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REMOVAL OF CU (II) IONS FROM WASTEWATER BY USING DRIED EUCALYPTUS LEAVES USINGBATCH ADSORPTION AND STUDY THE ADSORPTION THERMODYNAMICS

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Abstract

Anew simple method for the treatment of waste water effluent containing Cu(II), was developed using dried eucalyptus leaves a low-cost natural . Batch experiments were conducted to determine the effects of varying adsorbent weight, pH, contact time, metal ion concentration and temperature of adsorption. The adsorption of cu (II) was found to be maximum(80%) at pH 8, at 25°C, metal ion concentration 100 ppm , contact time 60 min and Speed Shake(185rpm) . adsorption capacity of Cu (II) were found maximum (82.5%) at optimum conditions. Freundlich isotherm was found to be suitable for the adsorption of Cu(II) functional groups[(C-N), (C-O),(C=O),(O-H)] identification was given using FTIR spectrophotoscopy.

Keywords: adsorption, copper, Freudlich isotherm, Langmuir isotherm, dried eucalyptus leaves.

1.Introduction

The toxicity of heavy metals in the environment is still major concerns of human life; because they accumulate in living tissues throughout the food chain which has humans at its top. The danger of these heavy metals is due to poisoning, cancer, and brain damage[1].The treatment of water and waste water containing heavy metal is very demanding. Such methods of treatment include precipitation [2], flotation [3], biosorption [4][6], electrolytic recovery, membrane separation[7], removal by adsorption on minerals [8,9] and activated carbon adsorption [10,11]. Heavy metals are the most important pollutants in the environment and widely found on water surfaces from natural and industrial sources[11] . Among metals, the two important pollutant are Cu and Ni cations. Cu ions can deposit in brain, skin, liver, pancreas, and myocardium causing serious toxicological effects on humans[12, 13]. Cu (II) is a commonly toxic metal in natural ecosystems. The most common adverse health effect of nickel in humans is an allergic reaction in direct contact with the skin caused by jewellery or other items containing Cu. There are several methods for removing heavy metals from waste water such as adsorption, chemical precipitation, ion exchange, electrochemical treatment, solvent extraction, and membrane separation[14, 15].

Nowadays, a number of low cost adsorbent materials such as zeolites are available to remove metal ions[16-17-18].

1:1 EXPERIMENTAL SECTION

Adsorption experiments

For the adsorption experiment, the effect of adsorbent weight on the adsorption of the ions was investigated (0.5 -2g) of the adsorbent was weight respectively into conical flasks. 20 ml of 100 mg/L solution of each of the metal ions solution was added and the mixture shaken at 185 rpm for 60 min. After the biosorption experiment, the biosorbent was separated from the solution by filtering through a Whatman (0.45 μm) filter paper and the filtrate was analyzed for the Cu (II) ions concentration. The Cu (II) ions concentrations before and after the biosorption were determined by using Flame Atomic Absorption Spectrophotometer. (Shimadzu 6000). The equilibrium Cu(II) ions sorptioncapacity could be calculated as equation bellow;

$Qe = V(C° - Ce)/m$… (1) [19]

Where ; Qe is the equilibrium Cu (II)) ions sorption capacity (mg/g), V is the suspension volume (l), m is the mass of durian material (g),Co = Initial concentration of solution, Ce= Concentration of the solution after adsorption. To determine the effect of concentration on the adsorption of the metal ions, 2g of the adsorbent, being the optimum adsorbent weight in the previous experiment was added to 50 ml each of varying concentrations(between 5 - 100 mg/L) of the metal ion solutions. The mixtures were shaken and the concentration of the metal ions adsorbed was determined. The effect of contact time was also investigated by adding 2g of the adsorbent to 20 ml of50 mg/L of Cu (II) ions being their respective optimum adsorption concentrations; and shaking using varying contact times(30 –180 min) and the percentage of adsorbed ions determined. The effect of pH on adsorption of the metals was investigated using 0.5g of the adsorbent and 20 ml of 100 mg/L of Cu (II) ions. The mixture was shaken for 60 min for Cu (II) and the amount of ion adsorbed was determined[20].

Preparation of adsorbent

Eucalptus leaves were collected from gardens of AL-basrah University, basrah, Iraq. The leaves were extensively washed with deionize water to remove dirt ,dried in an oven at90C° for a period of 1.5 hr, then ground and screened to obtain the average particle size150μm.the powder was preserved in glass bottles for use as adsorbent, The some physical properties of the chosen adsorbent are listed in Table 1.

Table 1

Properties	Value
Porosity(%)	82.99 ±0.349
Langmuir surface area(m2 /gm) 2	1.7656 m^2/g
BET Surface Area	1.1312 m^2/g
Pore Volume	9.709 cm^3/g
Partical density	0.718 g/cm^3
Bulk density	0.688 gm/cm^3

2: RESULTS AND DISCUSSION

2:1. FT.IR Characterization of Eucalptus Leaves

FT-IRapparatus type shimadzu (4000-400 cmP-1 P) was carried out to identify the functional groups and structural in the Eucalptus leaf powder that might be involved in the adsorption process. FT-IR analysis was carried out in order to identify the functional groups in the Eucalptus leaf powder that might be involved in the adsorption process. The FTIR spectrum in the range of 400-4000cm is shown in Fig.1.as shown in the figure, the spectrum displays a number of adsorption peak, which indicates the complex natural of the material examined stretching, which is consistent with the peak at 1160.28 and1340cm assigned to alcoholic C-O and C-N stretching vibration. The absorption band wave numbers of 2990-2870 cm can be assigned to CH and $–CH_2$stretching, respectively [21].The absorption band wave number of ketone group is about1690cm.thatresult of binding of this group with the cations of metal .Show table(2).

Table (2)explains the effective groups

Wavelength(cmP-1P)	Structural and Functional group	Functional group
1600-1690	C=O	ketone group
1700-1720	C=O	carboxylate groups
3000-3600	O-H	Hydroxyl group
2870-2990	C-H	Hydrocarbon
1310-1340	N-H	Amines
1050-1160	C-O	Carbon oxygen group

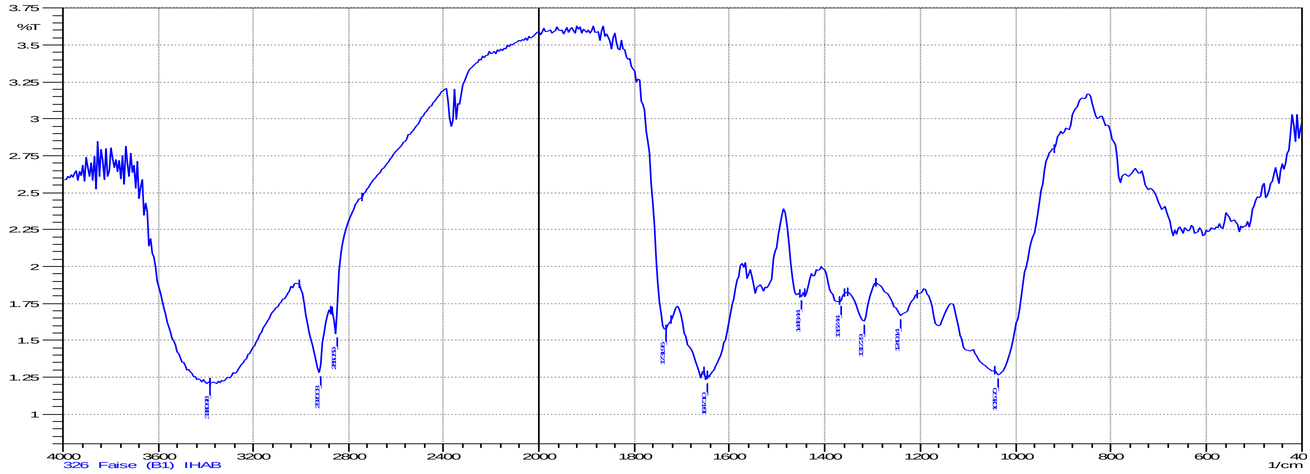

Fig (1)FT- IR Eucalptus leaves powder

2:2.Effect of pH

The pH is one of the most important parameters of biosorption of heavy metals, The biosorption of Cu (II) by Eucalptus erectus leaf powder at different pH values(3-10) is presented in Fig2. The optimal pH for removal of Cu (II) was(10). The removal percentages of, Cu (II) ion on Eucalptus powder at an initial concentration of 100 ppm and at an initial pH=(10) ,using 0.5g of the adsorbent with 100mLof Cu (II) ions solution (80%.).At pH higher than 10 both metals were precipitated due to the formation of hydroxides and removal due to sorption was very low .The minimal adsorption at low pH may be due to the higher concentration and high mobility of the H+, which are preferentially adsorbed rather than the metal ions . At higher pH values, the lower number of H+ and greater number of ligands with negatives charges results in greater Cu (II) adsorption. For example, carboxylic groups (–COOH) are important groups for metal uptake by biological materials . At pH higher than 3-4, carboxylic groups aredeprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced [22].

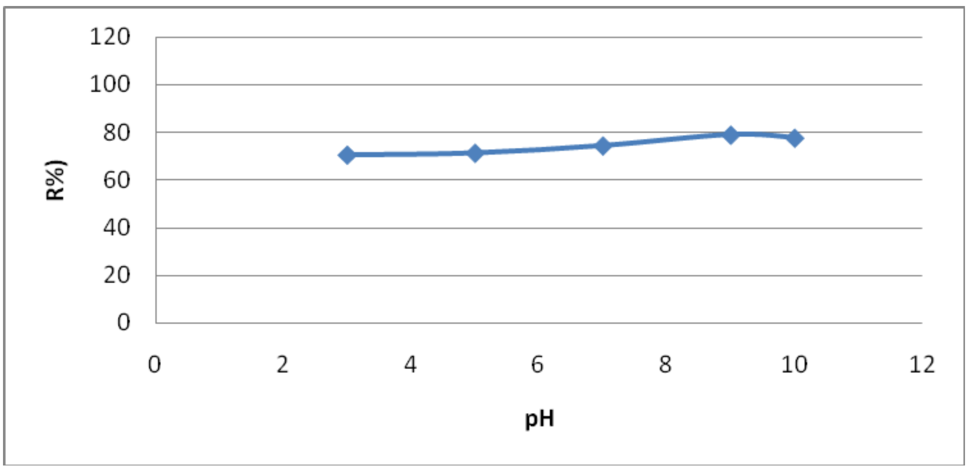

Fig (2) Effect of pH

2:3. Effect of adsorbent weight

One of the parameters that strongly affect the sorption capacity is weight of the adsorbents. With the fixed metal concentration it can easily be inferred that the percent removal of metal ions increases with increasing weight of the adsorbents as shown from Fig. 3This is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent[23] . the removal percentages of Cu(II) ion Eucalptus powder at an initial concentration of 100 ppm and at an initial pH=(8) ,using at different weight of the adsorbents(0.5_3g) with 50mLof Cu (II) ions solutions(96.9%).

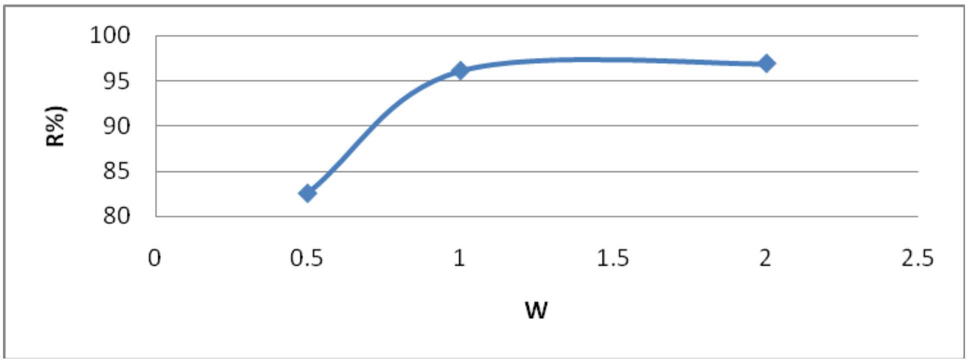

Fig (3) Effect of adsorbent weight

2:4. Effect of metal ions concentrations

The removable efficiency decreases with increasing initial concentrations from 10-100 mg L-1, shown in Figure 4. Maximum adsorption obtained at minimum concentration of metal ions. The different lead solutions with concentration ranging from 10mg/l to 100 mg/l were agitated at 250 rpm for 80 minutes with adsorbent dose of 0.5 gm,. The percentage adsorption of Cu(II) decreases as the initial concentration of increased from 10 mg/l to 100 mg/l. Maximum adsorption obtained at minimum concentration of metal ions. Such behavior can be because of the unchanging number of available active sites on the adsorbent here the amount of adsorbent was constant[24].

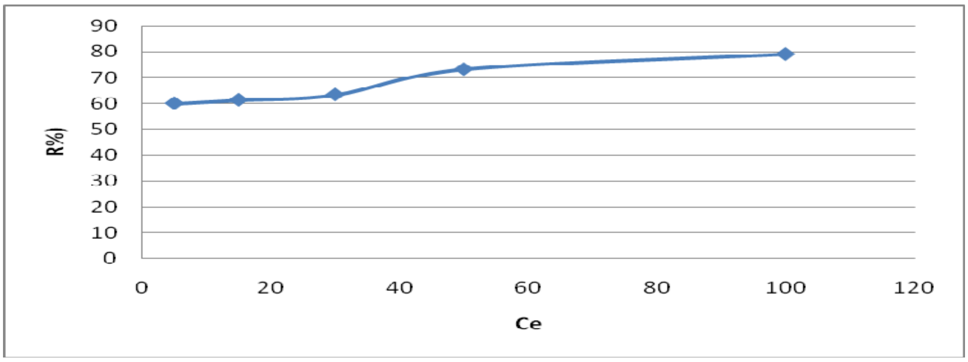

Fig (4) Effect of Initial Concentration of Pb(II)ions

2:5.Effect of contact time

The effect of contact time on the biosorption of lead and copper ions onto nano sawdust is studied at different times ranged from 30-180 min. and optimum pH Cu(II)]. Figure 5 shows that the removal of Cu(II) as a function of contact time, where the removal percentage of the two metal ions increase rapidly with increasing contact time (i.e., high adsorption rate). For lead, minimum percentage removal was 80.8% at time of 30 min and it increased to maximum value 82.5% at time of 60 min, whereas, for copper, minimum value was 82.6% at time of 90 min to maximum value of83% at time of 120 min. After maximal time, increasing in contact time is not effective in the adsorption process.[25] The rate of the biosorption of the two metal ions onto the surface of the nano sawdust occurred in two steps. The biosorption was very fast initially as a large number of vacant surface sites are available for binding with metal ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.[26] Then biosorption reached equilibrium as a result of the reduction of available sites which are difficult to be occupied due to repulsive forces between metal ions biosorbed onto the biosorbent surface and the bulk phase [27].

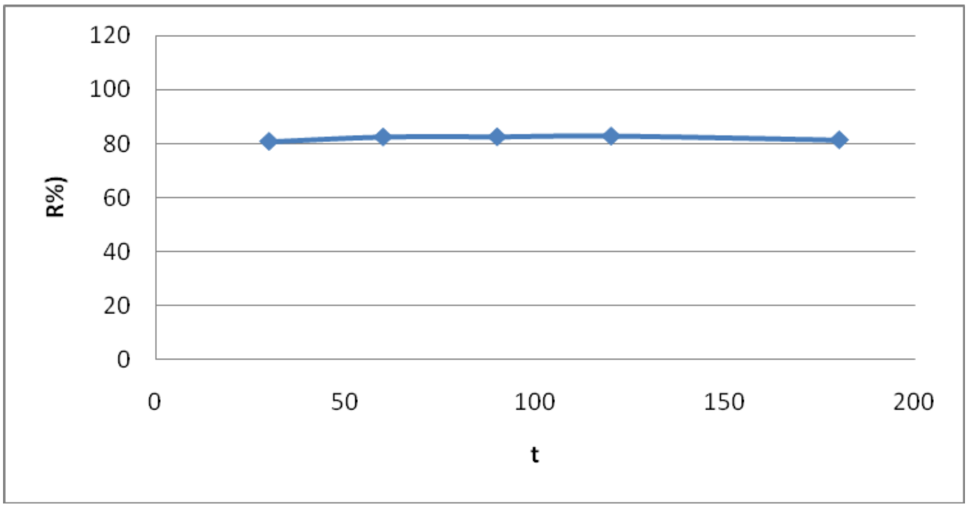

Fig (5) Effect of contact time

2:6. Effect of temperature on the adsorption rate

The Increase of temperature from 30 to 60 C° increased the adsorption ofCu (II) ions indicating the process to be endothermic. The increases in uptake of Cu (II) ions with temperature may be due to the desolvation of the adsorbing species, the changes in the size of pores, and the enhanced rate of intraparticle diffusion of adsorbate, as diffusion is an exothermic process. The biosorption was found to increase with increase in temperature at (30-55P OPC)and the sorption capacity (Q) was also found to increase. The interactions are found to be exothermic in nature [28],[29] for which the evaluation of thermodynamic. This is shown in Figure(6). The removal percentages of Cu (II)ions on Eucalptus powder was at different temperature from(30-60) and at an initial pH=8,using(0.5g of adsorbent)with 20mL of Cu (II)ions solutions (91.9%.) [30].

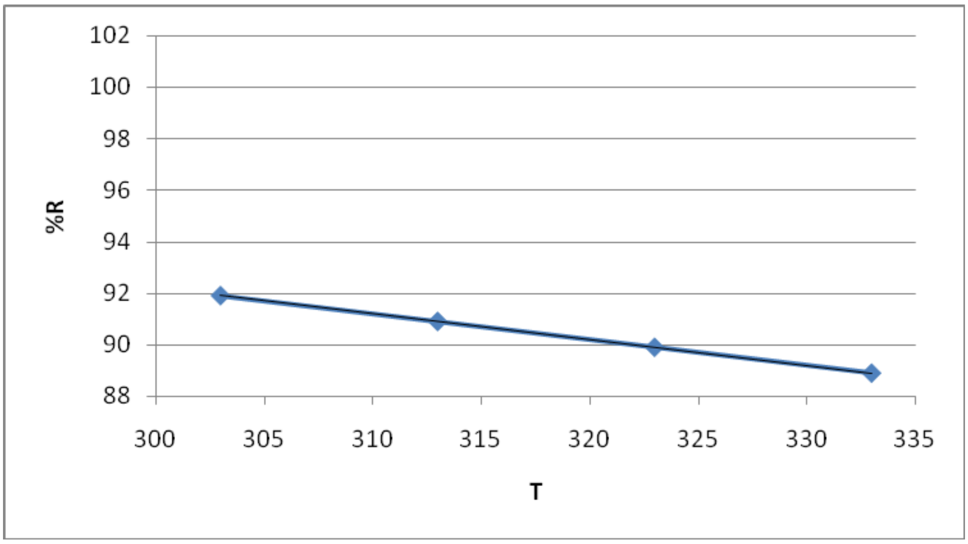

Fig (6) Effect of temperature on the adsorption rate

3. Isotherms

The adsorption isotherm experiment was carried out by mixing 1 gram of adsorbent and 100 mL of metal ion solution of various concentration; 20-100 mg/L with pH 8, shaking at 150 rpm about an hour for reaching equilibrium. Then the remaining concentration of metal ion in solutions were examined using AAS for Langmuir adsorption isotherm model and Freundlich adsorption isotherm model.

Langmuir model:

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

and can be linearized to be

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad \text{.........................(2)}$$

Freundlich model:

$$q_e = K_F C_e^{\frac{1}{n}}$$

which can be written in the linear form as

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \text{..................(3)}$$

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where Ce is equilibrium concentration (mg/L), qe is adsorption capacity (mg/g), qm is maximum adsorption capacity (mg/g), KL is Langmuir adsorption constant and KF is Freundlich adsorption constant. The plot of Ce/qe versus Ce for Langmuir's adsorption model will give the straight line with slope of 1/qm and intercept of1/(KL qm). For Freundlich's adsorption model, plot of log qe against log Ce also will be linear relationship. The relative coefficients of these models were calculated using linear least-squares fitting [31]. Since the relationship between the amount of substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in equilibrium, adsorption isotherm, is very important in determining the adsorption capacity of metal ions onto the adsorbent. Adsorption isotherm describes the interaction between adsorbate and adsorbent materials. The experimental results were fitted to the equations according to Langmuir adsorption model and Freundlich model as Eq(2) and Eq(3), respectively.

And the experimental data and calculated values are in Table 3. As shown in Figure (7) and regression coefficient in Table1, the experimental data fitted to Langmuir's adsorption model with R^2 around 0.58 and also fitted to Freundlich's adsorption model with R^2 around 0.95 as shown in Figure 4 for Cu (II) [32] .

Table (3)

Ion	Langmuir adsorption model			Freundlich adsorption model		
Cu	a (mg/g)	b (L/g)	R^2	n	K_f	R^2
	0.0538	0.0305-	0.88	0.04	0.736	0.96

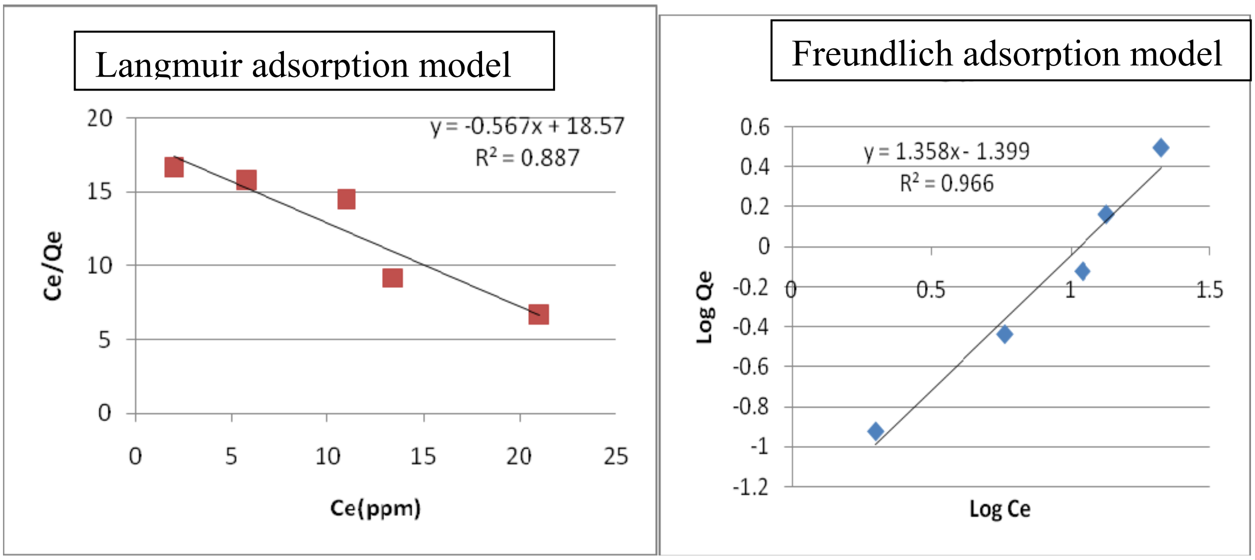

Fig (7) Isotherms

4.Thermodynamic Study

The consideration of energy and entropy in any adsorption process is important for determining whether the process will be spontaneous or not. As a result, thermodynamic parameters are significant for the application of this material and process to real life scenarios. Equations (4) ,(5) and (6) were used to calculate the change in free energy ΔG°, change in enthalpy ΔH°, and change in entropy ΔS° which:

$\Delta G^\circ = -RT \ln K$ ………….(4)

$\text{Log } K = (\Delta S^\circ/2.303R) - (\Delta H^\circ/2.303\, RT)$ ………… (5)

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ …………. (6)

As K is the equilibrium constant ,T is the absolute temperature (K°) and R is the gas constant (33).

Van,t Hoff equation was used to estimate the values of ΔH° and ΔS° from the intercept, and slope of the plot which was ln K vs. 1/T (fig. 8).Table (4) showed the thermodynamic parameters values for the adsorption processes. From this the table, adsorption was found exothermic (ΔH° was negative), reaction was spontaneous (ΔG° was negative), and solid solution interface was random because ΔS° was increased. The change in adsorption enthalpy was measured and found -20 to 40 KJ.mol-1, compared to chemisorption which was -400 and -80 KJ.mol-1.values of ΔH° physisorption was found the dominant mechanism(34,35).

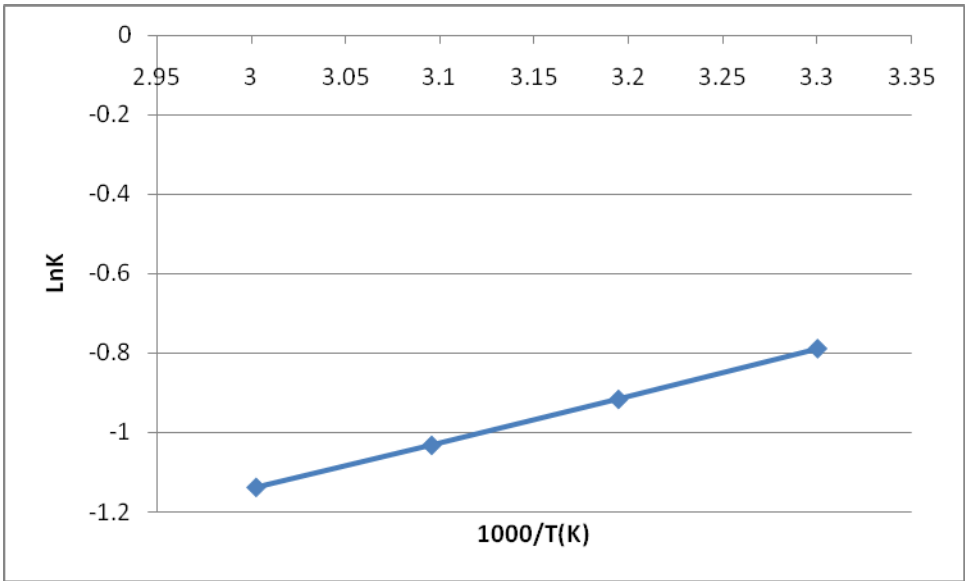

Fig (8) Effect of temperature on the adsorption rate.

Table (4)

heavy metal	Temperature K°	ΔG° KJ.mole-1	ΔH° KJ.mole-1	ΔS° J.mole-1.K-1
Cu	303	-15.41	-9.73	18.75
	313	-15.59		18.71
	323	-15.78		18.72
	333	-15.97		18.747

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