# Adsorption Isotherm and Kinetic Studies of Phenol on Meskeat Activated Carbon

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## Abstract

Adsorption is a commonly used process for the removal of pollutants from aqueous solutions utilizing many adsorbents. Phenol in water is one of the pollutants that can be removed by activated carbon. The Meskeat activated carbon sample was; crushed into fine powder (75µm), heated in an oven at temperature 110$^{o}$ C and kept in a desiccator. It was analyzed for pH, $pH_{pzc}$ and scanned by Electron Microscopy (SEM). It has been found that pH (8.1) and $pH_{PZC}$ (7.13). The sample contain calcium, potassium, chlorine, sulphur, oxygen and carbon. The morphological aspects of activated carbon were rich porous particles with fibrous morphology and also of angular- shaped particles as analyzed by SEM. The equilibrium time of phenol on activated carbon was found to be 150 min for phenol solution and the adsorption capacity increased with increase in the initial phenol concentration. The experimental data at equilibrium were analyzed using two adsorption isotherms models(Langmuir and Freundlich), and the Langmuir's isotherm model is better than Freundlich isotherm, according to the high value of correlation coefficient ($R^2$). Also the results of adsorbent dose from 0.5 g/L to 3 g/L indicated that an increase in the activated carbon mass decreases the residual concentration of phenol solution. The results show that pseudo-second order kinetics model is better than first order.

**Key words: Adsorption, Meskeat activated carbon and phenol**

## المستخلص

تعد عملية الامتزاز من العمليات التي تستخدم لإزالة الملوثات من المحاليل المائية وذلك باستخدام عدة مواد مازة. استخدم في هذه الدراسة الكربون المنشط لإزالة الفينول من المحاليل المائية. عينة كربون المسكيت المنشط تم سحقها إلى بدرة ناعمة ثم غربلت بواسطة غربال 75µm . جففت العينة في فرن عند درجة حرارة $110^{o}C$ وحفظت في مجفف لحين الاستخدام. حللت العينة بواسطة دراسة حمضية العينة، نقطة شحنة الصفر والماسح الالكترونى الضوئي. وجد أن حمضية العينة(8.1)، نقطة شحنة الصفر(7.13). توصلت الدراسة إلى أن التركيب الكيميائي في العينة هو الكالسيوم، البوتاسيوم، الكلور، الكبريت، الاكسجين والكربون. أيضاً النتائج المتحصل عليها بواسطة الماسح الالكتروني الضوئي أوضحت بأن السمات العامة لسطح عينة كربون المسكيت المنشط هي عبارة عن جزيئات مسامية ليفية وذات زوايا. خلصت الدراسة إلى أن الزمن اللازم لحدوث الاتزان على سطح الكربون المنشط يساوى (150 دقيقة) لمحلول الفينول وسعة الامتزاز تزيد بزيادة التركيز الابتدائي لمحلول الفينول. النتائج التجريبية عند الاتزان تم تحليلها باستخدام اثنين من ايسوثيرمات الامتزاز( لانكمير وفريندلش)، توصلت الدراسة إلى أن ايسوثيرم لانكمير أفضل من ايسوثيرم فريندلش وذلك اعتماداً على القيمة العالية لمعامل الارتباط($R^2$). بالإضافة إلى ذلك وجد أن زيادة كمية المادة المازة في المدى (0.5 - 3 g/L) يقلل من تركيز المتبقي للفينول في المحلول المائي. أظهرت النتائج أن تفاعلات الرتبة الكاذبة الثانية مفضلة أكثر من تفاعلات الرتبة الكاذبة الأولى.


**الكلمات المفتاحية: الامتزاز، كربون المسكيت المنشط والفينول**

# INTRODUCTION

Phenolic compounds are organic compounds that enter the aquatic environment through direct discharge from oil refineries. The contents of these pollutants in the industrial wastewater are usually higher than the standard limit (less than 0.5 ppm for phenolic compound). Activated carbon adsorption is one of the important unit processes that is used in the treatment of drinking water and renovation of wastewater(Alexander and Zayas, 1989). The studies of adsorption of organics onto activated carbon has been reported in a large number of literatures, and the results demonstrated that the adsorption behaviors depend mainly on the characteristics of the activated carbon, the molecular properties of the organics and the operational conditions. The characteristics of the activated carbon such as surface area, pore size distribution and surface functional groups play an important role in the adsorption, as they determine the interactions between the organics and the activated carbon at the interface(Li et al., 2002, Alam et al., 2009). The effects of the molecular properties of adsorbate such as molecular size, solubility, $pK_a$ and electron distribution have been revealed, which might influence the affinity between the organics and the carbon surface(Terzyk, 2004, Li et al., 2004, Zhang et al., 2006). Furthermore, the operational conditions such as solution pH and temperature are also involved in the adsorption, which might have implications on the adsorbent/adsorbate interactions(Vasiljevic et al., 2006, Al-Degs et al., 2008). This study focused on the potential for utilizing unconventional sorbents, such as Meskeat activated carbon for the removal of phenolic pollutants from water. On the basis of theoretical analysis it was assumed that the following factors will affect the course and effectiveness of the sorption process: (*i*) type and dose of applied sorbent, (*ii*) manner of process conductance (contact time, initial concentration, particle size), and (*iii*) Temperature of adsorptive solution. In the course of tests performed in static conditions, the adopted assumptions were subjected to experimental verification. Batch experiments were carried out for kinetic studies on the removal of phenol from aqueous solutions. The influence of various important parameters such as the contact time, adsorbent amount, and initial phenol concentration were investigated by varying any one of the process parameters and holding the other parameters constant. The Langmuir, Freundlich equations were used to fit the equilibrium isotherm models. Pseudo first-order, second-order and Elovich kinetic models were used to evaluate the mechanism of adsorption.

# MATERIALS AND METHODS

## Materials

The following materials were used: Commercial activated carbon was obtained from Kassala state-Sudan. The sample was crushed into fine powder using pestle and mortar and sieved through standard test sieves into different particle size. The sample was heated in an oven at temperature of ***110$^o$ C*** and then kept in the desiccators. A phenol stock solution (analytical standard, ***99%***) was prepared by dissolving (*1g*) of phenol in distilled water (*1 L*). Hydrochloric acid, sodium hydroxide, sodium chloride, and distilled water.

# MATERIAL CHARACTERIZATION

## Determination of pH

The determination of the hydrogen-ion activity or the pH of Meskeat activated carbon is by far the most common activated carbon test. The activated carbon pH was determined by placing 10 g of Meskeat activated carbon sample into a 100 ml beaker and 20 ml of distilled water was added to

the activated carbon sample and stirred for 30 min. The Meskeat activated carbon suspension was left to stand for a period of time to allow most of the suspended solids to settle from the suspension. The electrode of the pH meter was inserted into the solution and the pH was read and recorded(Owabor et al., 2012).

**Determination of $pH_{PZC}$**

The method proposed by(Rivera-Utrilla et al., 2001) was followed. The point of zero charge was determined from acid-base titration. For this, 50 ml of 0.01 M NaCl solution were prepared in six volumetric flasks. Their pH was adjusted with addition of 0.01 M solution of NaOH or HCl. When the pH value was constant, 0.15 g of Meskeat activated carbon sample was added to each flask and shaken for 24 h. The mixture was filtrated and the electrode of the pH meter was inserted into the six solutions and the pH was read and recorded. The $pH_{PZC}$ value is the point where the curve $pH_{Initial}$ vs. $pH_{Final}$ crosses the line $pH_{Initial} = pH_{Final}$.

**Scanning Electron Microscopic (SEM) Analysis**

The Meskeat activated carbon was characterized by Scanning electron microscopy (SEM), using the Oxford instrument X-max, Model TC110 made in Germany. The Scanning electron microscopy analysis was carried out on the activated carbon. The sample was fixed on standard aluminum SEM stub using sputter aluminum tape. The SEM analysis involved a detailed investigation and description of the sample material with special focus on the grain surfaces and textures. The morphology of the Meskeat activated carbon particles was observed by scanning electron microscopy with a coupled energy dispersive spectroscopy (EDS), at 20 kV.

**Adsorption Experiments**

The batch experiments were carried out in 100 ml conical flasks by agitating a pre-weighed amount of the activated carbon of meskeat with 50 ml of the aqueous phenol solution for a predetermined period of time (based on prior kinetic studies) at 30°C on a water bath-mechanical shaker (150 rpm). The effect of the contact time was studied with 90 mg/L phenol solutions. Experiments were also conducted to investigate the effect of varying the amount of activated carbon from 0.5-3.0 g/L with a phenol concentration of 90 mg/L. Adsorption isotherm studies were carried out with the different standard solutions (10-70 mg/L phenol) while maintaining the adsorbent dosage at 1 g/L. UV-visible spectrophotometer was employed to determine the concentrations of phenol remaining in the sample. The absorbance of solution was recorded at 270 nm. The filtrate was analyzed for the remaining phenol concentration. The amount of phenol adsorbed (mg/g) at time (t) was calculated using Equation (1):

$$q_t = \frac{C_o - C_t}{m_s} \times V \text{.....(1)}$$

Where ($C_o$) and ($C_t$ ) are the phenol concentrations in (mg/L) at time (0) and time (t), respectively, (V) is the volume of the phenol solutions in (L), and ($m_s$ ) is the weight of activated carbon in (g).

## RESULTS AND DISCUSSION

**Characterization of adsorbents**

The result of the pH meter reading is 8.1. The point of zero charge $pH_{pzc}$ is an important guides to these interfacial properties. The techniques for the determination of $pH_{pzc}$ are founded on the assumption that protons, $H^+$, and hydroxyl groups, $OH^-$, are potential determining ion. The pH at which the surface has zero net charge, Known as $pH_{pzc}$ is characteristic of amphoteric surface and determined by the type of surface sites on solid and their structures(Milonjić et al., 2007). The

result is shown in Figure(1). For values of pH < PZC, the Meskeat activated carbon surface has been positively charged. At pH > PZC the Meskeat activated carbon surface has been negatively charged. It was shown that the activated carbon particles shift the net surface charge of activated carbon from negative to positive and the point of zero charge (PZC) of Meskeat activated carbon is equal to 7.13

The morphology of the Meskeat activated carbon powder particles was observed by scanning electron microscopy with a coupled energy dispersive spectroscopy (EDS), at 20 kV. The morphological aspects of the powder particles of Meskeat activated carbon are outlined in Figure (2). The porosity of the surface is clearly visible. The scanning electron micrograph in this Figure shows the typical regular shapes of the Meskeat activated carbon particles. The powder is rich in porous particles with fibrous morphology and also of angular-shaped particles. The Meskeat activated carbon is also characterized by the utilization of dispersive energy of spectroscopy in the Figure(3).

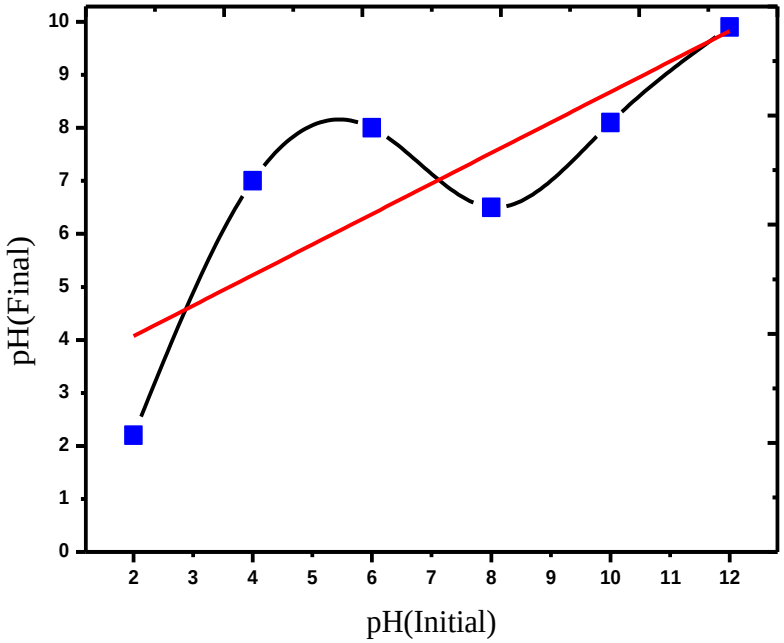



Figure (1): The pH(final) vs. pH( initial).

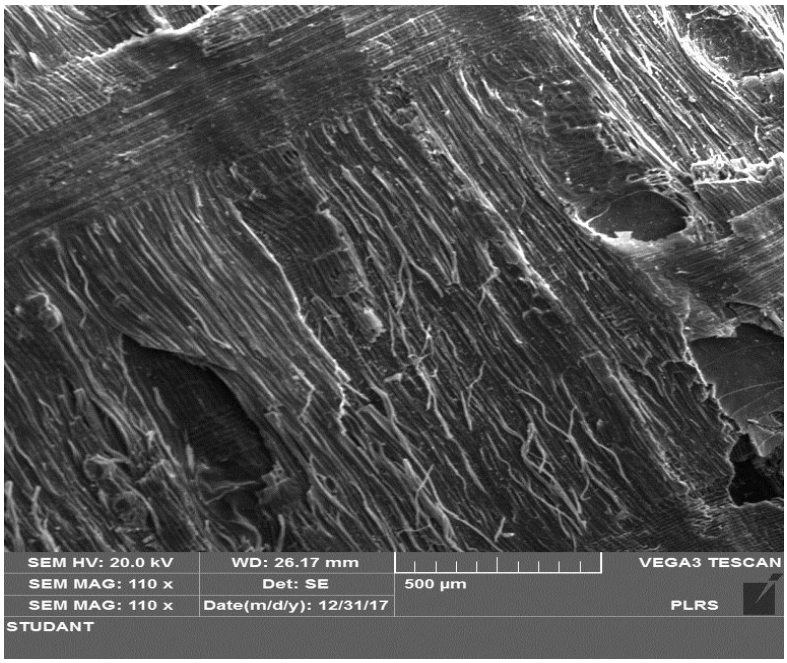



Figure (2): The SEM micrograph of the activated carbon

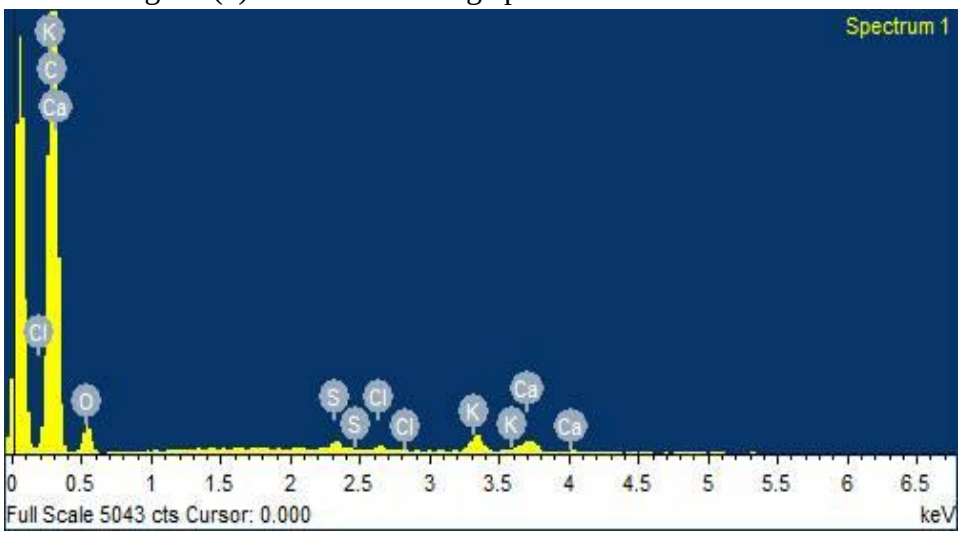
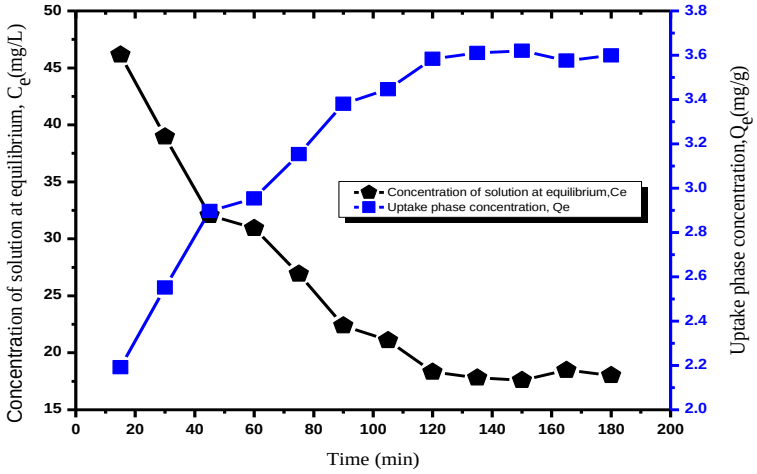



Figure (3): The dispersive energy spectrum of activated carbon spectroscopy.

**Effect of contact time:**

The amount of phenol adsorbed (mg/g) increased with increase in agitation time and reached equilibrium (Figure 4). The equilibrium time was found to be 150 min for 90 mg/L of phenol. The equilibrium time and the uptake of phenol are dependent on initial concentration. It shows that the adsorption at different concentrations was rapid in the initial stages and gradually decreased with the progress of adsorption until the equilibrium was reached. The initial rapid phase is due to the high number of vacant sites at the initial stage. As a result, there existed increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent. The curve also indicates that the adsorption led to saturation suggesting the possible monolayer coverage of phenol on the surface of adsorbent




Figure(4): Effect of contact time on the phenol adsorbed by Meskeat activated carbon

**Adsorption kinetics**

**Pseudo first-order kinetics**

Kinetic modeling of the removal of phenol by activated carbon was carried out using the well known Lagergren model(Tabak et al., 2009, Hameed, 2009) :

$$\log[q_e - q_t] = \log q_e - k_1 t/2.303 \text{.....(2)}$$

Where $q_e$ and $q_t$ are the amounts of phenol adsorbed (mg/g) at equilibrium and time $t$, respectively, and $k_1$ ($min^{-1}$) is the rate constant of the pseudo first-order adsorption operation. A plot of log $(q_e - q_t)$ versus t (Figure 5) was linear and represents the pseudo first-order kinetics for the removal of phenol using meskeat activated carbon. The first-order rate constants $k_1$ and $q_e$ were calculated for initial phenol concentrations (90 mg/L) with a constant amount of activated carbon (1g/L) (Table 1). The regression correlation coefficient was 0.858. The experimental values of $q_e$ obtained using initial phenol concentrations of 90 mg/L was 3.62 mg/g, which do not agree with the values predicted by the pseudo first-order model (Table 1).

**Pseudo second-order kinetics**

The pseudo second-order adsorption kinetic rate equation is expressed as Equation (3)(Ho and Mckay, 1998).

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \text{.....(3)}$$

Where $k_2$ is the rate constant of pseudo second-order adsorption (mg/g min). Ho and Mckay(1998) proposed

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \text{.....(4)}$$

With h (g/mg min), the initial adsorption rate, expressed by: Equation (5)

$$h = k_2 q_e^2 \text{.....(5)}$$

The plot of $(t/q_t)$ and t of Eq. (4) was linear (Figure 6), and $q_e$ and $k_2$ (Table 1) were determined from the slope and intercept, respectively. The calculated $q_e$ values agreed with the experimental values, and The regression correlation coefficient was 0.995. These results indicate that the

kinetics of phenol adsorption using activated carbon are explained better by a second-order kinetic model than a first-order one.

**Elovich kinetic equation:**

The Elovich equation is a rate equation based on the adsorption capacity, and is commonly expressed as Equation (6) (Chien and Clayton, 1980):

$$dq_t/dt = \alpha e^{-\beta q_t} \quad \text{.....(6)}$$

Where α(g/mg min) is the initial adsorption rate and β (mg/g) is the desorption constant. Equation (6) is simplified by assuming αβ>>t and by applying the boundary conditions $q_t$ = 0 at t = 0 and $q_t$ = $q_t$ at t = t, as given by: Equation (7):

$$q_t = 1/\beta \ln \beta\alpha + 1/\beta \ln t \quad \text{.....(7)}$$

The slope and intercept of the plot of $q_t$ versus ln t (Figure 7) were used to determine the kinetic constants α and β, respectively, and the regression correlation coefficients were calculated (Table 1). It is evident from Table (1). that the regression correlation coefficients for the second-order kinetic model are greater than those for the pseudo first-order and Elovich kinetic model for initial phenol concentrations. This indicates that the second-order kinetic model can be applied to the removal of phenol using meskeat activated carbon as an adsorbent.

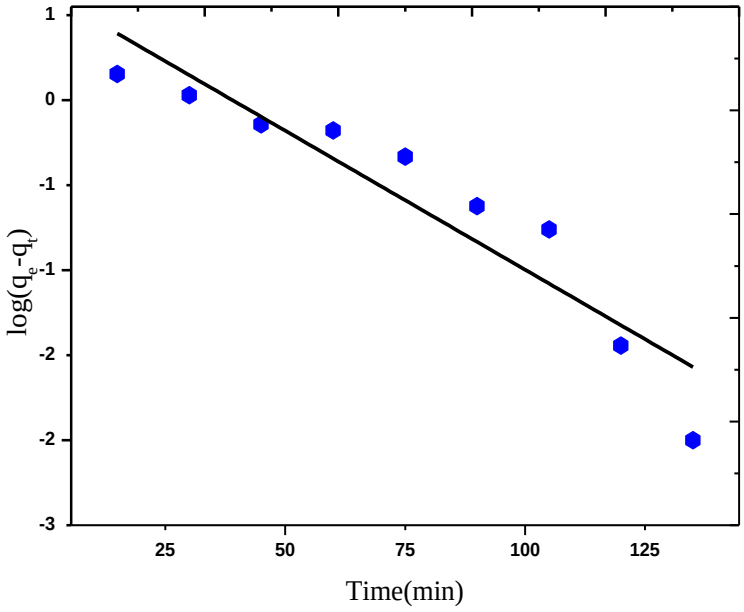



Figure (5): The pseudo First -order kinetic modeling plot.

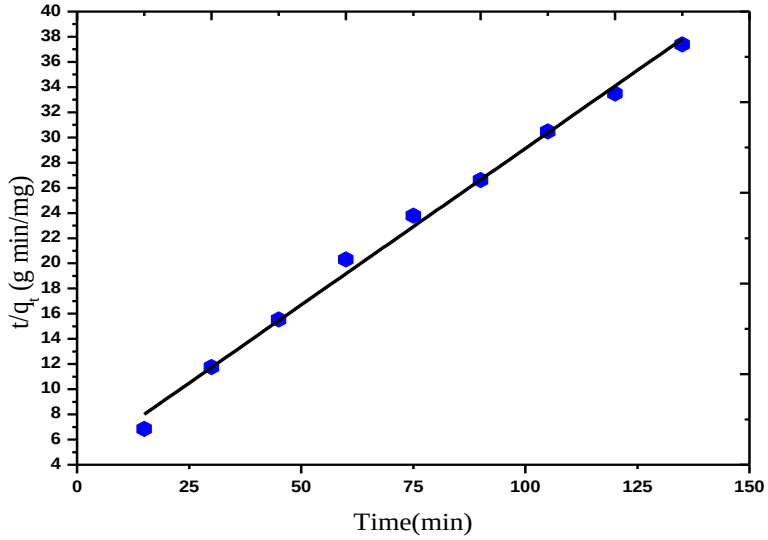



Figure (6): The pseudo second-order kinetic modeling plot.

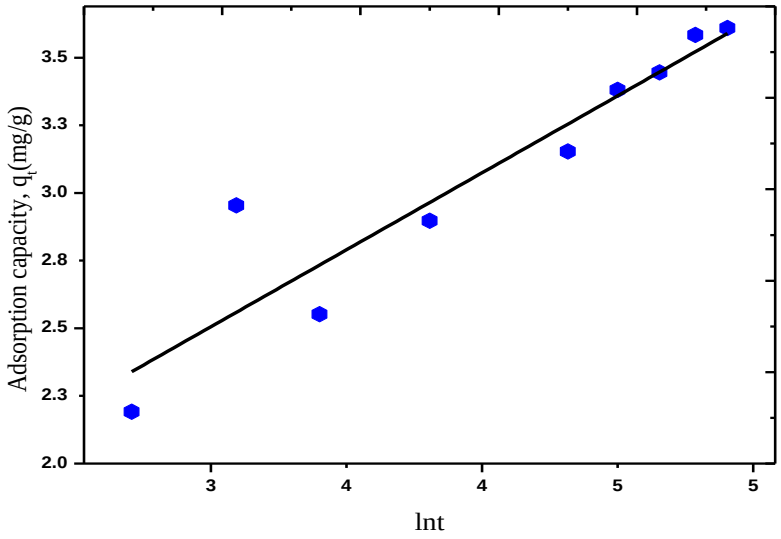



Figure (7): Elovich's plot for kinetic modeling

Table (1): Regression equations and $R^2$ values for the pseudo first-order, pseudo second-order, and Elovich rate equation plots.

| Initial Concentration | First order kinetic model | Second order kinetic model | Elovich kinetic |
|---|---|---|---|
| 90 | Y= -0.01636X+0.63878<br>$R^2$= 0.858 | Y= 0.248X+ 4.277<br>$R^2$= 0.995 | Y= 0.569X+ 0.799<br>$R^2$= 0.860 |

## Adsorption Isotherm

The equilibrium of adsorption is an important physicochemical parameter for evaluation of the adsorption process. The adsorption isotherm ($q_e$ versus $C_e$) obtained in this study showed that the adsorption capacity (mg/g) increased with increasing equilibrium phenol concentrations and eventually attained a constant value (Figure 8). To model the adsorption behavior, two adsorption isotherms were studied and

their correlation with the experimental data was assessed. These were the Freundlich and Langmuir isotherms, which are the earliest and simplest known relationships describing the adsorption equation(Muhamad et al., 1998).It is clear from Table(2) that the adsorption capacity of the commercial activated carbon used in this study far exceeded that of other activated carbons prepared from different materials

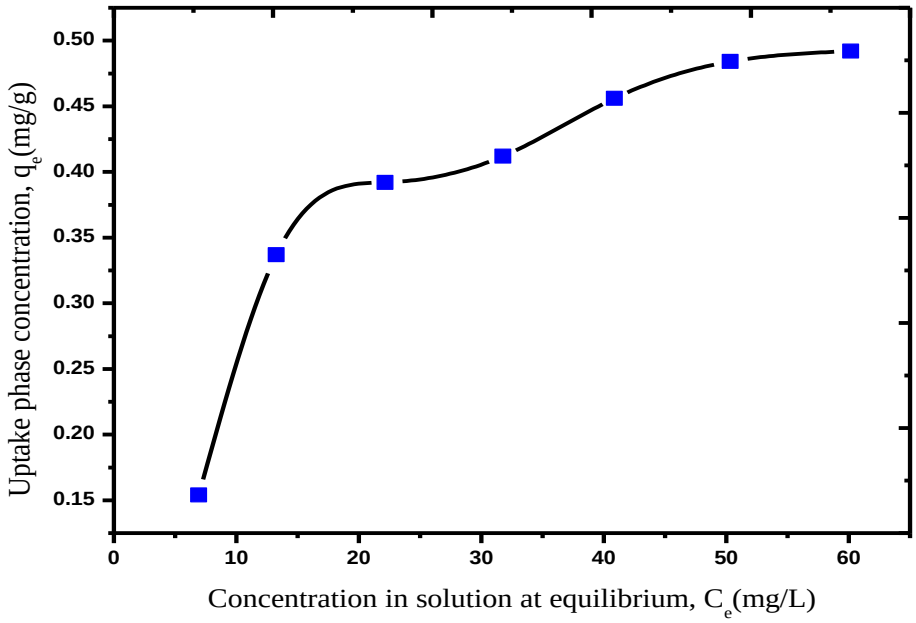



Figure (8): Adsorption isotherm of phenol .

**Langmuir isotherm:**

The linear form of the Langmuir equation is shown in Equation (8) (Ravikumar et al., 2007, Langmuir, 1916, Bulut and Aydin, 2006):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad \text{.....(8)}$$

Where b and $q_m$ are constants related to the apparent energy of adsorption and the adsorption capacity, respectively; and $q_e$ is the amount adsorbed per unit mass of the adsorbent (mg/g) with an equilibrium concentration of $C_e$ (mg/L). A plot of ($C_e/q_e$) vs. $C_e$ was linear (Figure 9) and the constants $q_m$ and b were determined from the slope and intercept of the plot (Table 2). The correlation coefficient obtained with the Langmuir equation was high ($R^2$ = 0.97), which indicated a good fit between the parameters.

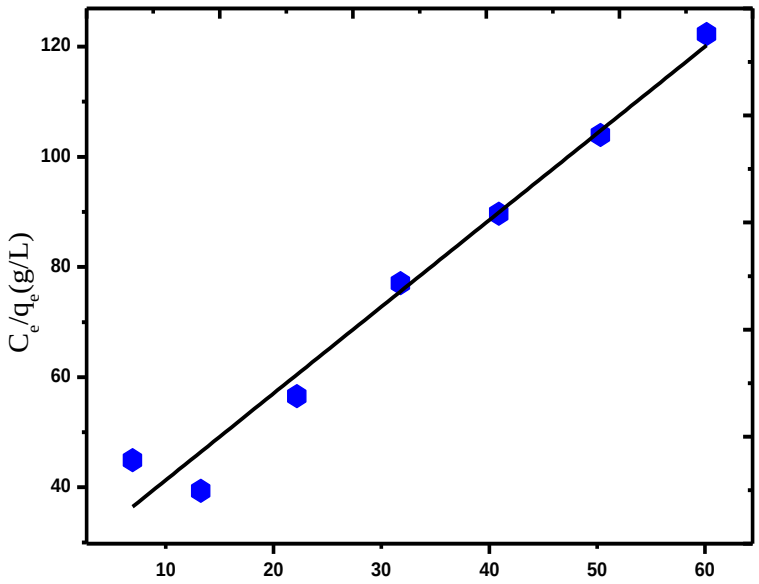



Figure (9): Linearized Langmuir isotherm.

**Freundlich isotherm:**

The Freundlich isotherm is expressed by Equation (9)(Freundlich, 1906) :

$$q_e = K_f C_e^{1/n_f} \text{.....(9)}$$

Where $K_f$ is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and $n_f$ is the heterogeneity factor representing how the absorption deviates from linearity. Values of $n_f$ less than one are an indication that significant adsorption takes place at low concentration, while high $K_f$ values indicate greater adsorption intensity. The linear form of the Freundlich isotherm is Equation (9):

$$\log q_e = \log K_f + 1/n_f \log C_e \text{.....(10)}$$

The Freundlich coefficients were determined from a plot of log $q_e$ versus log $C_e$ (Figure 10) and are given in Table (2).

The higher regression values showed that the equilibrium data for phenol fitted well to both the Langmuir and Freundlich isotherms in the studied concentration ranges. Based on the correlation coefficients ($R^2$), the equilibrium data was slightly better fitted in the Langmuir adsorption isotherm than the Freundlich equation (Table 2).

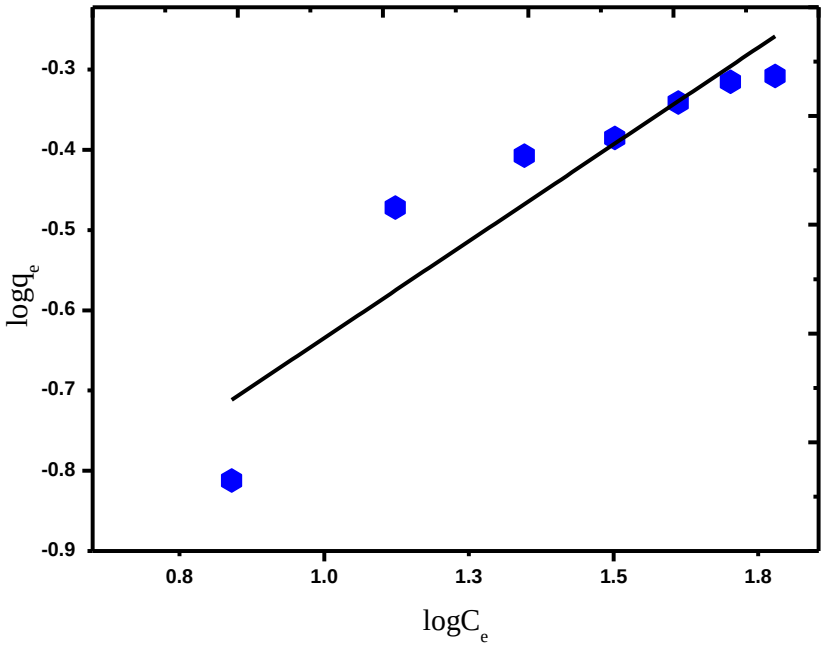


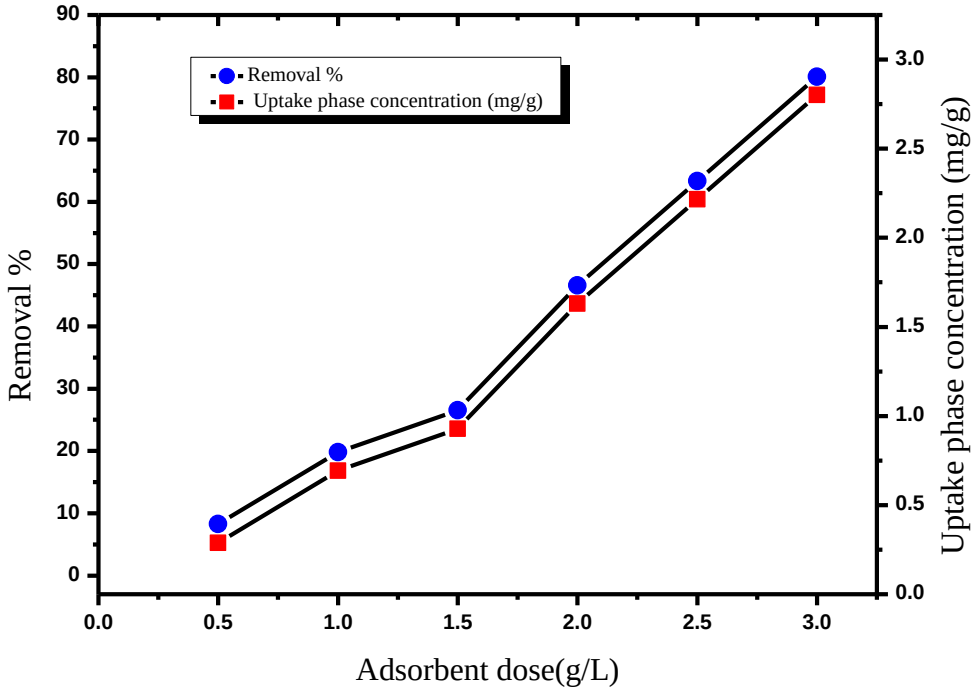

Figure (10): Linearized Freundlich isotherm.

Table (2): The Adsorption isotherm values for phenol.

| Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|
| b(l/mg) | $Q_o$ (mg/g) | $R^2$ | $k_f$ $(mg^{1-1/n}L^{1/n}/g)$ | $1/n_f$ | $R^2$ |
| 0.061 | 0.636 | 0.970 | 0.076 | 2.071 | 0.824 |

**Effect of adsorbent concentration**

The effect of adsorbent concentration on phenol removal was studied where various amounts of Meskeat activated carbon were contacted with a fixed initial phenol concentration (70 mg/L). The residual phenol was measured in the solution at equilibrium and results are shown in *(Fig. 11.)*. The percentage of adsorption increases with the increase in adsorbent concentration as the number of adsorbent particles increases and more phenol is attached to their surface.




Figure(11): The activated carbon mass effects on the equilibrium concentration and Removal % of phenol.

## CONCLUSIONS

In this work the commercial activated carbon can be successfully used for the adsorptive removal of phenolic pollutants from water. Langmuir is better representation of the equilibrium adsorption data. Kinetic studies showed that the sorption dynamics of phenols are predicted more accurately by the pseudo-second order rate model.

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