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Adsorptive Removal of Phenol by Coffee Residue Activated Carbon and Commercial Activated Carbon: Equilibrium, Kinetics, and Thermodynamics

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Carbons were prepared from coffee residue using chemical activation with $ZnCl_2$. Among five carbons prepared by varying the activating agent ratio (mass of $ZnCl_2$/mass of coffee residue) from 0 % to 100 %, the one with an activation ratio equal to 25 % (AC 25 %) was the most effective sorbent showing the maximum phenol uptake (68 %). Consequently, all the adsorption experiments were achieved with the carbon having an activation ratio equal to 25 %. A comparative study of prepared activated carbon (AC 25 %) and a commercial activated carbon (CAC) was undertaken to determine their capacities for phenol removal. For each adsorbent−phenol system, a pseudosecond-order kinetic model described the adsorption kinetics accurately at all concentrations and temperatures for the two systems. The thermodynamics of the phenol−CAC and phenol−AC 25 % systems indicate an exothermic process. Phenol adsorption isotherms onto the prepared and commercial activated carbons have been studied. They display two plateaus. The degree of coverage of the surface of two carbons by the phenol molecules was calculated, and it was revealed that the second plateau, appearing at high concentrations, is assigned to the desorption of water molecules fixed on the surface oxygen groups of the activated carbons and the occupation of these sites by phenol molecules in excess in the treated solutions. The Langmuir, Freundlich, and Elovich models were tested.

Introduction

Wastewater loaded by phenol presents a serious discharge problem due to its poor biodegradability, high toxicity, and other environmental aspects.[1] As a derivative of benzene, phenol is a product of chemical and allied industries such as petrochemicals, oil refineries, paint, pesticides, and pharmaceutical. Several methods for the treatment of phenolic wastewater have been proposed in the literature. There are physicochemical treatment processes, chemical oxidation and biological degradation. Among the physicochemical methods are adsorption and ion exchange. According to Srivastava for high strength, low volume phenolic wastewaters, phenol elimination by adsorption using granular/powdered activated carbon has been widely used. Nevertheless, the high cost of activated carbon is considered a disadvantage.[2] This problem has led to the search for cheaper carbonaceous substitutes to activated carbon such as lignocellulosic materials. Several wastes and agricultural residues such as nutshells, wood, plum kernels, date pits, and so on have been used as starting materials to produce activated carbon.[3] In this study, an agricultural low-cost byproduct, coffee residue activated carbon, was used as an adsorbent. It is an available waste since many domestic activities generate a large quantity of coffee residue. Algeria annually consumes between (100 000 and 110 000) tons of coffee, and all of these quantities end up in the form of coffee grounds in discharges. This could be recovered and used to produce activated carbon with good physical and chemical characteristics and at low cost; it is an alternative route for the exploitation of this waste. Coffee residue chemically activated with $ZnCl_2$ and H_3PO_4 has been used for removing phenol and its derivatives.[4]

The adsorption performance of an activated carbon from aqueous solution is affected by both surface physicochemical properties and solution characteristics. The presence of surface functional groups such as carboxylic, lactone, phenol, carbonyl, ether, pyrone, and chromene assigns to the activated carbon an acid−base nature.[5]

Phenol is a model compound which is largely used to test numerous carbons. It is reported from the literature that this molecule can be adsorbed on different orientations, and then, different sorption areas exist depending on its orientation on the surface of the solid.[6]

It is very important to know the adsorption isotherm corresponding to the studied system since it is an essential piece of information to understanding an adsorption process and the description of the isotherms can be based on models.[7]

The aim of this paper is multiple. Preparation of activated carbon from coffee residue was the first objective. The second was to characterize and then test the prepared activated carbon (AC 25 %) by submitting it for the adsorption of phenol and compare its efficiency with a commercial activated carbon (CAC).

Materials and Experimental Section

Materials. The precursor used is coffee residue which was collected from coffee houses and households. All the used chemicals were of analytical reagent grade. Zinc chloride and phenol of purities 95 % and 99.5 %, respectively, were obtained from BIOCHEM Chemopharm. Nitrogen gas was industrial grade of 99 % purity.

A stock phenolic solution was prepared by dissolving 5 g of phenol in 1000 mL of distilled water. Working standard solutions of initial concentrations ranging between (10 and 170) $mg \cdot L^{-1}$ were prepared by progressive dilution of the stock phenolic solution. The pH of the tested solutions was adjusted to the required value with 2 N H_2SO_4 or 1 N NaOH solutions before the experiments.

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Adsorbent Preparation. To obtain an activated carbon, the precursor underwent several treatments as follows: the waste was washed to remove any impurities and dried. The residue was chemicaly activated using $ZnCl_2$ in different activating ratios: 0 %, 25 %, 50 %, 75 %, and 100 %. The reagent was dissolved in 500 mL of hot water (85 °C) and then mixed with 400 g of coffee residue. The mixture was put in the oven at 85 °C for 7 h to facilitate the hydratation of the precursor and the swelling of the interior channels of lignocellulosic structure allowing for a better access of the $ZnCl_2$ into the interior of the particles. The temperature was raised to 110 °C, and the mixture was kept for 24 h at this temperature to cause complete evaporation of the water which will further force the incorporation of $ZnCl_2$ to the interior of the particles.

The carbonization was realized under the flow of nitrogen, and the resulting carbon was treated with HCl solution (10 % by mass) to eliminate residual zinc from the pores of the carbons followed by washing with hot distilled water (65 °C) to remove the acidity of the carbon and chlorides. The washing operation was stopped when the conductivity of the washing water reached the conductivity value of the distilled water used. The activated carbon resulting was dried and then ground.

Characterization of Activated Carbons. Activated Carbons Texture Characterization. The textural heterogeneity of the prepared and commercial carbons was characterized by N_2 adsorption−desorption isotherm measurements at the liquid nitrogen temperature (77 K) using a Quantachrome Novawin2 Analyzer to determine the specific surface area and pore volume of the samples. The surface areas (S_{BET}) were calculated by the BET method assuming that the surface area occupied by a nitrogen molecule was 0.162 nm^2. The total pore volumes were estimated on the basis of the liquid volume of nitrogen adsorbed at a relative pressure of 0.98. The microporous volumes (pores < 2 nm)[9] were calculated by two methods: V_{mic}(DR) was determined according to the Dubinin−Radushkevich equation (D−R plots)[8,9] and (S_{micro}) by a *t*-plot method. The external surface area (S_{ext}) was also obtained by the *t*-plot method. The microporous surface area (S_{micro}) was calculated by subtracting the external surface area from the BET surface area.[8,9] The mesoporous volumes (V_{mes}) were obtained by deducing the microporous volumes from the total pore volumes.

Evaluation of Surface Chemistry. Activated carbon (AC) samples (200 mg) were immersed in 250 mL Erlenmeyer flasks containing 50 mL of NaOH and HCl solutions at a concentration of 0.1 N. The glass vessel containing the solution and the sample was sealed and then shaken for 48 h at 150 rpm. Then, after filtration of the solutions, excess base and acid of the filtered solutions (10 mL) were titrated with HCl and NaOH, respectively. The number of acidic sites (acidic functions) and the number of basic sites (basic functions) were calculated from the amount of HCl and NaOH consumed by the titration, respectively.[10]

pH Point of Zero Charge (pH_{PZC}) Measurements. The point of zero charge of the activated carbon was determined by using the method reported by Rivera-Utrilla et al.[11]

The point of zero charge was determined from an acid−base titration. Aliquots with 50 mL of 0.01 M NaCl solution were prepared in different flasks. Their pH was adjusted with addition of 0.01 M solutions of NaOH or HCl. When the pH value was constant, 0.15 g of carbon sample was added to each flask that was then shaken for 24 h. Blank tests were also made without sample to eliminate the influence of CO_2 on pH. The pH_{pzc} value is the point where the curve pH_{final} vs $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$.

Infrared Spectroscopy. The nature of surface groups on the activated carbons was studied by IR analysis. Fourier transform infrared transmission spectra of carbon samples were obtained using the potassium bromide technique[5] on an FTIR spectrometer over the wavenumber range of (4000 to 400) cm^{-1}. Carbon powder was mixed with potassium bromide at a ratio of roughly 1/1000.

Morphology of Activated Carbons. The activated carbons were analyzed by using a scanning electron microscope to study their morphologies.

Phenol Adsorption. Kinetic Study. To determine the time required for reaching the adsorption equilibrium, batch experiments were conducted in a 5 L glass vessel. This was submerged in a water bath controlled at a predetermined constant temperature (precision: ± 0.1 °C). When the temperature of the adsorbate solution (1 L) was stabilized at a desired level, 0.5 g of activated carbon was left in contact with agitated phenol solution (stirring speed: 160 rpm). This was considered as the initial time for the kinetic experiment. Small volume liquid samples were withdrawn at different time intervals. Samples were filtered through glass filter paper to remove adsorbent particles. The filtrates were analyzed for residual phenol concentration using a UV−visible spectrophotometer (model JENWAY 6305 UV/vis.) at 270 nm.

The adsorption uptake of phenol at equilibrium q_e ($mg \cdot g^{-1}$) was calculated using the following relationship

$$q_e = \frac{(C_0 - C_e)}{m}V \tag{1}$$

where C_0 is the initial phenol concentration ($mg \cdot L^{-1}$); C_e is the equilibrium phenol concentration ($mg \cdot L^{-1}$); V is the volume of the solution (L); and m is the mass of the adsorbent (g).

Adsorption Isotherms and Modeling. The adsorption capacity of an adsorbent is important information which can be provided by an equilibrium study. An adsorption isotherm is characterized by constant values which express the surface properties and affinity of the adsorbent. This type of adsorption isotherm is generally fit to the Langmuir, Freundlich, and Elovich models. The first model is valid for monolayer adsorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. It is expressed as follows[7]

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

where q_m and b are Langmuir parameters related to the maximum adsorption capacity and bonding energy of adsorption, respectively.

The precedent equation can be linearized as shown in the following[7]

$$C_e/q_e = \left(\frac{1}{q_m}\right)C_e + \frac{1}{bq_m} \tag{3}$$

where b and q_m are calculated by plotting C_e/q_e versus C_e.

The Freundlich model is based on adsorption onto a heterogeneous surface suggesting that binding sites are not equivalent. It is characterized by the following equation[7]

$$q_e = K_F C_e^{1/n} \tag{4}$$

Table 1. Physicochemical Characteristics of Carbons—Phenol Adsorption Tests onto Prepared Carbons ($C_0 = 30$ mg·L^{-1}, $T = 25$ °C, pH =3, and 1 g of Carbon/L of Solution)

carbon	phenol removal (%)	microporosity ($V_{\mathrm{micro}}/V_{\mathrm{tot}}$)/%	acidic function/ basic function
nonactivated (0 %)	42.00	75.14	10.75
AC 25 %	67.86	95.70	1.94
AC 50 %	59.28	92.33	2.46
AC 75 %	57.81	81.55	3.79
AC 100 %	57.80	70.04	11.19

where K_F and n are Freundlich parameters indicating the adsorption capacity and the adsorption intensity, respectively. They were determined by plotting ln q_e versus ln C_e which is given as follows

$$\ln q_e = \ln K_F + (1/n)\ln(C_e) \tag{5}$$

The Elovich model is based on an increase of the adsorption sites exponentially with the adsorption process indicating multilayer adsorption. It is expressed by the following equation[7]

$$q_e/q_m = (K_E C_e)\exp(-q_e/q_m) \tag{6}$$

where K_E is the Elovich equilibrium constant (L·mg^{-1}) and q_m is the Elovich maximum adsorption capacity (mg·g^{-1}).

$$\ln(q_e/C_e) = \ln(K_E q_m) - (q_e/q_m) \tag{7}$$

The experimental values of q_e and C_e are treated with the previous models to establish the equation parameters, and the isotherms are reconstituted using the determined values.

The better criterion to find the best model for the experimental data for isotherm adsorption modeling is a parameter known as the normalized percent deviation (average percentage error) which is expressed as

$$\text{APE}\ (\%) = \left(\frac{100}{N}\right)\sum\left(\frac{I q_t^{\mathrm{exp}} - q_t^{\mathrm{pred}} I}{q_t^{\mathrm{exp}}}\right) \tag{8}$$

where q_t^{exp} is the experimental adsorption amount of the studied substance at any time t; q_t^{pred} are the values corresponding to predicted q_t according to the equation under study with best fitted parameters; and N is the number of data points: the lower the value of APE, the better the fit.

Results and Discussion

Effect of the Activating Ratio. The efficiency of the prepared carbons has been tested by subjecting them to adsorption of molecules of phenol with $C_0 = 30$ mg·L^{-1} at pH =3, at $T = 25$ °C, and in the presence of 1 g of carbon. The results are reported in Table 1.

These values show that the activated carbon prepared with an activation ratio of 25 % is the most successful compared to the other carbons, which can be explained by the presence of a large microporosity (95.69 %) in addition to the smaller ratio of the numbers of acidic to basic groups (ratio = 1.94). This result is in agreement with those of Koganovski et al.[18] who reported that the adsorption of phenol at low equilibrium concentrations on an activated carbon not only depends on the pore volume of the activated carbon but also on the ratio of the numbers of acidic to basic groups. The larger this ratio is, the lower the adsorption.[18]

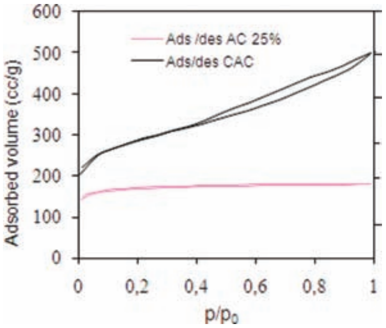

Figure 1. Adsorption and desorption isotherms of nitrogen at 77 K for prepared (AC 25 %) and commercial (CAC) activated carbons.

Consequently, the activated carbon prepared with an activation ratio of 25 % was used in all subsequent experiments. It will be designated as AC 25 %.

Characterization of the Activated Carbons. Activated Carbon Texture Characterization. Figure 1 shows the N_2 adsorption−desorption isotherms of the prepared (AC 25 %) and the commercial (CAC) activated carbons. According to the IUPAC classification, carbon prepared with a $ZnCl_2$/coffee residue ratio equal to 25 % exhibited steep type I. It is a characteristic of microporous solids.[9,12] The commercial carbon isotherm exhibited steep type IV with a hysteresis loop of type H_4, indicating the highly narrow pore size distribution microporous materials with slit-like or plate-like pores.

The porous structure parameters for CAC and AC 25 % obtained by applying the BET equation to nitrogen adsorption at 77 K, the Dubinin−Radushkevich equation (D−R plots), and the t-plot equation are listed in Table 2. The parameters concerning the nonactivated carbon and the prepared carbons with different ratios [(25, 50, 75, and 100) %] are reported in the previous study.[13]

It appears that the activated carbons include micropores and mesopores, but the percentage of micropores is greater than that of the mesopores according to the results given in Table 2; so, they are principally microporous carbons.

Surface Chemistry Determination. Table 3 presents the amounts of acidic and basic and the ratio of the numbers of acidic to basic groups. It can be observed that the prepared activated carbon has acidic character contrary to the commercial one. These results are confirmed by the obtained $\mathrm{pH_{pzc}}$ values.

FTIR Analysis. The FTIR spectra of the prepared carbons with different ratios [(25, 50, 75, and 100) %] are given in the previous study.[13] In Figure 2, we present both CAC and AC 25 % FTIR spectra. They display the following bands:

- 3370 cm^{-1} is the OH group of the phenol function.[14]
- The absorption bands observed in the area (3100 to 3600) cm^{-1} correspond to the vibration of hydroxyls fixed on the surface of carbon and water chemisorbed on carbon.[15]
- 2906 cm^{-1} and 2847 cm^{-1} correspond to stretching C−H groups, and they represent aliphatic, olefinic, and aromatic structures. The first one could correspond to bands of CH_2− groups while the second one to $-O-CH_3$ or two bands of aldehyde groups.
- 1556 cm^{-1}: C═O stretch of the carbonyl group in a quinone as well as representing γ-pyrone structure with strong vibrations from a combination of C═O and C═C.[14]
- 1424 cm^{-1}: C−O stretch or O−H deformation in carboxylic acids.[16]

Table 2. Porous Structure Parameters of the Activated Carbons[a]

	$V_{0.99}$	V_{micro}(DR)	microporosity	V_{mes}	S_{BET}	S_{ext}	S_{micro}	dp = $4V_{\text{tot}}/S_{\text{BET}}$
carbons	$\text{cm}^3\cdot\text{g}^{-1}$	$\text{cm}^3\cdot\text{g}^{-1}$	$V_{\text{micro}}/V_{0.98}$ (%)	$\text{cm}^3\cdot\text{g}^{-1}$	$\text{m}^2\cdot\text{g}^{-1}$	$\text{m}^2\cdot\text{g}^{-1}$	$\text{m}^2\cdot\text{g}^{-1}$	nm
AC 25 %	0.28	0.27	95.70	0.01	520	5.64	514.06	2.15
CAC	0.77	0.43	56	0.34	921	148	733	3.36

[a] $V_{0.99}$, total volume; V_{mic}(DR), microporous volume; V_{mes}, mesoporous volume; S_{BET}, BET surface; S_{ext}, nonmicroporous surface; S_{mic}, microporous surface; dp, average pore diameter.

Table 3. Surface Groups of Activated Carbons and pH_{pzc} Values

	carboxylic	carbonylic	phenolic	lactonic	acidic functions	basic functions		
carbon	$\text{mmol}\cdot\text{g}^{-1}$	$\text{mmol}\cdot\text{g}^{-1}$	$\text{mmol}\cdot\text{g}^{-1}$	$\text{mmol}\cdot\text{g}^{-1}$	$\text{mmol}\cdot\text{g}^{-1}$	$\text{mmol}\cdot\text{g}^{-1}$	acidic func/basic func	pH_{pzc}
AC 25 %	1.00	0.70	0.60	1.00	3.3	1.7	1.94	4.47
CAC	0.15	0.3	0.15	0.17	0.77	1.67	0.46	7

- The absorption around (1000 to 1350) cm^{-1} could be related to the existence of the C−O single bond in carboxylic acids, alcohols, phenols, and esters.[17]

The spectra of the prepared activated carbon (AC 25 %) and the commercial carbon (CAC) display practically the same functional groups. The difference is in the intensity of the peaks. The presence of hydroxyl groups of phenolic and carboxylic character causes acidic surface properties, whereas carbonyl and quinone groups bring about surface basicity. Hence, all the carbons exhibit both acidic and basic surface functional groups.

Morphology of Activated Carbons. The analysis of microstructures of all prepared activated carbons is also given in a previous study,[13] which presents scanning electron micrographs for different activating ratios.

Figure 3 represents the obtained micrographs of the morphology of both AC 25 % and CAC. Both the carbons contain different sizes and shapes of pores, but it can be noticed that the porous structure (size of the pores) is well developed for CAC compared to AC 25 %.

Kinetic Study. The adsorption process depends on contact time between absorbent and adsorbate. The study of the effect of contact time on the adsorbed quantity of phenol shows that the latter increases with the contact time. Figure 4 shows the adsorption of phenol onto AC 25 % and CAC. The process

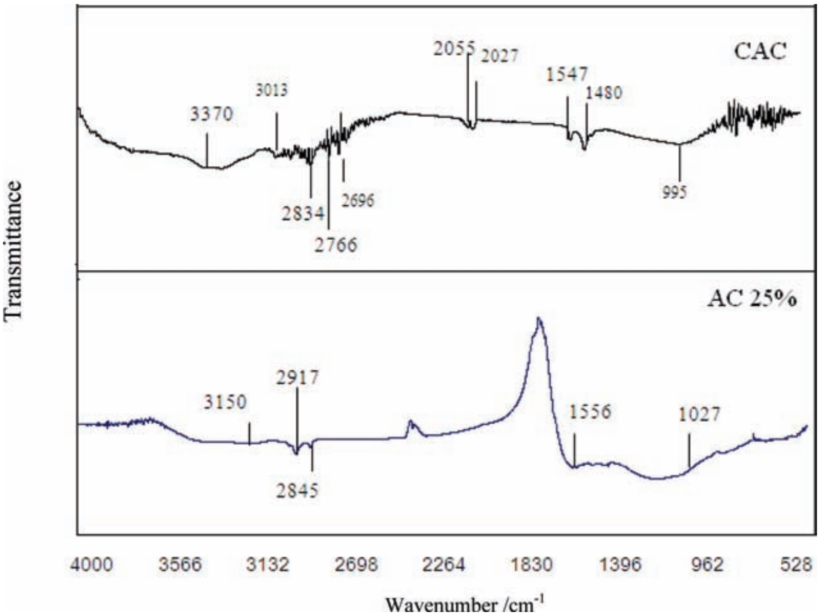

Figure 2. FTIR spectra of the prepared carbon (AC 25 %) and commercial carbon (CAC).

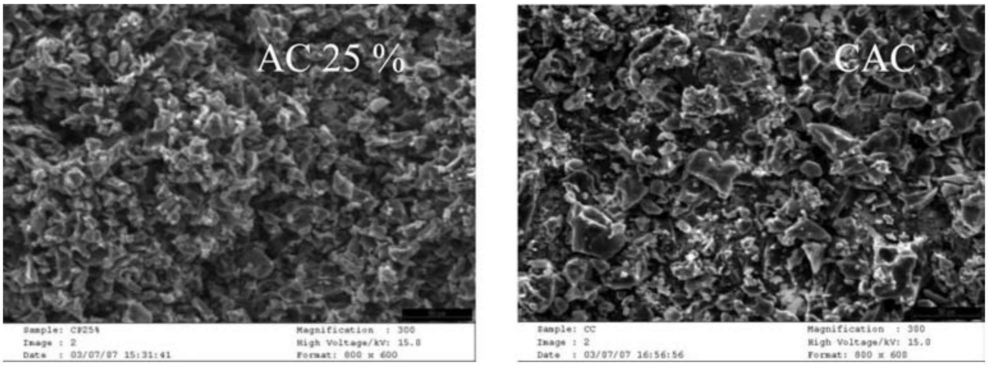

Figure 3. Scanning electron micrographs of AC 25 % and CAC.

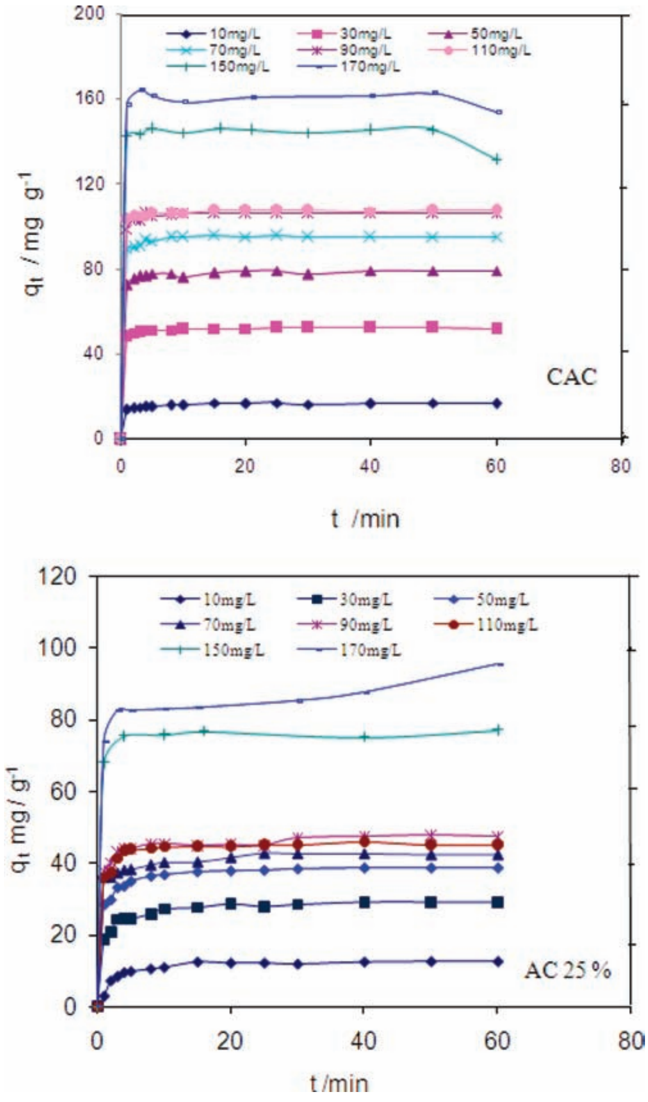

Figure 4. Effect of time and initial phenol concentration on removal of phenol by AC 25 % and CAC. Conditions: pH = 3; AC 25 % dosage = 1 g·L^{-1}; T = 25 °C.

increased linearly with time in the beginning and then more slowly until reaching equilibrium. It can be observed that the maximum uptake is reached in approximately 5 min for the phenol−CAC system and 10 min for the phenol−AC 25 % system.

To analyze the adsorption kinetics of the phenol, pseudofirst-order (Lagergren's equation) and pseudosecond-order models[18] are tested.

Pseudofirst-Order Model or Lagergren's Equation. This model is widely used for adsorption from the liquid phase.[18] Once rearranged and linearized, it presents as follows

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (9)$$

where q_e (mg·g^{-1}) and q_t (mg·g^{-1}) are the quantities of the adsorbed substance at equilibrium and at time t, respectively, and k_1 (min^{-1}) is the rate constant.

Plots of $\log(q_e - q_t)$ versus t did not give a straight line, and consequently, this indicates that the adsorption of phenol onto AC 25 % and CAC does not fit the pseudofirst-order model.

Table 4. Pseudosecond-Order Rate Constant, k_2, the Coefficient of Determination R^2, and Uptake of Phenol at Equilibrium

activated carbon	T / K	C_0 / mg·L^{-1}	k_2 / g·mg^{-1}·min^{-1}	q_e(cal) / mg·g^{-1}	q_e(exp) / mg·g^{-1}	R^2
CAC	298	10	0.218	16.95	16.85	0.999
		30	0.160	52.08	52.45	0.999
		50	0.201	78.74	79.18	0.999
		70	0.138	95.24	95.34	1
		90	0.147	106.38	106.44	1
		110	0.144	107.53	107.53	1
		150	0.031	147.06	144.67	0.999
		170	0.053	163.93	153.51	1
AC 25 %	298	10	0.067	14.65	13.41	0.999
		30	0.057	31.45	29.86	0.999
		50	0.058	38.02	39.04	1
		70	0.056	44.05	44.25	0.999
		90	0.046	48.78	48.50	0.999
		110	0.038	48.78	48.50	0.999
		150	0.034	76.92	77.68	0.999
		170	0.022	87.72	84.02	0.999

Pseudosecond-Order Model. This model[18] is represented by the following equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (10)$$

where q_t (mg·g^{-1}) and q_e (mg·g^{-1}) represent the amounts of adsorbed substance at time t and at equilibrium, respectively, and k_2 is the corresponding kinetic constant (g·mg^{-1}·min^{-1}).

The applicability of this model can be examined from plots of t/q_t versus t (not shown here). Our results (Table 4) showed high coefficients of determination (R^2) and similarity between the experimental capacities at equilibrium (q_e(exp)) and the calculated capacities from the model (q_e(cal)). These results suggest that the pseudosecond-order model fits the experimental data ($R^2 \geq 0.999$).

Thermodynamic Parameters of Adsorption. The thermodynamic parameters that must be considered to determine the process are enthalpy of sorption (ΔH), Gibbs energy change (ΔG), and entropy change (ΔS) due to transfer of a unit mole of solute from solution onto the solid−liquid interface. The important thermodynamic function (ΔH) is very useful whenever there is a differential change that occurs in the system. The negative value of ΔH indicates an exothermic process, and a positive value indicates an endothermic process. The other important thermodynamical parameter is the change in entropy, ΔS, which indicates the degree of freedom of the adsorbed species. The ΔG parameter is used to identify the spontaneity in the sorption process.[19]

Thermodynamic parameters of Gibbs energy, enthalpy, and entropy can be estimated using the equilibrium constant. The equilibrium constant (K_c) of the adsorption of phenol is defined as

$$K_C = \frac{C_0 - C_e}{C_e} \qquad (11)$$

where C_0 is the initial concentration and C_e is the equilibrium concentration of the phenol. The standard Gibbs energy ($\Delta G°$) is calculated from the following equation[19]

$$\Delta G° = -RT \ln K_C \qquad (12)$$

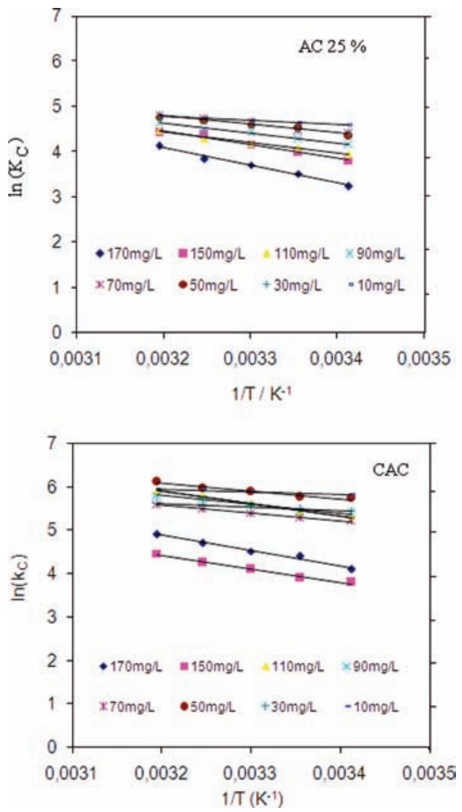

Figure 5. van't Hoff plots of phenol adsoption onto CAC and AC 25 %.

where R is the universal gas constant and T is the absolute temperature. The Gibbs energy change indicates the degree of spontaneity of the sorption process, and a higher negative value reflects a more energetically favorable adsorption.

The equilibrium constant may be expressed in terms of the enthalpy change of sorption ($\Delta H°$) and entropy change of sorption ($\Delta S°$) as a function of temperature. The relationship between K_C and temperature is given by the van't Hoff equation[19]

$$\ln K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{13}$$

$\Delta H°$ and $\Delta S°$ can be obtained from the slope and the intercept of a van't Hoff plot of $\ln K_C$ versus $1/T$. The van't Hoff plot for the adsorption of the phenol onto both AC 25 % and CAC is given in Figure 5. The thermodynamic parameters obtained are summarized in Table 5 and Table 6.

The exothermic nature of the process onto both CAC and AC 25 % is well explained by the negative value of the enthalpy change (Table 5). Moreover, we notice that all the values of the enthalpy are lower than 40 kJ·mol^{-1}; consequently, the process of adsorption of the phenol on activated carbons is purely physical.

The negative values of $\Delta S°$ correspond to a decrease in the degree of freedom of the adsorbed species, suggesting strong interactions between phenol and activated carbons. Positive $\Delta S°$ values were observed at 10 mg·L^{-1} for the phenol−CAC system (Table 6), indicating that the disorder is important at low concentrations and thus the phenol−CAC system has van der Waals interactions.

Positive $\Delta G°$ values were observed from 110 mg·L^{-1}, indicating that spontaneity of the adsorption process is not favored at high concentrations ($C_0 \geq 110$ mg·L^{-1}) for the phenol−CAC system (Table 6). Concerning the phenol−AC 25 % system, the process is only spontaneous for $C_0 = 10$ mg·L^{-1} and for $T \leq 35$ °C (Table 5).

Table 5. Thermodynamic Parameters for the Adsorption of Phenol onto AC 25 %

concentration (mg·L^{-1})	T K	K_C	$\Delta G°$ kJ·mol^{-1}	$\Delta H°$ kJ·mol^{-1}	$\Delta S°$ J·mol·K^{-1}
10	293	2.247	−1.869	−35.668	−115.356
	298	1.653	−1.292		
	303	1.212	−0.715		
	308	1.317	−0.139		
	313	0.780	0.438		
30	293	0.991	0.016	−14.524	−49.519
	298	0.938	0.231		
	303	0.809	0.479		
	308	0.766	0.727		
	313	0.681	0.974		
50	293	0.640	1.035	−11.490	−42.749
	298	0.611	1.248		
	303	0.580	1.462		
	308	0.508	1.676		
	313	0.481	1.889		
70	293	0.462	1.827	−9.722	−39.417
	298	0.445	2.024		
	303	0.429	2.221		
	308	0.388	2.418		
	313	0.359	2.615		
90	293	0.369	2.461	−9.646	−41.323
	298	0.335	2.667		
	303	0.318	2.874		
	308	0.301	3.081		
	313	0.283	3.287		
110	293	0.283	3.080	−10.480	−46.281
	298	0.263	3.311		
	303	0.244	3.543		
	308	0.228	3.774		
	313	0.216	4.006		
150	293	0.354	2.444	−6.112	−29.203
	298	0.349	2.591		
	303	0.363	2.737		
	308	0.327	2.883		
	313	0.299	3.028		
170	293	0.337	2.560	−7.320	−33.720
	298	0.328	2.728		
	303	0.351	2.896		
	308	0.298	3.065		
	313	0.277	3.234		

Adsorption Isotherms. The experimental isotherms obtained for the adsorption of phenol onto both the prepared and the commercial activated carbons are presented in Figure 6, and they of the are L$_4$-type according to the Giles et al.[20] classification.

L curves classified in the subgroups 2 and higher corresponding to Giles et al.[20] classification can identify a plateau or a "Point B". The latter is the end of the turning point with completion of the first monolayer and in special cases; the turning point may represent a change in the mode of packing of the adsorbate. The subsequent rise represents the development of a second layer, and in subgroup 4 this is completed.[20] Coughlin et al.[21] obtained the same isotherm shape for phenol adsorption onto carbon. The authors had assigned the two plateaus to the different orientation of phenol molecules. This suggests that the attraction of phenol for the carbon substrate lies probably in nonpolar forces operating over the entire phenol nucleus. This led Giles et al. to suggest that the second step in the isotherm may represent the uncovering of a portion of the original surface of carbon. Mattson et al.[22] had reported that Giles et al.[20] pointed out that the adsorption isotherm for phenol on carbons usually shows a two-step process, resulting in two plateaus. The oxidation−reduction studies of Coughlin and Ezra

Table 6. Thermodynamic Parameters for the Adsorption of Phenol onto CAC

concentration (mg·L^{-1})	T K	K_C	$\Delta G°$ kJ·mol^{-1}	$\Delta H°$ kJ·mol^{-1}	$\Delta S°$ J·mK^{-1}
10	293	4.213	−3.737	−2.125	5.500
	298	5.349	−3.764		
	303	4.841	−3.792		
	308	3.521	−3.819		
	313	4.841	−3.847		
30	293	6.180	−4.590	−5.980	−4.744
	298	6.963	−4.567		
	303	6.065	−4.543		
	308	5.638	−4.519		
	313	5.637	−4.459		
50	293	3.650	−3.287	−7.662	−14.932
	298	3.803	−3.212		
	303	3.741	−3.137		
	308	3.171	−3.063		
	313	3.101	−2.988		
70	293	2.373	−2.058	−8.412	−21.686
	298	2.135	−1.949		
	303	2.060	−1.841		
	308	2.015	−1.732		
	313	1.855	−1.624		
90	293	1.551	−1.087	−10.195	−31.085
	298	1.447	−0.932		
	303	1.376	−0.776		
	308	1.313	−0.621		
	313	1.165	−0.468		
110	293	1.008	−0.121	−7.471	−25.086
	298	0.956	0.004		
	303	0.937	0.129		
	308	0.947	0.255		
	313	0.850	0.380		
150	293	0.901	0.204	−0.592	−2.720
	298	0.931	0.218		
	303	0.935	0.231		
	308	0.894	0.245		
	313	0.901	0.259		
170	293	0.843	0.431	−2.622	−10.421
	298	0.823	0.483		
	303	0.808	0.535		
	308	0.771	0.587		
	313	0.800	0.640		

showed that this second plateau was apparently independent of the oxidation state of the carbon surface. Then Giles suggested that the second step of the isotherm involved an uncovering of part of the surface and readsorption of the phenol molecules in a different orientation. It is suggested that this reorientation involved a change from a flat configuration to an end-on configuration where the hydroxyl group is directed away from the carbon surface. Nevskaia et al.[23] also obtained an L_4-type isotherm for adsorption of phenol on oxidized carbons. The tentative explanation reported by the authors was that for the lower phenol concentrations in the solution the molecules may be displaced by adsorbed water molecules from the carbon surface free of functional groups to reach the first plateau. If the phenol concentration increases sufficiently, these molecules can displace the water molecules bonded to oxygen functional groups to form the second plateau.

To check if the second plateau corresponds to a second monolayer formed on the top of the first one, we have compared the degree of coverage θ of the two activated carbons for both the first and second plateaus. The degree of coverage θ is obtained using the equation

$$\theta = S_{\text{exp}}/S_{\text{BET}} \tag{14}$$

S_{exp} is calculated as follows

$$S_{\text{exp}} = (q_e N_A \sigma / M) \tag{15}$$

where N_A is the Avogadro constant; M is the molar mass of phenol; and σ is the cross-sectional area of phenol.

Three cross-sectional values have been reported for phenol depending on its orientation on the surface: 45 Å^2 according to Mattson et al.[22] or 52.2 Å^2 according to Puri et al. for a planar orientation, 28 Å^2 for edge-on, and 24.8 Å^2 for end-on orientation.[6]

We have considered the case in which the phenol molecules are adsorbed in a planar orientation (σ = 52.2 Å^2), and we have calculated the degree of coverage θ at different temperatures for both activated carbons. The obtained results are presented in Table 7.

According to the results presented in Table 7, we notice that the degree of coverage values θ (%) (eq 14) reached an average of 39 % and 28 % for the commercial and prepared activated carbons, respectively. Then, the first phenol monolayer is not complete for both the activated carbons, and a second monolayer cannot be formed. Moreover, the calculated degree of coverage values θ (%) using the maximal phenol adsorbed amounts are 55 % (commercial activated carbon) and 53 % (prepared carbon). These results show that about 50 % of the total activated carbon surfaces are not covered by phenol molecules. The second plateau cannot be assigned to the readsorption of phenol molecules in a different orientation but can be attributed to displacement of adsorbed water molecules from the carbon surface free of functional groups by phenol molecules at low

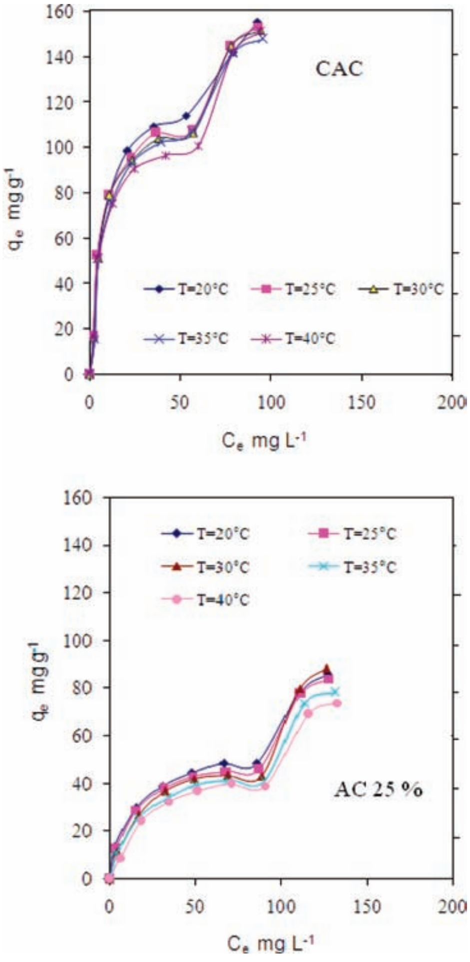

Figure 6. Adsorption isotherms of phenol onto AC 25 % and CAC conditions: pH = 3; AC 25 % or CAC dosage = 1 g.

Table 7. Degree of Coverage θ (%) of Prepared and Commercial Carbons at Different Temperatures

phenol/CAC	first plateau	second plateau	amount of basic groups 10^{-20}
T (°C)	θ (%)	θ (%)	
20	41.42	56.40	10.06
25	38.99	55.65	
30	38.59	55.10	
35	38.79	53.68	
40	36.65	54.79	

phenol/AC 25 %	first plateau	second plateau	amount of basic groups 10^{-20}
T (°C)	θ (%)	θ (%)	
20	31.18	55.09	10.23
25	29.50	54.01	
30	27.74	56.77	
35	26.24	50.18	
40	25.10	47.47	

concentration (first plateau). when the phenol concentration increases sufficiently, water molecules bonded to oxygen functional groups are moved by phenol, and then the second plateau is formed.

In addition, according to the numerical data listed in Table 7, 1 g of activated carbon (prepared or commercial) contains about 10^{21} basic groups, which is much higher than the amount of absorbed phenol molecules (9 10^{20} molecules for commercial activated carbon and 5 10^{20} for prepared activated carbon).

From Table 7, we can notice that adsorption uptake obtained on the commercial activated carbon is higher than the one obtained on the prepared activated carbon. This is due to the difference in the physicochemical properties of the two adsorbents.

Modeling of Phenol Adsorption. The adsorption data for phenol onto both AC 25 % and CAC were analyzed by a regression analysis to fit the linearized expression of the Langmuir isotherm model. Values of the Langmuir constants are presented in Table 8, and the isotherms are reconstituted using the determined values (Figure 7). The isotherm curves showed no superposition of experimental results (points) and the theoretical calculated points (lines) since the experimental curve shapes are stepped isotherms and the reconstituted one is L-shaped.

The coefficient of determination (Table 8) for the Langmuir isotherm equation was found to be lower for the phenol−CAC system ($0.91 \le R^2 \le 0.97$) and better for the phenol−AC 25 % system ($0.95 \le R^2 \le 0.98$). In spite of the acceptable coefficients of determination obtained for the second system, this model does not describe perfectly the equilibrium data because of the higher values of average percentage errors. Thus, it is not appropriate to use the coefficient of determination of the linear regression method for comparing the best-fitting isotherms (Table 8).

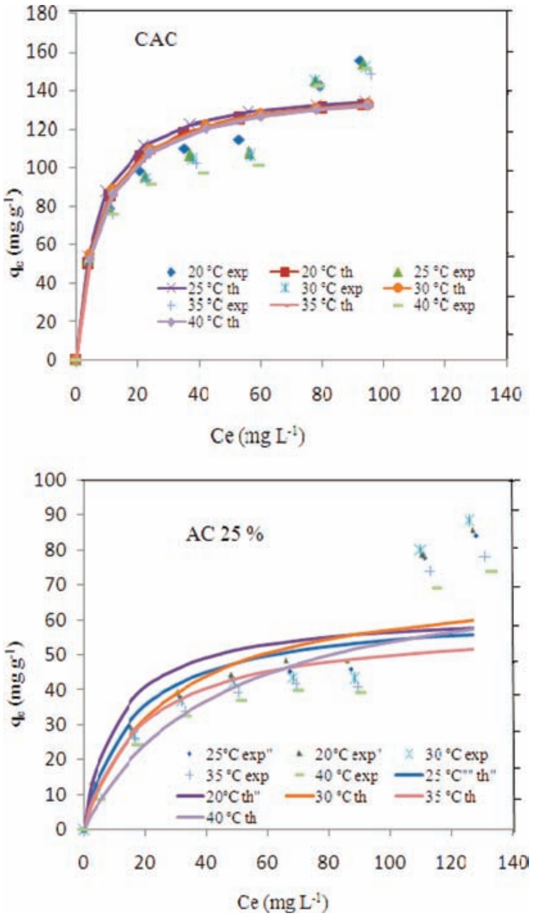

Figure 7. Comparison of experimental and predicted adsorption isotherms of phenol onto AC 25 % and CAC according to the Langmuir model.

According to Figure 8, the Freundlich isotherm slightly diverges from the experimental results for higher equilibrium concentrations. From Table 8, it was observed that the values of the coefficient of determination for the Freundlich isotherm equation fluctuate from 0.934 to 0.976 for the phenol−CAC system and from 0.922 to 0.95 for phenol−AC 25 %. The values of average percentage error evaluated using eq 8 were higher

Table 8. Parameters of the Langmuir, Freundlich, and Elovich Isotherms for the Adsorption of Phenol onto CAC and AC 25 %

model/parameters	CAC					AC 25 %				
temperature (°C)	20	25	30	35	40	20	25	30	35	40
q_e exp	155.56	153.51	151.97	148.05	151.10	85.7	84.02	88.31	78.06	73.85
Langmuir										
b/L·mg^{-1}	0.13	0.16	0.13	0.12	0.13	0.09	0.06	0.04	0.05	0.02
q_m/mg·g^{-1}	142.86	142.86	142.86	142.86	142.86	62.5	62.5	71.43	58.82	76.92
R^2	0.97	0.94	0.95	0.95	0.91	0.95	0.97	0.97	0.97	0.98
APE (%)	8.22	9.76	10.31	9.37	11.38	18.36	13.78	15.67	14.13	16.27
Freundlich										
K_F	33.98	35.91	33.92	31.85	31.41	8.28	6.77	4.95	5.46	3.52
n	3.05	3.25	3.13	3.05	3.08	2.23	2.06	1.80	1.95	1.66
R^2	0.97	0.96	0.95	0.97	0.93	0.95	0.94	0.92	0.93	0.93
APE (%)	10.01	9.97	23.58	9.64	11.30	10.32	13.78	13.16	11.70	13.19
Elovich										
K_E/L·mg^{-1}	0.66	0.34	0.57	0,53	0.37	0.66	0.67	0.57	0.53	0.37
q_m/mg·g^{-1}	50.00	59.17	50.00	50.00	55.55	50.00	50.00	50.00	50.00	55.55
R^2	0.93	0.83	0.84	0.88	0.76	0.93	0.86	0.84	0.88	0.76

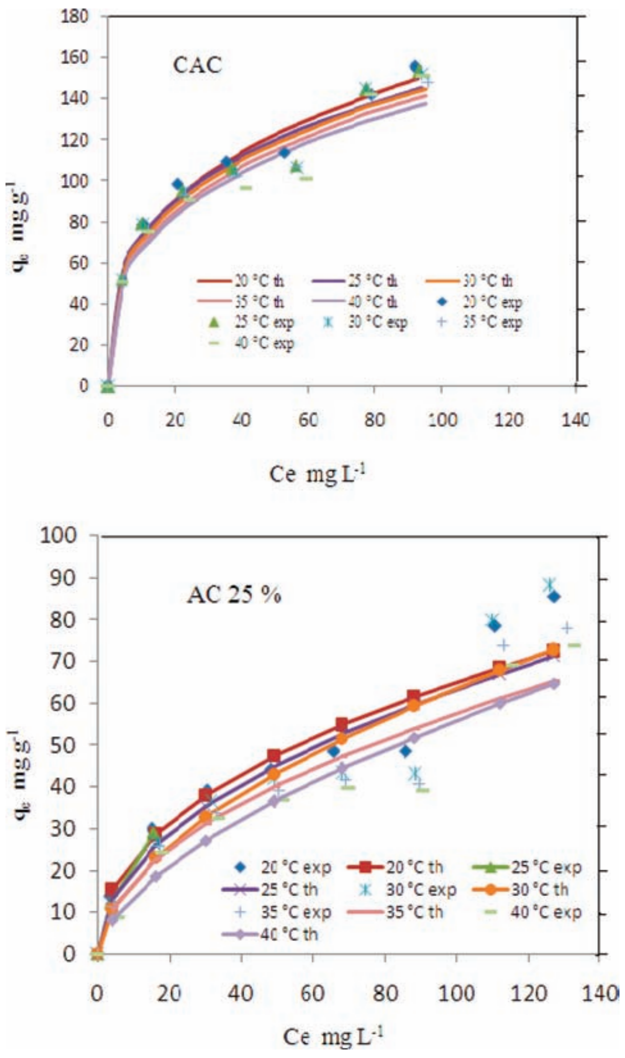

Figure 8. Comparison of experimental and predicted adsorption isotherms of phenol onto AC 25 % and CAC according to the Freundlich model.

(Table 8). Consequently, the Freundlich isotherm did not represent phenol adsorption data, at all.

The Elovich isotherm constants, K_E and q_m, as well as the coefficient of determination, R^2, for the phenol−CAC and phenol−AC 25 % systems were obtained using the linear form of the equation (Table 8). The values of the maximum adsorption capacities determined using the linear transformation of the model are much lower than the experimental adsorbed amounts at equilibrium corresponding to the plateau of the adsorption isotherms (Table 8). This suggests that this model is not appropriate and is unable to describe the adsorption isotherm of phenol onto the two activated carbons which means that the assumption of the exponential covering of adsorption sites that implies multilayer adsorption is not in agreement with the experiment in the studied concentration range, and this confirms the preceding results.

Conclusion

Activated carbon can be prepared from coffee residue by chemical activation with $ZnCl_2$. The determined surface area and total porous volume of the prepared carbon were $520\ m^2 \cdot g^{-1}$ and $0.28\ cm^3 \cdot g^{-1}$, respectively. It is essentially microporous compared to a commercial carbon since the prepared activated carbon microporosity is about 96 % while the commercial one is about 56 %.

Batch kinetic studies performed on the carbon−phenol systems indicated the adsorption capacity of both the prepared and commercial carbons. The kinetic data tended to fit well a second-order kinetic model, and the obtained thermodynamic data confirm the physisorption of phenol onto both prepared and commercial carbon particles.

Adsorption isotherms of phenol on prepared and commercial activated carbons were studied and modeled using the Langmuir, Freundlich, and Elovich equations. The phenol experimental isotherms onto the two carbons are L_4-type according to the Giles classification. The determination of the degree of coverage values θ (%) of phenol adsorption on the two activated carbons suggests that a second plateau may be attributed to displacement of water by phenol molecules when the phenol concentration increases sufficiently which means that multilayer adsorption is not in agreement with the experiment in the studied concentration range. These results are confirmed with no applicability of the Elovich model to the experimental data. Moreover, the low coefficients of determination values and the average percentage error values for the modeling of the phenol adsorption process onto the two activated carbons by the Langmuir and Freundlich models suggest that these are not appropriate, either.

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