Phenol Adsorption from Aqueous Phase onto Prepared Low-cost Carbons from Natural Sources: A Comparative Study

A. Ghanadzadeh Gilani[a,*], H. Ghanadzadeh Gilani[b], P. Azmoon[b] and N. Chaibakhsh[a]

[a]Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran
[b]Department of Chemical Engineering, University of Guilan, Rasht, Iran

This study demonstrates removal of phenol from aqueous solution using the carbons prepared from the natural sources, *i.e.*, olive-pit, date-pit, and pomegranate-kernel in a batch system. For comparison purpose, the adsorption tests were also carried out on a commercial activated carbon. Influences of effective parameters such as pH, adsorbent dosage, contact time, phenol initial concentration and temperature on the removal of phenol from water were investigated. The optimum conditions for maximum adsorption were determined. In this work, the Langmuir and Freundlich models were chosen to evaluate the adsorption isotherms of phenol. The experimental isotherms showed that Freundlich isotherm fits adequately the experimental data for all adsorbents used. The adsorption data followed closely the pseudo-second-order. In addition, thermodynamic analysis was carried out for phenol adsorption. In this work, the two conventional analysis techniques, Fourier transform infrared (FTIR), and scanning electron microscopy (SEM) were used to investigate the structural and morphological properties of the adsorbents surface.

Keywords: Phenol, Natural absorbents, Activated carbon, Adsorption, Isotherm models

INTRODUCTION

Phenol (C_6H_5OH) is an important aromatic compound that has many scientific and industrial applications. Pure phenol is a white crystalline solid at room temperature and pressure that melts at 41 °C. It forms a binary azeotrope with water at 9.2 wt% of phenol [1]. It is a common raw material for manufacturing a great variety of chemical and medical products such as plastics or related materials, detergents, and drugs. It has also significant applications in the production of phenolic resins [2]. Phenol and phenolic compounds are common contaminants in wastewater generated from many industrial operations such as petroleum and petrochemical, coal conversion, pulp and paper processes [3]. Phenol is a toxic and mutagenic chemical at high concentrations and may be absorbed by the human body through the skin. It is harmful to organisms even at low concentrations [4]. Due to its industrial importance, the removal of this compound from aqueous mixture and or wastewater is an important problem. Moreover, the removal of phenol from wastewater has taken on great environmental interest.

Various methods have been developed to remove phenol from water and wastewater, including electrochemical oxidation [5], biodegradation [6], solvent extraction [7], ion exchange [8], and adsorption [9]. However, adsorption technique has been preferred due to the low cost and high sorption capacity. Therefore, recovery of phenol from water or wastewater using adsorption method, by and agricultural by-products adsorbent, is industrially and economically important [10].

Commercial activated carbon has been widely used for the adsorption process due its high surface area and porous surface leading to the high adsorption capacity. However, from economical point of view, the commercial activated carbon has disadvantage of high-cost production process

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*Corresponding author. E-mail: aggilani@guilan.ac.ir

[11]. Recently, the production of carbon or activated carbon from natural sources and agricultural by-products has taken on great economical interest in adsorption method. Many attempts have been carried out to obtain activated carbons from agricultural by-products including coconut shell [12], date pit [13], peach core [14], rattan sawdust [15] , sewage sludge [16] and soybean straw [17].

In this study, olive-pit (OP), date-pit (DP), pomegranate-kernel (PK), and commercial activated carbon (AC), for comparison purposes, were chosen as adsorbents for the removal of phenol from aqueous solutions in a batch system. Effects of the different parameters such as pH, adsorbent dosage, contact time, phenol initial concentration, and temperature on the adsorption percentage were experimentally investigated. Some adsorption isotherm models were chosen to evaluate the adsorption capacity. The phenol adsorption process was analyzed using the kinetic, thermodynamic, and spectroscopic (FT-IR) data.

EXPERIMENTAL

Materials and Apparatus

Phenol (mass fraction > 0.99) was purchased from Chem-Lab NV Belgium. The commercial activated carbon was obtained from Merck Company. Deionized water was used in all experiments. The stock solutions of phenol (1000 mg l^{-1}) were prepared by dissolving accurately weighted phenol in deionized water. The stock solutions were prepared in 500 ml volumetric flask at room temperature. The testing solutions were prepared by diluting the stock solutions to proper concentrations. The sample weighting was carried out with an AND electronic analytical balance (model HR-200) with an accuracy of ±0.0001 g.

The aqueous solutions of phenol with known compositions were placed in a round bottle flask and were agitated by a shaker at a constant speed of 150 rpm. A temperature controlled water bath shaking was used for all experiments. A digital pH meter Genway model 3505 was used for determination of pH. All experiments were performed at room temperature. The residual phenol concentration was analyzed using a Cary 100 UV-Vis double-beam spectrophotometer at room temperature at 270 nm. FTIR of adsorbent was determined using a Bruker-Alpha spectrophotometer by the KBr disk method.

Preparation of the Carbon

Collected cores of olive, date and pomegranate were first washed several times with deionized water to eliminate the impurities. The color of pits was removed by dipping in acetone (Merck) for 4 days. Then, the pits were washed well with water and dried at 110 °C for 6 h. The clean and dried samples were crushed and placed in a sealed ceramic oven individually. The pomegranate, olive, and date pits were heated to 400, 500 and 600 °C for 2 h, respectively. Prepared carbon was milled and sieved through a 30-mesh size, and were stored in a vacuum desiccator.

Experimental Procedure

The aqueous phenol solutions were prepared with known concentrations by diluting the stock solution in 50 ml volumetric flasks. The initial concentrations of phenol were in the range of 25-300 (mg l^{-1}). The test phenolic samples were investigated and the obtained experimental data were used to calculate the adsorption isotherm models. The pH of the solutions was adjusted with sodium hydroxide and hydrochloric acid. The effect of pH on phenol adsorption was performed in the various pH values of 2 to 12. The next step was addition of accurate weighing of each adsorbent in the testing solutions. The adsorbent dosage was studied in different values: 0.05, 0.2, 1, 1.5, 2, 2.5 and 3 g.

The prepared batch systems were agitated at a constant rate (150 rpm) in a temperature-controlled shaker. The contact times or stirring times were set to be 15, 30, 45, 60, 90, 120, 150, 180 min. The experimental data were then used to determine the equilibrium time, which will be used in determination of adsorption kinetic models. After the desired times (stirring times), the solid materials (adsorbent) were separated from their solutions with filter paper and centrifuge. The final concentration of each solution was spectrophotometrically determined.

The adsorption capacity of phenol q (mg of adsorbate/g of adsorbent) was calculated using the following equation [18]:

$$q = \frac{(C_o - C_e)V}{m} \tag{1}$$

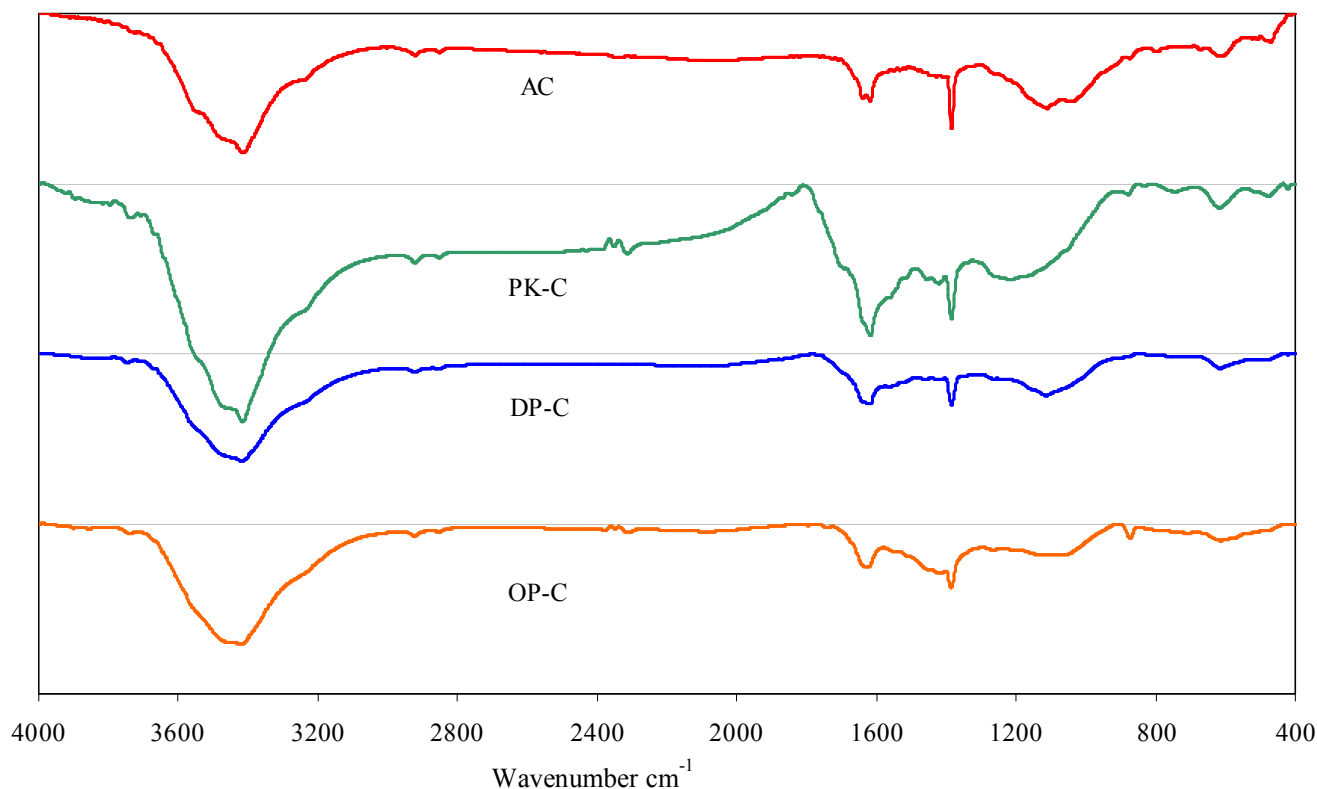where V is the volume of the solution in terms of L, C_0 the

Fig. 1. FTIR spectra of the studied absorbents.

initial concentration (mg l^{-1}), C_e the equilibrium concentration (mg l^{-1}), and m is the weight of the adsorbent (g). The phenol removal percentage was calculated by [19]:

$$Removal\% = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

Characterization Result

In this work, Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM) were used to characterize the adsorbents (olive-pit, date-pit, pomegranate-kernel carbons and commercial activated carbon).

FTIR. In order to obtain a qualitative analysis of the main functional groups that are involved in the adsorption process, the FTIR transmission spectra of the samples were

recorded on a Bruker-Alpha spectrophotometer using the KBr disk technique. The FTIR spectra of the adsorbents are compared and shown in Fig. 1.

As it can be seen from the figure, the broad band at around 3400 cm^{-1} can be attributed to the stretching vibrations of the surface hydroxyl groups or the adsorbed water. The band observed at around 1630 cm^{-1} corresponds to the C=C stretching vibration in the aromatic ring. This band also could be attributed to the H-O-H stretching vibration of absorbed water. The observed weak band at 2920 cm^{-1} is assigned to the C-H stretching mode, originated from the surface. The oxygen-containing functional groups can provide numerous adsorption sites, and therefore, increase the adsorption capacity for phenol molecules [20].

SEM. In this work, scanning electron microscopy (SEM) imaging was used to characterize the surface morphology of the adsorbents. The pore structures of OP-C,

DP-C, PK-C, and AC are shown in Fig. 2a-h, respectively. The images were recorded at different magnifications in order to visualize the overall sample and the morphology of the carbon. It can be seen from the micrographs that the surface of the adsorbents is approximately rough and are relatively organized with pores of different sizes and shapes. Fig. 2 (g and h) indicates that the external surface of the AC is heterogeneous with porous structure that giving large surface areas. The images captured from AC surface confirm the high porosity of AC particles and shows different pore structures compared with the other adsorbents surface. From the SEM images, it can be seen that DP-C is highly porous and its morphology is more similar to the commercial AC compared to OP-C and PK-C. Thus, DP-C might be expected to show a higher efficiency in phenol removal. The porosity of OP-C is lower than that of the other adsorbents.

Effect of pH on the Adsorption Equilibrium

If one accepts the existence of different forms of phenol (molecular and ionic forms) in aqueous acidic and alkaline solutions, it may have a strong influence on the adsorption properties of phenol [21]. Therefore, effect of pH on the adsorption of phenol with a fixed phenol concentration of 100 mg l^{-1} was evaluated at different pH values in the range of 2-12 in room temperature.

As can be seen from Fig. 3, for the OP-AC, DP-AC and PK-AC, the phenol amount adsorbed decreases as the pH increases. The highest adsorption percentage was observed at a pH of 2 over the pH range of 2-12. Bohli *et al.* [22] investigated phenol adsorption from aqueous solutions by activated carbon prepared from olive stones. The results showed that the phenol adsorption percentage was decreased by increasing the pH. They were found that the pH$_{pzc}$ of olive stone activated carbon was equal to 3 confirming this trend of adsorption process.

The variation of phenol adsorption on AC in the various pH ranges is not significant. However, the maximum adsorption percentage was found at pH = 5. It is due to this fact that the molecular form of phenol was favorable for the adsorption. Phenol has a pK$_a$ value of 9.99, hence, it exists totally in its molecular form in acidic solutions. Therefore, the adsorption of molecular phenol on the positively charged surface of carbon adsorbent can be attributed to

several interactions such as electrostatic interaction, London dispersion interaction, and π-π interaction between aromatic structures of phenol and the carbon surface [23].

In alkaline medium, *i.e.*, in the presence of OH$^-$, phenol is in its ionic form, thus, the ionic phenol adsorption is reduced by electrostatic repulsion between phenolate anions (C$_6$H$_5$O$^-$) and negatively charged carbon surface [24]. Therefore, based on the experimental results, the optimum pH value for further experiments on OP-C, DP-C and PK-C was selected 2. The optimal condition for AC was obtained in pH value of 5.

Effect of Adsorbent Dosage

In order to investigate the influence of adsorbent dosage on the phenol adsorption, a range of adsorbent amounts (0.05−3 g) were stirred with water for 2 h with initial phenol concentration of 100 mg l^{-1}. The effect of adsorbent dosage on the adsorption percentage and adsorption capacity of phenol is shown in Figs. 4a and b, respectively. It was found that the adsorption percentage increases with an increase in adsorbent concentration. This is expected, as increasing the adsorbent concentration has provided more available adsorption sites for the removal phenol at a fixed phenol initial concentration [25]. Nevertheless, when the adsorbent dosage increased, the adsorption capacity (the amount adsorbed per unit mass of adsorbent) decreased. The decrease in adsorption capacity with increasing the adsorbent dosage is mainly due to the adsorption sites remaining unsaturated during the adsorption reaction.

From Fig. 4, it was also found that with 0.05 g adsorbent dosage, percentages of phenol adsorption on OP-C and PK-C were 10.92% and 31.89%, respectively. However, the percentage reached about 92% when OP-C and PK-C dosages were increased to the 1.5 g and 2.5 g, respectively. Therefore, the experimental runs were carried out with these optimum adsorbent dosages of OP-C and PK-C. As can be seen in Fig. 4, the phenol adsorption on AC increases about 6.85% with the increase in adsorbent dosage up to 0.5 g. The adsorption percentage changes just 1.26% when adsorbent dosage increases from 0.5 to 1 g. As it can be seen from the figure, the phenol adsorption remains approximately unchanged with the further increase of AC dosages, thus, increasing the adsorbent is not economical. Similar result was also reported by Özkaya [11], which the
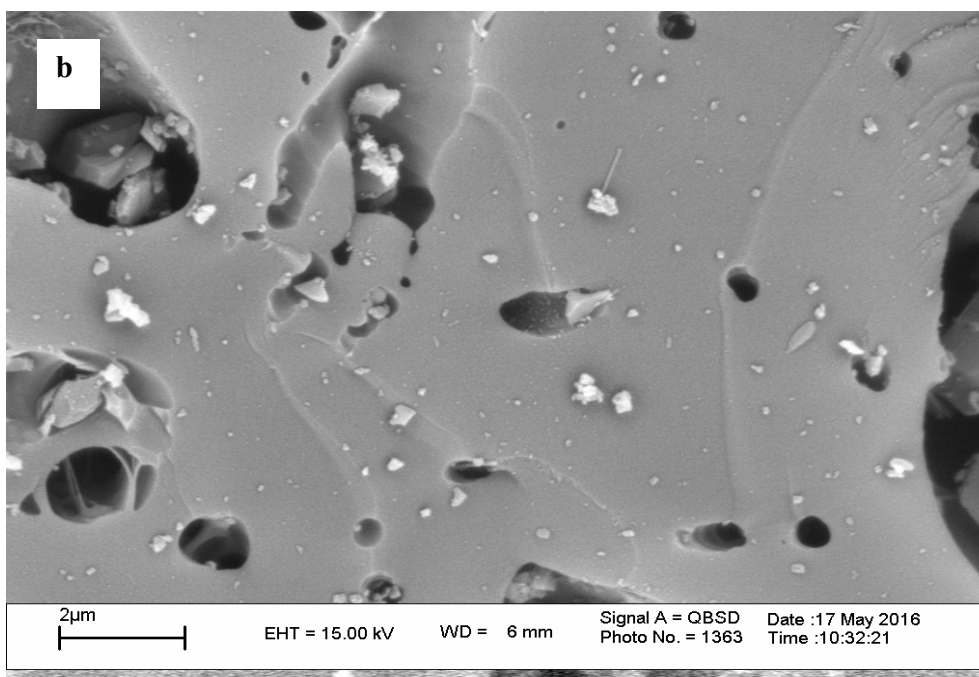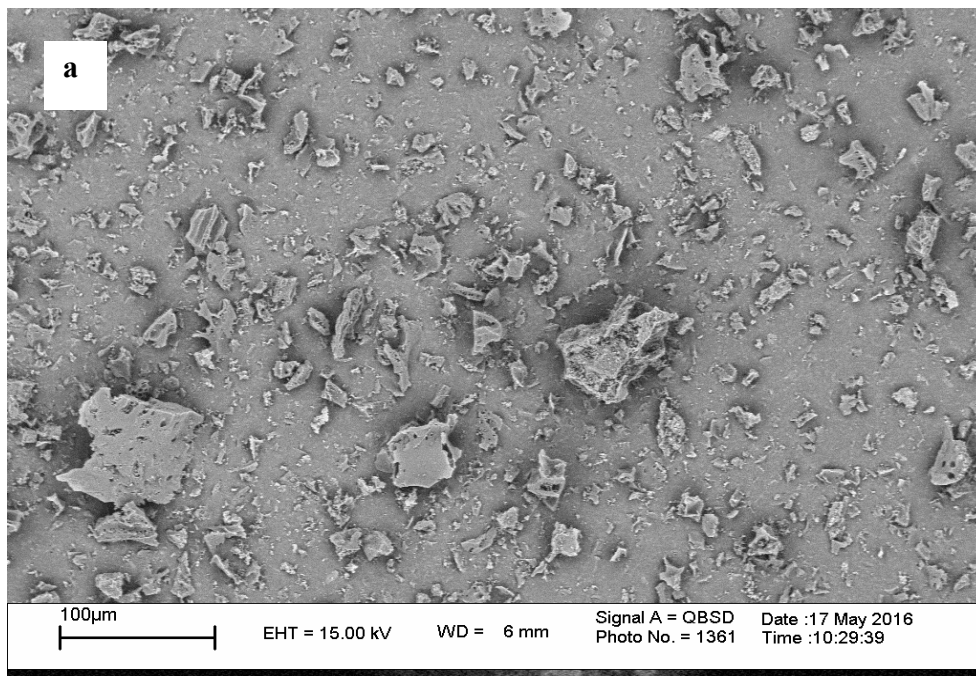
Fig. 2. SEM images of the carbons produced from (a, b) olive-pit, (c, d) date-pit, (e, f) pomegranate-kernel, and (g, h) the commercial activated carbon at the two different magnifications.
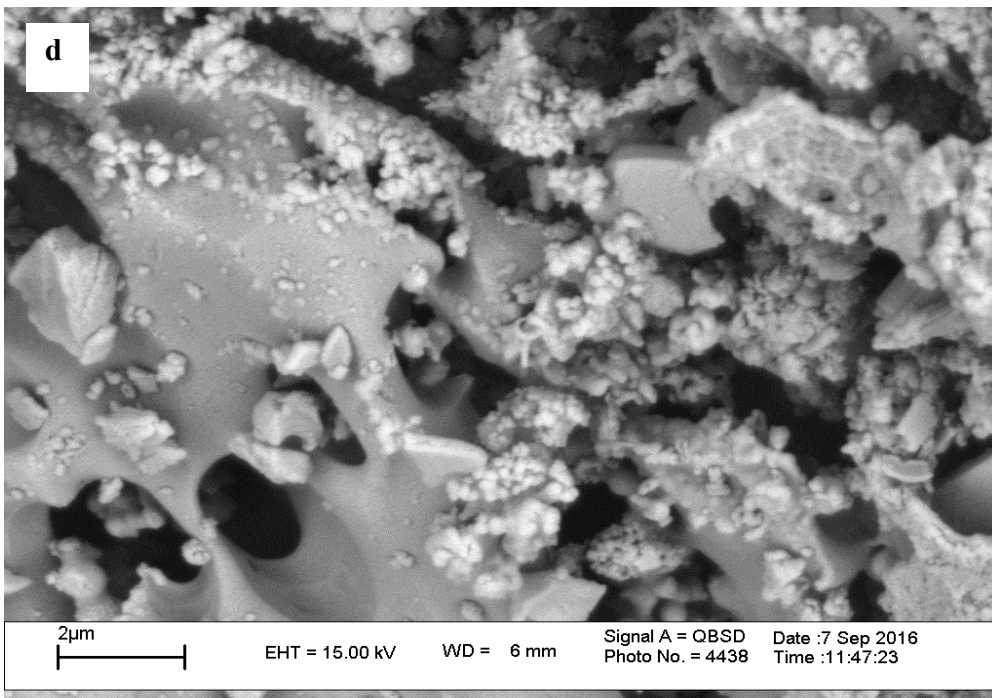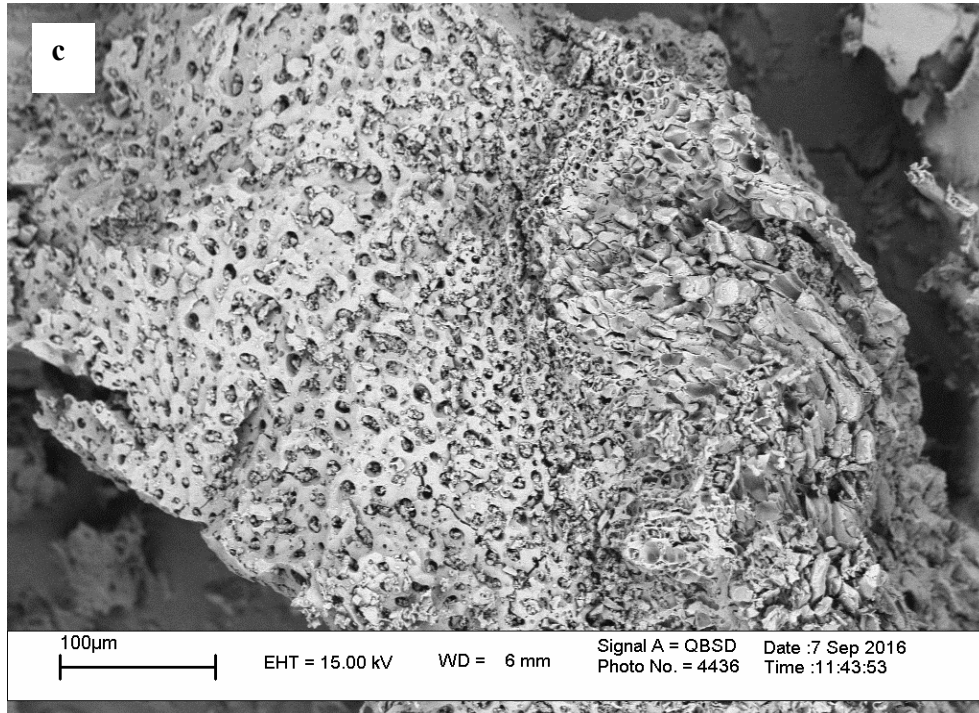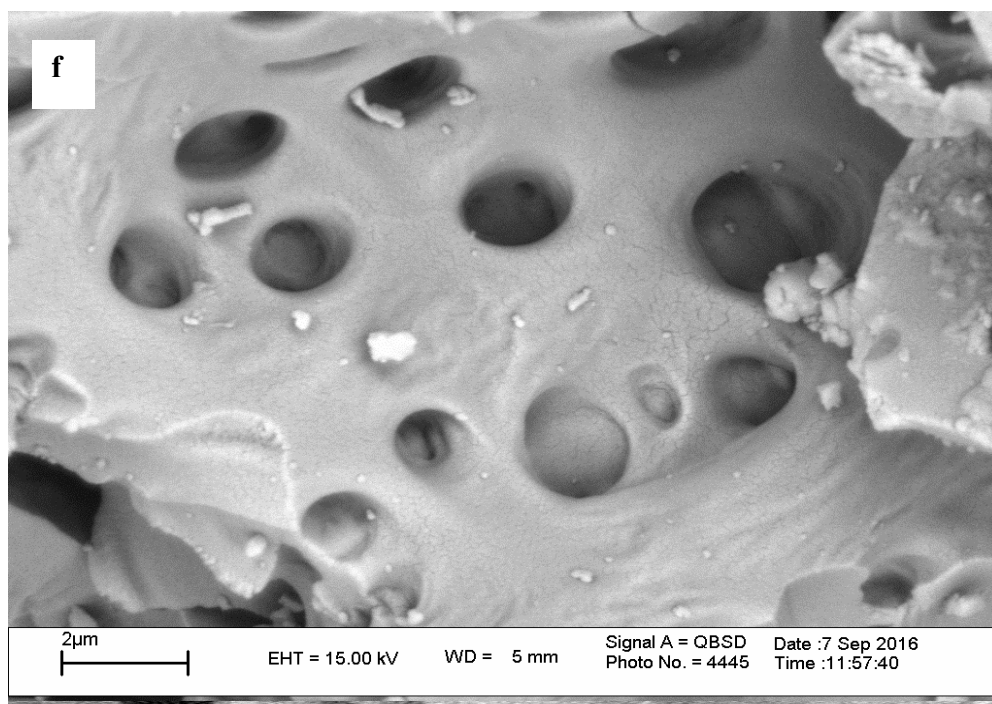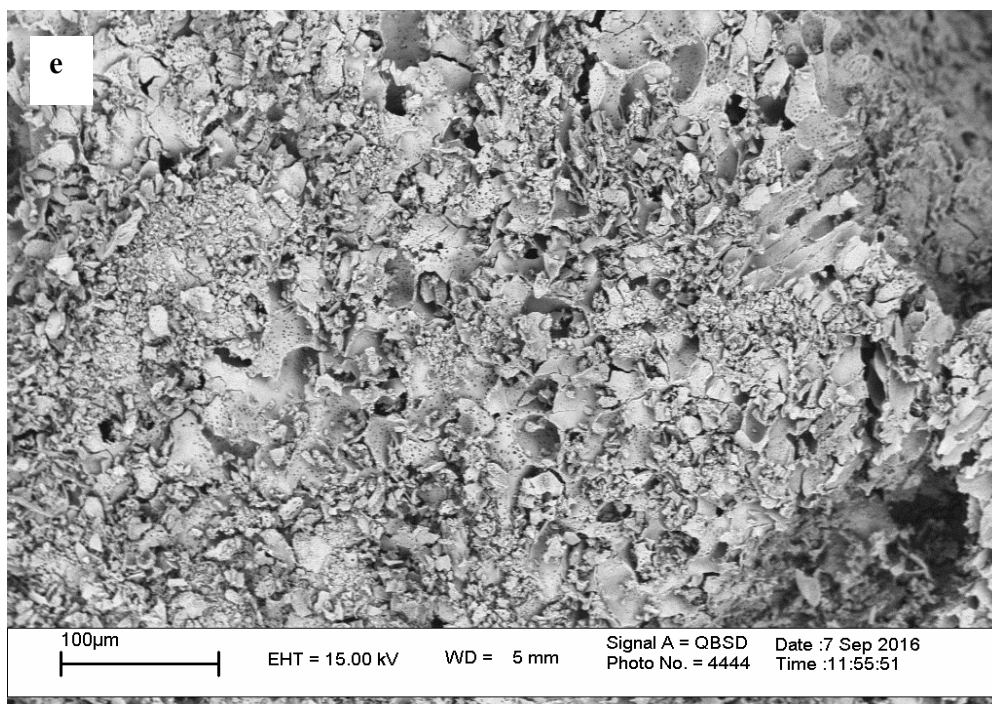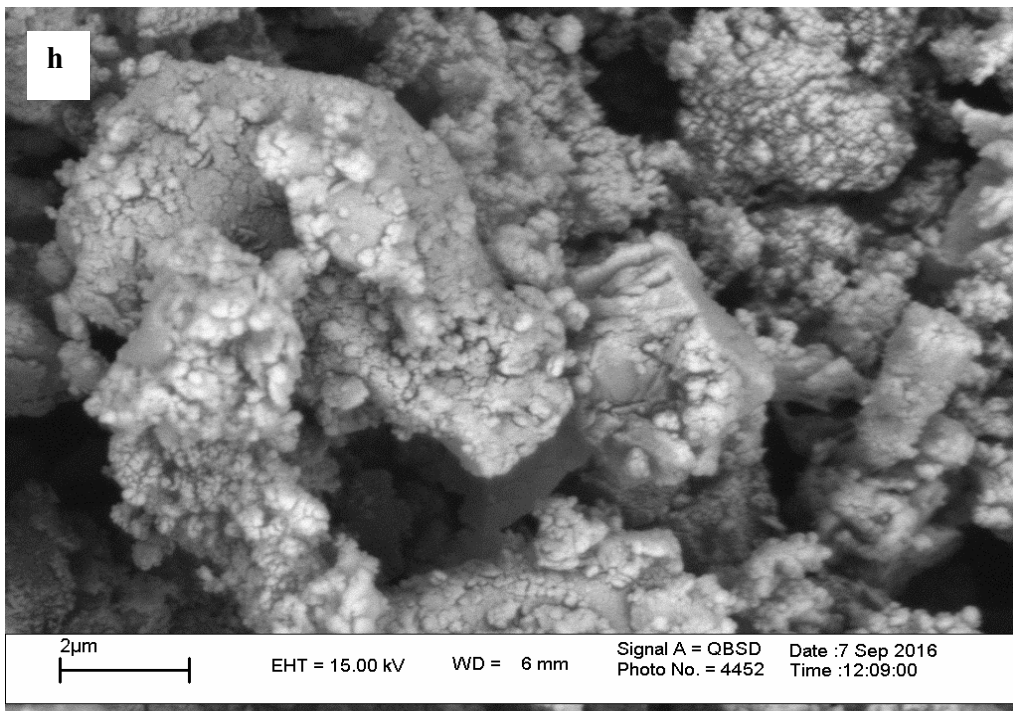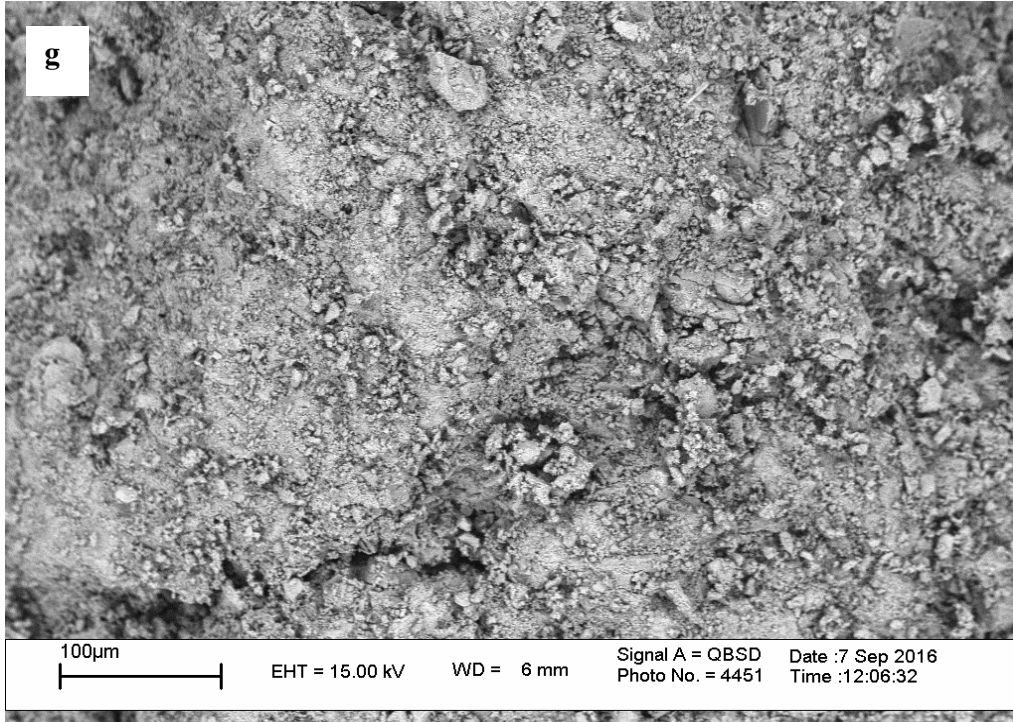
Fig. 2. Continued.

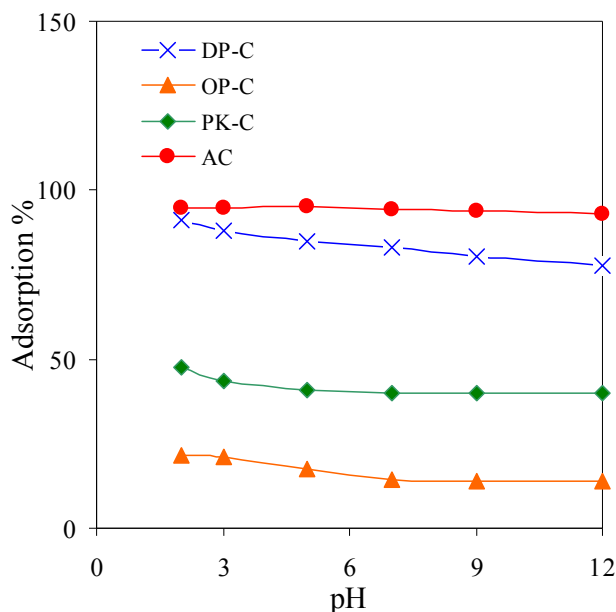**Fig. 2.** Continued.

Fig. 2. Continued.

Fig. 3. Effect of pH on the adsorption percentage of phenol on olive-pit (OP-C), date pit (DP-C), pomegranate-kernel (PK-C) carbons, and commercial activated carbon (AC).

optimum dosage of carbon for phenol removal was obtained 0.5 g. The similar trend was also observed for DP-C. Thus, 0.5 g of date-pit carbon was selected as the optimum adsorbent dosage for phenol adsorption.

Effect of Contact Time

The effect of contact time on the removal of phenol (initial concentration 100 mg l^{-1}) was investigated. Figure 5 shows a sharp increase of phenol adsorption at first, and then the adsorption reached the equilibrium for all types of adsorbents. The time required to attain the equilibrium and the amount of phenol adsorbed at this state reflected the maximum phenol adsorption capacity of the adsorbent under these particular conditions. Therefore, the optimum contact time for OP-C and AC was obtained 90 min and for the DP-C and PK-C were found to be 60 and 90 min, respectively. A similar trend has been reported for the effect of contact time on phenol removal 3, 26.

For comparison purpose, the effect of contact time on the phenol removal using the different absorbents was demonstrated for the same range of starting and ending time points. As it was previously mentioned, the porosity of DP-C is higher than that of PK-C and OP-C, therefore, its

removal efficiency is higher.

As shown in Fig. 5, the different behaviors of phenol onto PK-AC prior to about 30 min might be due to the higher external surface porosity of PK-C respect to OP-C, which hence the initial diffusion rate in the first 30 min of the reaction might be higher for PK-C. However, due to the data fluctuation caused by the experimental error, the interpretation should be performed by care.

The Kinetic Models

The kinetics of phenol adsorption was investigated with the pseudo-first-order and pseudo-second order models. The pseudo-first-order equation of Lagergren [27] is given in linear form by:

$$ln(q_e - q_t) = \ln q_e - (k_1 \times t) \tag{3}$$

where q_t and q_e are the amounts of phenol adsorbed at t and equilibrium time (mg g^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The slope and intercept of plots of ln(q_e - q_t) vs. t determine the k_1 + and q_e, respectively (Fig. 6a).

The pseudo-second-order equation [28] is given by:
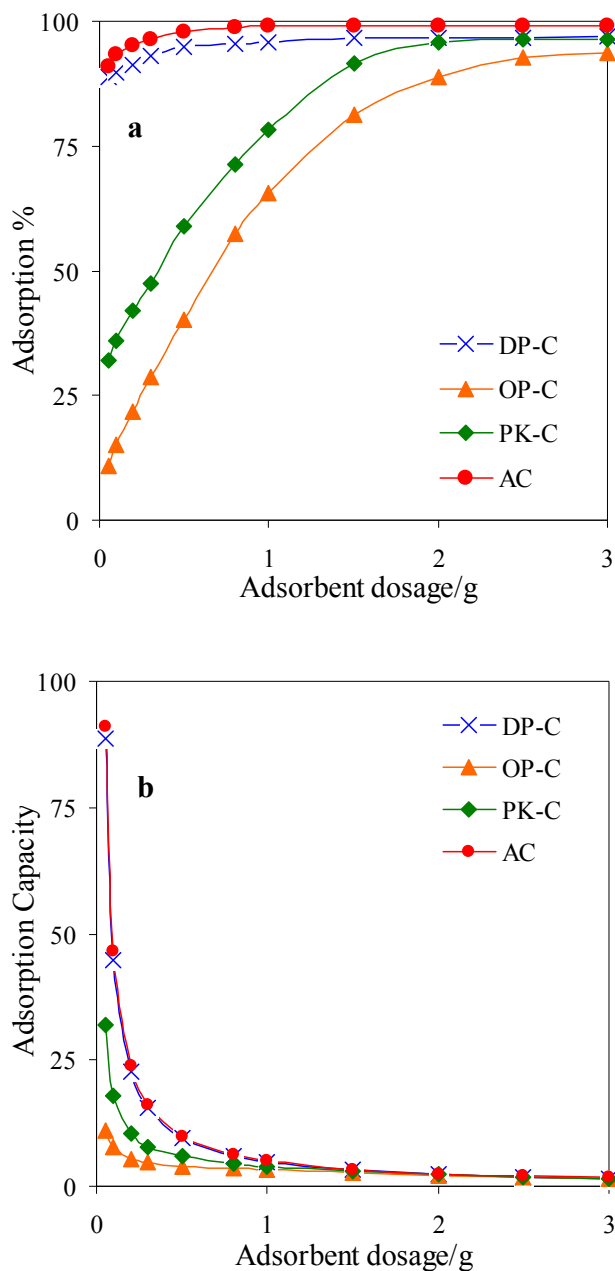
Fig. 4. Effect of adsorbent dosage on the (a) adsorption percent, and (b) adsorption capacity of phenol on
OP-AC, DP-AC, PK-AC, and AC.

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (4)$$

where k_2 is the pseudo-second-order process rate constant (g
mg^{-1} min^{-1}). k_2 and q_e can be calculated from the slope and
intercept of the plot of t/q_t *vs. t*, respectively (Fig. 6b). The

calculated kinetic parameters and correlation coefficients
for these models are listed in Table 1. Figures 6a and 6b
compare the kinetic models with the experimental data
using pseudo-first-order and pseudo-second-order
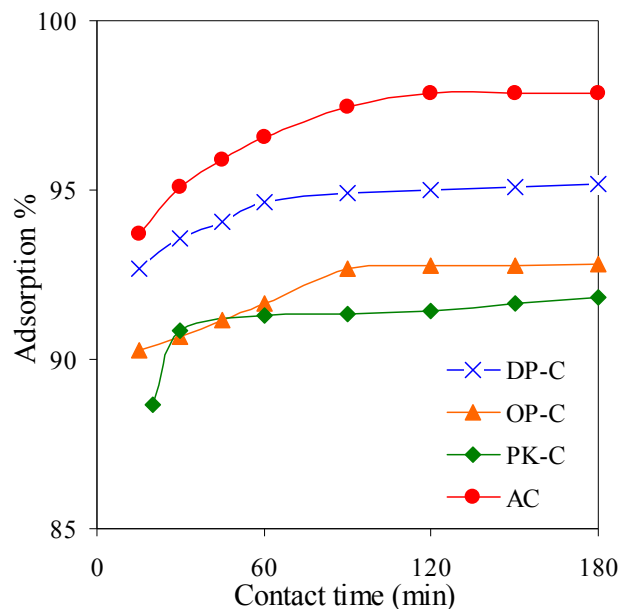equations, respectively. As can be seen from Table 1, the

Fig. 5. Effect of contact time on the adsorption percentage of phenol on OP-C, DP-C, PK-C and AC.

Table 1. Kinetic Constants for Phenol Adsorption onto OP-C, DP-C, PK-C and AC

Adsorbent	Experimental	Pseudo-first-order			Pseudo-second-order		
	q_e	q_e	K_1	R^2	q_e	k_2	R^2
OP-AC	1.853	0.067	0.0193	0.9762	1.865	0.671	1.000
DP-AC	9.46	0.373	0.0425	0.9994	9.54	0.192	1.000
PK-AC	3.025	0.207	0.0199	0.9986	3.07	0.463	1.000
AC	9.75	0.621	0.0315	0.9948	9.84	0.1026	1.000

pseudo-first-order model has high correlation coefficient values. The correlation coefficients (R^2) for this model are higher than 0.97 for OP-C and higher than 0.99 for another adsorbents.

It can be seen that the correlation coefficients of the pseudo-second order model are also high and equal to unity for all ACs. Although, there is no major difference in R^2 values of the models, the calculated values of the adsorption capacity (q_e) for pseudo-first-order model are very low compared with those of the experimental values, which is not an acceptable result. It can be concluded that the

pseudo-first-order model is not a suitable model for describing the kinetics of the adsorption systems. On the other hand, the pseudo-second order model has the advantage of the close q_e values of the experimental and calculated data.

As a result, it can be calculated that the kinetic of phenol adsorption on OP-C, DP-C, PK-C and AC follows the pseudo-second order model. The same shape of kinetic was found by Bohli *et al.* [22] that studied the adsorption of phenol using an activated carbon from olive stones. This confirms that the kinetic of phenol adsorption onto OP-AC
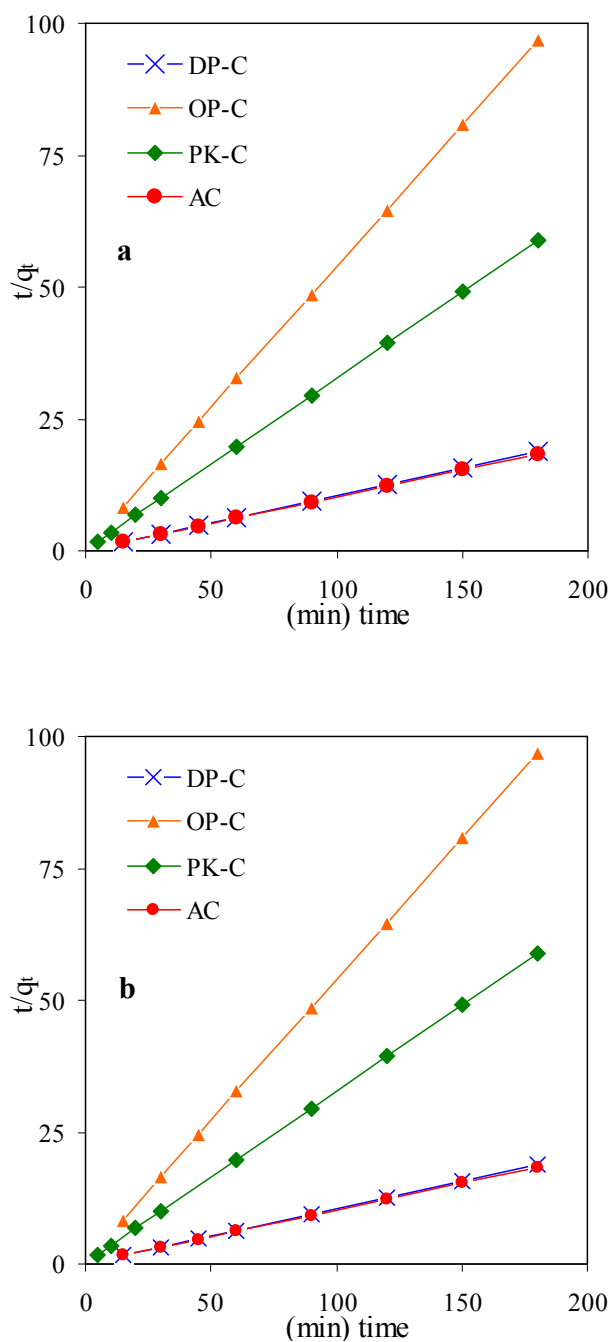
Fig. 6. (a) Pseudo-first-order and (b) pseudo-second-order model plots for adsorption of phenol on OP-C, DP-C, PK-C and AC.

was following a pseudo-second-order model.

Effect of Initial Phenol Concentration

Following the addition of an optimum amount of

adsorbent, solutions of phenol with different initial concentrations (25-300 mg l⁻¹) were prepared by dilution of appropriate volume of stock solutions into 100 ml volumetric flasks. The flasks were shaken on a shaker with
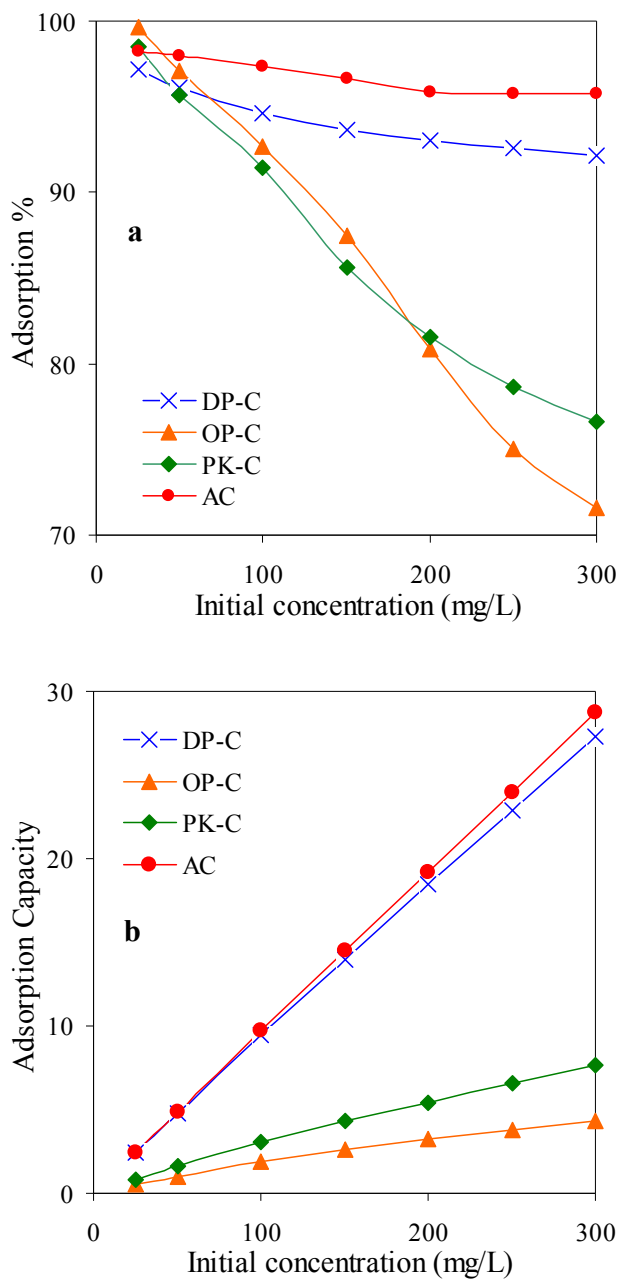
Fig. 7. Effect of initial concentration on the (a) adsorption percentage and (b) adsorption capacity of phenol on OP-C, DP-C, PK-C and AC.

a constant rate at 150 rpm for the time needed to reach equilibrium. Then, the samples were filtered and the phenol concentration was determined. This process was performed at atmospheric pressure and temperature.

As can be seen from Figs. 7a and b, when initial phenol concentration increases, adsorption or removal percentage decreases, which are in agreement with the study of Dakhil [29]. It is due to the fact that at a fixed adsorbent dosage, the

active sites are constant, while the phenol concentration increases. Conversely, the adsorption capacity increases because the driving force for phenol adsorption between the aqueous and solid phases increases [29]. As seen from Fig. 7, all the adsorption systems (including OP-C, DP-C, PK-C, and AC) show similar trend.

Isotherm Models

In this study, two well-known adsorption isotherms, namely Langmuir and Freundlich models were chosen to evaluate the adsorption of phenol on OP-C, DP-C, PK-C and AC. According to Langmuir isotherm model the homogeneous and monolayer adsorption of molecules occurred on the surface. In addition, the tendency of active sites for adsorption should be equal. The linearized form of Langmuir model can be written as follows [30]:

$$C_e / q_e = 1 / b_L q_{max} + C_e / q_{max} \qquad (5)$$

Where q_e and q_{max} are monolayer adsorption capacity and maximum monolayer adsorption capacity of adsorbent, respectively, b_t is the Langmuir constant. Isotherm parameters for this model can be calculated from the slope and intercept of the linear plot of C_e / q_e *vs.* C_e.

The Langmuir isotherm is shown in Fig. 8a. The Langmuir equation might be expressed by dimensionless constant called "separation factor" (R_t), which is defined as $R_t = 1/(1 + b_t C_0)$ [31]. The value of R_t indicates the type of isotherm. For irreversible adsorption $R_t = 0$, favorable adsorption $0 < R_t < 1$, and linear adsorption $R_t = 1$. However, R_t values greater than unity indicates unfavorable adsorption [32].

The Freundlich isotherm as well as Langmuir model is the most widely used isotherm to analyze the adsorption data. The logarithmic linear form of the Freundlich equation is given according to the following equation [33]:

$$\log q_e = \log k_f + (1/n_f) \log C_e \qquad (6)$$

where K_f and n_f are the Freundlich adsorption constants. K_f indicates the capacity of the adsorbent and n_f is a measure of the deviation from linearity of the adsorption [34]. The Freundlich constants (K_f and n_f) can be obtained using the

linear plot of $\log q_e$ *vs.* $\log C_e$. The results of the Freundlich isotherm analysis are illustrated in Fig. 8b.

The calculated Langmuir and Freundlich isotherm parameters are summarized in Table 2. As seen in this table, the phenol uptake by all the absorbents is favorable. As can be observed, the correlation coefficient (R^2) value of the Freundlich model is better than that of the Langmuir model. For all the adsorption systems the $1/n_f$ values are between 0 and 1, this indicates that the adsorption process is favorable. Also, the results show that the $1/n_f$ values for the DP-C and AC are more close to unity indicating that the adsorbents surfaces are more homogeneous [35].

Effect of Temperature

Effect of temperature on the adsorption of phenol was studied in different temperatures of 295.2, 308.2, 318.2 and 328.2 K. As shown in Fig. 9, increasing the temperature leads to decrease in the adsorption percentage of phenol. It means that the phenol adsorption is an exothermic process. The maximum adsorption was observed at 293.2 K, indicating that phenol uptake was favored at lower temperatures. This is in agreement with the results found in some other studies performed by Li *et al.* [36], Zhu *et al.* [37], and Ocampo-Perez *et al.* [38]. This effect can be due to the weakening of the adsorptive forces between the active sites on the adsorbent and the phenol species. This result implies that the adsorption process of phenol is favored at lower temperatures.

Thermodynamic Parameters

Thermodynamic functions such as standard Gibbs free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$) can be calculated using the following equations [39]:

$$\Delta G^o = -RT \ln K_c \qquad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (8)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and K_c is the equilibrium constant as the following equation [40]:

$$K_c = C_{Ae} / C_e \qquad (9)$$
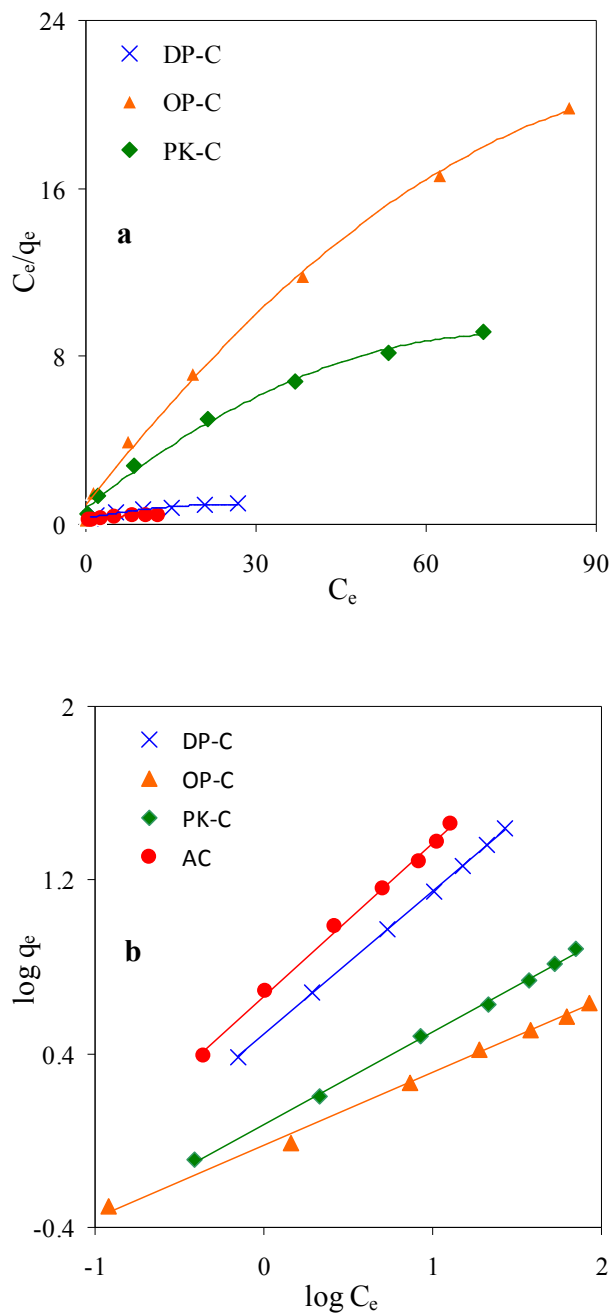
Fig. 8. (a) Plots of the Langmuir and (b) the Freundlich models for adsorption of phenol on OP-C, DP-C, PK-C and AC.

here C_{Ae} and C_e are the phenol equilibrium concentration on the adsorbent and in the solution, respectively. A plot of $\Delta G°$ *vs.* T (Fig. 10) should be linear with a slope equal $\Delta S°$

and with an intercept equal $\Delta H°$. The calculated values of adsorption thermodynamic parameters are presented in Table 3. The standard Gibbs free energy change $\Delta G°$ of

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Table 2. Constants and Correlation Coefficients of Langmuir and Freundlich Models for Phenol Adsorption onto OP-C, DP-C, PK-C and AC

Adsorbent	Langmuir				Freundlich		
	q_{max} (mg g^{-1})	b_L (l mg^{-1})	R^2	R_L	K_f	$1/n_f$	R^2
OP-AC	4.39	0.128	0.975	0.238	0.987	0.323	0.993
DP-AC	39.37	0.067	0.920	0.374	3.09	0.661	0.999
PK-AC	8.16	0.085	0.947	0.320	1.195	0.281	0.999
AC	44.25	0.113	0.916	0.262	4.620	0.705	0.997

Table 3. Thermodynamic Parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) and the Equilibrium Constants (K_c) for the Phenol Adsorption on the Different Adsorbents (OP-C, DP-C, PK-C and AC) at Different Temperatures

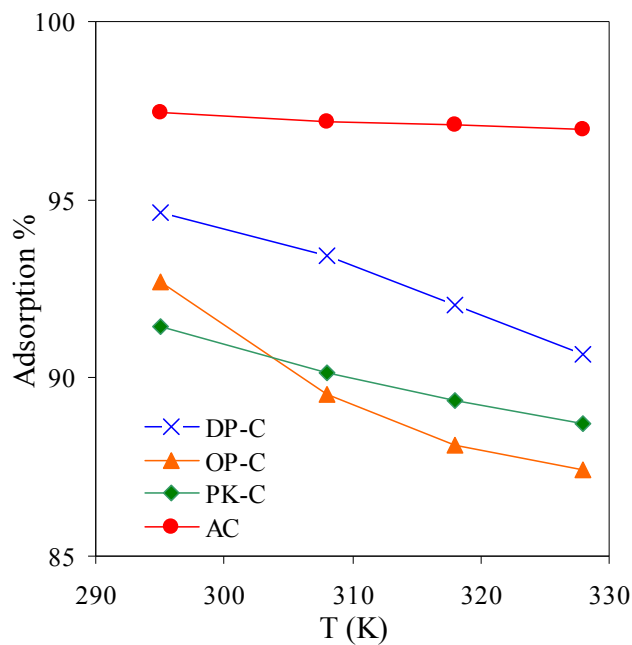| Adsorbent	T (K)	K_c	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1})
OP-C	295.2	12.64	-6.227		
	308.2	8.56	-5.502	-14.47	-28.5
	318.2	7.42	-5.304		
	328.2	6.95	-5.290		
DP-C	295.2	17.62	-7.042		
	308.2	14.2	-6.798	-14.69	-0.0258
	318.2	11.56	-6.476		
	328.2	9.72	-6.205		
PK-C	295.2	10.7	-5.816		
	308.2	9.16	-5.676	-7.44	-5.6
	318.2	8.39	-5.627		
	328.2	7.87	-5.635		
AC	295.2	38.37	-0.3834		
	308.2	34.46	-0.252	-4.29	0.0157
	318.2	33.48	-0.2167		
	328.2	32.22	-0.2006		

Fig. 9. Effect of temperature on the adsorption percentage of phenol onto OP-C, DP-C, PK-C, and AC.
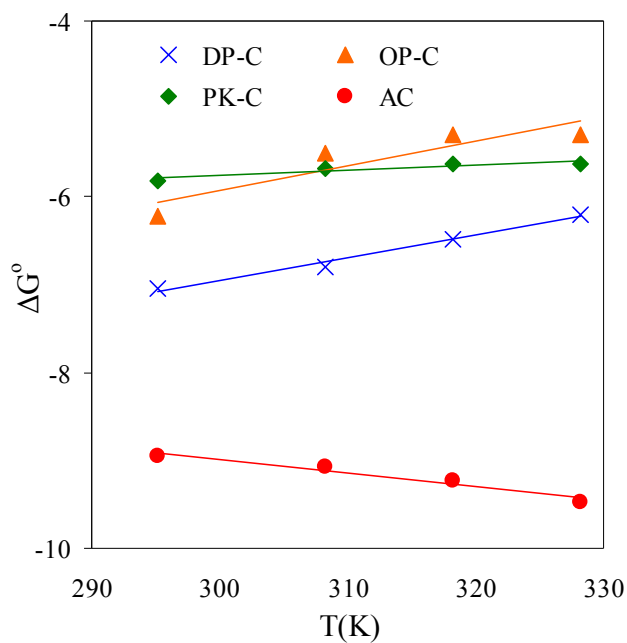

Fig. 10. Variation of the standard free Gibbs energy *vs*. temperature for OP-C, DP-C, PK-C, and AC.

adsorption was negative at all investigated temperatures. The negative values of $\Delta G°$ confirmed that the adsorption of phenol onto OP-C, DP-C, PK-C and AC was thermodynamically possible and spontaneous.

Note that for physical adsorption $\Delta G°$ is between 0 to -20 kJ mol^{-1}, and for chemical adsorption it is in the range of -80 to -400 kJ mol^{-1} [41]. The absolute values of $\Delta H°$ in the range of 2.1-20.9 could be due to the physical adsorption and in the range of 80 to 200 kJ mol^{-1} for the chemical adsorption [41]. As seen from Table 3, the absolute values of $\Delta H°$ are in the range of 2.1-20.9. The Gibbs free energy changes for all the adsorbents were in the range of 0 to -20 kJ mol^{-1} indicating that the phenol adsorption is physical. The negative values of $\Delta H°$ indicate that the phenol adsorption is exothermic in nature.

The positive value of $\Delta S°$, for phenol adsorption on the AC, confirms the increased randomness at the adsorbent-solution interface during the adsorption process [42]. In contrast, the negative value of entropy changes for OP-C, DP-C and PK-C suggests the decreased randomness at the interface during the adsorption process. Similar results were also found by Jain *et al.* [40] and Liu *et al.* [41].

CONCLUSIONS

The effectiveness of carbons prepared from olive-pits, date-pits and pomegranate-kernel for the removal of phenol from aqueous solution was evaluated and compared with that of commercial activated carbon. The optimum pH for the maximum phenol adsorption onto produced carbons and commercial activated carbon was obtained 2 and 5, respectively. The optimum adsorbent dosages were observed at the amount of 2.5 g and 1.5 g for OP-C, PK-C, respectively, and 0.5 g for DP-C and AC. The kinetics and equilibrium data for the adsorption of phenol were obtained and fitted to the two types of kinetic and isotherm models. The experimental data were fitted to a pseudo second-order model well and the equilibrium data followed the Freundlich isotherm. Thermodynamic studies demonstrate that the phenol adsorption is spontaneous and exothermic, and the adsorption process is physical in nature. It was found that among the produced adsorbents, the carbon from date-pit has higher efficiency than that of the other adsorbents. The present study concludes that olive-pit, date-

pit and pomegranate-kernel carbons prepared under these conditions can be used effectively for the removal of phenol from aqueous solutions because of low-cost and locally available adsorbents.

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