Phenol Adsorption from Aqueous Solutions onto Activated Carbon Produced from Iraqi Date-Stones

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Phenol Adsorption from Aqueous Solutions onto Activated Carbon Produced from Iraqi Date-Stones.

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Abstract:

This study is conducted to synthesize an activated carbon from date-stones using different concentration (20%,35%,50%) of phosphoric acid as activater. The carbon was soaked for 72 hours followed by carbonization at (500°C) for two hours. Specific surface area and pH were measured. The adsorption of phenol at different temperatures (283 K , 293 K , 313 K , 333 K) from aqueous solutions onto activated carbon was investigated .The determination of phenol concentration at equilibrium solution was measured using U.V. spectrophotometer with an adsorbance wavelength of (211nm). The activated carbon exhibited high ability to adsorbe phenol from aqueous solutions. The maximum adsorption rates were 98.76% , 98.9% and 97.5% at an initial concentration of (240 mg/l) of phenol and at 333K for activated carbon , (20% ,35% and 50%) , respectively. Adsorption isotherm was studied using Langmuir and Freundlich isotherm models .The characteristic parameters for each isotherm and related correlation coefficient have been determind .The results showed that the adsorption process of the synthetic activated carbon fits very well with the Freundlich isotherm model and in a lesser degree with Langmuir isotherm model . Thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ have also been evaluated and it has been found that the sorption process was feasible, spontaneous and endothermic.

Key words : phenol , adsorption , activated carbon , date-stone.

Introduction

Phenols at low concentration are considered as priority pollutants , since they are harmful for humans and animals . However , phenols might be classified as hazardous pollutants , because of their high potential harm for human health (1-3) . Phenols have high instant solubility in water which cause great bad effects on drinking water (4,5) . Many techniques have been considered for removing phenols from aqueous solutions such as solvent extraction , precipitation , adsorption and ion-exchange (6-8).

Adsoription is a powerful and well established technique for treating industrial and domestic wastes (9,10). Adsorption onto the surface of activated carbon is the most widly used method in water treatment (11,12) .

Organic materials that rich in carbon are used for the production of activated carbon , such as data-stones , rice huck , wood , cornstalk and peat (13). The preparation of activated carbon with different pore sizes can be divided into two processes , physical or chemical activations . Physical activation uses oxidizing gases such as CO2 , NO2 and O2 . This activation normally takes place at temperatures between (700°C - 800°C). In the chemical activation process , chemicals such as zinc salts or phosphoric acid are added to the carbon precursors at some intermediate temperatures (400°C -700°C) to produce the activated carbon (14, 15)

In this study we had prepared activated carbon (AC) invented from date-stones by using a chemical activation agent with phosphoric acid as a vital activator element. The capacity of adsorption with activated carbon for phenol from aqueous solution was studied.

Methods

Materials.

Ortho phosphoric acid (%85) , ethylene glygol monoethyl ether , anhydrous calcium chloride and phenol were purchased from BDH chemicals LTD , England.

Precursors used for the production of activated carbon(AC) was date_stone collected from Heet city in Al-Anbar-Iraq.

Method of preparation

Prepration of Activated Carbon (AC).

Samples of dried date-stone were washed thoroughly with distilled water and then dried again in oven at (383K). After cooling to room temperature, they were cut into small pieces with

blander and soaked for (72h.) in various concentrations of phosphoric acid (20% , 35% , 50%). The treated stones were then carbonized at a temperature of (500°C) for (2h.) , using muffle furnace.

The activated carbon (AC) was washed with bi-distilled water. The sample was then dried at (383K) overnight and finally kept in diseccators for subsequent use.

The weight of content is expressed as follows

Total AC%=(W1/W2)*100

W1= weight of sample (g)

W2= weight of AC (g)

Measurements

- Determination of surface area.

The specific surface area was measured using ethylene glycol monoethyl ether method (EGME) (16).

- pH measurements.

Determination of pH was performed by mixing (1g) of sample with (10 ml) distilled water , then measured by pH meter.

Adsorption Equilibrium.

The phenol stock solutions of concentration 1000 ppm was used to prepare different concentrations (40,80,120,160,200,240) ppm for adsorption isotherm.

An aqeous solution of phenol were added to activated carbon, shaking for (2h.) by shaker and stand for (24h.) until equilibrium reached at different temperatures (283 K ,293 K ,313 K ,333 K). The extract was then measured using U.V. spectrophotometer with wavelength of (211nm).

The quantity of adsorption was calculated by using the following equation

$$Qe = Vsol(Co - Ce)/M$$

Where :

Qe= quantity of adsorbate (mg/g)

Vsol= Total volume of adsorbate solution (l)

Co= Initial Concentration of adsorbate solution (mg/l)

Ce= Concentration of adsorbate solution at equilibrium (mg/l)

M= Weight of activated carbon (g).

While the Removal percentage was calculated by using the following equation;

$$Qe\% = [Co-Ce/Co]*100$$

Where:

Qe% = Adsorption percentage.

Results and discussion

Adsorption Isotherms

Isotherm information is significant in order to advance an equation that correctly explains the results and could probably be used for design aims. The carbon surface specialty and adsorption can affinily be identified by equilibrium studies , with enough information on the capacity of the adsorbent .

The Langmuir equation relates the soild phase adsorbate concentration (Q_e) or uptake to the equilibrium liquid concentration (C_e) as follows:

……1

$$Q_e = bC_e \setminus (1+aC_e)$$

Where a and b are the Langmuir constants , representing the maximum capacity for the solid phase loading and the energy constant related to the heat of adsorption , respectively (Table1). This can be seen from figures(1 - 3).

The adsorption isotherms in figures (4 - 6) represent the Freundlich model with high correlation coefficient ($R^2 = 0.98$).

The linear form of the Freundlich isotherm model is given by the following relation.

$$\log Q_e = \log K_f + (1/n) \log C_e \qquad \ldots\ldots 2$$

Where: Qe is the amount adsorbed of equilibrium (mg/mg)

C_e is the equilibrium concentration of the adsorbate (mg/l).

K_f and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity respectively , of the sorbent (Table1).

The values of K_f and 1/n can be obtained from the intercept and slope respectivel, of the linear plot of experimental data of $\log Q_e$ versus $\log C_e$.

This isotherm is usually used in special cases for heterogeneous surface by multilayer adsorption and the amount of adsorbate increases infinitely with increases in concentration, where it is characterized by the heterogeneous factor 1/n . The heterogeneous factor (n) was calculated and the estimated value ranged between (2.4 to 12.5) . It is known that when the n value is greater than 1.0, the conditions are favorable to adsorption [17].

Thermodynamic Study

Thermodynamic parameters such as entropy (ΔS^o),the free energy (ΔG^o) , and enthalpy (ΔH^o) changes during adsorption can be evaluated from the following Equations (3,4 and 5)

…….3

$$K_c = C_A/C_e$$

$$\Delta G^o = -RT \ln K_c \quad Kc \qquad \ldots 4$$

$$\ln K_c = \Delta S^o/R - \Delta H^o/RT \qquad \ldots\ldots..5$$

Where K_c is the equilibrium constant , C_e is the equilibrium concentration in solution (mg/l) and C_A is the solid-phase concentration at equilibrium (mg/l). ΔG^o, ΔH^o and ΔS^o are changes in Gibbs free energy (kJ/mol) , enthalpy (kJ/mol) and entropy (J/mol/K) , respectively. R is the gas constant (8.314J/mol/K) and T is the absolute temperature (K) . The values of ΔH^o and ΔS^o were determined from the slope and the intercept of the plots of $\ln K_c$ versus 1/T (figure7) .The ΔG^o

values were calculated using Equation (4). The plots were used to compute the thermodynamic parameters (Table 2). The values of the enthalpy change (ΔH^o) and the entropy change (ΔS^o) , in this work they were 83.3 J/mol and 16.462kJ/mol/K , respectively , for phenol concentration (160 mg/l). The negative ΔH^o value indicates the exothermic nature of adsorption .

Surface Area:

Table (3) shows that the values of the surface area increased with the addition of phosphoric acid until 35% , and then deccreased .The maximum values could be obtained at 35% of acid.

Conclusions:

1-The activated carbon prepared from date_stones exhibits high adsorption abilities for phenol from their aqueous solution.

2-The adsorption process is exothermic.

3-The equilibrium sorption data fitted the Freundlich isotherm model better than the Langmuir model.

4-Activated carbon showed high adsorption capacities , and can be successfully used for the removal phenol from waste water.

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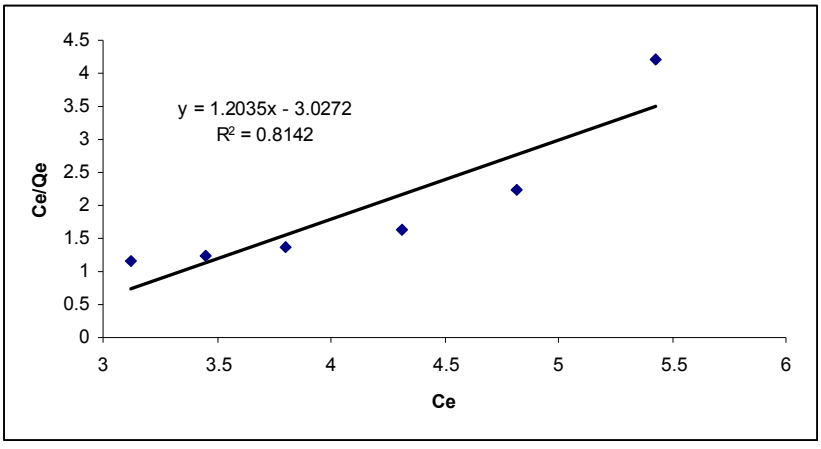

Fig 1: The linearized langmiur adsorption isotherm for phenol with date-stones activated carbon %20

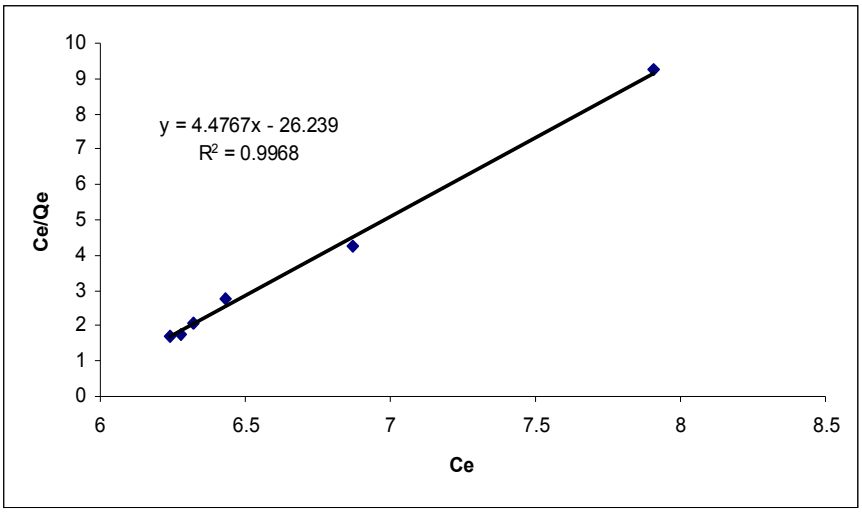

Fig 2: The linearized langmiur adsorption isotherm for phenol with date-stones activated carbon %35.

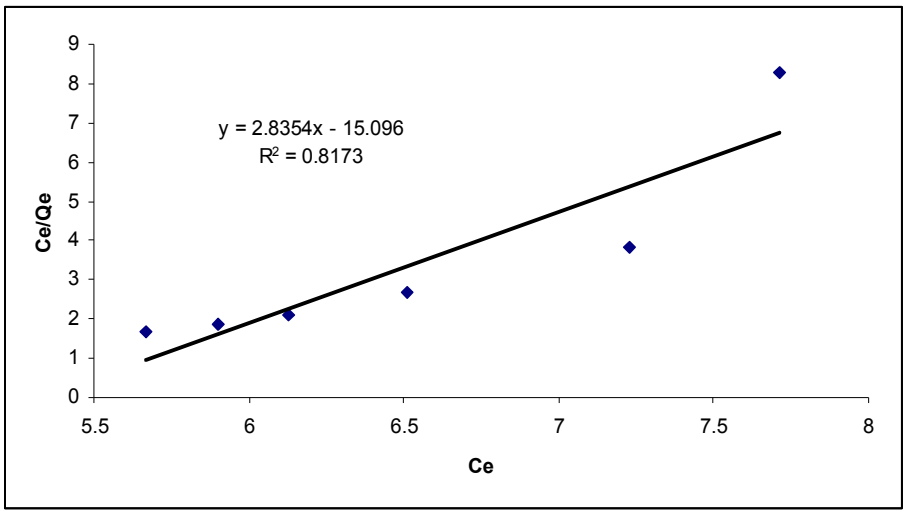

Fig 3: The linearized langmiur adsorption isotherm for phenol with date-stones activated carbon %50.

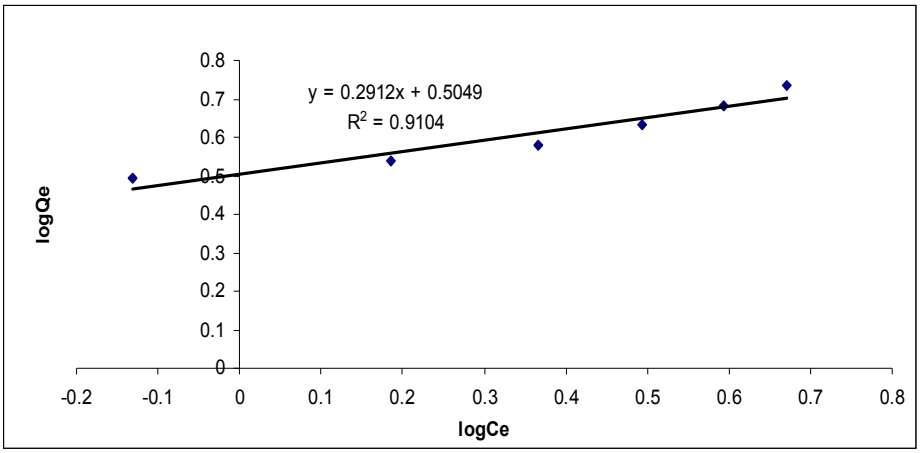

Fig 4: The linearized freundlich adsorption isotherm for phenol with date-stones activated carbon %20

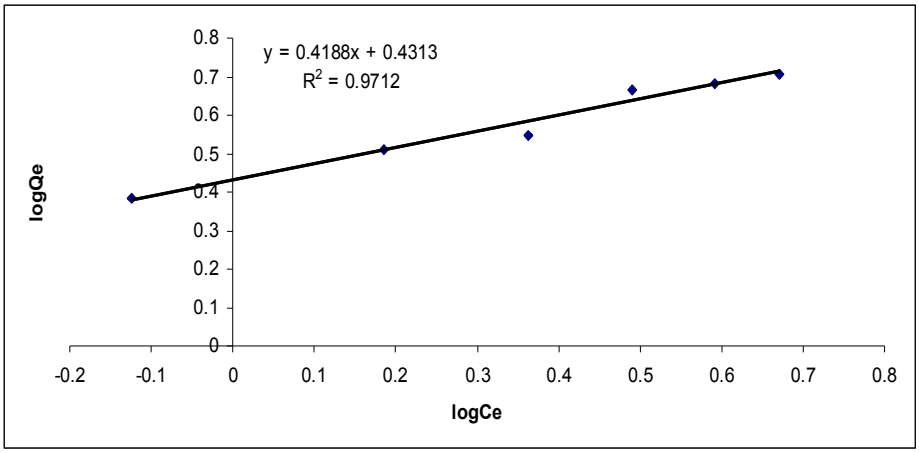

Fig 5: The linearized freundlich adsorption isotherm for phenol with date-stones activated carbon %35.

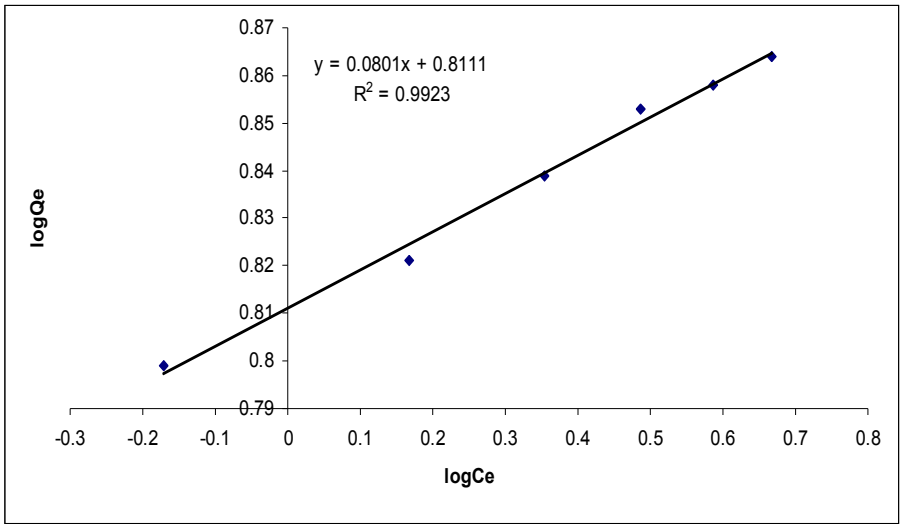

Fig 6: The linearized freundlich adsorption isotherm for phenol with date-stones activated carbon %50.

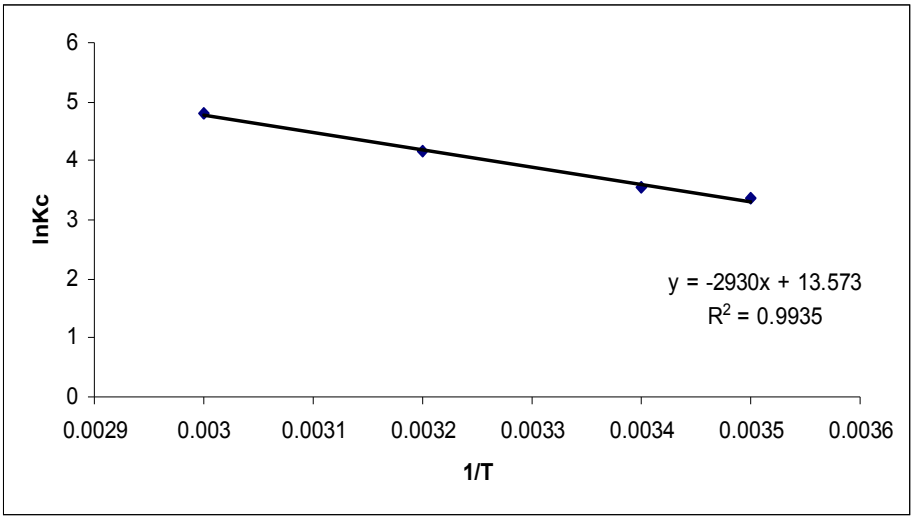

Fig.7:Relation shipe between lnkc and 1/t for date-stones activated carbon %20.

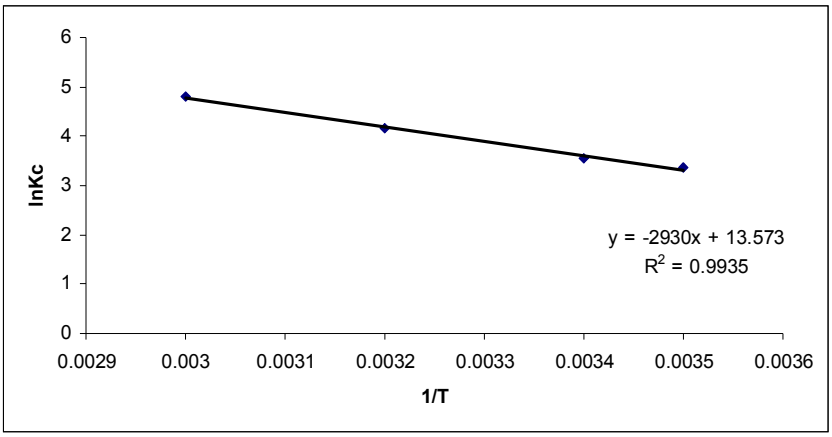

Fig. 8: Relation shipe between lnkc and 1/t for date-stones activated carbon %35.

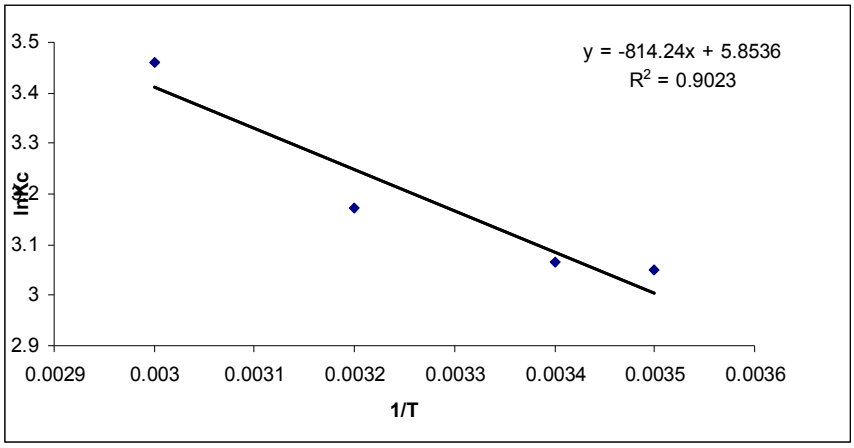

Fig.9:Relation shipe between lnkc and 1/t for date-stones activated carbon %50.

Table1: Parameters of freundlich and langmuir isotherm models.

Absorbent	Langmuir isotherm			Freundlich Isotherm		
	a mg/mg	b l/mg	R^2	K_f	n	R^2
AC. With %20 phosphoric acid	-0.54	-1.05	0.814	3.2	3.27	0.91
AC. With %35 phosphoric acid	-0.33	-0.578	0.997	2.7	2.77	0.97
AC. With %50 phosphoric acid	-0.038	-0.171	0.817	6.5	10.91	0.99

Table:2 Thermodynamic parameters for the adsorption of phenol onto date-stones activated carbon

Initial phenol conc.(mg/l)	Activated carbon	ΔHº (kJ/mol)	ΔSº (J/mol/K)	ΔĠº (kJ/mol)			
				283K	293K	313K	333K
160	20%	16.46	83.3	-7.97	-8.72	-10.19	-12.16
	35%	24.32	112.66	-3.63	-8.54	-10.84	-13.29
	50%	6.76	48.58	-7.16	-7.45	-8.24	-9.56

Table:3 Characteristics of activated carbon

Phosphoric acid conc.(v/v)	Surface areas (m^2/gm)	PH	C% (W/W)
20%	401.57	5.5	60.5
35%	1012.12	4.1	80.8
50%	335.45	3.0	70.8

Table:4 Adsorption percentage of phenol onto activated carbon

c_o of phenol mg/l	AC with H_3PO_4 20% Q_e%				AC with H_3PO_4 35% Q_e%				AC with H_3PO_4 50% Q_e%			
	283K	293K	313K	333K	283K	293K	313K	333K	283K	293K	313K	333K
40	89.25	92.2	94.5	96.37	92.9	93.95	95.4	96.	83.8	84.25	84.4	85.83
80	94.29	95.6	97	97.7	95.9	95.93	97.25	97.69	91.6	91.73	92.15	92.63
120	95.99	96.8	97.6	97.95	96.2	97.1	98.	98.35	94.38	94.24	94.73	94.89
160	96.75	97.3	98	98.5	96.6	97.4	98.4	98.65	95.47	95.54	95.98	95.93
200	96.95	97.59	98.2	98.76	97.3	97.6	98.7	98.8	96.35	96.40	96.57	96.79
240	97.33	97.73	98.5	98.8	97.6	97.8	98.8	98.9	96.91	96.95	96.70	97.5

امتزاز الفينول من المحاليل المائية له على سطح الكاربون المنشط المحضر من نوى التمر

مي فهمي عبد الرحمن
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الخلاصة:

تم في هذه الدراسة تحضير مادة الكاربون المنشط من نوى التمر .استخدمت الطريقة الكيميائية التي يستعمل فيها حامض الفسفوريك وبتراكيز مختلفة كعامل منشط,نقعت لمدة زمنية مقدارها (72) ساعة لكل تركيز .اجريت بعد ذلك عملية الكربنة بدرجة حرارة (500) درجة مئوية ولمدة ساعتين.تم دراسة سعة الكاربون المنشط على الامتزاز والتي تم اختيارها بامتزاز الفينول وبدرجات حرارية مختلفة (283 ,293 , 313 , 333) درجة مطلقة , ثم قيست الامتصاصية للمحاليل المائية للفينول قبل وبعد الامتزاز عند طول موجي (211) نانو متر .وكانت نسبة امتزاز الفينول (98.76% ,98.9 %, 97.5%) على سطح الكاربون المنشط (20% , 35 % ,50 %) بالتتابع من التركيز الابتدائي للفينول (240) ملغم/اللتر وعند درجة حرارة (333) مطلقة . استخدمت معادلة لانكمير وفريندلش لحساب الامتزاز الاعظم. وبينت النتائج تطابق اكبر مع معادلة فريندلش. كما تم قياس الدالة الحامضية والمساحة السطحية للكاربون المنشط. تم حساب الدوال الثرموديناميكية مثل الانتروبي والانثالبي ودالة كبس وبينت النتائج ان التفاعل تلقائي ماص للحرارة .