Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: Equilibrium, kinetics and thermodynamics

Murat Kilic, Esin Apaydin-Varol, Ayşe E. Pütün *

Department of Chemical Engineering, Anadolu University, Eskişehir 26470, Turkey

ARTICLE INFO

ABSTRACT

This study consists of producing high surface area activated carbon from tobacco residues by chemical activation and its behavior of phenol removal from aqueous solutions. K_2CO_3 and KOH were used as chemical activation agents and three impregnation ratios (50, 75 and 100 wt.%) were applied on biomass. Maximum BET surface areas of activated carbons were obtained from impregnation with 75 wt.% of K_2CO_3 and 75 wt.% of KOH as 1635 and 1474 m^2/g, respectively. Optimum adsorption conditions were determined as a function of pH, adsorbent dosage, initial phenol concentration, contact time and temperature of solution for phenol removal. To describe the equilibrium isotherms the experimental data were analyzed by the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models. Pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models were used to find out the kinetic parameters and mechanism of adsorption process. The thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated for predicting the nature of adsorption. According to the experimental results, activated carbon prepared from tobacco residue seems to be an effective, low-cost and alternative adsorbent precursor for the removal of phenol from aqueous solutions.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health [1]. The major sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coal conversion, polymeric resin, gasoline, rubber proofing, steel, petroleum and petrochemical industries [2,3]. Excessive exposure to phenol may cause health effects on the brain, digestive system, eye, heart, liver, lung, skin and others on human beings [4]. Therefore, removal of phenols from industrial effluents is required before sewage disposal [5]. Accordingly, various technical processes such as oxidation, biodegradation, chemical coagulation, solvent extraction, incineration, reverse osmosis and adsorption have been proposed to remove phenolic compounds from contaminated waters, among which adsorption is one of the most effective techniques in either laboratory or industrial scale [6]. There are many adsorbents in use. Activated carbons are the most widely used adsorbents due to their large surface area, micro-porous nature, high adsorption capacity, high purity and easy availability [1,2].

Production of activated carbon can either be through physical or chemical activation. The nature of the precursor, activation method, and activation conditions determine the characteristics of porosity in activated carbons, including pore size distribution, pore shape, and surface chemistry [7]. Physical activation is a two-step process [8]. The material is carbonized under inert atmosphere and then activated at high temperature using either steam or carbon dioxide as the activating reagent to produce more porous structures [9]. In chemical activation, raw material is impregnated with an activation reagent and heated in an inert atmosphere. The carbonization step and the activation step proceed simultaneously. By dehydration and oxidation reactions of the chemicals, pores are developed. Produced char is then washed to rid it from residual impurities [8]. The advantages of chemical activation are: its low energy and operating cost, high carbon yields and large surface areas with porous structure when compared with physical activation [9,10].

Activated carbons are produced from a variety of carbonaceous materials. The choice of precursor largely depends on its availability, cost, and purity, but the manufacturing process and intended applications of the product are also important considerations [10]. Therefore evaluation of biomass is getting increased attention in all over the world as it is renewable, widely available, cheap, and environmental friendly [11]. There are a number of biomass sources, such as forest residues, low grade plants, agricultural residues and municipal solid wastes, which can be utilized for activated carbon precursor [12].

---

* Corresponding author. Tel.: +90 0 222 321 3550 6504; fax: +90 0 222 323 9501.
E-mail address: aeputun@anadolu.edu.tr (A.E. Pütün).

Nomenclature

q_e (mg/g)   adsorption capacity at equilibrium
q_m (mg/g)   complete monolayer adsorption capacity
q_t (mg/g)   adsorption capacity at time t
C_i (mg/L)   initial phenol concentration
C_e (mg/L)   equilibrium phenol concentration
C_0 (mg/L)   highest initial phenol concentration
V (L)   solution volume
W (g)   mass of adsorbent
K_L (L/mg)   Langmuir adsorption constant
K_F ((mg/g) (L/mg)$^{1/n}$)   Freundlich adsorption constant
n empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the material (dimensionless)
β (mol^2/kJ^2)   adsorption energy constant
ε Polanyi potential
R (8.314 J/(mol K))   gas constant
T (K)   absolute temperature
E (kJ/mol)   mean free energy
b_T (J/mol)   Tempkin constant related to the heat of adsorption
K_T (L/mg)   Temkin constant related to the equilibrium binding energy
t (min)   contact time
k_1 (1/min)   rate constant of pseudo-first order adsorption
k_2 (g/mg min)   rate constant of pseudo-second order adsorption
k_p (mg/g min$^{1/2}$)   intraparticle diffusion rate constant
C intercept
ΔG° Gibbs free energy change (kJ/mol)
ΔH° enthalpy change (kJ/mol)
ΔS° entropy change (kJ/mol)
K_e equilibrium constant

Turkey is one of the major tobacco producer and exporter country. Tobacco production is nearly 100,000 t/yr. Thus, tobacco residue generated from tobacco harvest has a major economic importance and exhibits a high affinity for phenols. Therefore, in this study, adsorption of phenol from aqueous solutions on activated carbon prepared from tobacco residue by chemical activation was studied. Experimental parameters affecting the adsorption process such as pH, adsorbent dosage, initial phenol concentration, contact time and temperature of solution for phenol removal were optimized. The equilibrium, kinetic and thermodynamic data of the adsorption was studied to describe the adsorption process.

1.1. Equilibrium modeling

Adsorption is a well-known equilibrium separation process for wastewater treatment. Adsorption isotherms are the equilibrium relationships between the concentrations of the adsorbed phenol and phenol ion in the solution at a given temperature. In this study Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models were used to investigate the adsorption equilibrium between the phenol solution and the activated carbon phase.

The Langmuir model is a non-linear model that suggests a monolayer uptake of the phenol on a homogenous surface, having uniform energies of adsorption for all the binding sites without any interaction between the adsorbent molecules [13]. The linear form of the Langmuir isotherm equation [14,15] is represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \tag{1}$$

The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using dimensionless separation factor (R_L). R_L is calculated by the following equation [16]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{2}$$

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm is an empirical model that is based on adsorption on heterogeneous surface and active sites with different energy. The linearized Freundlich isotherm equation [17] is represented by the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

The D-R isotherm is another model for the analysis of isotherms of a high degree of rectangularity. The D-R isotherm is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential. The linear form of D-R isotherm equation is as follows [18]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

where β is a constant and gives the mean free energy (E(kJ/mol $= 1/\sqrt{2\beta}$)) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution (mol^2/kJ^2) and ε can be correlated as;

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \tag{5}$$

Temkin and Pyzhev [19,20] considered the effects of indirect adsorbent/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent/adsorbate interactions. The linear form of Temkin isotherm equation is as follows:

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

where $B = RT/b_T$. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [1].

1.2. Kinetic modeling

The kinetics of adsorption is an important characteristic to define the efficiency of adsorption. In order to investigate the mechanism of adsorption and kinetic parameters sorption data was analyzed using pseudo-first order [21,22], pseudo-second order [23,24] and intraparticle diffusion [25] models.

The pseudo first-order rate equation of Lagergren based on solid capacity is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

Integration of Eq. (7) for the initial conditions $t = 0$ and $q_t = 0$ gives the linearized from of the pseudo-first order rate equation as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \tag{8}$$

Pseudo-second order model predicts the behavior over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step comparing with the pseudo-first order model [1]. The pseudo-second order kinetic model equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

Integration of Eq. (9) for the initial conditions $t = 0$ and $q_t = 0$ gives the linearized from of the pseudo-second order rate equation as:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{10}$$

Eq. (10) can be rearranged to

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

The pseudo-first order and pseudo-second order kinetic models cannot generally identify the diffusion mechanism and rate controlling steps affecting the kinetics of adsorption. The kinetic results were then analyzed by using intraparticle diffusion model. The intraparticle diffusion equation can be written as:

$$q_t = k_p t^{1/2} + C \tag{12}$$

According to this model, the plot should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate-controlling step. If the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously [26,27].

1.3. Thermodynamic modeling

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process [28]. Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and the entropy change (ΔS°) can be estimated using equilibrium constants changing with temperature. The Gibbs free energy change of the adsorption reaction can be determined from the following equation:

$$\Delta G^\circ = -RT \ln K_e \tag{13}$$

The K_e value was calculated using the following equation:

$$K_e = \frac{q_e}{C_e} \tag{14}$$

Relation between ΔG°, ΔH° and ΔS° can be expressed by the following equations:

$$\Delta G^\circ = DH^\circ - T \Delta S^\circ \tag{15}$$

Eq. (15) can be written as

$$\ln K_e = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{16}$$

according to the Eq. (16), ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K_e$ versus $1/T$, respectively [28–30].

2. Experimental

2.1. Materials

Tobacco residue was collected from Aegean Region of Anatolia. Tobacco was harvested between July and August and the residue was collected after harvest. Tobacco residue first washed with distilled water to remove impurities like dust, dried at room temperature, ground in a high-speed rotary cutting mill, sieved and stored in a cool and dark room.

2.2. Preparation of activated carbon

Tobacco residue with a particle size of 0.85–0.425 mm was activated using chemical activation technique. K_2CO_3 and KOH were used as chemical activation agents and three impregnation ratios (50, 75 and 100 wt.%) were applied on biomass samples. Samples were kept overnight at room temperature for 24 h and then dried at 85 °C for 72 h to prepare impregnated sample. The impregnated samples then carbonized at 700 °C under nitrogen (N_2) flow of 100 cm^3/min and at a heating rate of 10 °C/min in a stainless steel fixed bed reactor, details of which were given elsewhere [31]. After being cooled, all the carbonized samples were washed several times with hot water until the pH became neutral and finally washed with cold water to remove residual chemicals. The washed samples were dried at 105 °C for 24 h to obtain the final activated carbons. The activated carbons were classified as ACK1 and ACK2, where the first two characters, AC, represents activated carbons, the last two characters K1 and K2 represents K_2CO_3 and KOH impregnation, respectively.

2.3. Batch adsorption experiments

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ/cm conductivity) was used for all solutions. The initial pH of each phenol solution was adjusted by using 0.1 mol/L NaOH and 0.1 mol/L HCl solutions. A portable Sartorius PT-10 Model pH meter was used for measuring pH values in the aqueous phase. Batch equilibrium adsorption experiments were performed using 50 mL of phenol solution. After adsorption process the adsorbent separated from the samples by filtering and the filtrate was analyzed using UV–vis spectrophotometer at 270 nm wavelength. To investigate the effects of adsorption parameters on adsorption of phenol onto tobacco residue derived activated carbon such as, pH (5–9), adsorbent dosage (0.5–8.0 g/L), initial phenol concentration (1–12 mg/L), contact time (10–240 min) and temperature (20–50 °C) were studied in a batch mode of operation.

The amount of phenol adsorbed per unit mass of the adsorbent (q_e) was calculated by using the following mass balance equation,

$$q_e = \frac{(C_i - C_e)V}{W} \tag{17}$$

and the percent adsorption of phenol was calculated as follows:

$$\text{adsorption}(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{18}$$

3. Results and discussion

3.1. Characterization of activated carbon

Table 1 represents the characteristics of raw tobacco residue. High carbon and low ash content indicated that the precursor is suitable for activated carbon production. Characteristics and BET surface areas of activated carbons are given in Table 2. Activated carbons have higher carbon content than raw tobacco residue which makes them more carbonaceous material. Also BET surface area of activated carbon is important because, like other physical and chemical characteristics, it may strongly affect the reactivity and adsorption behavior. The maximum surface areas were obtained with the activation of 75% K_2CO_3 and 75% KOH impregnated samples as 1634 and 1474 m^2/g, respectively. The higher surface areas are probably due to the opening of the restricted

Table 1
Characteristics of raw tobacco residue.

Proximate analysis (%)	
Moisture	8.13
Ash	11.73
Volatiles	67.55
Fixed C	12.59
Ultimate analysis (%) (dry-ash basis)	
C	40.95
H	5.21
N	5.99
O[a]	47.85
H/C	1.52
O/C	0.88
HHV (MJ/kg)	15.07
Structural analysis (%)	
Lignin	8.75
Cellulose	42.30
Oil	3.30

[a] By difference.

Table 2
Characteristics of activated carbons (as received).

Sample code	Impregnation ratio	Elemental analysis (wt.%)				Surface area (m²/g)
		C	H	N	O[a]	
ACK1	50	54.09	0.46	1.35	44.10	1571
	75	55.25	0.22	0.95	43.58	1634
	100	58.11	0.76	1.63	39.05	1250
ACK2	50	58.71	0.64	1.06	39.59	1215
	75	49.40	0.28	1.52	48.80	1474
	100	48.03	1.16	1.49	49.32	998

[a] By difference.

pores with the help of activating reagents. Above 950 K, the carbon reduced the impregnated K_2CO_3 and was consumed through the formation of CO, leading an increase in surface area and pore volume [32]. Thus the specific area of K_2CO_3 impregnated sample was higher than KOH impregnated sample. All adsorption experiments were conducted with obtained by impregnation with 75% K_2CO_3 and 75% KOH.

Scanning electron microscopy (SEM) technique was used to observe the surface physical morphology of the samples. SEM micrograph of raw tobacco residue and the activated carbons for the highest surface areas are given in Fig. 1. It is seen that a thick wall structure exists along with a little porosity for the raw material. SEM images of activated carbons show that thick wall gets opened and a wider porosity is created, thus the external surfaces of the chemically activated carbons are full of cavities. After carbonization, K_2CO_3 and KOH impregnated samples forms sponge-like morphology activated carbons. Pores of different size and different shapes were obtained from two different chemical activation agents.
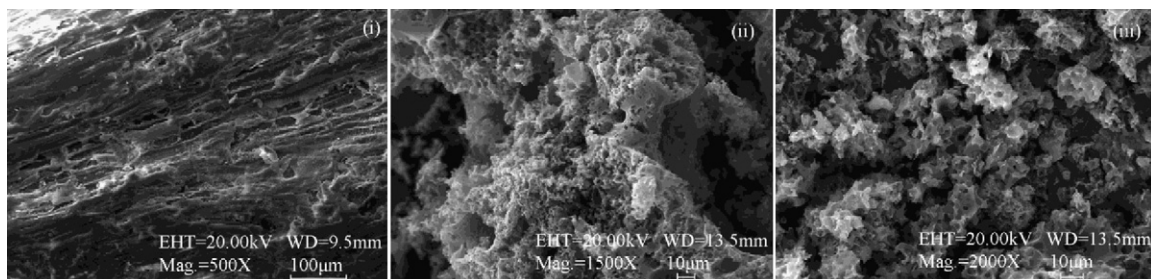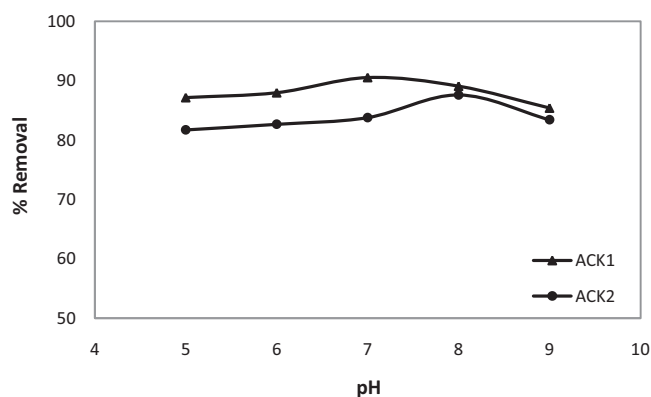

Fig. 2. Effect of pH on phenol removal onto ACK1 and ACK2.

3.2. Adsorption of phenol

3.2.1. Effect of pH

Hydrogen ion concentration in the adsorption is considered to be one of the most important parameters that influence the adsorption behavior of phenol in aqueous solutions. It affects the solubility of phenol ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction [33].

The effect of initial pH on the adsorption of phenol was determined within the pH range of 5–9 and the results are represented in Fig. 2. The maximum adsorption was determined at pH 7 as 90.5% for ACK1 and at pH 8 as 87.6% for ACK2. This may be due to the difference in the concentrations of H^+ and OH^- in the solutions. Adsorbent particles have active sites with negative charges. The H^+ ions within low pH environments can neutralize those negative sites, reduce the hindrance to diffusions of phenol ions and consequently increase the chances of their adsorption. High pH environments led to high concentration of OH^-, which can increase the hindrance to the diffusions of phenol ions and thus reduce the chances of their adsorption [34]. Therefore, for this study all the adsorption experiments were carried out at pH 7 for ACK1 and pH 8 for ACK2 where the highest adsorptions were obtained.

3.2.2. Effect of adsorbent dosage

The adsorbent dosage is an important parameter because this parameter determines the capacity of adsorbent for a given phenol concentration and also determines sorbent–sorbate equilibrium of the system. The effect of adsorbent dosage on the adsorption of phenol was determined within the adsorbent dosage range of 0.5–8 g/L and the results are represented in Fig. 3. It is known that the increase in adsorbent concentration resulted in an increase in percent adsorption of phenol due to the greater availability of the exchangeable sites or surface area, but decreased the adsorption amount due to the partial aggregation or overlapping of activated
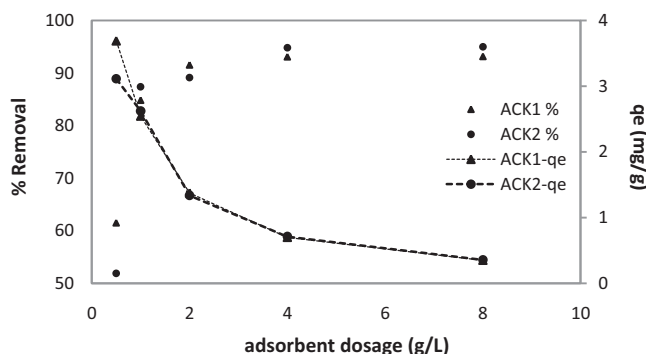

Fig. 1. SEM images of (i) raw tobacco residue, (ii) ACK1, and (iii) ACK2.

Fig. 3. Effect of adsorbent dosage on phenol removal onto ACK1 and ACK2.

Fig. 4. Effect of initial phenol concentration on phenol removal onto ACK1 and ACK2.

Fig. 5. Effect of contact time on phenol removal onto ACK1 and ACK2.

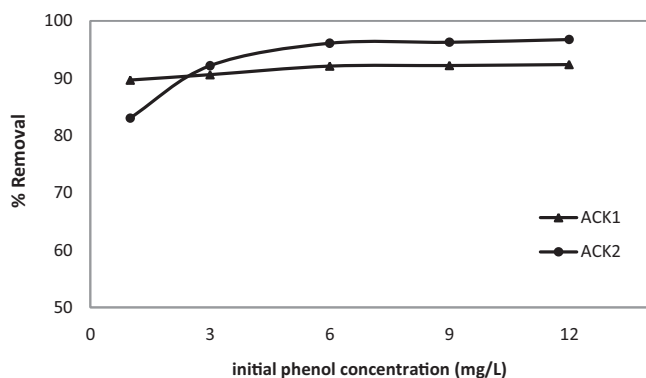**Fig. 6.** Effect of temperature on phenol removal onto ACK1 and ACK2.

carbon, which results in a decrease in effective surface area for the adsorption. It is seen from Fig. 3 that adsorption efficiency increased with increasing adsorbent dosage for both ACK1 and ACK2, but adsorption amount decreased with increasing adsorbent dosage. After a certain dosage, the adsorption efficiency was not increased significantly. Therefore, the optimum amounts of ACK1 and ACK2 for further adsorption experiments were selected as 2 and 4 g/L for ACK1 and ACK2, respectively.

3.2.3. Effect of initial phenol concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of phenol between the aqueous and solid phase. Fig. 4 represents the results of initial concentration effect on phenol adsorption within range of 1–12 mg/L. The equilibrium adsorption efficiency of activated carbon increased slightly with increasing initial phenol concentration up to 6 mg/L. Then adsorption efficiency decreased as the initial phenol concentration was increased. The higher adsorption at lower concentrations may be due to the presence of more available sites on the adsorbent than the number of phenol ions which are available in the solution. However, at higher concentrations the number of phenol ions is relatively higher than available sites for adsorption. The maximum adsorption was determined at 6 mg/L as 92% for ACK1 and 96% for ACK2.

3.2.4. Effect of contact time

Contact time is an important parameter to determine the equilibrium time of adsorption process. The characteristics of activated carbon and its available sorption sites affected the time needed to reach the equilibrium. The experimental results for the determination of equilibrium time are given in Fig. 5 and it is obviously seen that adsorption capacity increased with increasing contact time. Large amounts of phenol was removed in the first 60 min and equilibrium was reached in 120 min for both ACK1 and ACK2.
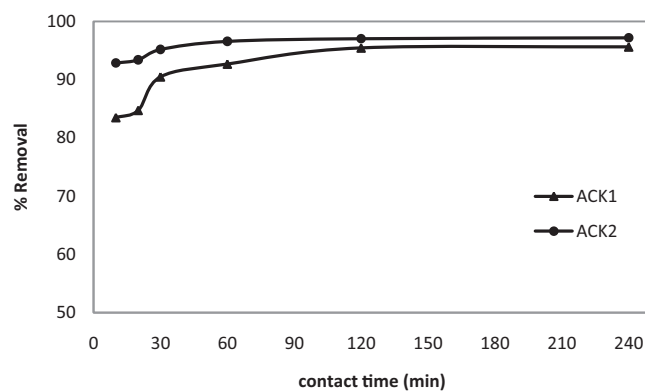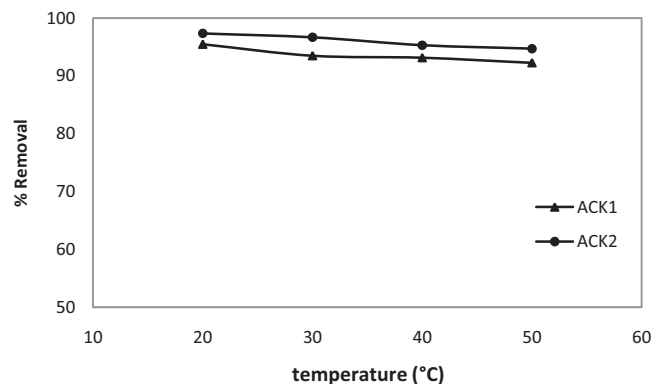
After the equilibrium, adsorption efficiency was not increased significantly.

3.2.5. Effect of temperature

Fig. 6 shows the experimental results obtained from phenol adsorption when temperature was varied from 20 to 50 °C. The adsorption efficiency decreased with an increase in temperature. The decrease in adsorption efficiency indicates an exothermic process. This may be due to the increasing trend to desorp phenol from the interface to the solution or the distorted active sites on adsorbent. The optimum solution temperature was selected as 20 °C for both ACK1 and ACK2.

3.3. Adsorption isotherms

The Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm parameters for adsorption of phenol onto activated carbon are given in Table 3. Comparison of the R^2 values shows that the Langmuir isotherm fitted quite well with the experimental data obtained from ACK1 with a high correlation coefficient ($R^2 = 0.9992$). In other words, this result may be due to the homogenous distribution of active sites on the surface of ACK1. Maximum monolayer adsorption capacity q_{max} of phenol onto ACK1 was 17.83 mg/g. R_L value was calculated as 0.15, which is greater than zero and less than unity, showing favorable adsorption of phenol onto activated carbon obtained from tobacco residue by chemical activation with K_2CO_3.

The Dubinin-Radushkevich isotherm fitted quite well with the experimental data obtained from ACK2 with a high correlation coefficient ($R^2 = 0.9991$). From the intercept of the plots, the q_m value was found to be 45.49 mg/g. The mean adsorption energy was calculated and the result indicated that the

Table 3
Isotherm constants for the adsorption of phenol onto ACK1 andACK2.

Isotherms	Parameters	
	ACK1	ACK2
Langmuir		
q_m (mg/g)	17.83	0.55
K_L (L/mg)	0.46	2.68
R^2	0.9992	0.9273
R_L	0.15	0.03
Freundlich		
K_F ((mg/g)(L/mg)$^{1/n}$)	12.48	134.64
n	0.86	0.31
R^2	0.9986	0.9914
Dubinin–Radushkevich		
q_m (mg/g)	11.26	45.49
β	8×10^{-8}	2×10^{-7}
E	2500.00	1581.14
R^2	0.9502	0.9991
Temkin		
K_T (L/mg)	9.11	5.78
B	4.51	6.43
R^2	0.8940	0.9329

Table 4
Kinetic parameters for the adsorption of phenol onto ACK1 andACK2.

	Parameters	
	ACK1	ACK2
Pseudo-first order		
k_1 (1/min)	0.083	0.192
q_e (mg/g)	1.490	0.791
R^2	0.8195	0.8023
Pseudo-second order		
k_2 (g/mg min)	0.082	0.52
q_e (mg/g)	5.79	2.92
R^2	1.000	1.000
Intraparticle diffusion		
k_p (mg/g min$^{1/2}$)	0.06	0.011
C	4.95	2.78
R^2	0.7714	0.7613

adsorption of phenol onto ACK2 may be carried out via chemically.

3.4. Adsorption kinetics

Pseudo-first order, pseudo-second order and intraparticle diffusion kinetic parameters are represented in Table 4. The correlation coefficient for the pseudo-second order kinetic model was higher than the one for pseudo-first order kinetic model for both ACK1 and ACK2 ($R^2 = 1.000$). This indicates that the adsorption perfectly complies with pseudo-second order reaction and the adsorption of phenol process appeared to be controlled by the chemisorption process. As it mentioned before according to the intraparticle diffusion model, the plot should be linear if intraparticle diffusion is involved in the adsorption process and when these lines pass through the origin then intraparticle diffusion is said to be the rate-controlling step. If the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. It is shown in Fig. 7 that the plots were not linear over the whole time range, implying that more than one process affected the adsorption and the adsorption process contains both the surface adsorption and intraparticle diffusion.
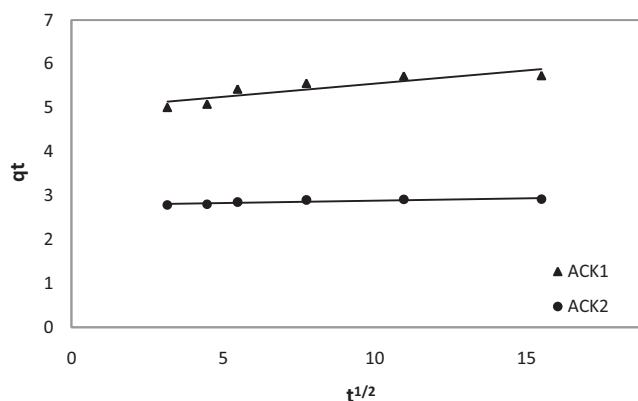
Fig. 7. Intraparticle diffusion plots for the adsorption of phenol onto ACK1 and ACK2.

Table 5
Thermodynamic parameters for the adsorption of phenol onto ACK1 andACK2.

T (°C)	$\Delta G°$ (kJ/mol)		$\Delta H°$ (kJ/mol)		$\Delta S°$ (J/K mol)		R^2	
	ACK1	ACK2	ACK1	ACK2	ACK1	ACK2	ACK1	ACK2
20	−7.423	−7.070						
30	−6.710	−6.732	−13.97	−19.73	−22.96	−43.18	0.8804	0.9756
40	−6.789	−6.021						
50	−6.657	−5.875						

3.5. Adsorption thermodynamics

The calculated values of Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes are given in Table 5. The negative $\Delta G°$ values indicate that process is thermodynamically feasible, spontaneous and chemically controlled. The negative value of $\Delta H°$ indicates that the nature of adsorption process is exothermic. This is also supported by the decrease in value of uptake capacity of the sorbent with the increase in temperature (Fig. 6). The negative value of $\Delta S°$ shows the decreased randomness at the solid/solution interface during the adsorption process.

4. Conclusions

Batch adsorption studies for the removal of phenol from aqueous solutions have been carried out using activated carbon obtained from tobacco residue by chemical activation using K_2CO_3 and KOH as activation agents. Activation with different chemical agents and ratios strongly affects characteristics of the activated carbons and optimum impregnation ratio should be selected to produce higher surface area and pore volume activated carbons. Maximum BET surface areas of activated carbons were obtained as 1635 and 1474 m^2/g impregnation with 75 wt.% of K_2CO_3 and 75 wt.% of KOH, respectively. Under the optimum conditions maximum phenol removal efficiencies were obtained as 95.5% and 97.4% from 75 wt.% of K_2CO_3 and 75 wt.% of KOH impregnated activated carbons.

The adsorption isotherm studies showed that Langmuir adsorption isotherm model for ACK1 and Dubinin–Radushkevich model for ACK2 adequately described the adsorption of phenol onto activated carbon and the maximum adsorption capacity (q_{max}) was found to be 17.83 and 45.49 mg/g for ACK1 and ACK2, respectively. It was shown that the pseudo-second order kinetic model better described the sorption kinetics with a high correlation coefficient (1.000). The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ showed a chemically favored, spontaneous and exothermic adsorption.

It can be concluded that activated carbon produced from chemical activation of tobacco residue seems an effective and alter-

native adsorbent for the removal of phenol from aqueous solution, because of its high surface area, adsorption capacity, availability, and low cost.

References

[1] B.H. Hameed, A.A. Rahman, Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material, J. Hazard. Mater. 160 (2008) 576–581.

[2] Md. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface Sci. 143 (2008) 48–67.

[3] S. Lin, R. Juang, Adsorption of phenol and its derivates from water using synthetic resins and low-cost natural adsorbents: a review, J. Environ. Manage. 90 (2009) 1336–1349.

[4] O. Jia, A.C. Lua, Effects of pyrolysis conditions on the physical characteristics of oil–palm–shell activated carbons used in aqueous phase phenol adsorption, J. Anal. Appl. Pyrolysis 83 (2008) 175–179.

[5] P. Gridos, A. Dufour, V. Fierro, Y. Rogaume, C. Rogaume, A. Zoulalian, A. Celzard, Activated carbons prepared from wood particleboard wastes: characterization and phenol adsorption capacities, J. Hazard. Mater. 166 (2009) 491–501.

[6] B. Pan, B. Pan, W. Zhang, Q. Zhang, Q. Zhang, S. Zheng, Adsorptive removal of phenol from aqueous phase by using a porous acrylic ester polymer, J. Hazard. Mater. 157 (2008) 293–299.

[7] Ç. Şentorun-Shalaby, M.G. Uçak-Astarlıoğlu, L. Artok, Ç. Sarıcı, Preparation and characterization of activated carbons by one-step steam pyrolysis/activation from apricot stones, Microporous Mezoporous Mater. 88 (2006) 126–134.

[8] O. Ioannidou, A. Zabaniotou, Agricultural residues as precursors for activated carbon production—a review, Renew. Sustain. Energy Rev. 11 (2007) 1966–2005.

[9] M.K.B. Gratuito, T. Panyathanmaporn, R.A. Chumnanklang, N. Sirinuntawittaya, A. Dutta, Production of activated carbon from coconut shell: optimization using response surface methodology, Bioresour. Technol. 99 (2008) 4887–4895.

[10] D. Prahas, Y. Kartika, N. Indraswati, S. Ismadji, Activated carbon from jackfruit peel waste by H$_3$PO$_4$ chemical activation: pore structure and surface characterization, Chem. Eng. J. 140 (2007) 32–42.

[11] S. Karagöz, T. Tay, T. Ucar, M. Erdem, Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, Bioresour. Technol. 99 (2008) 6214–6222.

[12] F. Sh, W.A. Mohamed, M.R. Khater, Mostafa, Characterization and phenols sorptive properties of carbons activated by sulphuric acid, Chem. Eng. J. 116 (2006) 47–52.

[13] M.F. Sawalha, J.R. Peralta-Videa, J. Romero-Gonzales, J.L. Gardea-Torresdey, Biosorption of Cd(II), Cr(III), and Cr(IV) by saltbush (*Atriplexcanescens*) biomass: thermodynamic and isotherm studies, J. Colloid Interface Sci. 300 (2006) 100–104.

[14] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[15] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[16] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed bed adsorbents, J. Am. Inst. Chem. Eng. 20 (1974) 228–238.

[17] H.M.F. Freundlich, Über die adsorption in lösungen, Z. Phys. Chem. 57 (1906) 385–470.

[18] M.M. Dubinin, L.V. Radushkevich, Equation of the characteristic curve of activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect. 55 (1947) 331.

[19] M.J. Temkin, V. Phyzev, Recent modifications to Langmuir isotherms, ActaPhysiochim, USSR 12 (1940) 217–222.

[20] M.J. Temkin, V. Phyzev, Kinetic of ammonia synthesis on promoted iron catalysts, ActaPhysiochim, USSR 12 (1940) 237–356.

[21] S. Lagergren, Zurtheorie der sogenannten adsorption gelosterstoffe, KungligaSvenskaVetenskapsakademiens, Handlingar 24 (1898) 1–39.

[22] J. Febrianto, A.N. Kosasih, J. Sunarso, Y.H. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies, J. Hazard. Mater. 162 (2009) 616–645.

[23] Y.S. Ho, G. McKay, Pseudo-second order model for sorption process, Process Biochem. 34 (1999) 451–465.

[24] Y.S. Ho, G. McKay, D.A.J. Wase, C.F. Foster, Study of the sorption of divalent metal ions on the peat, Adsorp. Sci. Technol. 18 (2000) 639–650.

[25] W.J. Weber, J.C. Morriss, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civil Eng. 89 (1963) 31–60.

[26] K.G. Bhattacharyya, A. Sharma, Azadirachtaindica leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo red solutions, J. Environ. Manage. 71 (2004) 217–229.

[27] J.P. Chen, S. Wu, K.H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, Carbon 41 (2003) 1979–1986.

[28] H. Ucun, Y.K. Bayhan, Y. Kaya, Kinetic and thermodynamic studies of the biosorption of Cr(VI) by *Pinus sylvestris* Linn., J. Hazard. Mater. 153 (2008) 52–59.

[29] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X. Wang, Biosorption of cadmium(II), zinc(II) and lead(II) by *Penicillium simplicissimum*: isotherm, kinetics and thermodynamics, J. Hazard. Mater. 160 (2008) 655–661.

[30] A. Sarı, M. Tuzen, Ö.D. Uluözlü, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladoniafurcata*) biomass, Biochem. Eng. J. 37 (2007) 151–158.

[31] A.E. Pütün, E. Apaydin, E. Pütün, Bio-oil production from pyrolysis and steam pyrolysis of soybean-cake: product yields and composition, Energy 27 (2002) 703–713.

[32] J. Hayashi, T. Horikawa, K. Muroyama, V.G. Gomes, Microporous Mesoporous Mater. 55 (2002) 63–68.

[33] R. Vimala, N. Das, Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: a comparative study, J. Hazard. Mater. 168 (2009) 376–382.

[34] S. Mukherjee, S. Kumar, A.K. Misra, Maohong Fan, Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal, Chem. Eng. J. 129 (2007) 133–142.