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Sawdust-based activated carbon ability in the removal of phenol-based organics from aqueous media

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ABSTRACT

The ability of an activated carbon prepared from sawdust-based activated carbon to remove phenol and its compounds from aqueous solutions has been investigated. Activation was achieved by impregnating sawdust in phosphoric acid with concentrations ranging from 20 to 85% and heating the sawdust-acid mixture starting from 600 to 800°C. The results showed that the Brunauer–Emmett–Teller (BET) surface area exhibited by the prepared material varied significantly with experimental conditions such as impregnation time, solution pH, adsorbent dose, initial concentration, and pyrolysis temperature, and attained a value of 2,257 $m^2 g^{-1}$ in comparison to the as-supplied Merck commercial activated carbon (Merck-AC) attaining 1,030 $m^2 g^{-1}$. Characterization of the prepared materials was carried out through the determination of the BET surface area, functional groups, and surface area accessible to small and fairly large molecules (iodine and methylene blue). Batch adsorption tests were performed and the experimental data analyzed using the Langmuir, Freundlich, and Temkin models. The estimated adsorption capacities from the fitting of the Langmuir model to the equilibrium data are 200, 334, and 500 mg g^{-1} for phenol, parachlorophenol, and pentachlorophenol, respectively. The application of the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models to the experimental data showed that pseudo-second-order model is more representative. Thermodynamic tests revealed a spontaneous ($\Delta G < 0$) but an endothermic sorption process (5.10/127 kJ/mol) for all the phenolic compounds investigated.

Keywords: Sawdust; Valorization; Pyrolysis; Adsorption; Phenolic compounds

1. Introduction

Because of its size and scope, industrial pollution can impact on the environment in a range of ways. One of its most common forms is water pollution generally caused by releasing wastewater charged with organic compounds causing widespread environmental problems. By being widely used in industry as chemical intermediates for the manufacture of drugs, pesticides, dyestuffs, disinfectants, tanning agents, and

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phenolic compounds even at low concentrations, can also have a negative environmental impact when discharged directly into receiving wastewater system without any prior treatments. As a result, these pollutants, by carrying significant quantities of aromatic materials end up in estuaries and streams leading to negative impact on human lives and health and can disrupt ecosystems. A growing awareness on industrial pollution and its consequences has led to tighter restrictions on pollution caused by this type of toxic pollutants [1]. New environmental regulation has been imposed and various methods for phenolic derivatives removal have been proposed to comply with the new legislation such as extraction, aerobic and anaerobic biodegradation, and ion exchange by resins and oxidation by ozone. Although well developed [2–4], these methods proved to be less efficient and more costly. Activated carbon adsorption in its most common physical forms (powdered or granular) has proved to be one of the most effective and the most frequently used technique for removing phenolic compounds from wastewater [5,6]. Besides activated carbon, a variety of solid adsorbents, ranging from macroporous polymeric resins [7,8] to microporous zeolites [9,10] have been used. Currently, activated carbon is by far the preferred adsorbent, and it is generally derived from a selection of local natural products as alternatives to the commercial activated carbons prepared from the usual coconut shell, apricot stones, etc. In the last decade, several raw materials-based activated carbon have been used for phenolic compounds removal such as vetiver roots [11], coconut shell [12], petroleum coke [13], bamboo [14], bagasse and rice husk [15], pecan shells [16], olive kernels [17], date stones [18], globe artichoke [19], and coffee grounds [20].

As reported in the literature, one of the most investigated of all liquid-phase applications of carbon adsorbents is adsorption of phenol and its derivatives from aqueous solutions by activated carbons [21].

In this study, attention was focused on the removal by adsorption of three phenolic compounds, namely phenol, parachlorophenol, and pentachlorophenol, frequently present in industrial liquid effluents, by lignocellulosic-activated carbon.

The adsorption equilibrium data for the considered pollutants were fitted with well-known isotherm models namely Langmuir, Freundlich, and Temkin models. Pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models were tested on the prepared adsorbents. Thermodynamic parameters such as Gibb's free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were also evaluated.

2. Materials and methods

2.1. Preparation of adsorbent and adsorbate solution

Sawdust sample was collected from a nearby carpentry, washed several times with distilled water (to eliminate impurities and dust), and dried in sunlight for a week then in an oven overnight at 378 K. The samples were then grinded, sieved through 0.07 mm using a Vierzen Crosshop grinder before activation. The samples were activated in a two-step process involving a chemical impregnation of 40 g of sawdust in 100 mL of phosphoric acid (acting as a dehydrating and pore stabilizing agent) at various concentrations (20, 40, 60, 70, and 85%) at 443 K for 180 min followed by pyrolysis (thermal activation) of the samples at 973 K during 180 min. The obtained adsorbents were washed with hydrochloric acid (0.1 M) and distilled water until the washing water tested with lead acetate revealed no phosphorous presence.

The supplied commercial activated carbon from Merck was used as a reference material for comparison purposes.

All reagents used in this study were of analytical grade. A $10^3\ \mathrm{mg\,L^{-1}}$ of stock solutions of phenol (Merck), parachlorophenol (Sigma-Aldrich), and pentachlorophenol (Aceros-Orga) was prepared separately according to standard procedure by dissolving the required amount in distilled water. Successive dilutions were used to obtain work solutions of the desired concentrations. Iodine standard solutions (0.1 N) were prepared from sublimed iodine dissolved in potassium iodide and titrated with (0.1 N) sodium thiosulfate which was standardized with chemically pure potassium iodate. Table 1 summarizes some important characteristics of three phenolic compounds used in this study.

2.2. Characterization of the prepared samples

Nitrogen adsorption tests were carried out on the prepared materials to assess their specific surface area. Additional characterization including adsorption porosity, microporous and mesoporous available areas, zero point of charge, and Fourier transforms infrared spectroscopy (FTIR) were done on selected samples using the methods described below.

2.2.1. Adsorbent porosity

Nitrogen at 77 K was used to determine the specific surface areas of the prepared carbons using an automated adsorption apparatus (Micromeritics apparatus

Table 1
Physicochemical properties of the phenolic compounds studied

	Phenol	Parachlorophenol	Pentachlorophenol
Molecular formula	C_6H_6O	C_6H_5OCl	C_6HOCl_5
Molecular weight (g mol^{-1})	94.11	128.56	266.34
Water solubility (g L^{-1})	77.50	27.10	0.02
pK_a	9.41	4.75	9.89
λ_{max} (nm)[a]	275	280	320

[a] Experimentally obtained values.

ASAP 2010). Prior to analysis, the samples were degassed at 150°C in a vacuum system at low pressure (10^{-4} Torr). The specific surface areas (S_{BET}) were determined using the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.3. The existence of micropores and mesopores of the prepared and the commercial activated carbons were also evaluated by both iodine number (ASTM D4607-94 method) [22] and methylene blue index (Chemviron Carbon company method TM-11), respectively [23]. It is assumed that 1 mg of iodine adsorbed corresponds roughly to a 1 m^2 of surface area determined by the BET method [24].

2.2.2. Mesoporous and microporous properties

Methylene blue adsorption on activated carbons has been largely used for surface area determination [25,26], especially mesoporosity. The adsorption process of methylene blue was studied by mixing 0.1 g of activated carbon with 25 mL of dye solution at different concentrations for 2 h. After filtration, the supernatant was analyzed for equilibrium concentration determination. The adsorption capacity obtained by Langmuir model can be used to evaluate the available area for mesopores (S_{MB}) using the following equation:

$$S_{MB} = b\frac{N_A}{M_{MB}}\sigma_{MB} \tag{1}$$

where b is the adsorption capacity (mg g^{-1}) obtained from previous Langmuir curves, N_A is Avogadro's number (6.023×10^{23}), M_{MB} is the molecular weight of methylene blue (319.86 g mol^{-1}), and σ_{MB} is the area occupied by an adsorbed methylene blue molecule (119 Å^2).

However, iodine number is a fundamental parameter for characterizing the performance of an activated carbon, especially its microporosity. Being a small molecule, it provides a good approximation of the surface area available for the adsorption of low-molecular weight compounds. Burn-off is defined as the ratio of percentage weight decrease of the material during the preparation of the original weight of the raw material that was calculated using the following equation:

$$\%\text{ Burn-off} = \frac{(W_i - W_f)\,100}{W_i} \tag{2}$$

where W_i is the initial weight (g) of the raw material and W_f is the product final weight (g). It was used in this work to evaluate the extent of activation for the prepared materials.

2.2.3. Zero point of charge determination (pH_{zpc})

Since the carbon surface requires a net positive charge due to H^+ adsorption at low pH and a net negative charge due to its release at high pH, then, the pH where the net charge is zero (absence of both positive and negative charges), called zero point of charge (pH_{zpc}), is of fundamental importance in carbon surface [27,28]. It determines how easily a substrate is able to adsorb potentially toxic ions. The pH_{zpc} was determined as follows: 50 mL of 0.01 M NaCl solutions were placed in each of a series of stoppered conical flasks. The initial pH (pH_i) of the solution in each flask was adjusted from 2 to 12 using HCl or NaOH (0.01 M) solutions. An amount of 0.15 g of activated carbon was added to each flask; the resulting suspensions were stirred for 48 h and the final pH (pH_f) value was measured for each solution. The difference between the initial and final pH value ($\Delta pH = pH_i - pH_f$) was plotted against (pH_i). The point of intersection of the resulting curve (not shown) with the abscissa, at which $\Delta pH = 0$, gave the point of zero charge values of the sawdust-based and the commercial activated carbons as shown in Table 2.

2.2.4. Fourier transform infrared spectroscopy

FTIR spectra (4,000–400 cm^{-1}) of the prepared sawdust-based activated carbon (SDB-AC) and the Merck-AC samples were recorded in the transmission mode

Table 2
Physical properties and chemical adsorption characteristics of SDB-AC and Merck-AC

	Adsorbent	
Properties	SDB-AC	Merck-AC
S_{BET} (m^2 g^{-1})	2,256.57	1,031
S_{BM} (m^2 g^{-1})	1,120.40	800
S_{ext} (m^2 g^{-1})	2,037.62	*
S_{mic} (m^2 g^{-1})	218.95	*
Iodine number (mg g^{-1})	1,205	830
Methylene blue index (mg g^{-1})	299	173
pH_{zpc}	7	6.45

*Values not available.

using an IR Prestige-21 SHIMADZU FTIR spectrophotometer. Samples of 1 mg of dried and finely grinded activated carbon were thoroughly mixed with 100 mg of KBr and compressed in order to make a thin-film disk for spectra analysis.

2.3. Phenolic compounds adsorption

Before applying the adsorption isotherm models, the effect of some parameters on the adsorption of the phenolic compounds studied by the activated carbons investigated was examined including acid concentration (20–85% range), adsorbent dosage (2–24 g L^{-1} range), contact time (30–400 min range), pH (2–12 range), and impregnation time (90–240 min range). Batch sorption tests were carried out using a series of capped 250 mL Erlenmeyer flasks at a temperature of 25 ± 1˚C. Twenty five mL of phenol or parachlorophenol or pentachlorophenol solution of known concentrations was mixed separately with a 0.2 g of adsorbent, agitated magnetically at a constant speed of 200 rpm until equilibrium was reached then centrifuged at 4,000 rpm. The samples were then filtered, and the residual concentrations in the filtrate analyzed using a UV–visible 2121 Optizen spectrophotometer at predetermined values of maximum wavelength shown in Table 1. Experiments were done in duplicate and the average values were reported. Uptake of all phenolic compounds (q_e) was calculated according to the following mass–balance relationship:

$$q_e = \frac{(C_0 - C_e)\,V}{m} \tag{3}$$

where C_0 and C_{eq} are the initial and the equilibrium phenolic compounds concentration (mg L^{-1}), V is the volume of the liquid phase (mL), and m is the mass of the activated carbon sample (mg). Impregnation time was varied from 90 to 240 min and the pyrolysis temperature from 600 to 800˚C.

The distribution of molecules between adsorbate and adsorbent during the adsorption process once the equilibrium is reached can be indicated by adsorption isotherms studies. In order to find a suitable model that can be used for design purposes [29], three well-known and widely used adsorption isotherms, namely Langmuir [30] which assumes that the adsorption takes place at specific homogeneous sites within the adsorbent, Freundlich [31] which describes adsorption as taking place on a heterogeneous adsorbent surface, and Temkin [32,33] which indicates the linearity between the surface coverage and the energy of adsorption, were fitted to the obtained data to describe the adsorption of the phenolic compounds studied at the solid–liquid interface.

The linear form of Langmuir isotherm model is given by the following equation:

$$\frac{C_{eq}}{q_e} = \frac{1}{b\,K} + \frac{C_{es}}{b} \tag{4}$$

where C_{eq} is the equilibrium concentration of the adsorbate (phenolic compounds) (mg L^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of activated carbon (mg g^{-1}), b (mg g^{-1}) is the Langmuir maximum uptake of phenol-based organics per unit mass of adsorbent, and K (L mg^{-1}) is the Langmuir constant related to the rate of adsorption.

The logarithmic form of Freundlich model is given by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_{eq} \tag{5}$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_{eq} the equilibrium concentration of the adsorbate, K_f and n are Freundlich constants that can be obtained from the intercept and the slope of ln q_e vs. ln C_{eq} plot, with n indicating the favorableness ($n > 1$) of the adsorption process, and K_f the adsorption capacity of the adsorbent.

The general linear form of Temkin model is given by the following equation:

$$q_e = B \ln K_T + B \ln C_{eq} \tag{6}$$

where q_e (mg g^{-1}) and C_{eq} (mg L^{-1}) are the amounts of adsorbed phenolic compound per unit mass of adsorbent and nonadsorbed concentration left in the solution at equilibrium, respectively. $B = (RT)/b_h$. T is the absolute temperature (K), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), b_h is a constant related to the heat of adsorption (J mol^{-1}), and K_T is the Temkin constant corresponding to the maximum binding energy.

3. Results and discussion

The textural and physical characteristics of SDB-AC and Merck-AC used in this study were determined using N_2 adsorption isotherms at 77 K. Table 2 summarizes their textural properties.

The adopted method of activation made it possible to obtain a specific surface (available for nitrogen) of 2,256 m^2 g^{-1} for the prepared carbons, which is very appreciable. Fig. 1 gives the adsorption/desorption isotherm of N_2 for the prepared carbon. There is an increase in the amount adsorbed under specified relative pressure values. At low P/P_0, the isotherm is of type I with a considerable uptake indicating that the SDB-AC is microporous material in accordance with the obtained iodine number (1,205 mg g^{-1}). While at intermediate and higher values of P/P_0, the presence of mesopores (type IV) can be seen from the isotherm curve in the presence of a certain hysteresis slope in accordance with the obtained methylene blue index (299 mg g^{-1}).

In order to also estimate the mesoporosity present, the adsorption capacity of methylene blue was determined using a molecular cross section of 119 Å^2 for this molecule.

3.1. H_3PO_4 concentration effect

Activated carbon samples were prepared using phosphoric acid as a chemical activating agent at concentrations ranging from 20 to 85%. The results showed that both iodine number and methylene blue index improved clearly with the concentration of H_3PO_4 except for the acid concentrations of 70 and 85% where both numbers decrease. This decrease may be explained by the fact that the biological constitution of the used material disaggregates and becomes disordered at a strong acid concentration; this favors pores destruction instead of their creation leading then to a reduction in microporosity.

According to the values summarized in Table 3, the prepared activated carbons are mainly microporous due to a fairly high iodine number of about 745 mg g^{-1}, which is an indication of appreciable carbon micoporosity. The samples exhibit also some mesoporosity as indicated by the obtained methylene blue number of 298 mg g^{-1} using 60% H_3PO_4 at an activating temperature of 600˚C.

3.2. Impregnation time effect

The activated carbon showing good characteristics seems to be the one prepared at the following

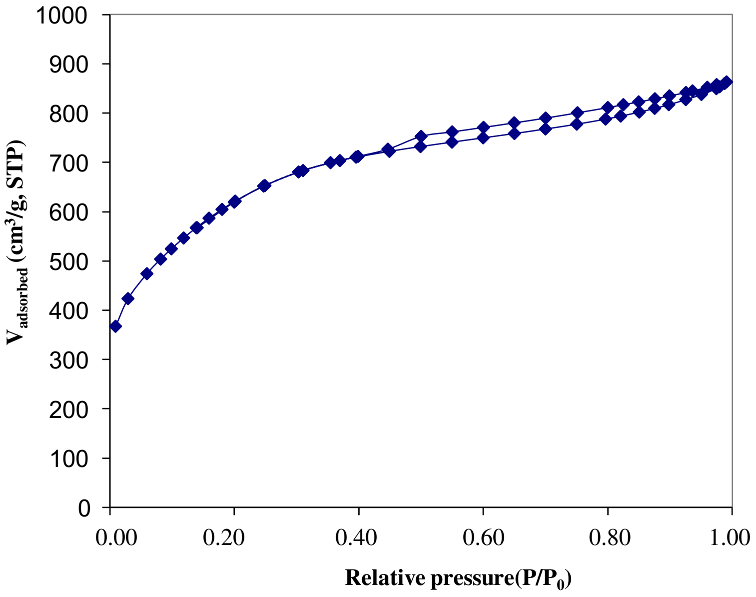

Fig. 1. BET adsorption–desorption isotherms for the SDB-AC.

Table 3
Iodine number and methylene blue index values as a function of H_3PO_4 concentration, impregnation time, and activation temperature

	H_3PO_4 concentration (%)					
	0	20	40	60	70	85
Iodine number (mg g^{-1})	187.22	550.46	559.64	744.90	644.64	634.98
Methylene blue index (mg g^{-1})	9.00	281.50	293.075	298.72	298.84	299.12
	**Impregnation time (min)					
	90	120	180	240		
Iodine number (mg g^{-1})	744.90	1,038.66	1,119.83	891.63		
Methylene blue index (mg g^{-1})	298.72	299.425	299.525	299.125		
	**Temperature (°C)					
	600	700	750	800		
Iodine number (mg g^{-1})	1,119.83	1,205.01	1,210.69	1,210.69		
Methylene blue index (mg g^{-1})	299.53	299.55	299.6	299.6		
Burn-off (%)	49.5	53.5	63.0	90.0		

**Both impregnation time and activation temperature experiments were done at 60% H_3PO_4 concentration.

conditions of 60% (acid concentration: Fig. 2(a)), 180 min (time of impregnation: Fig. 2(b)), and 700°C (activation temperature: Fig. 2(c)). An increase in iodine number is observed with impregnation time in phosphoric acid up to 180 min followed by a decrease at 240 min as shown in Fig. 2(b). This behavior can be explained by the pore destruction for impregnation time exceeding 180 min. As shown in Table 3, this prepared sample has an iodine number of 1,038 mg g^{-1} and methylene blue index of 299 mg g^{-1} indicating a developed mixed microporous–mesoporous structure, foreshadowing good adsorbing properties.

3.3. Activation temperature effect

Further tests were carried out by varying the activation temperature from 600 to 800°C. To limit high adsorbent weight loss at high temperatures, 700°C was selected as the activation temperature. The results shown in Table 3 indicate burn-off ranging from 49 to 90% for the activation temperature range. This mass loss may be due to the removal of most disorganized carbons once the activating agent and the precursor come into contact during the activation stage. More tarry material removal from the carbon was observed at high values of burn-off (90%) and temperature (800°C) leading to higher values of iodine number and methylene blue index and, consequently, of BET surface area. Lower values of these parameters were also found at lower activation temperatures indicating that the porosity of char is not always accessible due to pores being filled by disorganized carbon resulting from tar deposition [34].

Enhancement of iodine number to up to a maximum value of 1,210 mg g^{-1} and methylene blue index to up to 299.52 mg g^{-1} was observed at 800°C for a 3 h activation time, but due to the high weight loss and poor carbon yield, these working conditions were discarded. On the other hand, results obtained at 700°C were taken into account being a compromise between yield and physical properties (BET, iodine, and methylene blue values) as shown in Table 3. From Fig. 2(a–c). it can be seen that at the working conditions (60% acid concentration, 3 h impregnation time, and 700°C pyrolysis temperature), an iodine number value of 1,205 mg g^{-1} and a methylene blue index of 299 mg g^{-1} were obtained.

3.3.1. Functional groups determination

Fig. 3(a) and (b) shows the IR spectra of the SDB-AC and the Merck-AC samples with main adsorption bands which can be attributed as follows: strong vibrations (O–H) hydrogen-bounded alcohols (3,341 cm^{-1}), medium stretching vibrations (2,889 cm^{-1}), and strong vibration phenols (1,031 cm^{-1}) on the other hand, the most important functional groups for both SDB-AC and Merck-AC are summarized in Table 4. The peak detected at 1,175 cm^{-1} may be ascribed to P=O and P–O–C. These function groups are due to the presence of H_3PO_4 during activation for the preparation of activated carbon, then disappear during water washing as revealed by lead acetate test. In conclusion, the main functional groups that could be responsible for phenolic compounds adsorption

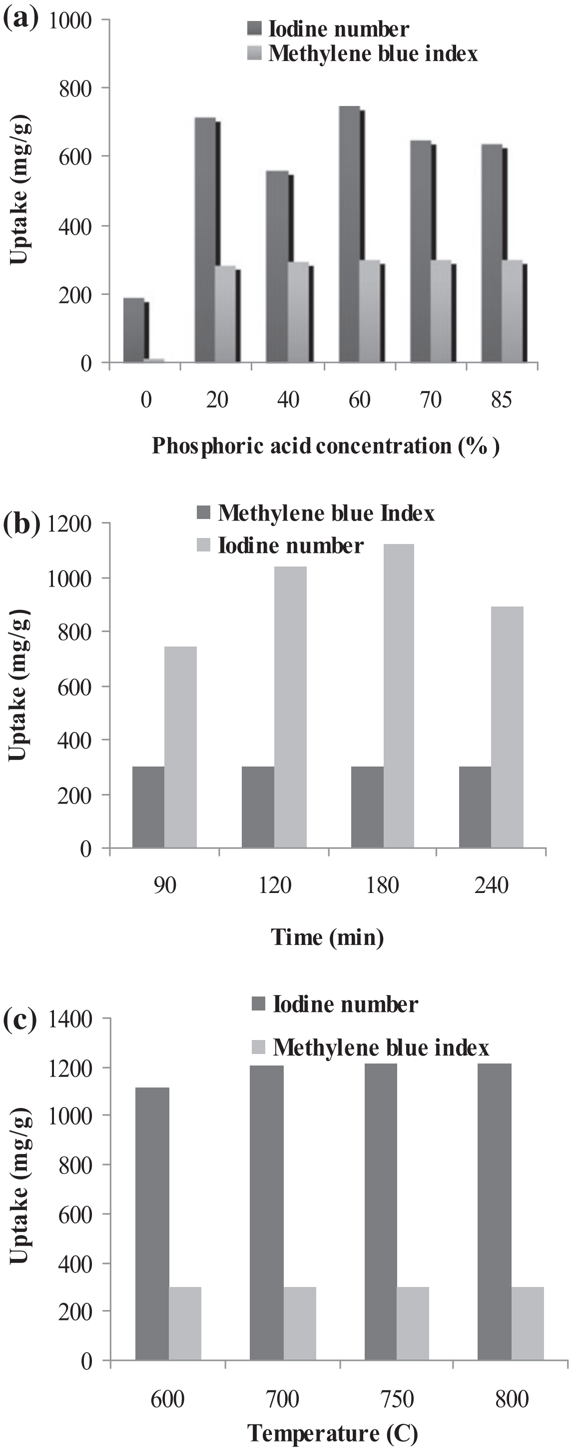

Fig. 2. Iodine number and methylene blue index values of SDB-ACs as a function of (a) H_3PO_4 concentrations, (b) impregnation times, and (c) pyrolysis temperatures.

through complex electron donor receiver interactions and hydrogen bonding are oxygen containing groups present on the activated carbon surface.

3.4. *Adsorption experiments*

3.4.1. *Adsorption equilibrium time determination*

Batch adsorption tests of phenolic substances (used in this study) onto the prepared activated carbons as a function of time were conducted in batch mode in order to determine the contact time necessary for each adsorption system to attain equilibrium. A 25 mL of known initial concentration of phenol or parachlorophenol or pentachlorophenol were mixed with 0.1 g of each adsorbent separately and agitated from 30 to 300 min. Fig. 4. shows the % removal vs. contact time for all three pollutants onto SDB-AC and Merck carbons. The equilibrium times observed were reached after a contact time of 3 and 4 h for all the three phenolic components onto SDB-AC and Merck, respectively.

3.4.2. *Adsorbent dose effect*

Among the factors influencing the properties of adsorption, the amount of the activated carbon (dose) is particularly important because it determines the degree of adsorption and can also be used to predict the cost of the activated carbon per unit of treated solution. In order to optimize the adsorbent dose for phenolic compounds removal from aqueous solution, adsorption experiments were carried out using different adsorbent dosage ranging from 2 to 24 $g\,L^{-1}$ in fixed pH, contact time, temperature, and adsorbate concentration. The percentage of the dye removed by adsorption on SDB-AC as a function of carbon dosage is shown in Fig. 5. Maximum uptakes (>99%) were obtained at an adsorbent dosage of 8 $g\,L^{-1}$ for all the three phenolic compounds. It can also be shown in Fig. 5, that the increase in adsorption from 40, 60, and 80 to over 99% for phenol, pentachlorophenol, and parachlorophenol, respectively, with the adsorbent dosage starting from 2 $g\,L^{-1}$ to up to 8 $g\,L^{-1}$ is due to the increase of adsorbent sites available for phenol and its compounds entailing better adsorption [35] followed by a saturation step. Thus, in all subsequent studies the optimum amounts of SDB-AC and Merck-AC were chosen as 8 and 4 $g\,L^{-1}$, respectively.

3.4.3. *pH effect on adsorption*

Functional group dissociation on the active sites of the activated carbon as well as its surface charge, are strongly affected by the solution pH which is an important parameter during the phenolic compounds adsorption process. Adsorption of the phenolic pollutants from aqueous solutions with known concentration

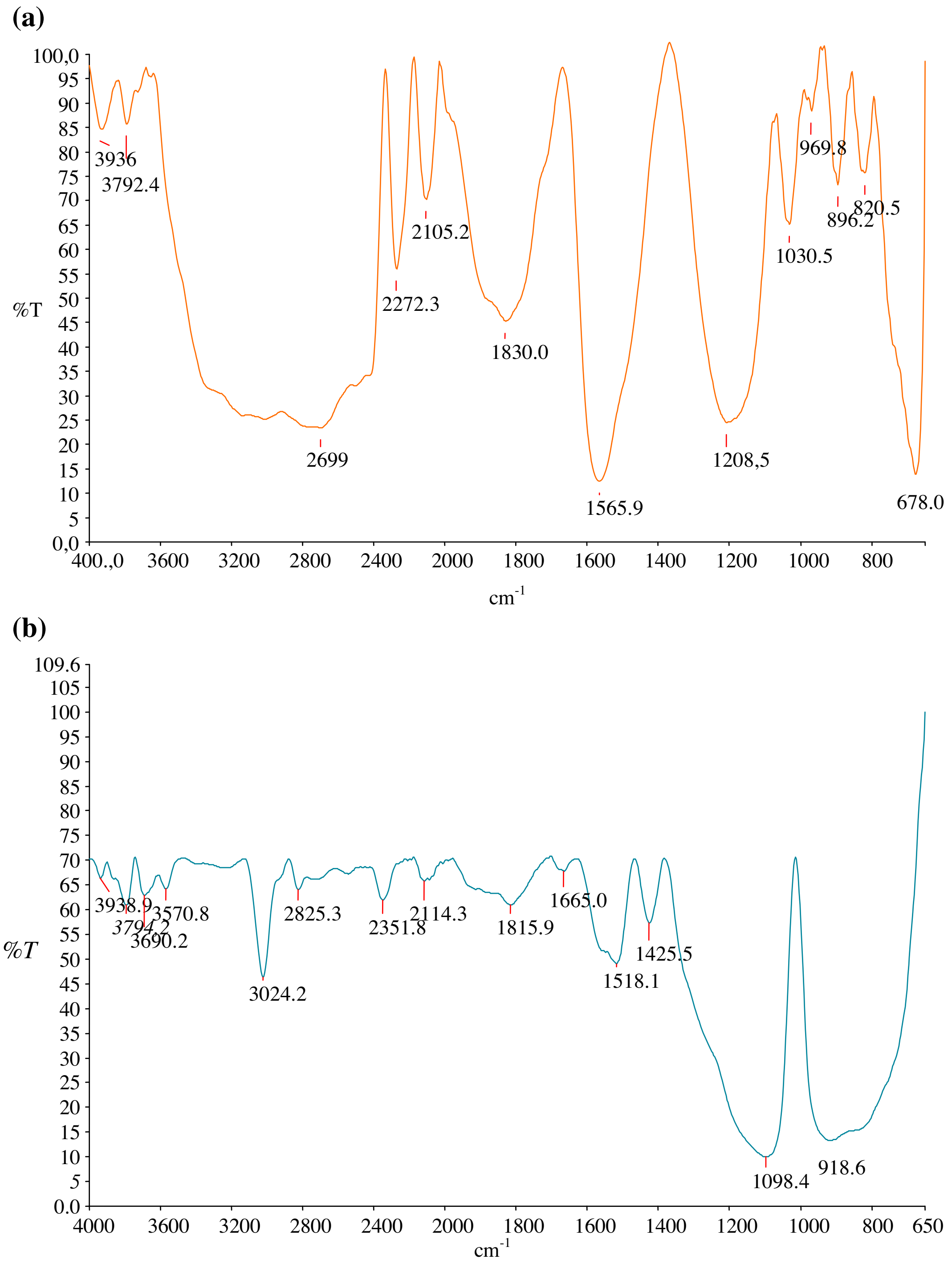

Fig. 3. FTIR spectrum of (a) SDB-AC and (b) Merck-AC.

(600 mg L^{-1} for phenol and pentachlorophenol, and 500 mg L^{-1} for parachlorophenol) onto a known amount (dose) the prepared and commercial materials was studied by varying pH from 2 to 12 at ambient temperature by adding either 0.1 N HCl or NaOH solutions. The mixture was agitated and filtered and the quantity adsorbed was determined by a mass balance according to Eq. (3). Maximum uptake capacities were found at pH 5.0 for phenol, 6.5 for both parachlorophenol and pentachlorophenol as shown in Fig. 6. Phenol may exist in two forms: a noncharged form and an anion or phenolate form depending on the pH.

Table 4
Characteristic FTIR wave numbers for the SDB-AC and Merck-AC

Sawdust-based activated carbon		Merck-activated carbon	
Band position (cm^{-1})	Assignment	Band position (cm^{-1})	Assignment
3,424	Stretching vibration of hydrogen-bonded groups	3,620–3,893	Stretching vibration of O–H groups
3,288	Stretching vibration (≡C–H)	3,021	O–H and $-NH_3^+$ groups
2,924	Stretching vibration (asymmetric) $=CH_2$	2,147	–C=CN, –N=C–H and –N=C=S groups
1,724	C=O stretching band from the carboxyl or ester groups	1,518	Related to N–H bending and C–N stretching
1,581	Stretching vibration (C=C) aromatic cycle, -deformation vibration (=NH)	1,107–1,000	C–O bond, characteristic peak for phosphate band
1,297	Symmetric stretching vibration, carboxylates	809–842	Alkenes, =C–H bond, stretching vibration N=O
1,047–1,126	Stretching vibration C–O (of alcohols), =C–O–C= and C–C alkenes		

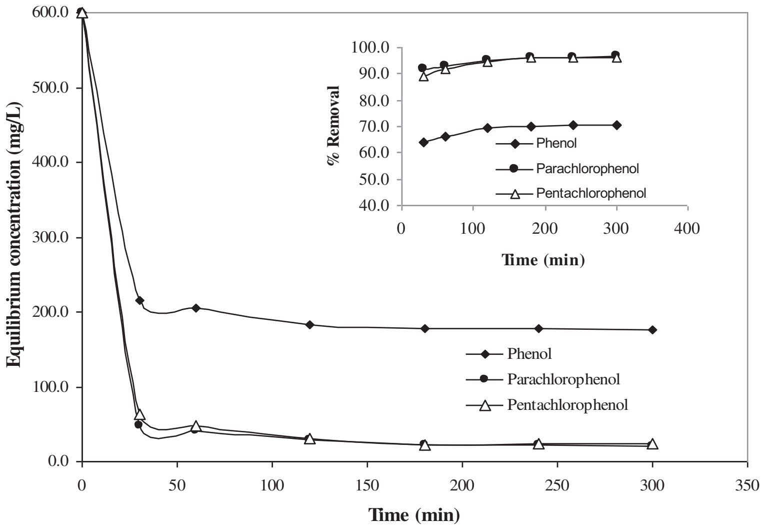

Fig. 4. Variation of phenolic compounds equilibrium concentration with time ($C_{initial} = 600$ mg L^{-1}). Inset: time-dependent phenolic compounds uptake.

The nature of interactions between the adsorbents used and the adsorption capacity will be affected by pH. Phenol uptake decreases as pH exceeds $pK_{a\ phenol}$ (9.89). This reduction in phenol adsorption is due to the repulsion between the activated carbon surface and the negatively charged phenalate form obtained at $pH > pK_a$. The same phenomenon has been reported in the literature [36]. In this case, the interactions of the electrostatic type take a particular importance because in very acid medium, the protons are adsorbed on carbonyls sites, thus competing with the phenol [21,37]. A maximum parachlorophenol uptake was found at pH 6.5 in the studied systems. At higher pH values, there is a repulsion between the adsorbate and the adsorbent due to the lesser acid character of parachlorophenol associated to an attractable effect of electrons (presence of chlorine in the aromatic ring). Dispersion effects such as interaction ring electron, interaction donor–acceptor of electrons, and an electrostatic attraction–repulsion in the presence of ions [38] are mainly responsible for this decrease in adsorption of the parachlorophenol. In general, it was observed that the adsorption of organic molecules is considerably influenced by the solution pH. The more the acidic pH is, the higher adsorption will be. However, for $pH < pK_a$, the molecules exist in neutral form and adsorption is favored contrary to high pH values where adsorption is favored for anion species.

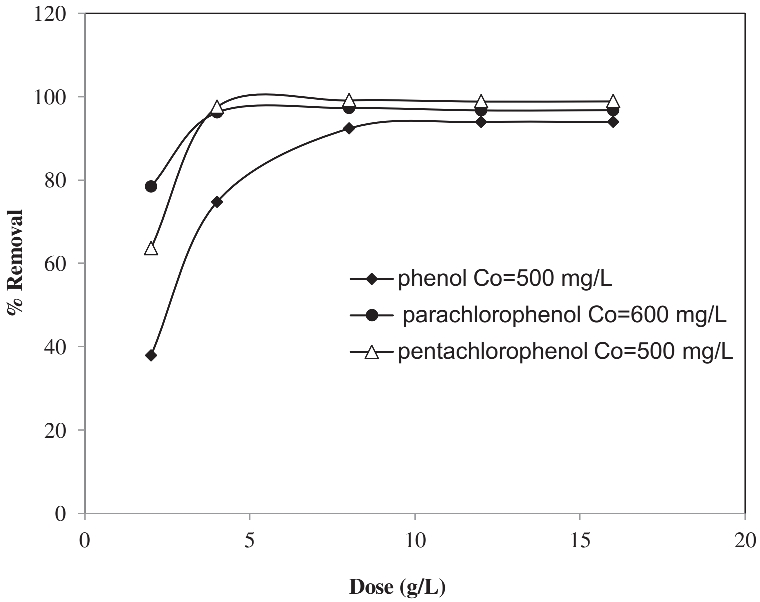

Fig. 5. Dose effect on phenolic compounds adsorption by SDB-AC.

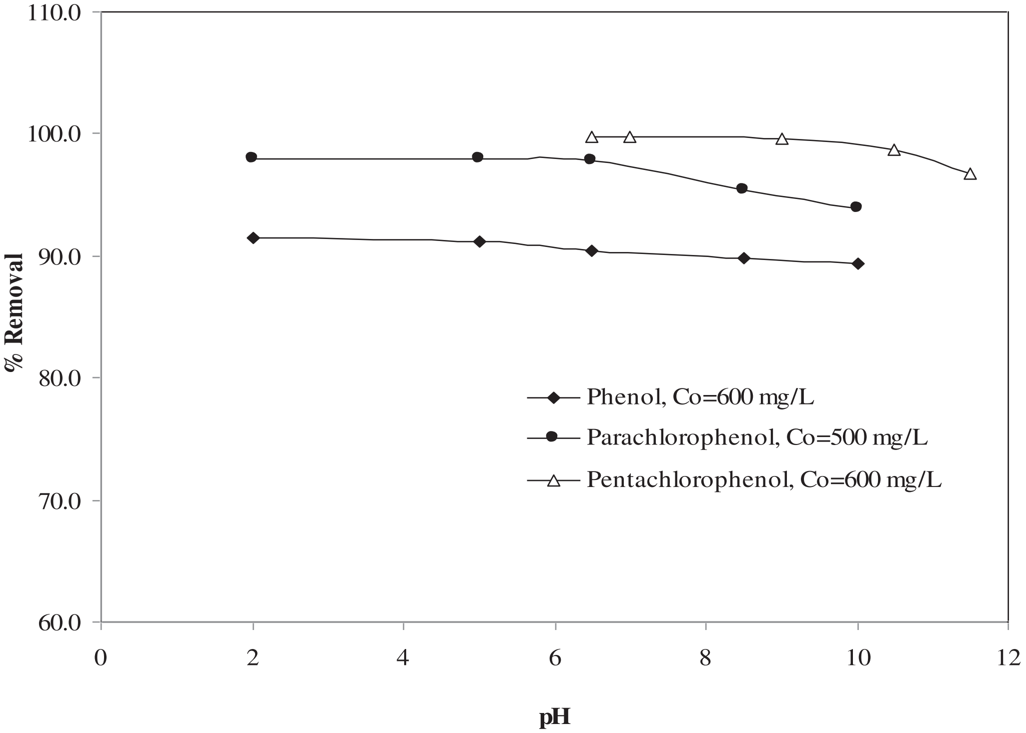

Fig. 6. pH effect on phenolic compounds adsorption by SDB-AC.

3.5. *Adsorption isotherms*

The adsorption isotherms of the phenolic compounds on the prepared activated carbons at ambient temperature, pH of 5 and 6.5 (determined previously) and a solid–liquid ratio of 8 g L^{-1} are presented in Figs. 7–9. As it can be seen from Fig. 7, the adsorption of phenolic compounds onto activated carbons have a typical Langmuir L-type isotherm of Giles classification

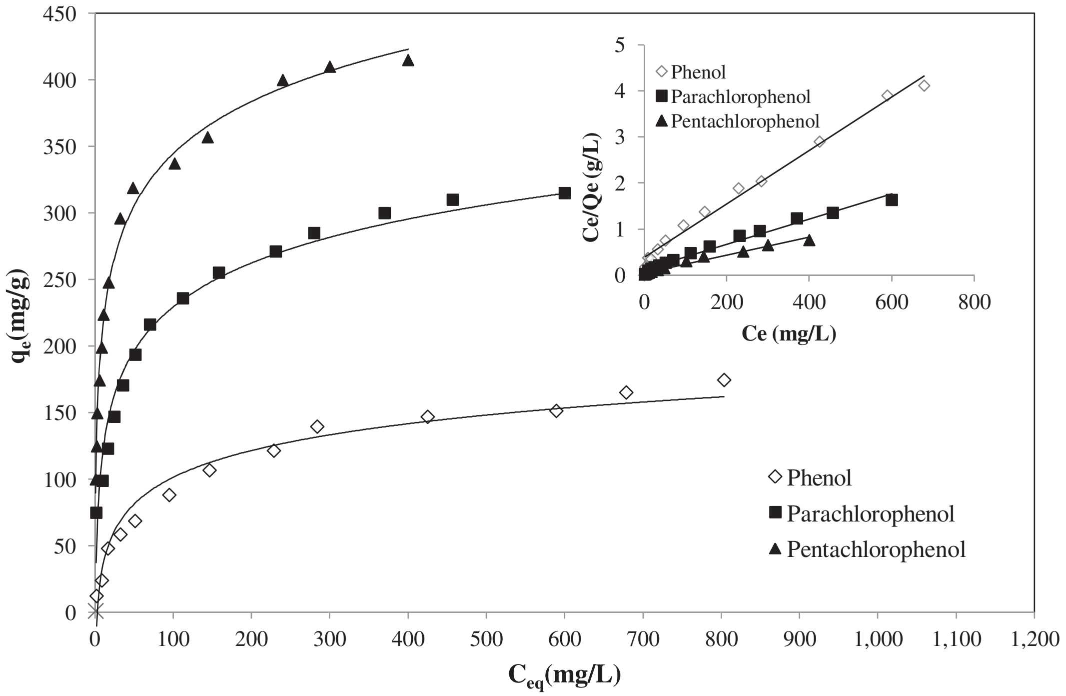

Fig. 7. Plots of Langmuir adsorption isotherms of phenolic compounds onto SDB-AC. Insert: linear forms of Langmuir adsorption isotherms of phenolic compounds onto SDB-AC.

[39,40]. The adsorbed amount of the pollutant increases quickly for weak concentrations in solution then attenuates to reach a plateau corresponding to adsorption sites saturation with values of 200, 334, and 500 mg g^{-1}, respectively, for phenol, parachlorophenol, and pentachlorophenol (Table 5). Values are compared to some

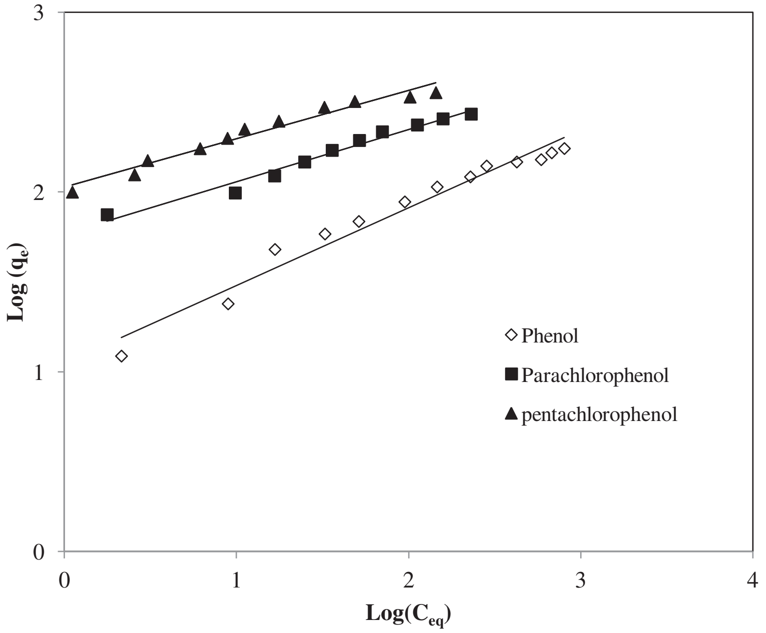

Fig. 8. Plots of Freundlich adsorption isotherms of phenolic compounds onto SDB-AC.

Table 5
Langmuir, Freundlich, and Temkin parameters for the removal of phenolic compounds by the prepared and the commercial adsorbents

		Langmuir			Freundlich			Temkin		
Adsorbent	Adsorbate	b (mg g^{-1})	K_L (L mg^{-1})	R^2	K_f (mg g^{-1})	n	R^2	B	K_T	R^2
SDB-AC	Phenol	200.0	0.010	0.99	2.36	11.43	0.96	13.33	0.13	0.99
	Parachlorphenol	333.3	0.042	0.99	3.75	106.66	0.96	18.12	1.49	0.94
	Pentachlorophenol	500	0.118	0.99	3.44	58.210	0.97	21.51	4.38	0.98
Merck-AC	Phenol	166.7	0.122	0.99	2.91	28.18	0.89	17.90	3.80	0.98
	Parachlorphenol	250.0	0.133	0.99	11.49	146.22	0.85	32.99	1,583.3	0.85
	Pentachlorophenol	166.7	0.111	0.99	4.12	42.27	0.72	18.26	5.03	0.89

values obtained from the literature as shown in Table 6. The Langmuir model is more representative indicating that the adsorption might look to the filing of a monolayer of solute molecules on adsorbents surfaces.

Linear plots for Temkin adsorption isotherm shown in Fig. 9 fit well the experimental data for all the considered phenolic compounds by the SDB-AC (high values of R^2 shown in Table 5) in comparison with commercial Merck-AC, which shows a relatively poor agreement with experimental data especially for pentachlorophenol and parachlorophenol (lower values of R^2). Lower values of B which are an indication of the heat of adsorption indicating a physical process.

3.6. Adsorption kinetics

To study the kinetics of adsorption of the phenol compounds, a volume of 25 mL of stirred solution containing the pollutant of known concentration is put in contact with 0.2 g of adsorbent in a 50 mL beaker. After filtering, the concentration was determined using Eq. (1) with q_t (mg g^{-1}) and C_t (mg L^{-1}) which are, respectively, the quantity adsorbed per gram of adsorbent and the liquid phase concentration at time t. In order to analyze the kinetic data, three models were chosen for simplicity reasons, namely, the pseudo-first-order [46,47], the pseudo-second-order, and the intraparticle diffusion models [48]. These models can be expressed as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{7}$$

Pseudo-first-order model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

Pseudo-second-order model

$$q_t = K_{int} t^{0.5} + C \tag{9}$$

Intraparticle diffusion model

Table 6
Adsorption isotherms of phenolic compounds on various activated carbons

Pollutant	Adsorbent	Max. capacity (mg g^{-1})	References
Parachlorophenol	Rattan sawdust	188.68	[41]
	Coconut shell	72.769	[12]
	Kenaf-AC	140.84	[42]
	Functional chitosan	179.73	[43]
	Sludge-based AC	1,080	[44]
	SDB-AC	333.33	This study
Phenol	Functional chitosan	131.50	[43]
	Vetiver roots AC	145	[11]
	Sludge-based AC	348.02	[44]
	SDB-AC	200	This study
Pentachlorophenol	Bentone SD3 (Clay type)	54.5	[45]
	SDB-AC	500	This study

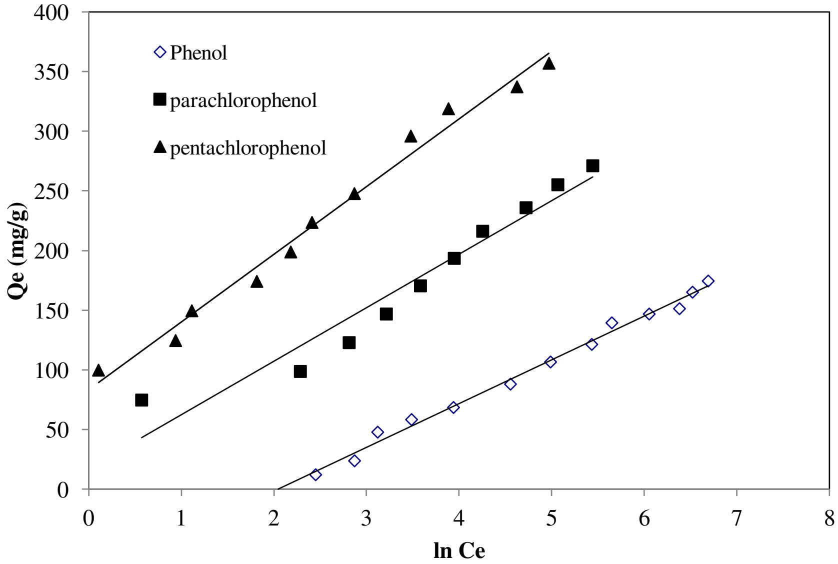

Fig. 9. Plots of Temkin adsorption isotherms of phenolic compounds onto SDB-AC.

where q_e and q_t (mg g^{-1}) are the amount of phenol compounds adsorbed at equilibrium and at time t (min), respectively, k_1 (min^{-1}) is the adsorption rate constant, k_2 (g mg^{-1} min^{-1}) is the rate constant of second order equation, K_{int} (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant, and C (mg g^{-1}) is a constant that gives an idea about the thickness of the boundary layer [38].

From Table 7 and Fig. 10, we notice that the pseudo-second-order model is the most reliable to describe the kinetics of adsorption of the phenolics onto SDB-AC and Merck-AC, Merck with good correlation coefficients ($R^2 = 0.99$). In the same way, it is noticed that the calculated (q_{cal}) values using the pseudo-second-order model are very close to the experimentally (q_{exp}) obtained ones. This corroborates the fact that the kinetics of adsorption of phenol and parachlorophenol onto the adsorbents investigated are well represented by the pseudo-second-order model. On the other hand, the difference between the calculated and the experimental adsorption capacities shown in Table 7 indicates that the pseudo-first-order model is poorly adequate (figures not shown). The intraparticle diffusion model expressed by Eq. (9) was also applied to the experimental data in order to elucidate the mechanism of diffusion by plotting q_t as a function of $t^{1/2}$ for two different concentrations of each of phenol, parachlorophenol, and pentachlorophenol. K_{int} (constant rate) and C (boundary layer effect) parameters obtained from the slope and the intercept, respectively, from this plot are listed in Table 7. It is seen that these parameters increase with increasing initial adsorbate concentrations. The increase in the boundary layer thickness leading to a good contribution of the surface sorption in the rate controlling step is due to the increase of C values with initial concentrations [38].

3.7. Thermodynamic parameters

Thermodynamic parameters in terms of the change in free energy (G), enthalpy (H), and entropy (S) were applied to evaluate the thermodynamic behavior of the adsorption of phenol and its compounds onto the SDB-AC and Merck-AC at three different temperatures (298, 303, and 313 K). These parameters were calculated from the distribution coefficient for adsorption (K_d) using the following equations:

$$K_d = \frac{q_e\ (m/V)}{C_e} \tag{10}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{T} \tag{11}$$

$$\Delta G = -RT \ln K_d = T\Delta S - \Delta H \tag{12}$$

Plots of ln K_d vs. T^{-1} from which ΔS and ΔH were obtained from the intercept and the slope, respectively, (figures not shown). The calculated values of ΔG, ΔH, and ΔS are listed in Table 8. The results indicate that the adsorption capacities increase from 61.96 to 124.53 mg g^{-1} for parachlorophenol and from

Table 7
Kinetic parameters for the adsorption of phenolic compounds by SDB-AC and Merck-AC

		Substance					
Adsorbent	Parameter	Phenol		Parachlorophenol		Pentachlorophenol	
SDB-AC	C_{initial} (mg L^{-1})	500	600	600	800	600	800
	q_{exp} (mg g^{-1})	59.36	70.09	74.86	99.2	74.93	99.86
	Pseudo-first-order						
	q_{cal} (mg g^{-1})	1.54	16.26	2.27	2.55	1.79	2.21
	k_1 (min^{-1})	0.025	0.045	0.0119	0.0069	0.011	0.012
	R^2	0.97	0.98	0.66	0.67	0.51	0.85
	Pseudo-second-order						
	q_{cal} (mg g^{-1})	59.52	71.43	74.63	99.01	76.92	100
	k_2 (g mg^{-1} min^{-1})	0.046	0.008	0.02	0.02	0.028	0.025
	R^2	1.00	1.00	1.00	0.99	1.00	1.00
	Intraparticle diffusion						
	k_{int} (mg g^{-1} min–$^{0.5}$)	0.049	0.226	0.126	0.239	0.112	0.142
	C (mg g^{-1})	58.7	67.23	73.01	95.73	73.3	97.86
	R^2	0.97	0.85	0.74	0.77	0.77	0.89
Merck-AC	C_{initial} (mg L^{-1})	500	1,000	500	1,000	500	600
	q_{exp} (mg g^{-1})	104.7	137.6	124.03	221.6	61.97	74.43
	Pseudo-first-order						
	q_{cal} (mg g^{-1})	0.93	3.77	0.94	137.0	1.188	1.598
	k_1 (min^{-1})	0.052	0.036	0.03	0.052	0.022	0.017
	R^2	0.75	0.98	0.84	0.50	0.97	0.90
	Pseudo-second-order						
	q_{cal} (mg g^{-1})	105.26	142.86	123.46	250.00	62.5	76.92
	k_2 (g mg^{-1} min)	0.150	0.049	0.109	0.001	0.0512	0.0338
	R^2	1.00	1.00	1.00	0.99	1.00	1.00
	Intraparticle diffusion						
	k_{int} (mg g^{-1} min–$^{0.5}$)	0.022	0.216	0.032	9.873	0.017	0.065
	C (mg g^{-1})	104.5	135.4	123.6	121.5	61.7	73.44
	R^2	0.99	0.91	0.52	0.72	0.95	0.91

74.13 to 74.41 for pentachlorophenol. Therefore, increasing in temperature facilitated the adsorption of both phenolic compounds on sawdust-based activated. The negative values of ($\Delta G < 0$) indicate the spontaneous nature of their adsorption onto the SDB-AC. For all considered cases in study, there is an increasing in (ΔG) values with increasing temperature. The degree of disorder at the solid–liquid interface increased during the adsorption of pentachlorophenol and parachlorophenol indicating that significant change in the internal structure of the prepared adsorbent surface might have occurred as showed by positive values of ($\Delta S > 0$). The negative value of ($\Delta S < 0$) for the only case of phenol, indicates that the measure of the degree of randomness decreased. This ($\Delta S < 0$) may also imply that no significant change occurred in the internal structure of the prepared adsorbent as observed by other researchers [49]. In general, ΔH can be used to distinguish between physical (weak) and chemical (strong) interactions during adsorption process. In this study, the ΔH values show that the adsorption process of some phenolic compounds such as pentachlorophenol onto SDB-AC and Merck-AC taking place via physisorption (low values of ΔH) associated with endothermicity [38,50]. On the other hand, higher values of ΔH are clear evidence that chemisorption governs the adsorption of parachlorophenol by both adsorbents.

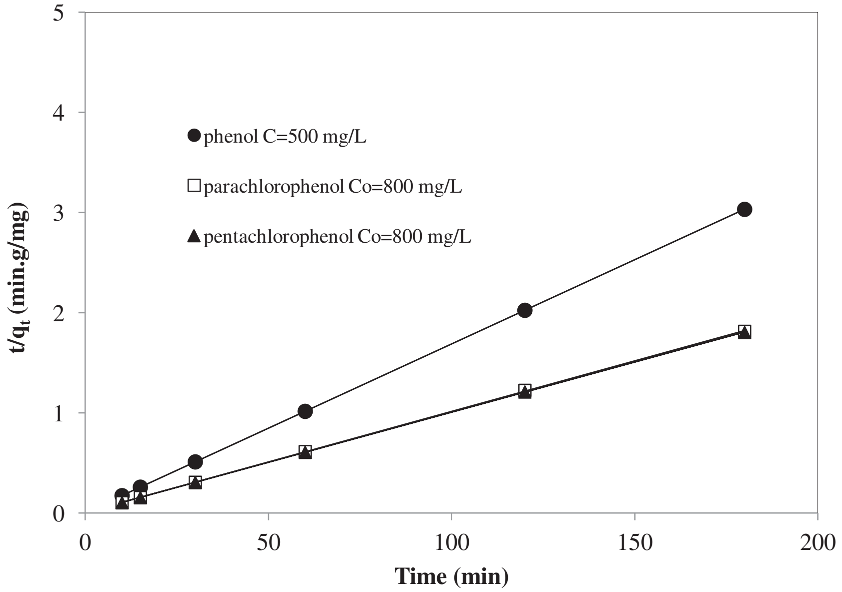

Fig. 10. Pseudo-second-order plots of phenolic compounds adsorption onto SDB-AC.

Table 8
Thermodynamic parameters of phenolic compounds onto SDB-AC and Merck-AC

		ΔG (kJ mol^{-1})			ΔH	ΔS
Adsorbent	Adsorbate	298 K	303 K	313 K	(kJ mol^{-1})	(kJ mol^{-1} K^{-1})
SDB-AC	Phenol	−1.44	−1.37	−1.22	−5.79	−0.015
	Parachlorophenol	−6.88	−9.06	−13.64	127.70	0.452
	Pentachlorophenol	−11.15	−11.60	−12.64	18.64	0.100
Merck-AC	Phenol	−8.53	−8.75	−9.21	5.10	0.046
	Parachlorophenol	−6.59	−8.48	−10.90	77.15	0.282
	Pentachlorophenol	−5.87	−6.25	−7.18	20.37	0.088

4. Conclusion

The use of a lignocellulosic waste as a suitable precursor for activated carbons preparation by chemical activation using H_3PO_4 and heat was investigated. The two-step activation process of sawdust has improved considerably its adsorptive capacity. The obtained adsorbents of developed surface area (2,270 m^2 g^{-1}) and pronounced adsorption activity were used to remove some toxic phenolic pollutants from aqueous media. Experimental conditions of 180 min (time of impregnation), 700°C (pyrolysis temperature), 60% H_3PO_4 (acid concentration), and pH 6 yielded an activated carbon with maximum uptake values of 200, 334, and 500 mg g^{-1} for phenol, parachlorophenol, and pentachlorophenol, respectively, in comparison to corresponding values of 167, 167, and 250 mg g^{-1} for the commercial activated carbon.

This significant adsorption capacity showed that the activated sawdust can be used as an alternative to the commercially adsorbents in removing phenolic compounds from industrial wastewater.

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