 ml of Rhodamine B solution of each known initial concentration (from 0.5 – 10 mg /L) were added to 0.1 g of each adsorbent followed by shaken for 1 hr and left to stand for 2 hr, these were centrifuged for 10 min at 7000 rpm before the solution was measured by UV/Vis –spectroscopy at λ_{max} = 552 nm. The amount of adsorbed dye was calculated according to the following equation [20].

$$q_e = \frac{(C_i - C_e)V}{m} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

where :-

q_e = amount of dye adsorbed (mg/g) .

C_i = initial concentration of adsorbed (mg/L).

C_e= the concentration at equilibrium time (mg/L).

m = mass of adsorbent (g).

V=Volume of dye solution (ml).

Effects of contact time

The effect of contact time and initial concentration of Rhodamine B dye solution on sorption was studied using a series bottles labeled from (1-20) at fixed temperature, 25 °C. A 0.1 g sample of TiO_2 powder was placed in each bottle then 25 ml volume of 5 mg/L Rhodamine B solution as shown the chemical structure in figure (1) was added to each bottle. At chosen times, a required volume from each bottle was taken and centrifuged at 7000 rpm for 10 min, (Hermle Z 160 M centrifuge), then the dye absorbance measured by UV/Vis-spectroscopy at λ_{max} =552 nm .

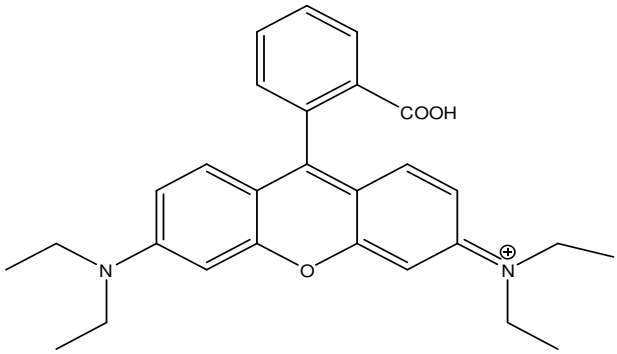

Figure 1 : Chemical structure of Rhodamine B dye.

Results and discussion

Figure (2), shows the maximum absorbance of Rhodamine B dye in solution at 552 nm when measured by UV – Vis spectrophotometer. Using these fixed wavelength measurements, a calibration curve of Rhodamine B solutions was determined and all example with a good correlation coefficient is illustrated in figure (3).

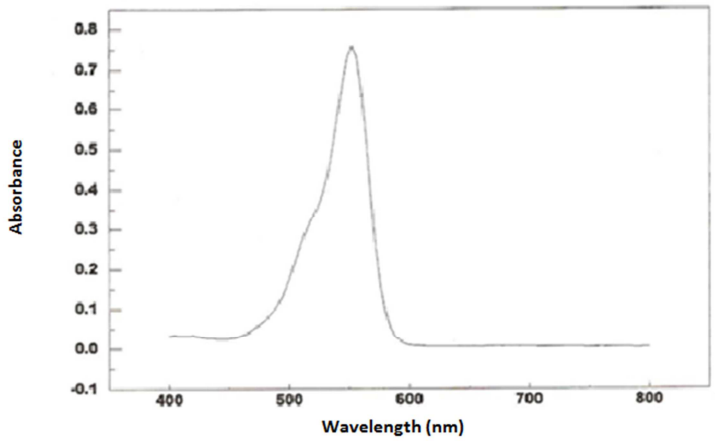

Figure (2): UV/Vis –spectra of (5 mg/L) Rhodamine B dye at 25 °C.

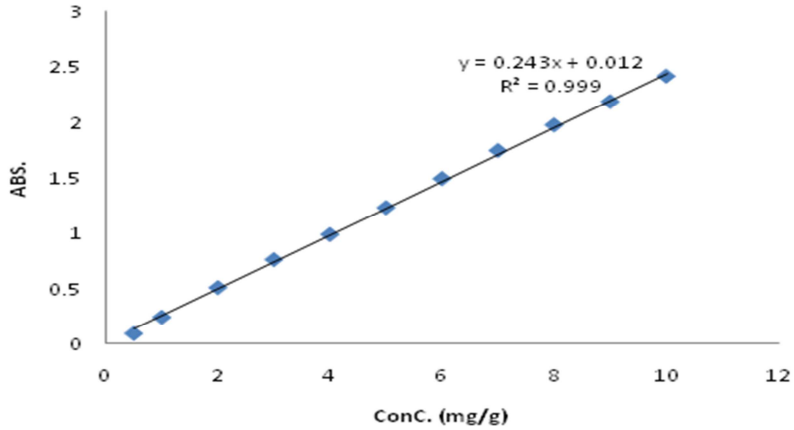

Figure 3: Calibration curve of Rhodamine B dye at fixed λmax = 552 nm at 25 °C.

Effect of contact time.

Suring data at interval time for the adsorption of Rhodamine B dye on TiO2, ZnO aThe effect of contact time was investigated by conducting a series of experiments using 25 ml of an initial concentration of 5 mg/L of Rhodamine B dye with 0.1 g of each adsorbent (TiO_2, ZnO or bentonite clay), Figure (4) shows that adsorption of dye reaches to equilibrium after 40 min and the meand bentonite for kinetic study are listed in table (1), (2) and (3)

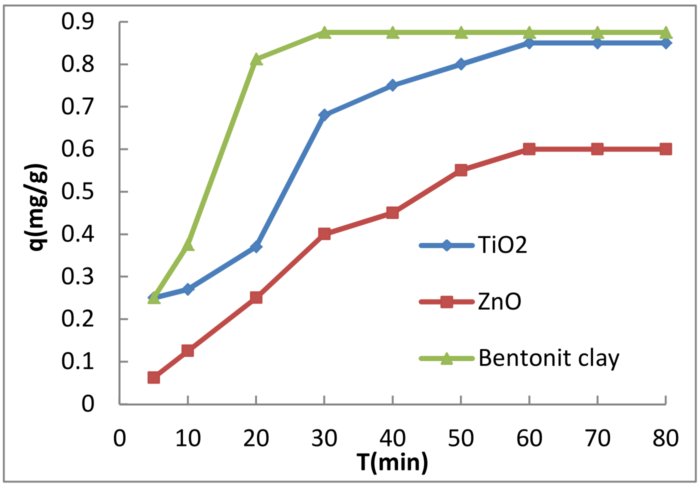

Figure 4: Effect of contact time on the adsorption of (5 mg/L) Rhodamine B on (0.1 g) of different adsorbents.

3.4. Kinetic studies

Kinetics of sorption, it is necessary to measure rate of adsorption. This is important to determine the efficiency of sorption and to identifying the amount of adsorbed dye over time. In the present study, the adsorption kinetics of Rhodamine B on various adsorbents has been studied. The second–order kinetics of adsorption was analyzed by using Largerger equation expressed as [21].

$$\frac{dq}{dt} = k_{2(q_e - q_t)}2 \quad \text{...}(2)$$

When arranged equation (2), obtain to the following equation:-

$$\frac{d(q_{e-}q_t)}{(q_{e-}q_t)2} = -k_2\, dt \quad \text{...}(3)$$

When we apply the conditions of integration if t=0 , qt =0 , whereby the dye not adsorbed on the adsorbent at time equal to zero , but after duration of time the molecules of dye adsorbed on adsorbent surface at t = t , $q_t = q_t$ the integrated form of the equation (3), becomes:-

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad \text{...}(4)$$

Equation (4) can be rearranged to obtain a linear equation form:-

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \quad \text{...}(5)$$

Where K_2 is the rate constant of second order in mg g^{-1} min^{-1} , and q_e is the equilibrium adsorption capacity in mg /g , the values of q_e and k_2 obtained from the slope and intercept respectively when (t/qt) plot against in equation (5). For the first –order kinetics used the equation proposed by Kannan and Sundaram

$$\frac{1}{q_t} = \left(\frac{k}{q_{max}}\right)\frac{1}{t} + \frac{1}{q_{max}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (6)$$

Where q_t is the amount of dye adsorbed in mg g^{-1} at time (t), q_{max} is the maximum adsorption capacity and k is the first-order rate constant in (min^{-1}). The plot ($1/q_t$) versus ($1/q_{max}$) gives a slope equal to (k/q_{max}) and the intercept equal to ($1/q_{max}$) .The experimental data in tables (2), (3), (4), and (5) were analyzed using equation (5) and (6) to determine the adsorption capacity and adsorption rate constants as shown in figures (5-10). The results of kinetics parameters are listed in Table (6), the results show the sorption of Rhodamine B dye uptake on ZnO fitted to first order reaction. This means that adsorption process is independent of the initial concentration of Rhodamine B dye. The sorption of Rhodamine B on TiO_2, and Bentonite fitted with second order adsorption kinetics indicating by increasing initial dye concentration the amount of adsorbed increases due to high surface area for these adsorbents.

Table (1): The data for kinetics studies of (5 mg/L) Rhodamine B dye sorption on (0.1 g) TiO_2.

t (min)	C_e g/L	$q_e$mg/g	1/t	1/q	t/q
5	4.00	0.25	0.20	4	20.00
10	3.90	0.27	0.10	3.7	37.03
20	3.50	0.37	0.05	2.7	54.00
30	2.25	0.68	0.033	1.47	44.11
40	2.00	0.75	0.025	1.33	53.33
50	1.80	0.8	0.02	1.25	62.50
60	1.60	0.85	0.016	1.17	70.50
70	1.60	0.85	0.014	1.17	82.35
80	1.60	0.85	0.012	1.17	94.11

Table (2): The data for kinetics studies of (5 mg/L) Rhodamine B dye sorption on (0.1 g) ZnO.

t (min)	C_e mg/L	q_e mg/g	1/t	1/q	t/q
5	4.75	0.062	0.2	16.6	83.3
10	4.5	0.125	0.1	8	83.3
20	4	0.25	0.05	4	80
30	3.4	0.4	0.033	2.2	75
40	3.2	0.45	0.025	1.8	88.8
50	2.8	0.55	0.02	1.6	90.9
60	2.6	0.6	0.016	1.6	100
70	2.6	0.6	0.014	1.6	116.6
80	2.6	0.6	0.012	1.6	133.3

Table (3): The data for kinetics studies of (5 mg/L) Rhodamine B dye sorption on (0.1 g) Bentonit clay.

t (min)	C_e mg/L	q_e mg/g	1/t	1/q	t/q
5	4	0.25	0.2	4	20
10	3.5	0.375	0.1	2.7	27.02
20	1.75	0.812	0.05	1.23	24.69
30	1.5	0.875	0.033	1.15	34.48
40	1.5	0.875	0.025	1.15	45.97
50	1.5	0.875	0.02	1.15	57.47
60	1.5	0.875	0.016	1.15	68.96
70	1.5	0.875	0.014	1.15	80.45
80	1.5	0.875	0.012	1.15	91.95

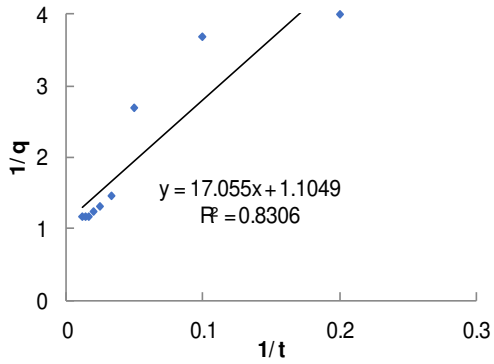

Figure 5: First order kinetics plot for the sorption of RB dye on TiO_2

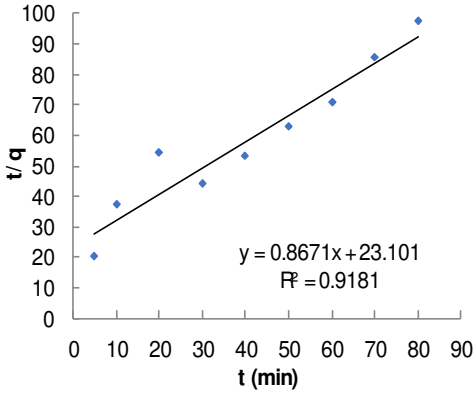

Figure 8: Second order kinetics plot for the sorption of RB on TiO_2.

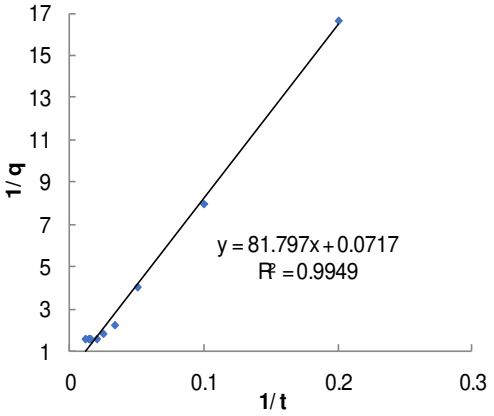

Figure 6: first order kinetics plot for the sorption of RB dye on ZnO

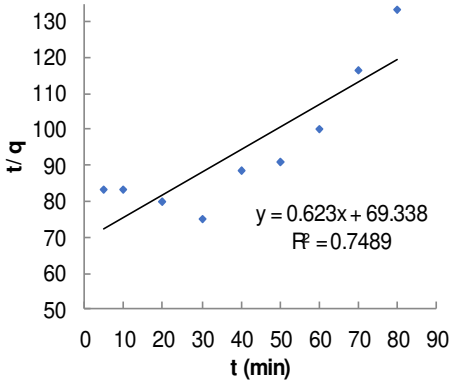

Figure 9 : Second order kinetic plot for the sorption of RB on ZnO

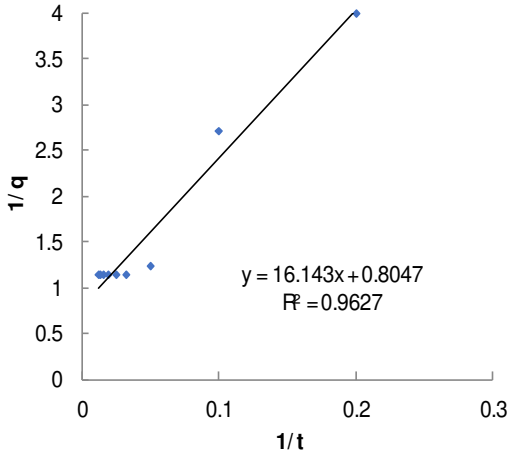

Figure 7: First order kinetics plot for the sorption of RB dye on Bentonite clay.

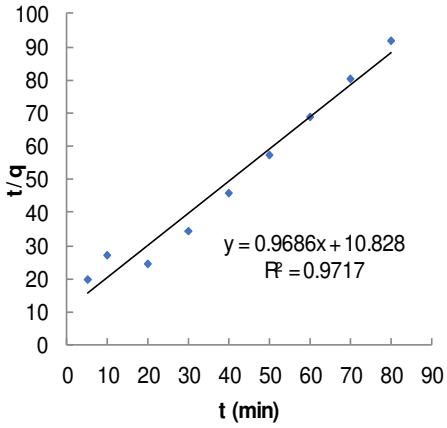

Figure10: Second order kinetics plot the sorption of RB on Bentonite.

Table (4): Kinetic parameters for Rhodamine B uptake on the studied adsorbents.

Adsorbents parameters		TiO_2	Bentonite	ZnO
1 st order	R^2	0.83	0.962	0.994
	K min^{-1}	15.43	20.07	20.07
	q_{max} mg/g	0.905	1.243	1.243
2 nd order	R^2	0.944	0.971	0.748
	K_2g.mg^{-1}.min^{-1}	5.599	0.086	5.599
	q_e mg/g	1.605	1.033	1.605

The solid to solution partition coefficient (K_d) was determined from the following equation.

$$K_d = \frac{C_{total}}{C_e} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Where:-

$$C_{total} = C_e + q_e \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (8)$$

The results of partition coefficient K_d are shown in Table (7). The partition coefficient kd for the sorption of Rhodamine B increases with time until equilibrium and becomes constant. We can conclude that the proportion of RB dye on each adsorbent increase because of the large number of adsorption sites available with the rate slowing with time as sites fill up [22].

Table (5): Partition coefficients (K_d), for the adsorption of Rhodamine B dye on different adsorbents.

Time (min)	5	10	20	30	40	50	60	70	80
TiO_2	1.06	1.07	1.1	1.3	1.37	1.44	1.51	1.51	1.51
Bentonite	1.06	1.1	1.46	1.58	1.58	1.58	1.58	1.58	1.58
ZnO	1.01	1.02	1.06	1.11	1.14	1.19	1.23	1.23	1.23

Adsorption isotherms

The adsorption isotherm usually describes the adsorption system indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The experimental data have been analyzed by the linear forms of the Freundlich and Langmuir model isotherms represented by the following equations. Freundlich isotherm expressed as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \dots\dots\dots\dots\dots\dots\dots\dots (9)$$

Where:-

q_e = amount of adsorbed at equilibrium mg g^{-1}

C_e= concentration at equilibrium mg L^{-1}

K_f =Freundlich constant refers to the adsorption capacity.

n= Freundlich constant related to the intensity of adsorption.

The plot log q_e against log C_e gives a slope equal to (1/n), with intercept equal to log k_f.

And Langmuir isotherm is equal to;-

$$\frac{C_e}{q_e} = \frac{1}{bk_l} + \frac{C_e}{k_l} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (10)$$

Where:-

q_e= amount of adsorbed at equilibrium mg g^{-1}

C_e=the concentration of adsorbed at equilibrium mg L^{-1}

K_L=Langmuir constant related to adsorption capacity mg g^{-1}

b= Langmuir constant related to intensity of adsorption L mg^{-1}

The plot (C_e/q_e) against C_e it gives a straight line producing a slope equal to ($1/K_L$) with intercept equal to ($1/bk_L$).

The experimental adsorption isotherms of rhodamine B dye on TiO2, ZnO and bentonite surface at 25 ^oC, are presented in figures (11) to (13) for Freundlich model by plot log(qe) versus log(Ce) and in figures (14) to (16) for Langmuir model by plot Ce/qe versus Ce. Langmuir and Freundlich isotherm constants have been determined from the slops and intercepts from the equations 10 and 9 respectively and listed in table 7. The obtained results in Table (7), that the adsorption of Rhodamine B dye on ZnO observed more fit to Freundlich model it means the Rhodamine B adsorbed weakly to the surfaces of ZnO, physical adsorption is achieved between the adsorbed and adsorbent, but the adsorption on TiO_2 and bentonite better fit to Langmuir model. Composition of the Bentonite is presented in table (6) composed of SiO_2 and Al_2O_3 as a majority metal oxides with other trace oxides it has a high surface area included positive and negative charge therefore contact strongly with dye molecules to form a monolayer on the Bentonit surface also TiO_2 which has a surface area 80.8 $m^2.g^{-1}$ conducted strongly to RB dye molecules, whereby the sorption between RB dye and TiO_2 is chemical adsorption [23].

Table (6): Chemical composition of Iraqi Bentonite clay. (*)

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO_2	LOI	Total
Wt%	45.91	9.8	4.85	11.8	4.16	2.94	1.37	0.69	0.07	17.25	98.84

(*):- State company of geological survey and mining in Iraq

Table (7): Isotherms constants of Freundlich & Langmuir for adsorption of Rhodamine B on different adsorbents at 25 ^oC.

Adsorbents	Freundlich constants			Langmuir constants		
	K_f (mg/g)	n (L/mg)	R^2	K_L (mg/g)	b (L/mg)	R^2
TiO_2	0.685	2.79	0.908	1.07	3.314	0.986
Bentonit	0.758	1.96	0.927	1.47	1.57	0.984
ZnO	0.212	1.47	0.98	1.09	0.257	0.873

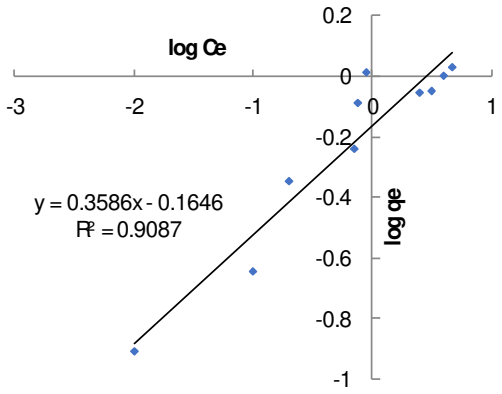

Figure 11: Freundlich isotherm for the sorption RB dye on TiO_2.

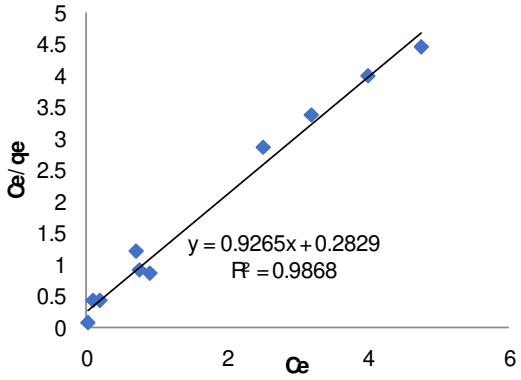

Figure14: Langmuir isotherm for the sorption of RB dye on TiO_2.

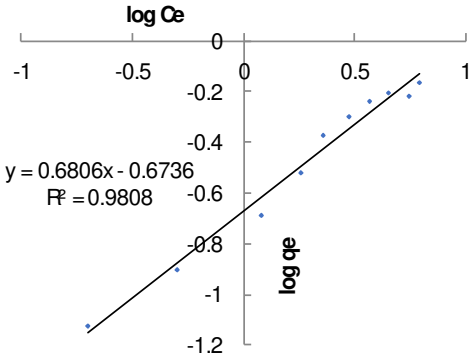

Figure 12: Freundlich isotherm for the sorption of RB on ZnO.

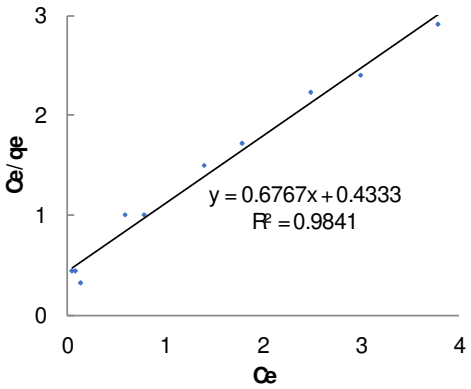

Figure 15: Langmuir isotherm for the sorption of RB dye on ZnO.

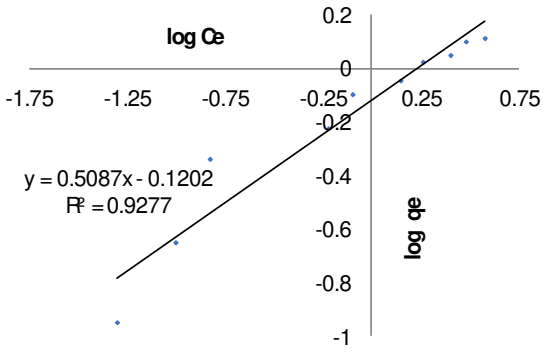

Figure13: Freundlich isotherm for the sorption of RB dye on Bentonite.

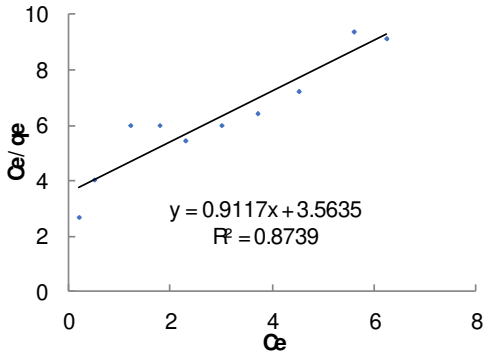

Figure16: Langmuir isotherm for the sorption of RB dye on Bentonite.

Effect of temperature

Thermodynamic parameters are an essential factior of proposing adsorption mechanism to confirm the adsorption nature of the present study. To evaluate the free energy change ΔG^{o} the following equation has been used:

$$\Delta G° = -RTln\ \frac{q_e}{C_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

where R is the constant of perfect gas (R = 8.314 J/mol. K), T is the absolute temperature of solution Ce is the equilibrium dye concentration (mg/L) and q_e maximum amount of adsorption (mg/g). The ratio of the qe and Ce were determined from the isotherms for each adsorbent at different temperatures as shown in figures (17) , (18 and (19). The enthalpy (ΔH) and entropy (ΔS) changes can be estimated by van't Hoff equation as follows:

$$\Delta G° = \Delta H° - T\Delta S° \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

A plot of Gibb's free energy change, $\Delta G°$, versus temperature, T, was found to be linear figures (20), (21) and (22). The enthalpy change, $\Delta H°$, and the entropy change, $\Delta S°$, for the adsorption processes were obtained from the intercept and slope of Eq. (12). The thermodynamic parameters of Gibb's free energy change, $\Delta G°$, enthalpy change, $\Delta H°$, and entropy change $\Delta S°$, for the adsorption of rhodamine B dye on the surfaces each of TiO_2 , ZnO and bentonite were calculated and listed in table 7. The results shows that The decrease in the value of $\Delta G°$ with an increase in temperature indicates that the adsorption process of rhodamine B on each of TiO_2 , ZnO and bentonite becomes more favorable at higher temperatures [24].

The enthalpy of adsorption of rhodamine B on TiO2, + 4.09 kJ/mol, on ZnO +15.25 kJ/mol and on bentonite +4.01 kJ/mol indicates that the process is endothermic. Whereas the positive value of $\Delta S°$as a result of rhodamine B adsorption due to an increased degree of freedom in the system and indicates high affinity of the adsorbent for Rhodamine molecules [25].

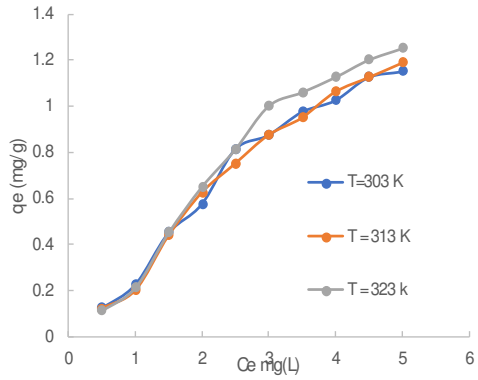

Figure 17: Adsorption isotherm of RB on TiO_2 at different temperatures

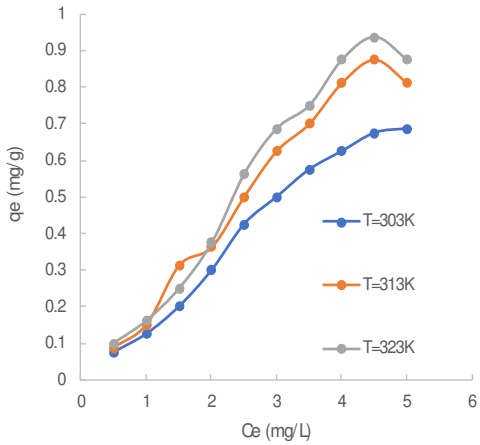

Figure 18: Adsorption isotherm of RB on ZnO at different temperatures

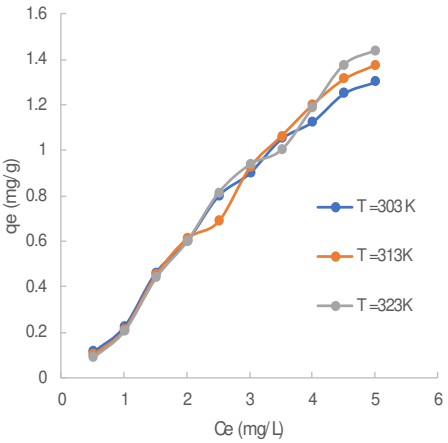

Figure 19: Adsorption isotherm of RB on Bentonite at different temperatures

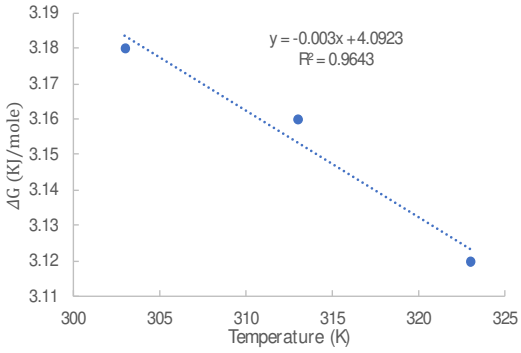

Figure 20: Plot of Gibbs free energy change, ΔG°, versus temperature, T for the sorption of RB on TiO_2.

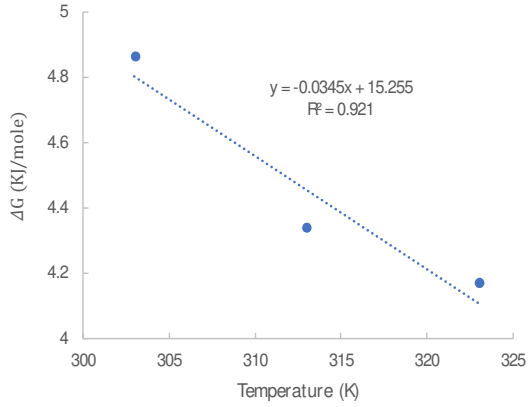

Figure 21: Plot of Gibbs free energy change, ΔG°, versus temperature, T for the sorption of RB on ZnO.

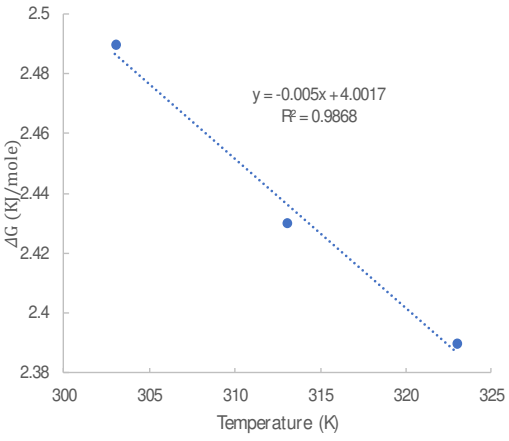

Figure 22: Plot of Gibbs free energy change, ΔG°, versus temperature, T for the sorption of RB on Bentonite.

Table 8: A comparison of thermodynamic parameters for the adsorption of Rhodamine B by different adsorbents

Adsorbent	T (K)	ΔG KJ/mole	ΔH KJ/mole	ΔS KJ/mole
TiO_2	303	3.18	4.09	0.003
	313	3.16		
	323	3.12		
ZnO	303	4.86	15.25	0.034
	313	4.26		
	323	4.17		
Bentonite	303	2.49	4.01	0.005
	313	2.43		
	323	2.39		

Conclusion

In the present study, different adsorbents for the removal of Rhodamine B dye from aqueous solution have been studied using an Iraqi bentonite clay, TiO_2 and ZnO as an adsorbents. The adsorption Rhodamine B on TiO_2 surface is better than bentonite and ZnO modeled by Langmuir model. On the other hand, the adsorption equilibrium of RB on ZnO and bentonite predicted by Freundlich approach. The results also show that the sorption of Rhodamine B dye uptake on ZnO fitted to first order reaction. And the sorption with TiO_2, and Bentonite fitted with second order adsorption kinetics indicating by increasing initial dye concentration the amount of adsorbed increases due to high surface area for these adsorbents. The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the sorption of rhodamine B dye on TiO_2 , ZnO and bentonite at different temperatures also have been calculated and the results shows that free energy $\Delta G°$ values decreased with increases in temperature. The values of $\Delta H°$ and $\Delta S°$ were also obtained from a slope and intercept of the relationship between $\Delta G°$ and reaction temperature. The positive value of $\Delta H°$ and $\Delta S°$ indicates that the adsorption process of rhodamine B on the adsorbents TiO_2, ZnO and bentonite were endothermic and randomness at the solid/liquid interface during the adsorption, respectively.

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