

# Study of the Adsorption of Copper Ion on a New Type of Activated Carbon

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## Abstract

In this study, a new type of activated carbon is prepared from spent lubricant oils by chemical treatment. This carbon is used as adsorbent for the removal of copper ions from aqueous solutions. The adsorption capacity of the carbon is estimated. The effect of contact time, concentration and temperature are investigated. The experimental data of adsorption were fitted to three different isotherms, namely; Langmuir, Freundlich and DKR. The isotherms equations were applied at different temperatures. The results obtained showed that, the Langmuir isotherm is better fitted to the experimental data of the studied system than the other isotherms. In addition the fitting is good at low temperature. Deviations are noticed when temperature is increased. The thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H$ , and  $\Delta S$  are determined at two initial concentrations. Their values and signs indicated that, the adsorption process could occur spontaneously at room temperature. The increase of temperature activates the departure of adsorbed molecules towards the solution. The adsorption system is exothermic in nature. The adsorption process increases the order of the studied system.

## Introduction

In recent years the growing health risk to the public caused by the increase in the amount and types of waste discharged into the environment as a result of rapid industrialization, and resulted an environmental pollution. The pollution treatments becoming some of the most important and widespread studies around the world. Industrial liquid wastes, particularly those containing heavy metal ions, have become a serious threat to the ecosystems of plants, animals, and humans. Methods for their safe treatment have, therefore, been intensively investigated.

Adsorption can be defined as an accumulation of the substance (adsorbate) onto the surface of adsorbent solids. Activated carbon is deemed to be an efficient and competitive adsorbent for usage in this field.

The wide use and various applications of copper increased its level in the wastewater discharged to the ecosystems leading to the growing threat of toxicity. This makes its removal as a vital task.

Sorption of copper ion from water is very important method in the pollution control of water. Many experiments were carried out on the adsorption of copper ions in a laboratory packed bed of activated carbon. The reason of applying activated carbon because of its large surface area, and it has no toxic effects in the solutions[1]. The prepared activated carbon from solid waste called Terminalia Catappa Linn shell used for adsorbing copper ion from aqueous solution. The effectiveness of such carbon has been studied as a function of agitation time, adsorbent dosage, initial metal ion concentration, temperature and pH. Adsorption data were modeled using both Langmuir and Freundlich classical adsorption isotherms[2]. In another study, Granular Activated Carbon (F-400) loaded with oxine and its derivatives were employed to remove copper from aqueous solutions. This transition metal was chosen since it forms one of the major constituents of industrial streams. The results obtained from equilibrium studies showed significant uptake of copper. The adsorption data fitted well with the Freundlich isotherm[3]. In a kinetic study, eucalyptus bark was employed as a raw material for the

production of activated carbon utilized for treating synthetic wastewater containing copper and lead ions. The results was found to match well with pseudo second-order model, where equilibrium adsorption capacities and adsorption rate constant increased with initial metal concentration. The adsorption isotherm followed Langmuir isotherm[4]. In other study, a serious of batch experiments were performed in order to investigate the feasibility of Elais Guineensis Kernel activated carbon for the removal of copper from aqueous solution by the adsorption process. Investigation was achieved by studying the influence of initial solution pH, adsorbent dosage and initial concentration of copper. The single component equilibrium data was analyzed using Langmuir, Freundlich, Redlich-Peterson, Temkin and Toth adsorption isotherms[5]. Palm shell activated carbon was modified via surface impregnation with polyethyleneimine (PEI) to enhance removal of  $\text{Cu}^{+2}$  from aqueous solution in this study. PEI modification clearly increased the  $\text{Cu}^{+2}$  adsorption capacities. The data on PEI-modified Activated carbon (AC) for both initial solution pH of 3 and 5 fitted the Langmuir and Redlich-Peterson isotherms[6]. Other studies were conducted in batch mode involved removing copper onto oxidized activated carbon with  $\text{HNO}_3$ . Oxidation strongly influenced the AC surface chemical structures by increasing the concentration of acidic groups which significantly improved  $\text{Cu}^{+2}$  ion adsorption[7]. A Gracilaria was used to prepare activated carbon used for the removal of copper ions from wastewater. The effect of pH, contact time, adsorbent dose and metal ions concentration were investigated. The data fitted to Langmuir and Freundlich isotherms. This study showed the benefit of using low cost sorbent for the removal of  $\text{Cu}^{+2}$  from wastewater[8]. The effect of pH, dosage, contact time, initial metal concentration and temperature were investigated for the adsorption of copper ion from aqueous solution by activated carbon prepared from rice hulls (ACRH). The constants of Freundlich and Langmuir isotherm were calculated at 298 K and 313 K. The adsorption of copper was found to be

exothermic. The other thermodynamic data ( $\Delta G^\circ$  and  $\Delta S^\circ$ ) were also determined[9]. Another study utilized commercial activated carbon (Merck 2514) to adsorb the copper ion among other heavy metals from aqueous solution. The Freundlich equation was applied on the experimental data in order to determine the isotherm constants. Rate constants were estimated by applying the kinetic model of first order reaction[10].

The aim of this study is to investigate the adsorption efficiency of an activated carbon prepared by the chemical treatments of spent lubricant oils[11] for the removal of  $\text{Cu}^{+2}$  ions from synthetic aqueous solutions at natural pH. The factors affecting the adsorption process, such as concentration and temperature were studied. Three isotherm models are applied to fit the experimental data obtained from the results of adsorption process. The isotherms parameters were determined at different temperatures.

### Experimental

#### 1-Preparation of stock solution of $\text{Cu}^{+2}$ ion

An exact weight of copper nitrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was dissolved in deionized water in a 250ml volumetric flask in order to prepare a solution of 1000mg/liter concentration. The prepared sample was kept in a reagent bottle and used for preparing other solutions.

#### 2-Effect of concentration

The experiments were achieved in batch mode. 50ml of  $\text{Cu}^{+2}$  ion solution of different concentrations (10, 20, 30, 40, 50, 60)mg/liter was put in six dry and closed flasks in sequence. 0.1g from the adsorbent was added to each flask. The solutions were shaken for 70min with speed of 140rpm at  $25^\circ\text{C}$ . The solutions were then filtrate, and the amount of adsorbed substance was determined by atomic absorption spectroscopy.

#### 3-Effect of temperature

The same steps those followed in finding the effect of concentration were repeated here with using the same concentration and keeping other conditions constant but under various temperatures (25, 35, 45,  $55^\circ\text{C}$ ).

#### 4-Adsorbent

The activated carbon used in this work is supplied by an other group of our research work. It was synthesized from spent lubricant oils by chemical treatment. The properties of the prepared sample could be concluded as follow: Iodine number 950mg/g, M. B.(Methylene Blue) 300mg/g, moisture %9.85, Ash content %1.52, and density  $0.3904\text{g/cm}^3$ [11].

### Results and Discussion

From the quality point of view of drinking water, it is very important that toxic heavy metals, such as the  $\text{Cu}^{+2}$  ion, must be removed. Complete purification or at least a reduction in amount is, therefore, vital task. This study is aimed to investigate the efficiency of the prepared carbon for the removal of  $\text{Cu}^{+2}$  ion by adsorption. The effect of variation of parameters such as concentration and temperature is determined. The

study of the affected factors on the adsorption is carried out at equilibrium where the adsorption process is independent of time, the surface of adsorbent is saturated and the rate of desorption and adsorption are equal. To achieve this study, the required equilibrium must be performed at optimum conditions. Such conditions are obtained at 70min when shaking 50ml of solution with 0.1g of the activated carbon and speed of 140rpm.

#### Effect of concentration:

The effect of varying concentration is carried out by keeping other reaction parameters constant. The results obtained are given in Table (1).

**Table (1): Effect of initial Cu(II) concentration on the adsorption efficiency (% adsorption) of Cu (II) onto activated carbon at  $(25)^\circ\text{C}$  and natural pH of  $\text{Cu}^{+2}$  solution (pH = 4.6)**

Ci mg/l	Ceq mg/l	qeq mg/g	% Adsorp.
10	2.47	3.765	75.3
20	8.68	5.66	56.6
30	16.59	6.705	44.7
40	27.14	6.43	32.15
50	34.46	7.77	31.08
60	44.66	7.67	25.57

The value of adsorption capacity (qeq mg/g) is calculated by the following equation.[8,9]

$$q_{eq} = \frac{C_i - C_{eq}}{m} * \frac{v}{1000} \quad \text{--- (1)}$$

Where  $C_i$  is the initial concentration of  $\text{Cu}^{+2}$  ions,  $C_{eq}$  is the concentration of  $\text{Cu}^{+2}$  in the solution at equilibrium,  $m$  is the weight of adsorbent and  $V$ (liter) is the volume of the solution of  $\text{Cu}^{+2}$  used.

The adsorption efficiency is determined by the equation.

$$\% \text{ Adsorption} = (C_i - C_{eq} / C_i) * 100 \quad \text{-- (2)}$$

The results in Table (1) show that, the adsorption process is concentration dependent and it is more efficient at low concentration and decreases as the concentration increase. This may be attributed to that, as the saturation of the active pores those available for the adsorption on the carbon surface is occurred, the number of residual ions in the solution increases with the increase of concentration leading to the decrease in the adsorption ratio. In addition to that, the increase of concentration increases the number of ions those compete to be adsorbed on a definite number of active sites that present on the surface of a specific weight of the adsorbent which in turn causes a decrease in the binding energy between the adsorbent surface and metal ion [12, 13].

#### Effect of temperature:

The adsorption is also performed at various temperature ranged between  $25-55^\circ\text{C}$ , and at different initial concentrations (10-60 mg/liter).

**Table (2): Effect of temperature on the adsorption efficiency of Cu(II) The activated carbon**

Initial conc. (mg/l)	Adsorption efficiency of Cu(II) at various temperatures			
	298°K	308°K	318°K	328°K
10	75.30	49.70	46.00	41.00
20	56.60	43.30	36.30	35.00
30	44.70	36.77	33.90	32.00
40	32.15	30.08	27.98	25.75
50	31.08	27.20	22.56	20.40
60	25.57	21.33	11.97	11.27

The results indicate that, the adsorption efficiency of Cu ions by activated carbon decreases with increasing the temperature no matter was the initial concentrations. This observation could lead to a conclusion that, adsorption under the studied conditions is mainly of exothermic nature over the activated carbon. Increasing temperature acts on breaking the attraction forces between the adsorbent surface and metal ion, and increasing the rate of desorption[9]. The high adsorption efficiency at room temperature is very important if it is considered in the economic point of view.

#### Adsorption isotherms:

Three isotherms of Freundlich , Langmuir and DKR are employed to test the experimental data of adsorption mathematically. The results of applying Freundlich (eq.3) and Langmuir (eq.4).[3] isotherms on the adsorption data are listed in Table (3).

$$\ln q_{eq} = \ln K + 1/n \ln C_{eq} \quad \text{----- (3)}$$

Where n is the intensity of adsorption and K is a function of the adsorption capacity.

$$C_{eq}/q_{eq} = 1/bQ + C_{eq}/Q \quad \text{----- (4)}$$

where Q is the maximum sorption capacity (mg/g) and b is related to the sorption energy.

**Table (3): Results of the application of Freundlich and Langmuir isotherms on the system studied.**

Temp. °K	n	K	R	Q (mg/g)	B (L/gm)	R
298	4.132	3.166	0.9698	8.230	0.255	0.9929
308	2.289	1.370	0.9615	8.091	0.102	0.9926
318	3.407	1.686	0.6946	4.202	-1.187	0.9240
328	3.234	1.476	0.6980	3.984	-2.919	0.9259

The Freundlich and Langmuir isotherms are applied on the experimental data of the adsorption of Cu<sup>+2</sup> ion on activated carbon by plotting  $\ln q_{eq}$  versus  $\ln C_{eq}$  and  $C_{eq}/q_{eq}$  versus  $C_{eq}$  respectively. The results in Table (3) show that, the Langmuir isotherm is better fitted on this system than the Freundlich. Deviations from the linear relationship are seen as the temperature increases. This is clearly indicated by the value of correlation coefficients.

The values of K constant of Freundlich equation decrease with increasing temperature. It is an indication of the physical nature of adsorption as the values of K exhibit the adsorbent ability of

adsorption[14]. Increasing temperature weakens the power of the effective pores on the adsorbent surface and that depresses thier ability of adsorption as a result. The value of n describes the adsorption intensity in this system and reveals the ability of the adsorbate to connect on the rough surface. When the value of n lies between 1 – 10 refers to a good adsorption[15]. Accordingly, the values of n obtained in this study give good indication to the ability of the employed activated carbon for adsorption of Cu<sup>+2</sup> ions. The values of n also show that, the adsorption intensity decreases with the increase of temperature which support the exothermic nature of the adsorption. The maximum adsorption capacity (Q) and b values in Langmuir isotherm equation decreases when temperature turns higher. This style of change corresponds with the exothermic and physical nature of adsorption of the studied system.

Isotherm DKR is also applied on the experimental data of Cu<sup>+2</sup> ion adsorption on the activated carbon used. Various concentrations (10-60 mg/liter) were used at four different temperatures (25, 35, 45, 55)°C. This study is done by the batch technique which aims to investigate the possibility of fitting this isotherm to the experimental data of the adsorption system under study. In addition the effect of varying concentration and temperature of isotherm's constants are investigated.[3,15].Results of applying DKR isotherm are portrayed in Table (4).

$$\ln C_{ads} = \ln X_m - \beta \epsilon^2 \quad \text{----- (5)}$$

$$\epsilon = RT \ln(1+1/C_{eq}) \quad \text{----- (6)}$$

$$E = 1/\sqrt{-2\beta} \quad \text{----- (7)}$$

Where  $C_{ads}$  is the amount of adsorbed Cu<sup>+2</sup> ions,  $X_m$  is the maximum adsorption capacity (mg/g),  $\epsilon$  is polanyi potential,  $\beta$  is the activity coefficient related to sorption energy, and E is the sorption energy, R is the gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>)

**Table (4):Results of application of the DKR isotherm on the system studied**

Temp. °K	$\beta$ mol <sup>2</sup> /J <sup>2</sup>	$X_m$ (mg/g)	E(J/mole)	R
298	-9 * 10 <sup>-7</sup>	6.9532	745.379	0.9295
308	-4 * 10 <sup>-6</sup>	6.2028	353.557	0.9706
318	-4 * 10 <sup>-6</sup>	4.8861	353.557	0.8446
328	-4 * 10 <sup>-6</sup>	4.6080	353.557	0.8758

Looking carefully at the values in table (4), it is clear that they present weak linear relationships especially at high temperatures indicated by the values of correlation coefficient (R) that are obtained from plotting  $\ln C_{ads}$  versus  $\epsilon^2$  and up to a certain concentration, which refers to the lack of possibility in utilizing this isotherm on the considered adsorption system. DKR isotherm factors are estimated from the slope and the intercept of the straight lines mentioned above. The adsorption capacity ( $X_m$ ) decreases with the increase of temperature and that agrees with the results found from applying Langmuir isotherm and the exothermic and physical nature of adsorption.

Moreover the values of E and  $\beta$  do not influence by the variation of temperature and that corresponds

with what is realized in the literatures[15]. It confirms the fact that the adsorption power does not rely on temperature, but it varies according to the nature of both adsorbate and adsorbent in the adsorption system.

### Thermodynamic functions:

Depending on the effect of temperature and using two different initial concentrations (10 and 20 mg/liter) on the adsorption of  $\text{Cu}^{+2}$  ions on activated carbon, the thermodynamic parameters are estimated. The values of  $\Delta G^\circ$ ,  $\Delta H$ , and  $\Delta S$  are portrayed in Table (5).

The values of equilibrium constant (K) are determined from the ratio of the adsorbed ions on the solid phase (Cad) to that in the solution (Ci) at equilibrium.

$$K = \text{Cad} / \text{Ci} \quad \text{----- (8)}$$

The value of  $\Delta G^\circ$  is calculated by the equation:

$$\Delta G^\circ = -RT \ln K \quad \text{----- (9)}$$

and the value of  $\Delta H$  is evaluated by using Van't Hoff equation:

$$\ln K = -\Delta H/RT + \text{constant} \quad \text{----- (10)}$$

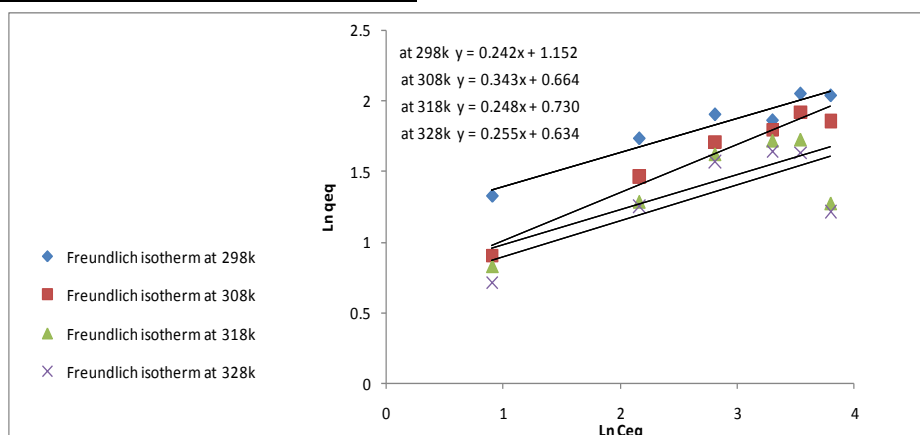
**Table (5): Thermodynamic parameters of Adsorption of  $\text{Cu}^{+2}$  ions on activated carbon**

I. C	Temp. °K	K	$\Delta G^\circ$ (J.mol <sup>-1</sup> )	$\Delta H$ (J.mol <sup>-1</sup> )	$\Delta S$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )
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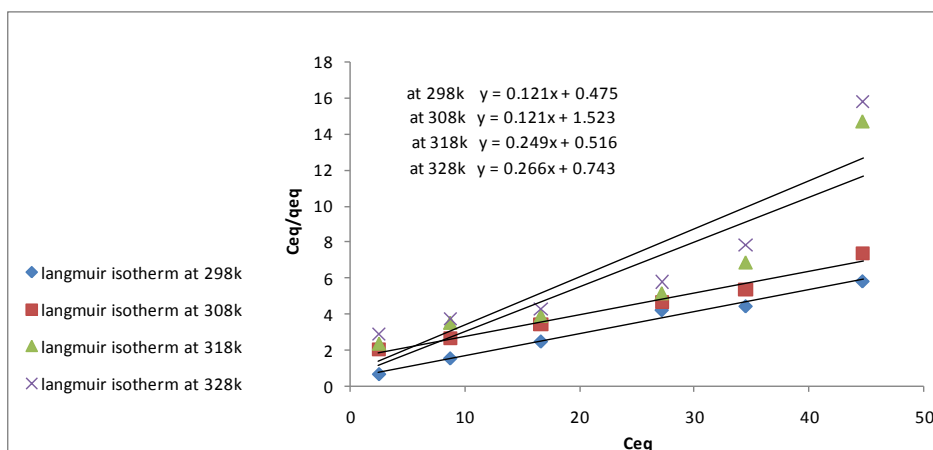
10 mg/l	298	3.049	-2762.031	-37706.484	-126.532
	308	0.988	+30.914		-122.424
	318	0.852	+423.463		-118.574
	328	0.695	+992.198		-114.959
20 mg/l	298	1.304	-657.638	-24192.077	-81.181
	308	0.764	+689.312		-78.546
	318	0.570	+1486.159		-76.076
	328	0.538	+1690.453		-73.756

The plot of  $\ln K$  versus  $1/T$  gives a straight line with slope equal to  $(-\Delta H/R)$ . Figures (13 and 14) show the plots obtained from the application of (eq.10) on the results of considered study.

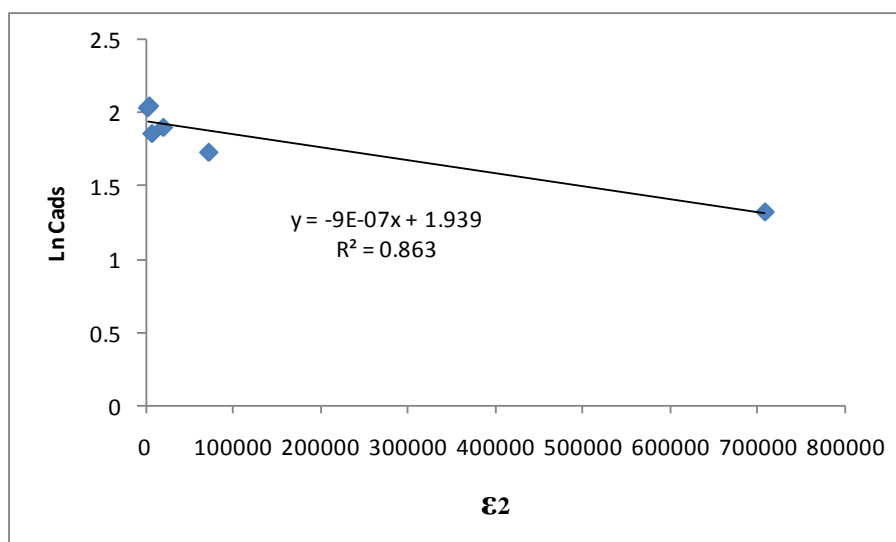
A close look on the results of Table (5) shows that, the adsorption is spontaneous at the room temperature. The increase of temperature increases the departure of  $\text{Cu}^{+2}$  ions from the surface of activated carbon toward the solution. This behavior is in consistent with the value of  $\Delta H$  which indicates to the physical nature of adsorption. The negative value of  $\Delta H$  refers to that, the adsorption process under study is exothermic system, while the negative value of  $\Delta S$  indicates to the increase in order of the studied system during adsorption.



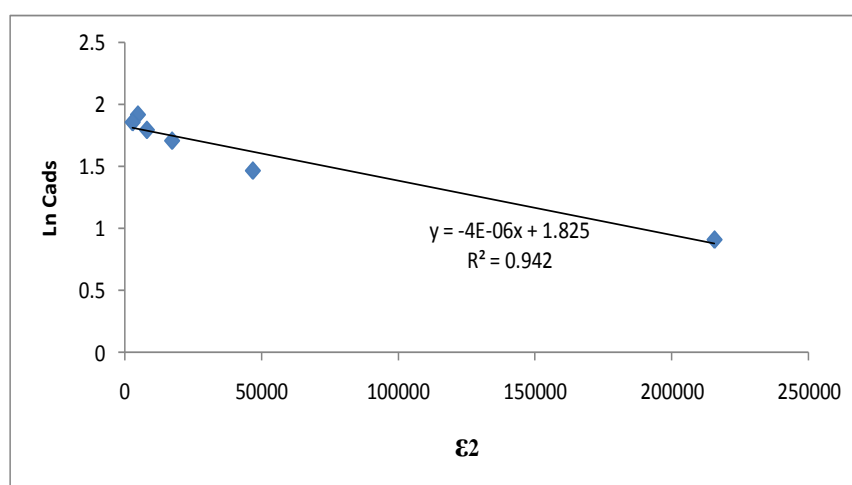
**Figures (1): Plot of the Freundlich relationship between  $\ln q_{eq}$  versus  $\ln C_{eq}$**



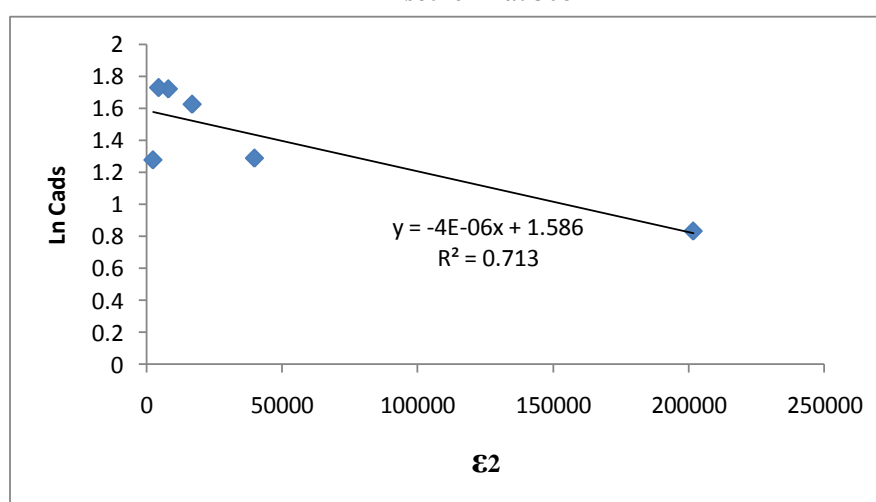
**Figures (2): Plot of the Langmuir relationship between  $C_{eq}/q_{eq}$  versus  $C_{eq}$ .**



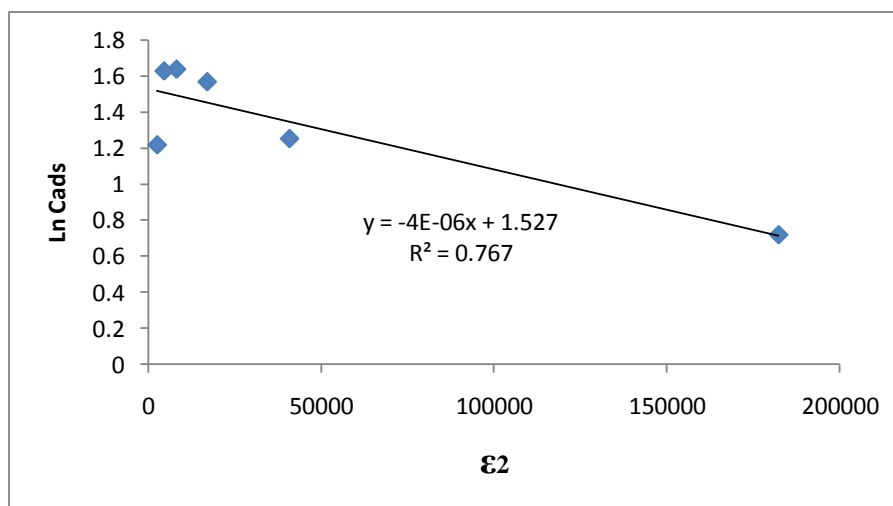
3-DKR isotherm at 298k



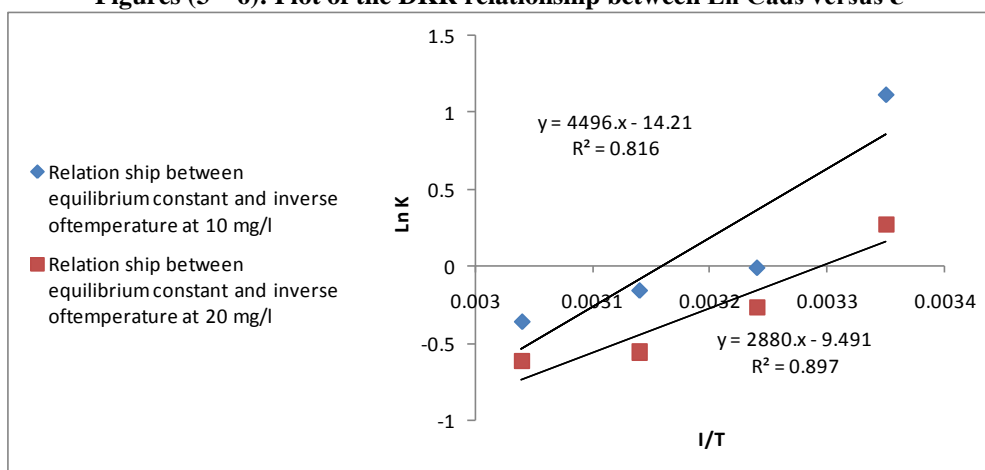
4-DKR isotherm at 308k



5-DKR isotherm at 318k



6-DKR isotherm at 328k

Figures (3 – 6): Plot of the DKR relationship between  $\ln C_{ads}$  versus  $\epsilon^2$ Figures (7): Plot of Van't Hoff relationship between  $\ln K$  versus  $1/T$ 

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## دراسة امتزاز ايون النحاس على نوع جديد من الكربون المنشط

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### الملخص

يتضمن هذا البحث استخدام الكربون المنشط والمحضر من الزيوت المستهلكة (زيوت المحركات) بمعاملة كيميائية، كمادة مازة لازالة ايونات النحاس من المحاليل المائية وتم قياس سعة الامتزاز للكربون. واشتمل ايضا على دراسة العوامل المؤثرة على كفاءة الامتزاز مثل زمن التماس والتركيز الابتدائي للايون الفلزي ودرجة الحرارة. واستخدمت النتائج التي تم الحصول عليها من دراسة تأثير درجة الحرارة في تطبيق المعادلات الرياضية لايزوتيرمات Freundlich و Langmuir و DKR على البيانات العملية للامتزاز. وقد اعطى ايزوتيرم Langmuir علاقات خطية بمعاملات ارتباط جيدة افضل من الايزوتيرمات الاخرى وعند درجة حرارية منخفضة وظهور انحرافات ملحوظة عند زيادة درجة الحرارة. كما حسبت قيم الدوال التيرموديناميكية  $\Delta G^\circ$  و  $\Delta H$  و  $\Delta S$  للتركيزين الابتدائيين (10 و 20 ملغم/لتر) عند درجات حرارية مختلفة. اشارت قيم  $(\Delta G^\circ)$  الى امكانية حدوث عملية الامتزاز بصورة تلقائية عند درجة حرارة الغرفة. وقد اظهرت نتائج الدراسة ان كفاءة الامتزاز تتناقص مع زيادة درجة الحرارة عند كافة التراكيز الابتدائية بسبب عودة الايونات الممتزة الى المحلول والذي يشير الى الطبيعة الفيزيائية الباعثة لحرارة الامتزاز. واعطت اشارة  $\Delta S$  السالبة وصفا للزيادة في حالة النظام الحاصل بسبب ارتباط الايونات الفلزية بالسطح الماز.