Adsorption Study Of Malachite Green Dye On To Cadmium Oxide Surface (Thermodynamic and Kinetic)

Adraa Abdul kadhim , Douaa Abdul hussain

Department of Chemistry, Faculty of Education for Girls , University of Kufa, Najaf, Iraq

الخلاصة

هو دراسة امتزاز صبغة الملاكات الاخضر على سطح اوكسيد الكادميوم, ضمن المدى الحراري (298-328 K)

وشملت الدراسة اختبار تطبيق نماذج إيزوثيرم لنكماير، فروندلش، إيلوفيتش و تمكين أعطت نتائج الاختبار علاقات خطية ومعاملات تصحيح جيدة، وخصوصا تمكين و فروندلش وكما تم ايضا دراسة حركيات الامتزاز باستخدام معادلة المرتبة الاولى الكاذبة والثانية الكاذبة ومعادلة إيلوفيتش الحركية واخيرا معادلة الانتشار بين الجزيئات ،وقد اظهرت النتائج ان معادلة المرتبة الثانية ومعادلة الانتشار بين الدقابق هي افضل علاقات اعطت معامل تصحيح جيده .

كما استخدمت نتائج الامتزاز للحصول على قيم الدوال الحرارية (طاقة كبس الحره ΔG، الانثالبيΔH و ΔS والعشوائية) ضمن المدى الحراري التجريبي (298-328 K) على أساس حساب قيم ثابت التوازن (Keq). وأوضحت النتائج أن الامتزاز هو ماص للحرارة والفيزيائية وأن العشوائية تزداد بزيادة درجة الحرارة وأن التفاعل يكون تلقائي ضمن ظروف تجريبية.

Abstract

The subject of the research is the study of adsorption of pigment dye malachite on to Metal oxide. One of these is metal oxides, cadmium oxide, was chosen as the adsorbents of this dye In the thermal range from 298K to 328K. The study included the test of applying the isotherm models of Langmuir, Freundlich, Elovich and Temkin to the practical adsorption data of the dye under study using the UV spectroscopy. The test results gave linear relations and good correlation coefficients, specifically Temkin and Freundlich .isotherm.

The kinetic data were modeled by using pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetics equations, The pseudo-second-order and intra-particle diffusion kinetic model was found to correlate with the experimental data well for the dye.

Adsorption adsorbents were also used to obtain the values of the thermodynamic functions (Free energy ΔG, enthalpy ΔH and ΔS entropy) within the experimental thermal range (328-298K) based on the calculation of the values of the equilibrium constant (Keq). The results indicated that adsorption is endothermic and physical and that entropy increases with increasing temperature and that the reaction is spontaneous in experimental conditions.

Keywords: adsorption , isotherm, kinetic , adsorbents , equilibrium .

Introduction

The dyes have been identified since antiquity since they can be obtained from animal or plant sources[1]. They are chemical substances and compounds that are used to produce and prepare long-lasting pigments on the surfaces of materials. The dyes are widely used in various industries such as paper, rubber, cosmetics , These dyes in general are dangerous and poisonous[2] because they contain metal ions that pollute the environment and affect the ozone layer so it is assumed to be disposed of in any way possible[3]. The most important of these methods is the method of adsorption[4].It's a physical phenomenon that combines the gas or liquid substance of molecules, atoms or ions of a material called adsorbate on the surface of another solid porous substance called adsorbent. The adhesion between the molecules of the substance absorbed by the active sites of the surface is either from through weak Vander waals or through chemical bonds[5-6]. In this research it is necessary to talk about the dye that called Malachite green (MG) is water soluble cationic dye that appears as green glassy dust and its classified in the dyestuff industry as a triarylmethane dye and also using in pigment industry. Formally, malachite green refers to the chloride salt $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$, although the term malachite green is used loosely and often just refers to the colored cation. The oxalate salt is also marketed. The anions have no effect on the color[7].

Experimental part

Preparation of Standard Solutions

Preparation a solution (stock solution) of the dye at a concentration of (100mg/L) by dissolving the weight of 0.1g in a specified amount of distilled water and then completing the volume to 1000ml. Different solutions were prepared with different concentrations ranging from 20-2 mg /L Of dye that conform to the Lambert law and the λ_{max} wavelength was measured for the greatest absorption using distilled water as a reference solution(Blank), as its shown in the next figure, and λ_{max} that we were used =618 .

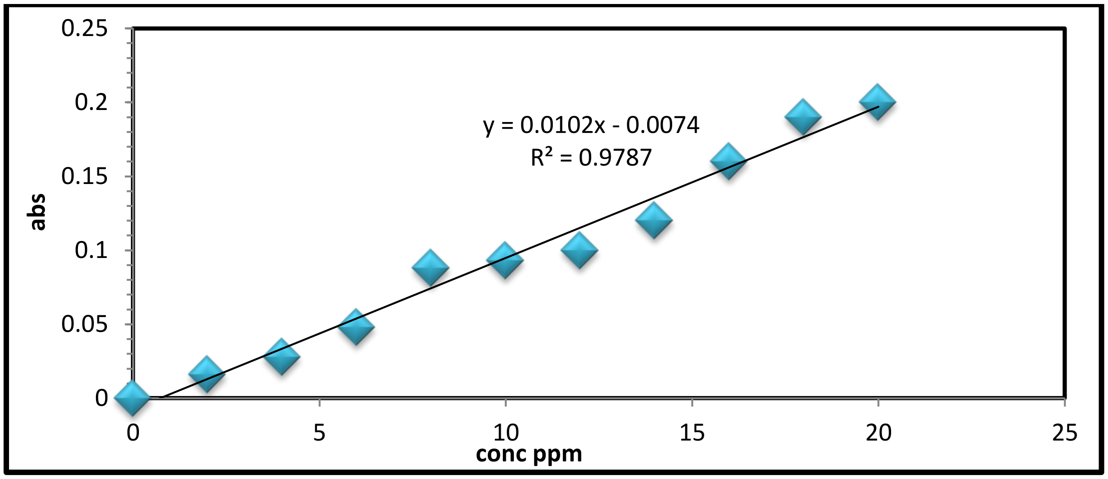

Fig1: Calibration curve for malachite dye.

Determination of the equilibrium time of adsorption systems

For the purpose of determining the equilibrium between the solvent solution and the absorbent material, all the conditions of pH, temperature functions were fixed with each change of time. 15 ml of the dye solution was taken at a specific concentration =14ppm and placed in a volumetric glass with a capacity of 50 ml and added 0.1g Of the adsorbent surfaces adopted in this study at room temperature and neutral acid function and then put in the device (shaker) and take samples at different time periods and measuring the absorption after the process of filtration at λ_{max} =618. The equilibrium time was determined by the minutes of the dye absorbed on the surface.the figure (2) showed that Equilibrium Time of Adsorption malachite green dye was = 40min.

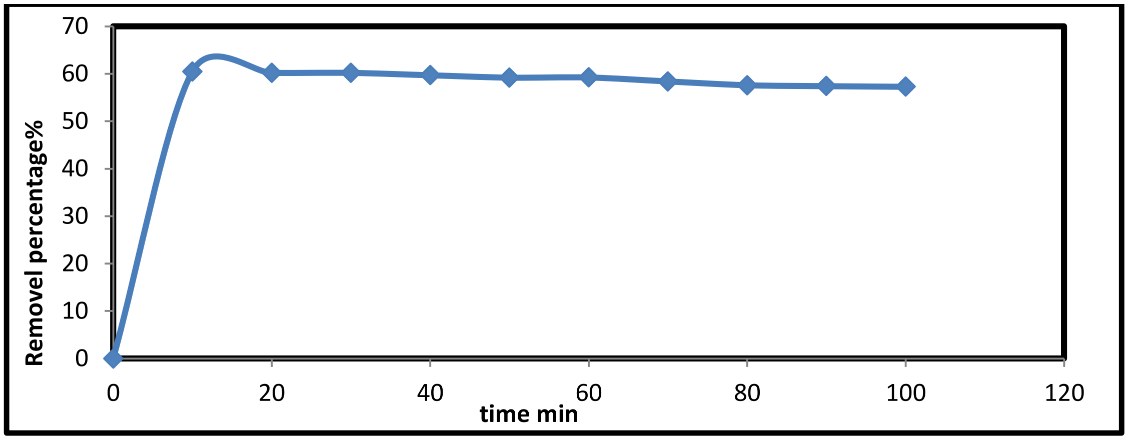

Fig 2: The Equilibrium Time of Adsorption malachite green dye on to cadmium oxide .

Determination best weight of the equilibrium of adsorption systems:

The effect of cadmium oxide weight on adsorption system was measured with the time required for the equilibrium process. At the temperature of 303K the acidic function (pH=7) and the primary concentration (14ppm) were used. Various weights were used (0.5, 0.45, 0.4, 0.35, 0.3 , 0.25, 0.2, 0.15, 0.1, 0.05gm) The best weight of the surface was determined=0.15g as showed in figure(3) .

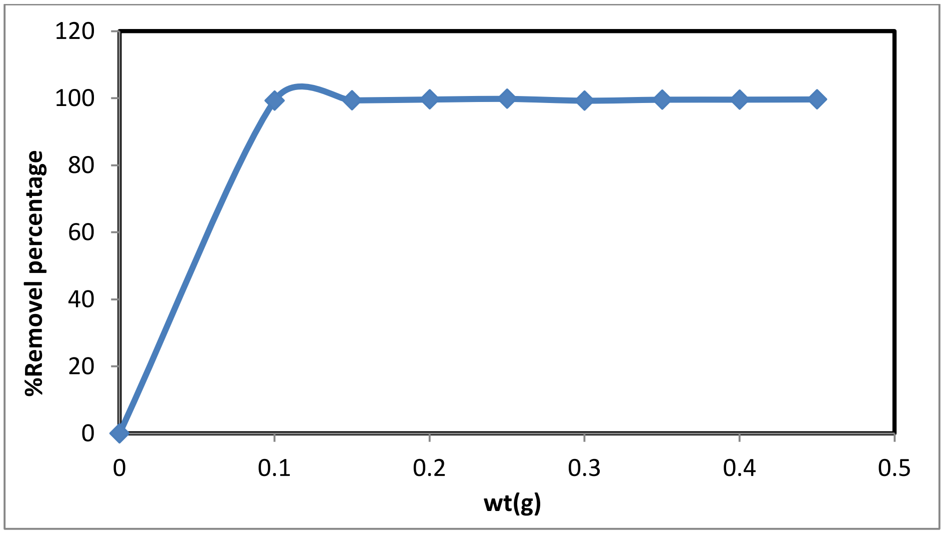

Fig 3: Best Weight of the Equilibrium of Adsorption malachite green dye on to cadmium oxide .

Adsorption Isotherm

The adsorption isotherm of the dye was obtained by preparing 10 concentrations of the absorbent material within the range (2-20 mg /L) in volumetric glass (100ml). The concentration was taken and placed in contact with a certain weight Of the adsorbate surface varies for the dye and placed in a conical flask capacity (50ml)) and then placed at a temperature controlled by water bath, equipped with shaking and after shaking for a certain period of time. When the pH was neutral ,then filtration of the solutions using filter sheets to get rid of the surface minutes. By means of the UV spectrometer at the λ_{max} of the dye to determine the absorbance values The concentration at the equilibrium (c_e) mg / L was determined from the calibration curve then the quantity of the absorbent substance (q_e) mg /g was found and the percentage of removal.

Temperature Effect:

The effect of the temperature of the dye on the surface of the adsorption within the thermal range (298-328K) was recorded on the adsorption process.

Results and discussion

1- Isotherm Models

Four Parameter Models were obtained including Langmuir, Freundlich, Temkin and Elovich the results show a good gave linear relations and good correlation coefficients

A- Langmuir isotherm

The Langmuir adsorption isotherm has been used to calculate the presentation of different biosorbents and is based on the statement that uptake occurs on a homogenous surface by monolayer sorption with-out interaction between adsorbed molecules. The linear form of the Langmuir isotherm equation can be expressed as follows[8],[9].figure (4) showed the Langmuir isotherm and table1 and the correlation coefficient for adsorption of pigment dye Malachite green on the surface of the cadmium oxide.

$$\frac{Ce}{qe} = \frac{1}{K_L\, q_m} + \frac{C_e}{q_m} \quad \text{......................(1)}$$

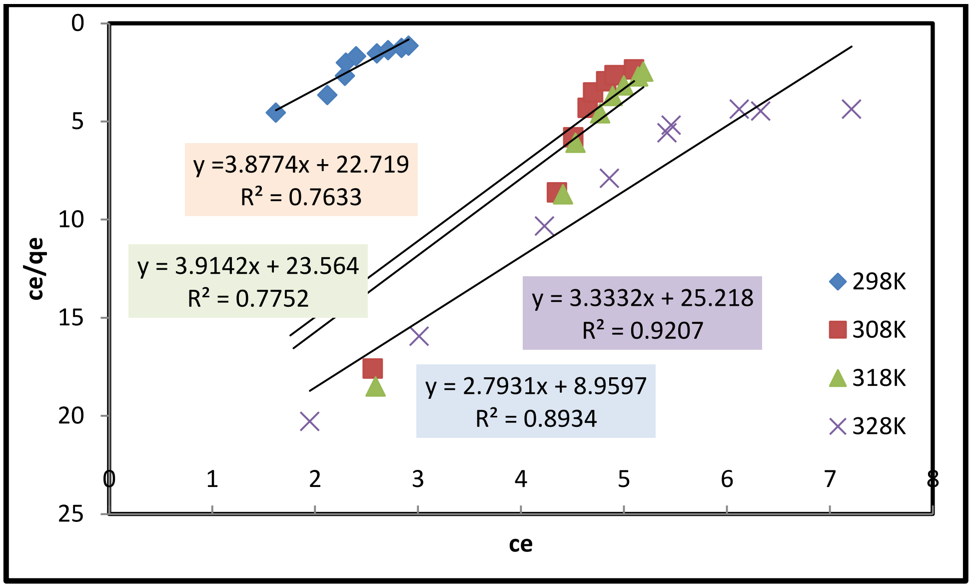

Fig.4. Langmuir adsorption isotherm.

B- Freundlich isotherm

The Freundlich sorption isotherm gives an appearance about the surface heterogeneity and the exponential dissemination of active sites and their energies, and is expressed by the following equation [8],[10] . the figure (5) showed Freundlich isotherm and table1 and the correlation coefficient for adsorption of pigment dye Malachite green on the surface of the cadmium oxide.

$\log q_e = \log K_f + 1/n \log C_e$ …………….(2)

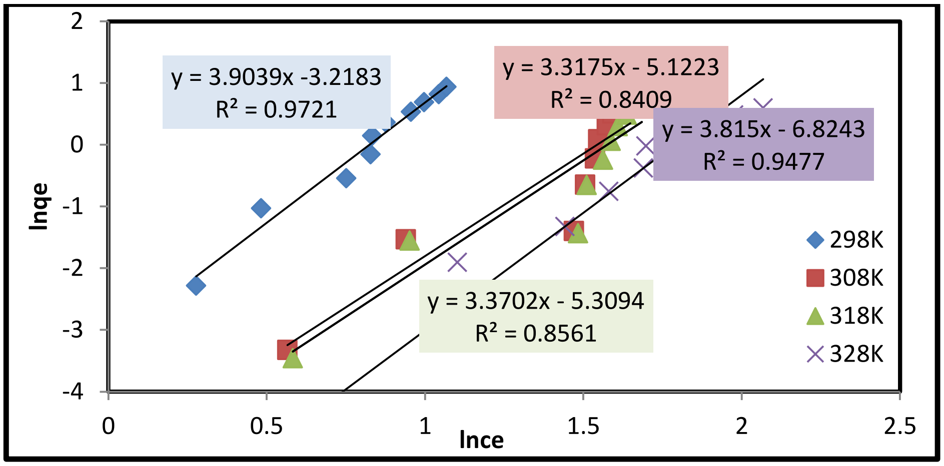

Fig.5. Freundlich adsorption isotherm

C-The Elovich isotherm

The equation significant the Elovich [8] model is established on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. It is expressed by the relation:

$$\ln\frac{q_e}{c_e} = \ln Kq_m - \frac{1}{q_m}q_e \ \ldots\ldots(3)$$

figure (6) showed the Elovich isotherm and table1 and the correlation coefficient for adsorption of pigment dye Malachite green on the surface of the cadmium oxide.

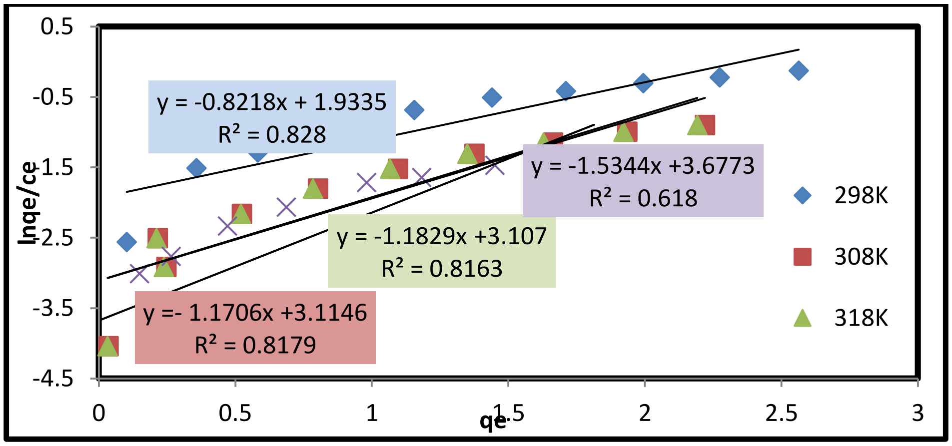

Fig: 6. Elovich adsorption isotherm

D-Temkin isotherm

The beginning of the Temkin isotherm assumes that the decrease in the heat of sorption is linear slightly than logarithmic as indirect in the Freundlich equation [8],[11]. The heat of sorption of all the molecules in the layer would decrease linearly with attention due to sorbate/sorbent interactions. The Temkin isotherm has usually been applied in the subsequent arrangement:

$q_e = B \ln K_T + B \ln C_e$ ………….(4)

and figure(7) showed the Langmuir isotherm and table1 and the correlation coefficient for adsorption of pigment dye Malachite green on the surface of the cadmium oxide.

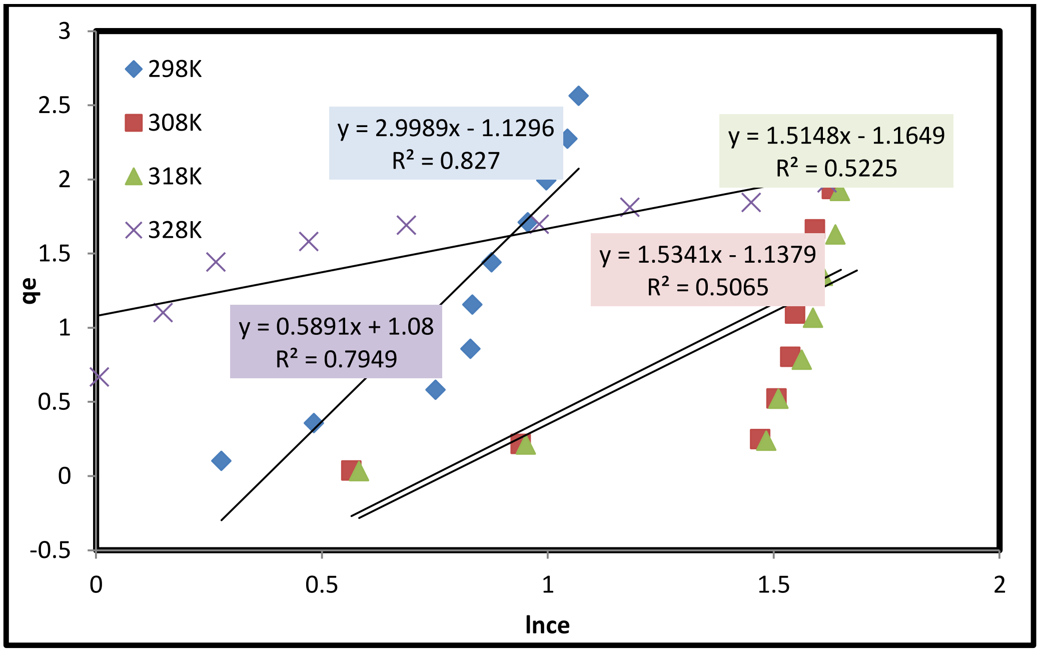

Fig. 7: Temkin adsorption isotherm.

Table1: show the comparison of the values of the adsorption equations of isotherm and the correlation coefficients for adsorption of pigment dye Malachite green on the surface of the cadmium oxide at a weight of 0.1g and the equilibrium weight of 30 min within the thermal range 298 to 328 K.

Dye	Isotherms Equation	Parameters	Temperature			
			298K	308K	318K	328K
Malachite Green	Langmuir $\frac{C_e}{q_e} = \frac{1}{K_L\, q_m} + \frac{C_e}{q_m}$	q_m	0.35802	0.2579	0.25548	0.3000
		K_L	0.04	0.01135	0.010842	0.0119
		R^2	0.8934	0.7633	0.7752	0.9207
	Freundlich $\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	N	0.25615	0.30143	0.29672	0.26212
		K_f	0.04003	0.00596	0.00495	0.00109
		R^2	0.9721	0.8409	0.8561	0.9477
	Temkin $q_e = B\ln K_T + B\ln C_e$	B	2.9989	1.5341	1.5148	0.5891
		K_T	0.68614	0.4762	0.46347	0.15988
		R^2	0.827	0.5065	0.5225	0.7949
	Elovich $\ln\frac{q_e}{c_e} = \ln Kq_m - \frac{1}{q_m}q_e$	q_m	1.21684	0.85426	0.84538	0.65213
		K_E	0.46307	1.31558	1.30163	0.17734
		R^2	0.828	0.8179	0.8163	0.618

2- Kinetics study

Different kinetic models including pseudo-first-order, pseudo-second-order, intra particle diffusion and Elovich model were experienced.

A. The Pseudo-First-Order Model

The Lagergren’s rate equation is one of the most generally used rate equation to describe the adsorption of an adsorbate from the liquid phase[12]. The linear formula of pseudo-first-order equation is given as:

$\ln(q_e - q_t) = \ln q_e - k_1 t$ …………..(5)

Figure(8) showed First order reversible reaction kinetics plot for the adsorption of Cd also table (2) showed the constants of the kinetic equations and the correlation coefficient for adsorption of the dye.

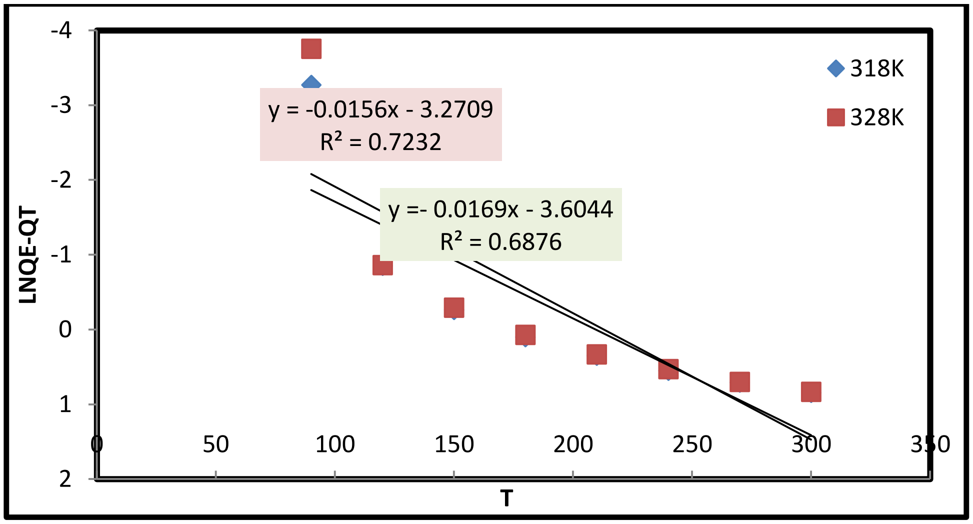

Fig. 8: First order reversible reaction kinetics plot for the adsorption of Cd.

B. The Pseudo-Second-Order Rate Equation

The pseudo-second order kinetic model[12] is founded on the assumption that chemisorption is the rate determining step and is given as:

$$\frac{t}{q_t} = \frac{1}{K(q_e)^2} + \frac{1}{q_e} t \quad ……(6)$$

Figure(9) showed second order reversible reaction kinetics plot for the adsorption of Cd also table (2) showed the constant of the kinetic equations and the correlation coefficient for adsorption of the dye.

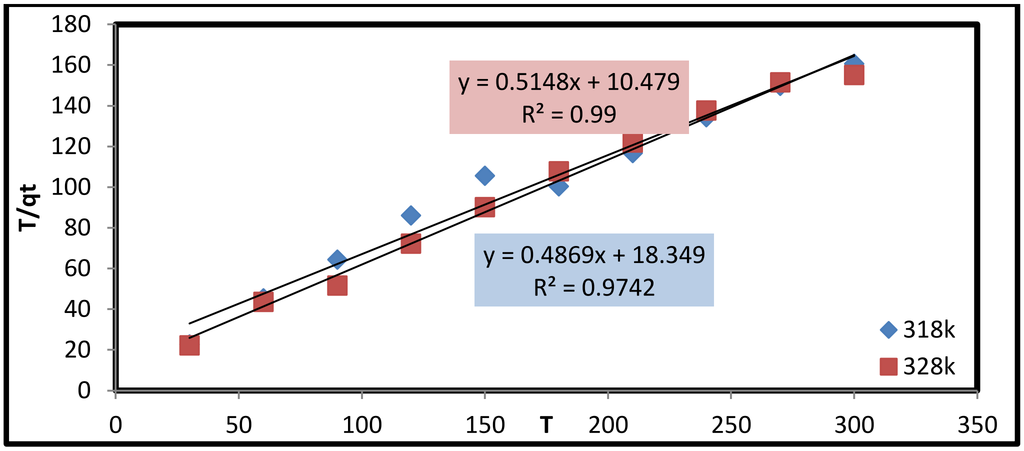

Fig.9: Pseudo Second order reversible reaction kinetics plot for the adsorption of Cd.

C-Elovich Model

The Elovich equation was first established to define the kinetics of chemisorption of gas onto solids [8]. The linear form of the Elovich model is obtainable by the following equation, and figure(10) showed Elovich kinetics plot.

$$q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t \ldots\ldots.(7)$$

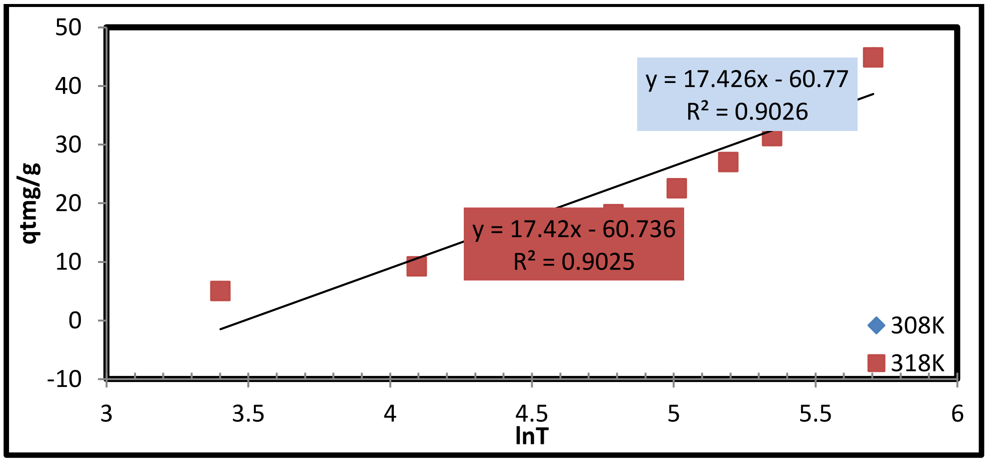

Fig.10: Elovich kinetics plot for the adsorption of Cd.

d-Intra-partical Diffusion Model

This model was developed by the researchers (McKay and Poots، Weber and Morri) [13-14], as they reached the following linear equation:

$q_t = K_{diff.} t^{1/2}$ ....(8)

Figure(11) showed Intra-partical Diffusion kinetics plot for the adsorption of Cd also table (2) showed the constant of the kinetic equations and the correlation coefficient for adsorption of the dye.

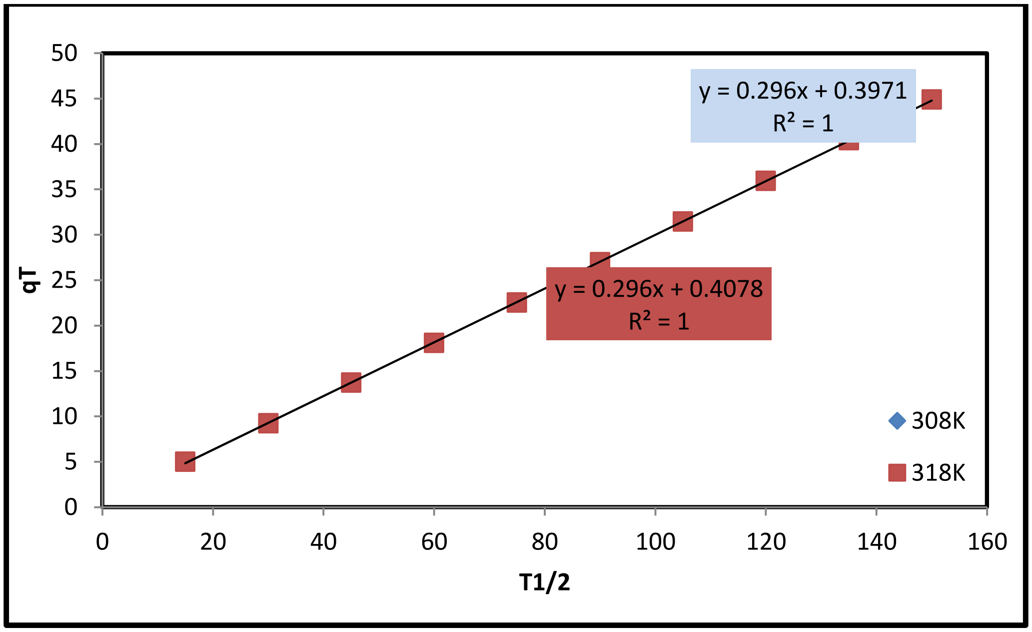

Fig.11: Intra-partical Diffusion kinetics plot for the adsorption of Cd.

Table2: show the constants of the kinetic equations and the correlation coefficient for adsorption of the dye at a weight of 0.10g of cadmium oxide and the acid function pH = 7 and at a primary concentration of 14 mg / L.

Dye	Linear equation of Kinetic model	Parameters	Temperature	
			318K	328K
Malachite Green	Pseudo-first- order $\ln(q_e - q_t) = \ln q_e - Kt$	k R^2	0.0156 0.7232	0.0169 0.6876
	Pseudo-second- order $\frac{t}{q_t} = \frac{1}{k\,q_e^2} + \frac{1}{q_e}t$	k R^2	0.01292 0.9742	0.02529 0.99
	Elovich $q_t = \frac{1}{\beta}\ln(\propto \beta) + \frac{1}{\beta}\ln t$	$\propto$ β R^2	0.96985 0.057405 0.9025	0.532936 0.057386 0.53293
	Intra – partical - diffusion $q_t = k_{diff}\, t^{1/2}$	k R^2	0.296 1	0.296 1

3-Thermodynamic study:

The reaction was endothermic and the adsorption is physical and the entropy increases within increases of the temperature and the figure (13) showed the Enthalpy and entropy thermodynamic plot for the adsorption of Cd also Table3 shows the equations of the thermodynamic functions of the adsorption of the malachite green dye on the cadmium oxide.

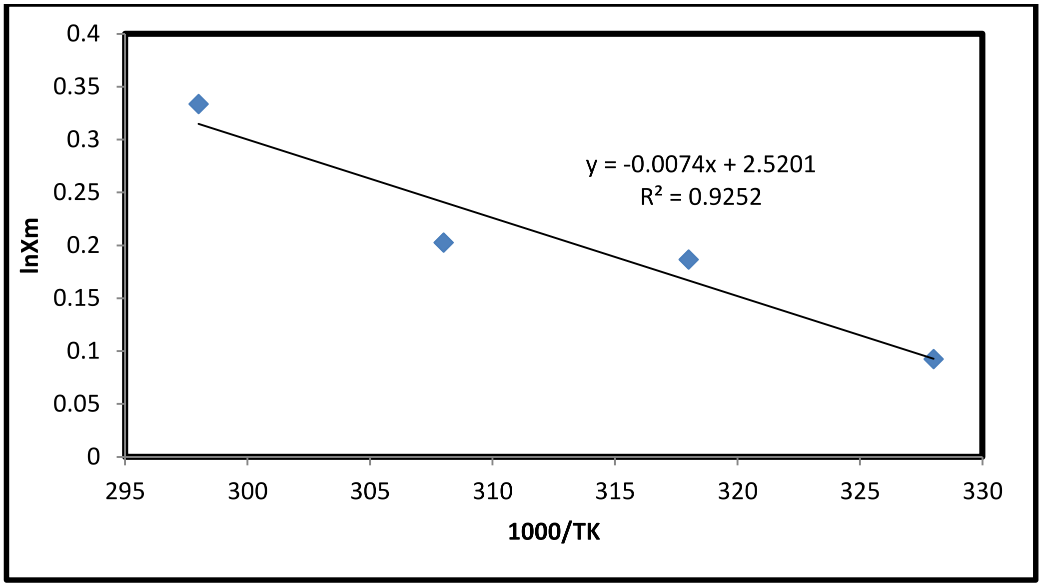

Fig 13: Enthalpy and entropy thermodynamic plot for the adsorption of Cd

Table3: shows the equations of the thermodynamic functions of the adsorption of the malachite green dye on the cadmium oxide.

dye	Equation parameter	Δ G $Jmol^{-1}$				ΔH $KJmol^{-1}$	ΔS $KJmol^{-1} K^{-1}$
	$lnX_m=-\Delta H/R+C$	298K	308K	318K	328K		
MG	$\Delta G=-RTln\ Xm$ $\Delta G=\Delta H-T\Delta S$	-826.67	-518.4	-492.99	-251.7	0.06152	2.7743

Conclusions

A biosorbents was successfully utilized for the removal of cadmium ions from aqueous solution by batch adsorption method. The equilibrium data were tested using the Langmuir, Freundlich, Temkin, Elovich isotherms. Correlation coefficients and Error analysis indicated the following order to fit isotherms Freundlich > Temkin> > Langmuir> Elovich, . Kinetic parameters were also analyzed using the pseudo-first order, Pseudo-second order, and Elovich and intra particle diffusion model. Kinetic studies showed that the adsorption of cadmium ions onto dye followed intra particle diffusion and Pseudo-second order kinetic model. Thermo dynamic effect showed that the adsorption is endothermic and the entropy is increase and its spontaneous within the limits of physical adsorption .

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