

Evaluation of the potential of using Iraqi local material to improve the fixed-bed adsorber for phenol removal from wastewater

**Prof. Dr. Dakhil Nasir Taha Lecturer: Isra'a Sadi Samaka Lecturer:
Amal Hamza Khalil**

**College of science
University of Babylon**

**College of Engineering
University of Babylon**

**College of Engineering
University of Babylon**

Abstract

The aim of the present study was to investigate the potential of increasing the adsorption efficiency for phenol adsorption onto activated carbon fixed bed with more economical and increasing the operating time using continuous system by adding local Iraqi porcellanite rocks as a weight ratio to the activated carbon bed . Two types of experiments were carried out, batch and continuous flow (column system) experiments. Batch study showed that equilibrium isotherms for the adsorbent used in this study is favorable type .After using SPSS (V.15) program for the statistical analysis of the experimental results, the equilibrium data of the phenol adsorption by using activated carbon in aqueous solutions was well represented by the Langmuir ($R^2=0.9775$) and Freundlich ($R^2=0.9879$) isotherm models. By the value of R^2 , it can be seen that the Freundlich model is the best to fit the data.

Column experiments carried out with using of natural porcellanite as different weight ratios to the activated carbon (0%, 5% ,10% and 15%) at similar operation conditions. It was found that adding 5% porcellanite weight ratio to the activated carbon bed increases the operating time of activated carbon – column by 24%, while adding 10% and 15% porcellanite weight ratio causes the operating time to decrease by (19% and 52%) respectively and therefore makes the adsorption process not efficient compared with pure (0% ratio) activated carbon bed.

The model provided a very high degree of correlation of experimental adsorption rate data suggesting that this model could be used in design applications.

الخلاصة

تهدف الدراسة الحالية زيادة كفاءة امتزاز الفينول بواسطة الكربون المنشط وبأكثر اقتصادية مع زيادة زمن التشغيل لعمود حشوة الكربون المنشط عند تطبيق تجارب النمط المستمر بواسطة إضافة صخور البورسيلانيت المحلية العراقية كنسب وزنيه لطبقة الكربون المنشط.

وتجارب النمط (batch) تم إجراء نوعين من التجارب تضمنت تجارب دفعية وقد أظهرت التجارب الدفعية أن علاقة التوازن (continuous system) المستمر للمادة المازة المستخدمة في الدراسة هي من النوع المفضل .

لإجراء التحليل الإحصائي للنتائج (SPSS (V.15 استخدم البرنامج الإحصائي التجريبية ، ووجد إن علاقة التوازن لامتزاز الفينول في المحاليل المائية باستخدام الكربون المنشط تتطابق جيداً مع نموذج لانكمر و فراندلش ، وقيم لمعامل التحديد تبين أن موديل R2 على التوالي . ومن خلال قيم (R2= 0.9879) و (R2=0.9775) فراندلش هو الأكثر ملائمة في تثبيت بيانات الاتزان .

إما تجارب النمط المستمر أجريت باستخدام البورسيلانيت الطبيعي وبنسب وزنية نسبة إلى طبقة الكربون المنشط (0% , 5% , 10% , 15%) وتحت نفس ظروف التشغيل

وجد إن إضافة نسبة (5%) من مادة البورسيلانيت إلى عمود الحشو الثابت للكربون المنشط يؤدي إلى زيادة زمن التشغيل لعمود الامتزاز بنسبة 24% أما إضافة (10% , 15% من البورسيلانيت يؤدي إلى تقليل زمن تشغيل العمود بنسبة (19% , 52%) على التوالي، وهذا ما يجعل عملية الامتزاز غير كفوءة بالمقارنة مع استخدام الكربون المنشط التجاري بمفرده (0%) .

يعطي الموديل درجة عالية جداً من الترابط للامتزاز التجريبي ويؤدي إلى إمكانية استخدام الموديل في التطبيقات التصميمية

Introduction:

Many industrial wastes contain organics which are difficult, or impossible, to remove by conventional biological treatment processes (Rengaraj et al.,2002).

Phenols as a class of organics are similar in structure to the more common compounds in that they are resistant to biodegradation, and it is extensively studied adsorbate for the adsorption of aqueous solutions on carbon , for practical(in wastewater treatment) as well as scientific reasons. It is a good model compound for organic pollutants in wastewater (Yang ,2003).

Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, epoxy resins, and polyamide for various applications (Banat et al., 2000).

Many wastewaters contain significant levels of organic pollutants of aquatic ecosystems such as phenols, especially the chlorinated once, are considered as priority pollutants since they are harmful to plants, animals and human, even at low concentrations (Theoparis et al.,1998). Because of extensive use of these compounds, they are readily enter ecosystems by industrial and municipal wastewater, by leachates emerging from waste deposits, by agricultural runoff of pesticides, etc.. (Yapar et al.,2004). Phenolics constitute the 11 th of the 126 chemicals which have been designated as priority pollutants by the United States Environmental Protection Agency (Rengaraj et al.,2002).

So that , the (EPA) regulations call for lowering content in the wastewater to less than 1 mg / l (Eahart et al. ,1977) and the (WHO) prescribed a concentration in drinking water (WHO, 1984).

Many water treatment technologies are available to remove phenol from receiving water bodies, the most important removal technology is adsorption (Laszlo et al.,2003 ; Tebbut ,1998).

Activated carbons are widely used as an adsorbent for the removal of a wide range of pollutants (Jankowska et al .,1991 and Ania et al .,2002).

Literatures on the adsorption study of organics contaminants onto activated carbon are abundant (Costa et al.,1988; Yang et al.,1994; Tseng et al.,2003; Dabrowski et al .,2004).

The main objective of this study is to prove that the flow system can be made more efficient and/ or economical by increasing the adsorption efficiency of the adsorbent through the reduction of dead zones between the activated carbon particles in a fixed bed system by adding filler material like natural porcellanite, and reduction the losses of adsorption process through the micro pores of activated carbon particles .

The experiments carried out batch's and fixed bed column. Laboratory batch studies were conducted to estimate the adsorption capacity of the adsorbent .

In this work, the Langmuir and Freundlich isotherm models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions. Four experiments in a fixed-bed column system with different weight ratios of natural porcellanite-activated carbon were done to investigate the main objective of this work.

The model can predict any data which is hard or cannot be known from the laboratory work and help engineers or column designers for better and economic design.

Materials and methods

Adsorbent : The commercial activated carbon with characteristics listed in Table (1) was supplied by (Unicarbo, Italian ,Lmt .Co.) to Iraqi local markets was used in this study .

The mesh size of activated carbon was ($0.5 \times 10^{-3} \text{m}$) and obtained by sieving analysis using the American Sieve Standards in the building materials Laboratory at the University of Babylon.

Iraqi natural porcellanite rocks kindly supplied by the General Establishment for Geological Survey and Mineralogy – Ministry of Industry and Minerals, from the Akashat site in the western region of Iraq. The characteristics of porcellanite are listed in Table (2) .

The porcellanite rocks were crushed and sieved to get granular porcellanite with particle size of ($0.1 \times 10^{-3} \text{m}$) to be used in present study .

For pre-treatment , these materials were firstly washed with distilled water and then dried in an electric oven at 120 C° over night (Yamin et al.,2007).

This time was usually enough to remove any undesired moisture within the particles .It was then placed in desiccators for cooling .

Adsorbate : The phenol solution was prepared with concentration of 0.2 kg/m^3 .

The pH solution was adjusted with (0.1 M HCL) using pH meter to its effective adsorption pH value ($\text{pH} = 5$) in this study .

Analytical technique : The phenol concentrations were measured using UV- 1650 PC SHIMATZU) with wavelength (500 nm) according to Wilfred,1959.

Linear calibration curve was used in the determination of equilibrium phenol .

The curve was based on standards in the concentration range (0.01 – 0.1 kg/m³).

For the concentration above (0.1 kg/m³), process of dilution was used in order to analysis the samples .

Triplicate samples were run and the results averaged .

Table (1) : Characteristics of the Activated carbon

Base	Coconut shell
Bulk density	0.3 * 10 ³ Kg /m ³
Particle density	1.5 * 10 ³ Kg /m ³
BET surface area	650 * 10 ³ Kg /m ³
Particle porosity	0.4
Bed porosity	0.2
Ash content (%)	5 (max)
Iodine No. (mg /g)	1100 - 1130
pH	10.2 -10.6
Moisture content (%)	5

Table (2) : Characteristics of the Iraqi natural Porcellanite rocks.

Kg /m ³ Density (gm / m ³)	1.323
Specific gravity	1.301
Surface area BET (m ² / g)	39.688
SiO ₂ (%)	62.02
MgO (%)	7.2
Fe ₂ O ₃ (%)	0.87
Al ₂ O ₃ (%)	2.71
CaO (%)	11.55

Experimental

The adsorption of phenol onto activated carbon was studied using two types of experiments , batch and column experiments.

Batch experiments : Bach experiments were carried out to study the adsorption isotherms of phenol at 30 ± 1 C° .

The experiments were adjusted at the initial pH of 5 for phenol (Banat et al.,2000 ;Mahvi et al.,2004). 100 ml of portions phenol solution of a 0.2 kg/m³ concentration were placed in 7 conical flasks 250 ml in volume, containing different accurately weighed masses of commercial activated carbon (0.1 , 0.2 , 0.3, 0.4 ,0.8 ,1 ,and 1.5 gm) .

The whole set was then placed on shaker for 30 hours . At the end of the equilibrium time the flasks were taken off the shaker and the samples were filtered using filter paper .Then , phenol equilibrium concentration was measured according to Wilfred,1959.

The amount of phenol adsorbed at equilibrium is calculated based on the following equation (Ho et al.,1996).

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

where:

q_e (mg/g) : is the amount of phenol adsorbed in adsorbent at equilibrium.

C_o and C_e (mg/l) : are the initial and equilibrium concentration of phenol solutions respectively.

m (g) : is the amount of adsorbent .

V (l) : is the volume of phenol solution .

Fixed bed column experiments :

Experimental arrangements

The schematic representation of experimental equipments is shown in Figure (1).

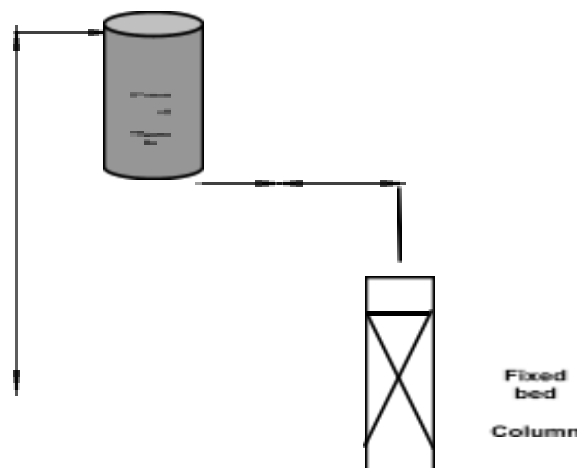
Adsorption column

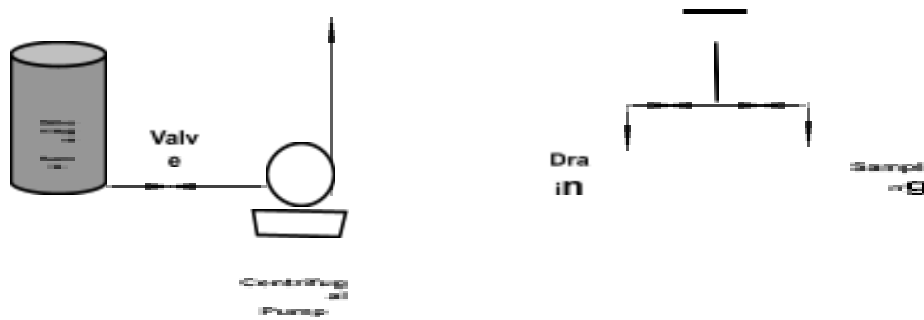
Continuous flow adsorption studies were conducted in a vertical glass column made of Pyrex glass tube (0.8 m) height , and (0.05 m) internal diameter .

The activated carbon bed was confined in the column by the means of the glass spheres placed on the top and bottom of bed to ensure a uniform distribution of influent phenol solution through the carbon bed .

Two cylindrical tanks were used as container, the first one as a storage tank (100* 10⁻³m³); the second one as a feed tank (50*10⁻³ m³); each tank was fitted with gate valves.

The bed column was (L=0.05 m) height of activated carbon with flow rate (\bar{Q} =1.78 *10⁻⁶ m³/sec), phenol concentration(C_o =0.2kg/m³), and pH=5 for all experiments.





.Fig. (1): A schematic representation of experimental equipment

Preparation of samples with different porcellanite–activated carbon ratios.

Different porcellanite–commercial activated carbon weight ratios were used starting from 0%, 5% ,10% ,and 15% of natural porcellanite. The added porcellanite was with a size of $(0.1 \cdot 10^{-3} \text{m})$ mixed with activated carbon particles with size of $0.5 \cdot 10^{-3} \text{m}$.

Each sample was mixed by a shaker for 1 hour .

Experimental procedure

After preparing the phenol solution with desired concentration in the storage tank.

The solution was pumped by means of centrifugal pump (KF-2, SAER, ITALA) with capacity $(0.05 \text{ m}^3/\text{hr})$ from the storage tank to the feed tank and then to the top of the column by gravity flow .

The volumetric method was used to adjust the flow rate to the desired value.

At first, every (10) minutes sample was taken from the outlet of the column and after phenol appeared in the sample the time interval of sampling became (20 minutes) until equilibrium state was reached .

To achieve the measurement of the breakthrough curve for phenol, four experiments were done, once with pure activated carbon, and other three experiments with different porcellanite–activated carbon weight ratio (5%, 10%, and 15%) . All experimental conditions are summarized in Table (3) .

Table (3) Column system-data

Experimental data									Data of results
Experimental No.	Adsorbent	Adsorbate	Adsorbate concentration (kg/m^3)	Bed depth (m)	Flow rate (\bar{Q}) (m^3/sec)	Particle Size of Activated carbon (m)	Particle Size of Porcellanite (m)	Porcellanite – activated carbon ratio (%)	Saturation time (min.)
1	Activated carbon	phenol	0.2	0.05	$1.78 \cdot 10^{-6}$	$0.5 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$	0	640
2	=	=	=	=	=	=	=	5	840
3	=	=	=	=	=	=	=	10	540
4	=	=	=	=	=	=	=	15	420

Results and discussion :

Batch experiments

This experiments were done to estimate the adsorption isotherm constants for commercial activated carbon. The Langmuir and the Freundlich equations were used to study data concerning the dependence of the adsorption on the phenol concentration, so that, the equilibrium data were fitted to these models to describe experimental data.

Analysis of the isotherm data is important in order to develop an model that represents the results and could be then used for design purposes .

The Langmuir isotherm defined by following equation (Langmuir ,1916):

$$q_e = \frac{QbC_e}{1 + bC_e} \dots\dots\dots (2)$$

or its linear form :

$$C_e/q_e = 1/Qb + C_e/Q \dots\dots\dots (3)$$

The linear form is made to yield Langmuir constants (Q ,b) by regression line . Where q_e (mg/g) is the amount of phenol adsorbed at equilibrium, C_e (mg/l) is the equilibrium concentration of adsorbate in solution, Q (mg/g) and b (L/mg) are the Langmuir constants related to the maximum adsorption capacity corresponding to complete monolayer coverage on the surface and to energy adsorption(affinity constant or heat of adsorption) (Weber,1972 ; Badmus et al ., 2007).

These constants are obtained from the slope and the intercept of the linear plot of experimental data of C_e/q_e versus C_e as shown in Figure (2).

C_e
/ q_e
(g
/L)

$$C_e/q_e = 0.432 + 0.014 C_e$$

$$R^2 = 0.9775$$

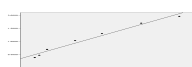


Fig.(2): linearized form of Langmuir adsorption isotherm of phenol onto commercial activated carbon at 30 ± 1 C°, $C_0 = 0.2$ kg/m³, pH = 5 .

Further, a dimensionless quantity r , defined as (Weber and Chakravorti , 1974):

$$r = 1/1 + C_o .b \dots\dots\dots (4)$$

is developed taking the Langmuir constant b (L/mg) and the adsorbate concentration C_o (mg /L).

The parameter indicates the shape of isotherm accordingly (Weber ,1972).

<u>r value</u>	<u>type of isotherm</u>
r > 1	unfavorable
r = 1	linear
0 < r < 1	favorable
r = 0	irreversible

Freundlich isotherm defined by the following equation : (Freundlich , 1906).

$$q_e = K.C_e^{\frac{1}{n}} \dots\dots\dots (5)$$

or its linear form

$$\log q_e = \log K + \frac{1}{n} \log C_e \dots\dots\dots(6)$$

Where K and $\frac{1}{n}$ are Freundlich constants related to maximum adsorption capacity or adsorption distribution and adsorption intensity, respectively of the sorbent (Chandra et al ., 2006).

The values of K and $\frac{1}{n}$ can be obtain from the intercept and slope, respectively, of the linear plot of experimental data of $\log q_e$ versus $\log C_e$ as shown in Figure (3).

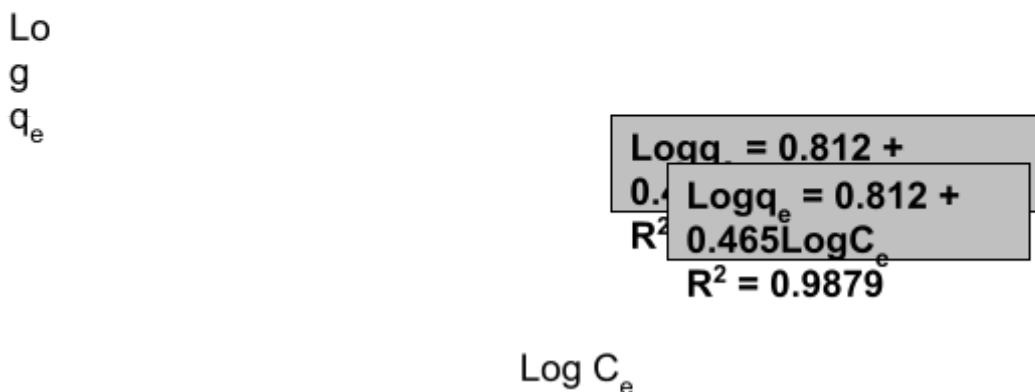


Fig.(3): linearized form of Freundlich adsorption isotherm of phenol onto

commercial activated carbon at $30 \pm 1 \text{ C}^\circ$, $C_0 = 0.2 \text{ kg/m}^3$, $\text{pH} = 5$.

The results are tabulated in Table(4). The values of correlation coefficient (R), determination coefficient (R^2), and the standard error of the estimate (S.E.) were obtained by linear regression using the least squares method. These estimated models parameters are measure of goodness of fit, show that both the Langmuir and Freundlich isotherm models can sufficiently, describes the adsorption data well for phenol compound study, but the value of R^2 was slightly higher for Freundlich than Langmuir .

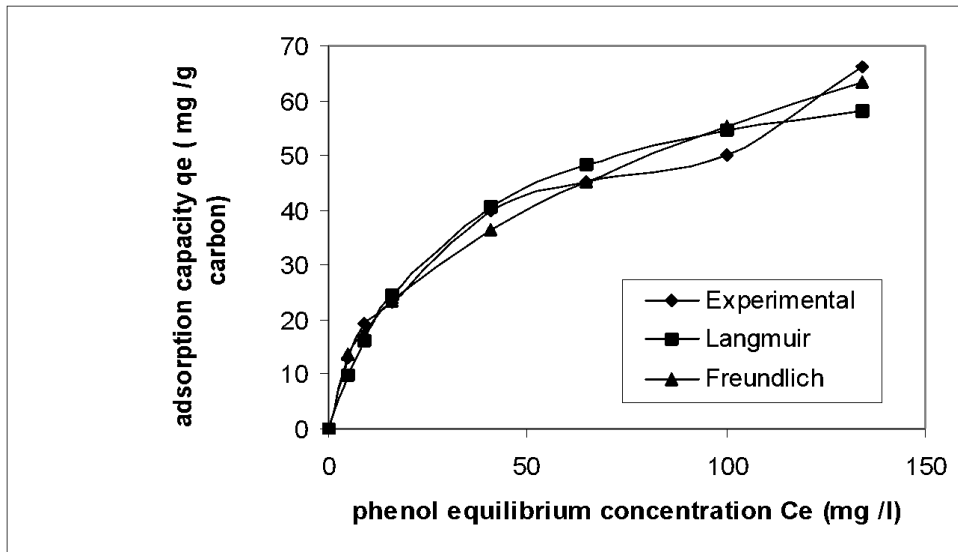
This indicates that the Freundlich isotherm is clearly the better fitting isotherm to the experimental data. Similar results were observed by Faust and Aly, 1987 for organic compounds such as phenolic compounds (Koh and Dixon ,2001).

The value of separation factor (r) for activated carbon with phenol concentration of 200 mg /l indicates that the adsorption process is favorable. Similar results were observed by (Weber and Chakravorti ,1974 ; Han et al ., 2005).

Table (4) : Langmuir and Freundlich parameters of isotherm for activated carbon used in this study.

Adsorbent	Langmuir isotherm (95 % confidence level)					Freundlich isotherm (95 % confidence level)					
	Q (mg/g)	b (L/mg)	Correlation coefficient (R)	Determination coefficient (R^2)	Standard error of the estimate (S.E)	R_L	Intercept (K) (L/mg) ^{1/n}	Slope (1/n)	Correlation coefficient (R)	Determination coefficient (R^2)	Standard error of the estimate (SE)
Granular activated carbon	71.4285	0.0324	0.9887	0.9875	0.101	0.1336	6.486	0.465	0.9939	0.9989	0.031

Figure(4) explains the experimental and theoretical results by using Langmuir and the Freundlich adsorption isotherm equations and showed favorable type of adsorption for experimental results .



ol onto
H = 5 .

Column experiments

The results of phenol adsorption onto commercial activated carbon fixed bed using continuous system (continuous flow) were presented in the form of breakthrough curves which showed the loading behaviors of phenol to be adsorbed from the solution expressed in terms of relative concentration defined as the ratio of the outlet phenol concentration to the inlet phenol concentration as a function of time (C / C_0 vs . time).

To study the effect of different natural porcellanite–commercial activated carbon weight ratios were investigated for phenol adsorption onto commercial activated carbon by adding different weight ratios of ($0.1 \cdot 10^{-3}m$ particle size) natural porcellanite to the activated carbon bed ($0.5 \cdot 10^{-3}m$ particle size). Four experiments were conducted using different weight ratios of (0%, 5%, 10%, and 15%). The experimental breakthrough curves are presented in Figure(5) and the data of results tabulated in Table (5).

All experiments were conducted at constant conditions, bed depth (0.05m) , initial phenol concentration ($0.2kg/m^3$), flow rate ($1.78 \cdot 10^{-6} m^3/sec$), particle size of granular activated carbon ($0.5 \cdot 10^{-3}m$), particle size of natural porcellanite ($0.1 \cdot 10^{-3}m$) and solution pH of 5 .

Figure(5) shows that a significant increase in the operating time by (24%) is achieved by adding (5%) porcellanite weight ratio to the activated carbon bed .

Increasing the natural porcellanite ratio to (10%, 15%) caused the operating time to decrease by 19% and 52% respectively and these additions were achieving lower operating time and removal efficiency than pure (0% ratio) activated carbon bed .

Therefore, it is very important to find the optimum weight ratio of natural porcellanite to activated carbon particles (5%).

Knowing that the matching between the two mechanisms; static hold-up and operating hold-up will save weight of activated carbon and minimize the losses in surface area for adsorption. Then, 5% ratio increases the adsorption efficiency of the activated carbon through the reduction of dead zones between particles in fixed bed, and reduction the losses of adsorption- process through the micro pores.

**Phenol adsorption, $C_o = 0.2\text{kg/m}^3$, EMBED Equation.3
 $=1.78 \text{ ml / sec}$, $L = 0.05 \text{ m}$, $\text{pH} = 5$**

Fig. (5) : Experimental breakthrough curves for phenol adsorption onto commercial activated carbon at different natural porcellanite ratios.

**phenol onto
 commercial
 pth=0.05m,**

Time (min)	0% Porcellanite	Time (min)	5% Porcellanite	Time (min)	10% Porcellanite	Time (min)	15% Porcellanite
	C /C _o		C /C _o		C /C _o		C /C _o
	0		0		0		0
	0		0		0		0
	0		0		0		0
	0		0		0		0.01
	0		0		0.02		0.035
	0.007		0		0.023		0.045
	7		0		75		0.055
	0.009		0		0.027		0.075
	8		0		5		0.08
	0.010		0.005		0.05		0.187
1	5	1	5	1	0.057	1	5
1	0.011	1	0.017	1	5	1	0.265
1	5	1	5	1	0.065	1	0.3
1		1		1	0.151	1	0.402

1	0.014	1	0.042	1	0.3	1	0.476
2	75	2	5	2	0.378	2	0.526
2	0.017	2	0.05	2	0.417	2	5
2	4	2	0.127	2	0.447	2	0.578
2	0.047	2	5	2	5	2	0.603
2	8	2	0.2	2	0.478	2	35
3	0.055	3	0.225	3	5	3	0.679
3	0.11	3	0.265	3	0.501	3	0.726
3	0.15	3	5	3	0.526	3	0.804
3	0.175	3	0.326	3	5	3	0.854
3	0.225	3	5	3	0.544	3	5
4	0.279	4	0.357	4	0.557	4	0.927
4	0.339	4	25	4	5	4	0.950
4	55	4	0.422	4	0.572		5
4	0.379	4	5	4	0.591		0.976
4	0.451	4	0.451	4	0.628		0.999
5	8	5	5	5	0.678		9
5	0.553	5	0.502	5	5		0.999
5	35	5	25	5	0.702		9
5	0.578	5	0.528		5		1
5	0.590	5	0.557		0.778		
6	5	6	0.578		5		
6	0.626	6	5		0.85		
6	5	6	0.593		0.903		
	0.655	6	0.604		35		
	0.676	6	0.617		0.954		
	0.707	7	0.643		0.978		
	25	7	0.652		0.999		
	0.79	7	5		9		
	0.84	7	0.675		0.999		
	0.901	7	6		9		
	5	8	0.702		1		
	0.952	8	0.718				
	5	8	0.754				
	0.979		0.809				
	0.993		5				
	85		0.839				
	0.999		0.869				
	9		2				
	0.999		0.903				
	9		5				
	0.999		0.936				
	9		5				
	1		0.962				
			5				
			0.978				

			0.981				
			5				
			0.985				
			0.991				
			0.995				
			0.999				
			9				
			0.999				
			9				
			1				

Conclusions

Wastewater containing phenolic compounds present a serious problem. Phenol containing wastewater may not be conducted into open water without treatment because of the toxicity of phenol. From the present study, the following conclusions based on the results are drawn :

- 1- The ability of commercial granular activated carbon to adsorb phenol from aqueous solution was investigated by batch and column systems. This study shows the potentialities of activated carbon in wastewater treatment and the adsorption process can be an alternative treatment method for this pollutant resistant to conventional methods. Therefore, it can be used for complete decomposition of phenol .
- 2- In batch experiments, the equilibrium isotherms for phenol adsorption onto the activated carbon used in this work are of favorable type. The data of phenol adsorption are correlated with Langmuir and Freundlich models and it is found that Freundlich model gives the best fit for the experimental data with higher correlation coefficient .
- 3- In continuous flow experiments, adding 5% ($0.1 \times 10^{-3}m$ particle size) of natural porcellanite as a weight ratio to the activated carbon bed ($0.5 \times 10^{-3}m$ particle size) increases the operating time by 24% compared to 0% ratio (activated carbon only). Increasing the porcellanite ratio to 10% and 15% decrease the operating time by 19% and 52% respectively, and therefore make the adsorption process not efficient compared with pure carbon bed (0% ratio) .
- 4- The model parameters would be useful for fabrication and designing of waste-water treatment plants.

Recommendations:

Based on the results achieved in this work, the following recommendations can be forwarded :

- 1- It is recommended to conduct further works with study the effect of using different natural porcellanite granular activated carbon ratios in continuous system to remove other pollutants such as pesticides and heavy metals from either domestic or industrial wastewater .
- 2- It is recommended using biological treatment before porcellanite-activated carbon columns for removing organic matter.

- 3- This study may be extended for using another type of adsorbent than activated carbon or activated carbon with another filler material.

References:

- Ania ,C.O.,J.B.Parra and J.J.Pis,2002, "Effect of texture and surface chemistry on adsorptive capacities of activated carbons for phenolic compounds removal", *Fuel Process. Technol.*, 77- 78 :337-343.
- Banata ,F.A.,B.AL – Bashir ,S.AL – Asheh and O.Hayajneh ,2000 , " Adsorption of phenol by bentonit " , *Environ. Pollut .* , 107 : 391 -398.
- Chandra,T.C.,Mirna,M.M.,Surdayanto,Y.and Ismadji, S.,2006,"Adsorption of basic dye onto activated carbon prepared from during shell: Studies of adsorption equilibrium and kinetics",*Chemical Engineering Journal*,127,121-29
- Dabrowski A,Podkoscielny P,Hubicki Z, Barczak M, 2004,"Adsorption of phenolic compounds by activated carbon-a critical review", *Chemosphere*,58(8):1049-1070.(Cited by Harry and Francisco,2006).
- Eahart ,J.P.,K. Won,H.Y.Wang and J.M.Prausnitz ,1977, " Recovery of organic pollutants via solvent extraction " , *Chem.Eng. Prog.*, 73 : 67 -73.
- E.costa,G.Calleja and L.Marjuan,1988," Comparative adsorption of phenol ,P – nitrophenol and P- hydroxyl benzoic acid on activated carbon " , *Adsorp. Sci.Tecnol.*,5(3),213-28.
- Faust, S.D. and Aly, O.M.,1987,"Adsorption processes for water treatment", Butterworths, Boston, MA.(Cited by Yang,2003).
- Freundlich, H.M.F.,1906,"Uber die adsorption in losungen", *Zeitschrift fur physikalische Chemie*(Leipzig), Vol.57A,pp.385-470.
- Han R, Zhang J, Zou W,2005,"Equilibrium biosorption isotherm for lead ion chaff", *J.Hazard. Mater*, B125: 266-271.
- Harry Marsh and Francisco Rodriguez –Reinoso ,2006 , " Activated carbon", Elsevier Science and Technology Books.
- Ho,Y.S,Wase,D.A.J.and Forster ,C.F.,1996, " Kinetic studies of competitive heavy metal adsorption by sphagnum peat " , *Environmental Technology* , 17, 71-77.
- Jankowska, H.Swiatkowski, A., and Ohoma, J.,1991,"Activated carbon",Ellis Harwood, New York, NY.(Cited by Yang, 2003).
- Koh, S.M. and Dixon, J.B.,2001, "Preparation and application of organo-minerals as sorbent of phenol, benzene and toluene", *Applied Clay Sci.*, 18: 111-122.
- Langmuir ,1916," The constitution and fundamental properties of solids and liquids" ,*J.Am.Chem.Soc.*38:2221-2295.
- Laszlo ,K.,Podkoscielny ,P. and Dabrowski ,A.,2003," Aqueous solutions of phenol and 2,3,4- trichlorophenol", *Langmuir* ,V.19 ,PP 97197-9723.
- M.A.O.Badmus, T.O.K.Audu and B.U.Anyata,2007,"Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells(*Typanotonus fuscatus*)",*Turkish J. Eng.Env. Sci.*, 31,251-263.
- Rengaraj ,S.,M.Seuny – Hyeon and R. Sivabalan ,2002, " Agricultural solid waste for the removal of organics : Adsorption of phenol from water and wastewater by palm seed coat activated carbon " , *Waste Manage.*,22: 543 -548.
- S.Yang,S.Guo and C.Luo,1994," Activated carbon for removing phenol using fluidized bed reactor", *Meitan Zhuankua* ,17 (2):25-30,*Chemical Abstract* 121:137330K (1994).
- Theopharis ,G.D.,Triantafyllos ,A.A., Dimitrios ,E.P.phlip, J.P., 1998, *Wat .Res.*, 32 ,295 -302.
- Tesng ,R.L., Wu,F.C. and Juang , R.S.,2003, " Liquid – phase adsorption of dyes and phenols using pinewood –based activated carbons , *Carbon* , 41 :487-495.

- T.H.Y.Tebbutt ,1998 " water quality control " 5 th Edition Butterworth–Heinemann.
- Weber, T.W and R.K. Charavorti, 1974,"Pore and solid diffusion models for fixed-bed adsorbers",J.Am.Inst.Chem.Eng.,20: 228-238, DOI:10.1002/aic.690200204.
- Weber W.J.,1972,"Phsiochemical processes for water quality control " ,Wiley Interscience ,9: 261-304.
- WHO Guidelines for drinking water quality , 1984, Vol.1, Recommendation World Health Organization ,Geneva.
- Wilfred W.,1959,"Standard methods of chemical analysis", New York.
- Yamin, Y.,Zobir, M., and Fujan, H.A.,2007," Adsorption of methylene blue onto treated activated carbon " , the Malaysian Journal of Analytiical Sciences , Vol. 11, No.11 ,PP.400-406.
- Yang , R.T., 2003," Adsorbents : fundamentals and applications " , John Wiley and Sons ,Inc., New Jersey, USA.