

Adsorptive removal of phenol by thermally modified activated carbon: Equilibrium, kinetics and thermodynamics

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

The purpose of this study was to remove phenol from aqueous solution using carbonized coir pith in batch mode technique. Batch adsorption studies were conducted to evaluate the effect of various parameters such as pH, contact time, concentration of phenol, adsorbent dose and temperature. The carbonized coir pith showed high surface area and best adsorption capacity. Lagergren first-order, second-order, Bangham's and intra particle diffusion model were used to fit the experimental data. Results of the kinetic studies show that the adsorption reaction is second order kinetic model with respect to phenol solution concentrations. The equilibrium time was obtained as 80 and 100 min for 10 and 20 mg/L and 120 min for 30 and 40 mg/L phenol concentrations. The adsorption equilibrium data obeyed the Langmuir, Freundlich, Dubinin-Radushkevich, and Tempkin isotherms. The adsorption capacity was found to be 48.31 mg/g, according to the Langmuir isotherm. Acidic pH was favorable for the adsorption of phenol. Studies on pH effect and desorption revealed that chemisorption was involved in the adsorption process. The change in entropy (ΔS°) and heat of adsorption (ΔH°) of coir pith carbon were determined as 85.76 J/mol/K and 24.99 kJ/mol, respectively. The negative value of change in Gibbs free energy indicates a feasible and spontaneous adsorption of phenol on coir pith carbon.

KEYWORDS

adsorption; coir pith carbon; isotherms; kinetics; phenol; temperature

1. INTRODUCTION

Phenol and its derivative compounds are generated by petroleum refining, leather and textile manufacturing, olive oil manufacturing etc. in appreciable quantities (Kent and Riegel's, 1992; Rengaraj et al., 2002; Cermola et al., 2004). Phenolic compounds have low permissible limit (0.5-1.0 mg/L) due to their toxicity to human and aquatic life and must be removed from wastewater in environmentally acceptable ways. Despite the existence of several physicochemical and biological treatment techniques (solvent extraction, ion exchange by resins, chemical oxidation by ozone, aerobic or anaerobic biodegradation, etc.) adsorption using activated carbon is the most effective and frequently used technique for phenol removal (Monahan, 1998; Tong et al., 1998;

Tchobanoglous et al., 2002; Dabrowski et al., 2005; Alves et al., 2010; Jaramillo et al., 2010).

For the treatment of aqueous phase by adsorption, activated carbon is the most widely used adsorbent. However, it is very expensive and has high operating costs (Gong et al., 2005). Therefore, in the past years, considerable attention has been devoted to explore different types of low-cost materials in order to remove the pollutants from aqueous phase. Many researchers prepared activated carbon from agricultural by-products like hard woods, grain hulls, corn cobs, nut shells, pecan shells, coconut shells, almond shells, saw dust, coffee grounds, cellulose residues, peach pits, oat hulls, rice hulls, rice straw, soya bean hulls and many others. Recent studies reported that adsorbents such as polymeric resin effluent (Victor-Ortega and Ochando-

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Received: 29-02-2016

Revised: 08-03-2016

Accepted: 16-03-2016

Available online: 01-04-2016

Pulido, 2016), palm oil mill effluent (Chonticha et al., 2016), curcumin formaldehyde resin (Saad et al., 2014), orange peel (Luis et al., 2016), coal, residual coal, residual coal treated with H_3PO_4 , rice husk and coke breeze (Ahmaruzzaman, and Sharma, 2005) have been used efficiently for the removal of phenols.

Most of the studies on phenol removal dealt with the adsorptive equilibrium and kinetics, both in batch and continuous mode. Experimental data were fitted to various isotherm equations to determine the best isotherm to correlate the experimental data. The equilibrium relationship was represented by various isotherm models. The adsorption capacity of the adsorbent has been studied using the adsorption isotherm technique. Temperature is known to have pronounced effect on adsorption phenomenon and intraparticle diffusion process. In the present investigation, coir pith carbon was prepared by thermal activation and the carbon with best surface area and adsorptive capacity was screened and subsequently used. The aim of the present work is to explore the possible utilization of coir pith as an adsorbent in the removal of phenol from aqueous solution and to determine suitable kinetic and isotherm model for data description.

2. MATERIALS AND METHODS

2.1. Preparation of adsorbent

Coir pith was collected from nearby coconut coir industries, dried in sunlight for 5 h and then grounded. The dried coir pith powder was sieved to 250-500 μm size. It was subjected to carbonization at 700 $^{\circ}C$ for 1 h using a muffle furnace under closed conditions. The carbonized material was taken out, sieved to 250-500 μm size again and used for adsorption studies.

2.2. Adsorbate

Phenol (C_6H_5OH) of analytical reagent (AR) grade supplied by S.D. Fine Chem. Limited (India) was used for the preparation of synthetic adsorbate solutions of various initial concentrations in the range of 10–40 mg/L. The required quantity of phenol was accurately weighed and dissolved in a small amount of distilled water and subsequently made-up to 1000 mL in a measuring flask. Fresh stock solution as required was prepared every day and was stored in a brown colour glass reservoir of 5 L capacity to prevent photo-oxidation. The initial concentration was ascertained

before the start of each experimental run.

2.3. Analytical measurements

The concentration of phenol was determined by finding out the absorbance of the solution at 270 nm wavelength using UV/Vis spectrophotometer (Hitachi, model U-3210, Tokyo). The calibration plot of absorbance versus concentration for phenol showed a linear variation up to 40 mg/L concentration. Therefore, the samples with higher concentration of phenol (>40 mg/L) were diluted with distilled water, whenever necessary, to make the concentration less than 40 mg/L, for the accurate determination of the phenol concentration with the help of the linear portion of the calibration curve. Adsorption studies for phenol by coir pith carbon were carried out at pH 2.0. Effect of pH was studied by adjusting the pH of phenol solutions with initial concentration of 10 and 20 mg/L using dilute 0.1 N HCl and/or 0.1 N NaOH solutions. The pH adjusted phenol solution (50 mL) was separately mixed with 100 mg of adsorbent and agitated for 80 and 100 min, respectively. Desorption studies involve utilizing the adsorbent that was previously used for the adsorption of 10 and 20 mg/L of phenol solution. The phenol loaded adsorbent was then filtered using Whatman filter paper and washed gently with distilled water to remove any unadsorbed phenol. Several such samples were prepared. Then, 100 mg of spent adsorbent was agitated for 80 or 100 min with 50 mL of distilled water, adjusted to different pH values (2 to 12).

2.4. Batch experimental procedure

For each experiment, 50 mL of the phenol solution with the known initial concentration, pH 2.0 and a known amount of the adsorbent were taken in a 100 mL of conical flask. This mixture was agitated at 35 $^{\circ}C$ by keeping the conical flask in a thermo stated rotary shaker (ORBITEK, Chennai, India) at a constant speed of 200 rpm. The phenol solution was separated from the adsorbent by centrifugation at 20,000 rpm for 20 min and its absorbance was measured. The initial pH of the adsorbate solutions was adjusted using 1 M aqueous solution of either HCl or NaOH. The percentage removal of phenol and equilibrium adsorption uptake, q_e (mg/g), was calculated using the following relationships:

$$\text{Per cent removal} = \frac{100(C_0 - C_e)}{C_0} \quad (1)$$

$$\text{Amount adsorbed } (q_e) = \frac{(C_0 - C_e)V}{w} \quad (2)$$

where C_0 is the initial adsorbate concentration (mg/L), C_e is the equilibrium adsorbate concentration (mg/L), V is the volume of the solution (L) and w is the mass of the adsorbent (g).

2.5. Effect of temperature and estimation of thermodynamic parameters

The effect of temperature on the adsorption characteristics was investigated by determining the adsorption isotherms at 35, 40, 50 and 60 °C. Apparent and net isosteric heats of adsorption at various surface of coverage were determined using classical thermodynamic equations. The concentration used was 10 mg/L using 50 mg of the adsorbent dosage and the initial pH of the solutions was maintained at 2.0.

3. RESULTS AND DISCUSSION

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3.1. Effect of contact time

The experimental adsorption results reveal that the uptake of adsorbate species was fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption was found to be nearly constant. This was obvious from the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

The nature of adsorption process will depend on physical or chemical characteristics of the adsorbent and also on the system conditions. The amount of phenol adsorbed (mg/g) increased with increase in agitation time and eventually reached equilibrium. The equilibrium time was 80 and 100 min for 10, 20 mg/L, respectively, and 120 min for 30 and 40 mg/L of initial phenol concentration. The amount of phenol removal at equilibrium increased from 3.38 to 12.43 mg/g with the increase in phenol concentration from 10 to 40 mg/L. It was clear that the removal of phenol depends on the concentration of the phenol. It was also observed that for an initial phenol concentration of 10 mg/L, the maximum amount (approximately 67.64% of total removal) of phenol was adsorbed within the first 80 min at an average adsorption rate of 0.0423 mg/g min and thereafter the adsorption rate tends to

decrease and proceeds at an average adsorption rate of 0.0249 mg/g min. A similar trend was observed for the remaining range of initial phenol concentrations (20–40 mg/L) studied. The initial rapid phase may be due to increased number of vacant sites available at the initial stage, and as a result of these there exist increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent.

3.2. Adsorption kinetic study

Four kinetic models, viz. Lagergren-first-order, pseudo second-order, Bangham's and intraparticle diffusion models were used to investigate the adsorption process of phenol on coir pith carbon.

3.2.1. Lagergren -first-order model

Various models can be used to analyze the kinetics of adsorption process. Lagergren (Lagergren and Svenska, 1898) suggested a rate equation for the adsorption of solutes from a liquid solution. This pseudo-first-order rate equation is

$$\frac{dq}{dt} = k_1(q_e - q) \quad (3)$$

Integrating Equation (3) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$ gives

$$\ln(q_e - q) = k_1 t \quad (4)$$

where q and q_e are the grams of solute adsorbed per gram of adsorbent at any time and at equilibrium, respectively, and k_1 is the rate constant of first-order adsorption. The pseudo-first order equation was used extensively to describe the adsorption kinetics (Ho and McKay, 1998; Ho and McKay, 1999; Ajmal, et al., 2000; Chenug et al., 2000; Reddad et al., 2002). Values of k_1 were calculated from the plots of $\log(q_e - q)$ versus t (Figure not shown) suggested the first order kinetics of the removal of phenol. The values of k_1 and q_e at different concentrations, calculated from the slopes and intercepts of these curves, are presented in Table 1.

3.2.2. The second-order kinetic model

Another model for the analysis of adsorption kinetics is pseudo-second-order (Ho and McKay, 1999). The rate law for this system is expressed as,

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (5)$$

Integrating Equation (5), for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$, gives

$$\frac{1}{(q_e - q)} = \frac{1}{q_e} + k_2 t \quad (6)$$

where k_2 is the pseudo-second-order rate constant of adsorption. Equation (6) can be rearranged to obtain a linear form,

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The initial adsorption rate, h (mg/g min), as $t \rightarrow 0$ can be defined as

$$h = k_2 q_e^2 \quad (8)$$

The plot of t/q versus t gives a straight line with slope of $1/k_2 q_e^2$ and intercept of $1/q_e$. Thus, the gram of solute adsorbed per gram of adsorbent at equilibrium (q_e) and adsorption rate constant (k_2) could be evaluated from the slope and intercept, respectively. The pseudo-second-order model was recently applied for analysis of adsorption kinetics from liquid solutions (Ho and McKay, 1999).

Two kinetic models for adsorption from liquid solution, represented above (first- and second-order models), were derived and used in the literature without any assumption or specialization of process conditions. In this step we want to derive these kinetic models by a general and different method. The advantage of our method is that it determines the conditions for using first-order or second-order models and also identifies the real meaning of their observed rate coefficients. Calculated correlations were closer to unity for second-order kinetics model; therefore the adsorption kinetics could be approximated more favorably by second-order kinetic model for phenol. The values of constants (k_2 (g/mg min) and h (mg/g min)) as calculated from the Figure 1 are listed in Table 1.

3.2.3. Intra-particle diffusion study

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related

by an apparent diffusion coefficient, which will fit the experimental adsorption-rate data. Generally, a process is diffusion controlled if its rate is dependent upon the rate at which components diffuse towards one another. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model (Weber Jr. and Morris, 1963; Poots et al., 1978; McKay et al., 1980; Allen et al., 1989).

$$q_t = k_{id} t^{1/2} + C \quad (9)$$

where, k_{id} is the intra-particle diffusion rate constant (mg/g min^{0.5}) and C (mg/g) is a constant that gives idea about the thickness of the boundary layer, i.e., larger the value of C the greater is the boundary layer effect (Kannan and Sundaram, 2001). If the Weber–Morris plot of q_t versus $t^{1/2}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. The mathematical dependence of fractional uptake of adsorbate on $t^{1/2}$ is obtained if the sorption process is considered to be influenced by diffusion in the cylindrical (or spherical) and convective diffusion in the adsorbate solution. It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stages of adsorption. This was represented by first sharper portion. The second linear portion was the gradual adsorption stage with domination of the intra-particle diffusion. Figure 2 presents the plots of mass of phenol adsorbed per unit mass of adsorbent versus $t^{1/2}$ for all phenol concentrations. In the figure the data points were related by two straight lines with the first straight portion depicting macropore diffusion and the second representing micropore diffusion (Allen et al., 1989). This represents the pore diffusion data. Extrapolation of the linear portions of the plot back to the y-axis gives the intercepts, which provide the measure of the boundary layer thickness. The deviation of straight lines from the origin (Figure 2) may be due to difference in rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step. The adsorption data for q_t versus $t^{1/2}$ for the initial period show curvature, usually attributed to boundary layer diffusion effects or external mass transfer effects (McKay et al., 1980; Crank, 1965; Asfour et al., 1985). The slope of the Weber and Morris plots q_t versus $t^{1/2}$ are defined as a rate parameter, characteristic of the rate of adsorption

in the region where intra-particle diffusion is rate controlling. The values of k_{id} as obtained from the slope of straight lines are listed in Table 1.

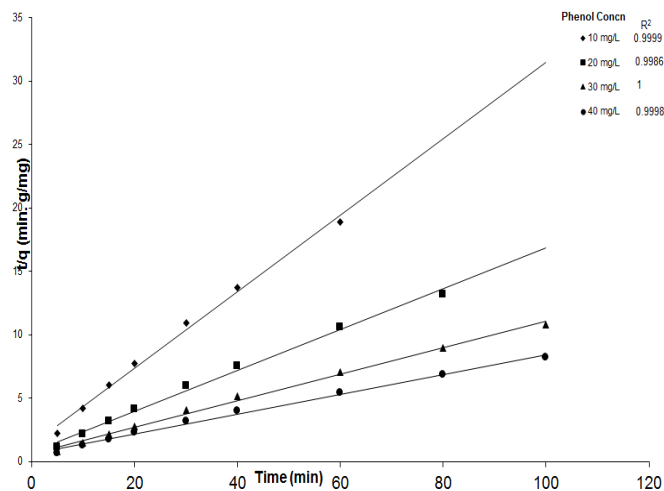


Figure 1. Second-order kinetics plots for the removal of phenol: at different initial concentrations of phenol: Adsorbent dose, 100 mg/50 mL; Initial pH, 2.0; Temp, 35°C.

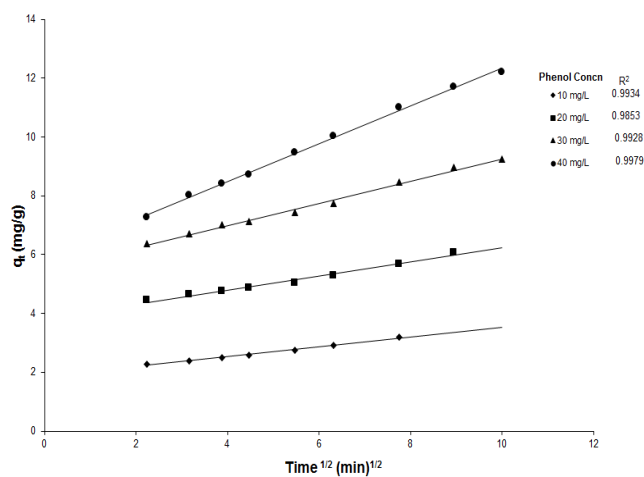


Figure 2. Weber and Morris intra-particle diffusion plots for removal of phenol: at different initial concentrations of phenol: Adsorbent dose, 100 mg/50 mL; Initial pH, 2.0; Temp, 35 °C.

3.2.4. Bangham's equation

Bangham's equation was used to evaluate whether the adsorption is pore-diffusion controlled (Aharoni et al., 1979).

$$\log \log \left(\frac{C_o}{C_o - q_t m} \right) = \log \left(\frac{k_o m}{2.303V} \right) + \alpha \log(t) \quad (10)$$

where C_o is the initial concentration of adsorbate in solution (mg/L), V is the volume of solution (mL), m is the weight of adsorbent per liter of solution (g/L), q_t (mg/g) is the amount of adsorbate retained at time t , and α (<1) and k_o are constants. The double logarithmic plot (Figure 3) according to above equation yielded perfect linear curves for phenol removal by carbon showing that the diffusion of adsorbate into pores of the adsorbent is not the only rate controlling step (Tutem et al., 1998). With increase in the contact time, the effect of diffusion process on overall sorption could be ignored. In another study, adsorption of phenol onto carbon rich bagasse fly ash, activated carbon-commercial grade and laboratory grade were studied (Srivastava et al., 2006). On fitting the kinetics data with Bangham's equation, the authors determined constant values of 5.026, 3637, 4.803 for k_o and 0.357, 0.309, 0.347 for α in the case of carbon rich bagasse fly ash, activated carbon-commercial grade and laboratory grade, respectively.

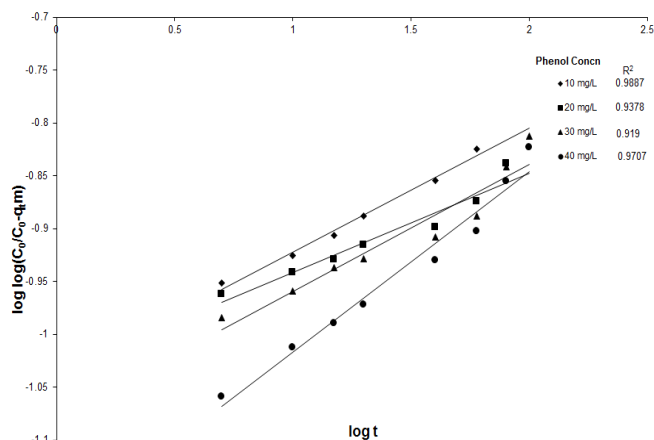


Figure 3. Bangham's plot for removal of phenol, at different initial concentrations phenol: Adsorbent dose, 100 mg/50 mL; Initial pH, 2.0; Temp, 35 °C.

3.3. Modeling of adsorption isotherms

The adsorption isotherm expresses the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. The adsorption capacity of coir pith carbon for phenol has been evaluated using different isotherms, namely Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R).

3.3.1. Langmuir isotherm

The Langmuir isotherm can be represented by the following equation (Langmuir, 1918):

Table 1. Kinetic parameters for the removal of phenol by coir pith carbon.

Pseudo-first-order constants							
C ₀ (mg/L)	k ₁ (min ⁻¹)	q _e (mg/g)	R ²	Temp (°C)	k ₁ (min ⁻¹)	q _e (mg/g)	R ²
10	0.030	1.412	0.976	35	0.098	3.317	0.9644
20	0.022	2.388	0.963	40	0.106	2.777	0.963
30	0.024	3.929	0.977	50	0.118	1.557	0.9843
40	0.031	6.852	0.960	60	0.103	0.856	0.9896
Pseudo-second-order constants							
C ₀ (mg/L)	h (mg/g min)	k ₂ (g/mg min)	R ²	Temp (°C)	h (mg/g min)	k ₂ (g/mg/min)	R ²
10	0.739	0.067	0.994	35	0.400	0.026	0.992
20	1.352	0.035	0.994	40	0.841	0.061	0.997
30	1.655	0.018	0.995	50	2.038	0.139	0.999
40	1.479	0.009	0.994	60	3.936	0.246	1.000
Bangham's equation constants							
C ₀ (mg/L)	k ₀ (mL/g/L)	α	R ²	Temp (°C)	k ₀ (mL/g/L)	α	R ²
10	15.957	0.1147	0.9915	35	26.353	0.1002	0.9959
20	8.276	0.1017	0.9901	40	19.228	0.1601	0.9683
30	5.799	0.0765	0.9939	50	22.984	0.1261	0.9909
40	4.429	0.0874	0.9808	60	16.249	0.1859	0.9846
Intra-particle diffusion constants							
C ₀ (mg/L)	k _{id} (mg/g.min)	R ²	Temp (°C)	k _{id} (mg/g.min)	R ²		
10	0.0852	0.9858	35	0.0681	0.9715		
20	0.1201	0.9728	40	0.0596	0.9451		
30	0.1038	0.993	50	0.0473	0.9288		
40	0.1288	0.9633	60	0.0377	0.9006		

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (11)$$

where C_e is the concentration of phenol solution (mg/L) at equilibrium. The constant Q₀ signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). Values of Q₀ and b were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e and are presented in Table 2. The adsorption capacity can be correlated with the variation of surface area and porosity of the adsorbent. Higher surface area and pore volume will result in higher adsorption capacity. It may be seen that the isotherm parameters differ widely in their values of origins of the activated carbons. Hence one should be cautious while using these values in design of adsorption systems. The adsorption capacities, as determined by the Langmuir isotherm model for Fe₂O₃, Al₂O₃ and TiO₂ nanoparticles-loaded activated carbon were 1.5106, 3.1530, 3.2875 and 3.5461 mg/g for raw activated carbon, activated carbon-TiO₂, activated carbon-Fe₂O₃ and activated carbon-Al₂O₃, respectively (Basim et al., 2016).

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L, as defined by Weber and Chakravorty (1974):

$$R_L = \frac{1}{(1 + bC_0)} \quad (12)$$

where b is the Langmuir constant and C₀ is the initial phenol concentration (mg/L), R_L values indicate the type of isotherm. The calculated R_L value in the range 0.52-0.81 indicates that adsorption was higher at low concentration.

Table 2. Isotherm parameters for removal of phenol by coir pith.

Langmuir constants			
C ₀ (mg/L)	Q ₀ (mg/g)	b (L/mg)	R _L
10	48.31	0.023	0.816
20			0.689
30			0.597
40			0.524
Freundlich constants			
C ₀ (mg/L)	k _f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R ²
10	0.546	0.575	0.9379
20	0.284	0.596	0.9271
30	0.678	0.863	0.8963
40	2.483	1.595	0.8321
Dubinin-Radushkevich constants			
C ₀ (mg/L)	q _s (mg/g)	E (kJ/mol)	R ²
10	10.89	5.774	0.8954
20			
30			
40			
Tempkin constants			
C ₀ (mg/L)	K _t (L/mg)	B ₁	R ²
10	1.969	5.733	0.9591
20			
30			
40			

3.3.2. Freundlich isotherm

The Freundlich isotherm (Freundlich, 1907) was also applied to plots of equilibrium adsorption data:

$$\log_{10}\left(\frac{x}{m}\right) = \log_{10} k_f + \frac{1}{n} \log_{10} C_e \quad (13)$$

where x is the amount of phenol adsorbed (mg), m is the weight of the adsorbent used (g), C_e is the equilibrium concentration of phenol in solution (mg/L), k_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and $1/n$ are Freundlich constants. n is related to the adsorption energy distribution, and k_f indicates the adsorption capacity. The increase in concentration of phenol decreases the correlation coefficients less than 0.9, in particular for 30 and 40 mg/L (Figure 4). The values of k_f and n were calculated from the intercept and slope of the plots and are presented in Table 2.

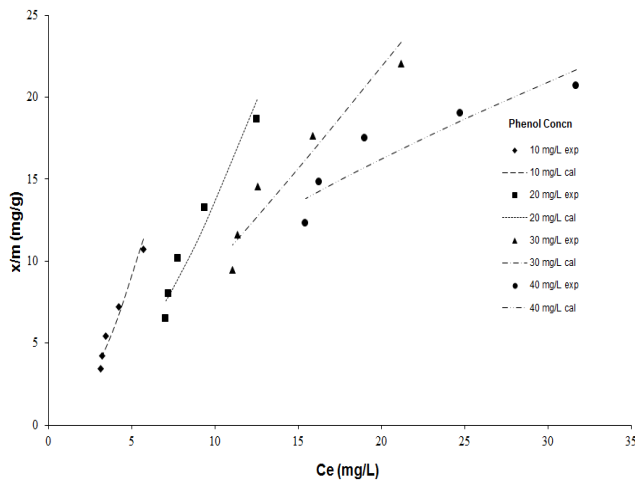


Figure 4. Freundlich plots for the adsorption of phenol by coir pith carbon.

3.3.3. Tempkin isotherm

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Aharoni and Ungarish, 1977). Tempkin isotherm can be represented by the following equation:

$$q_e = \frac{RT}{b \ln(K_t C_e)} \quad (14)$$

Equation (14) can be expressed in its linear form as:

$$q_e = B_1 \ln K_t + B_1 \ln C_e \quad (15)$$

$$\text{where, } B_1 = \frac{RT}{b} \quad (16)$$

The adsorption data can be analysed according to Equation (15). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants K_t and B_1 . K_t is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. The values of the parameters are given in Table 2.

3.3.4. Dubinin-Radushkevich isotherm

Another equation used in the analysis of isotherms was proposed by Dubinin-Radushkevich (Dubinin and Radushkevich, 1947).

$$q_e = q_s \exp(-B\varepsilon^2) \quad (17)$$

where q_s is D-R constant and ε can be correlated as

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (18)$$

$$E = \frac{1}{(2B)^{1/2}} \quad (19)$$

The calculated Dubinin-Radushkevich constants for the adsorption of phenol on coir pith carbon are reported in Table 2. The values of correlation coefficients were lower than 0.9, which were similar to the Freundlich isotherm results at high concentrations. In the present study, the D-R equation represents unsatisfactory fit of experimental data compared to the Langmuir and Tempkin isotherm equations.

3.4. Pore diffusion coefficient

Assuming spherical geometry for the adsorbent, the time for half adsorption can be correlated to the pore diffusion coefficient (Michelson et al., 1975).

$$t_{1/2} = \frac{0.03r_0^2}{D_p} \quad (20)$$

where $t_{1/2}$ is the time for half adsorption (s), r_0 is the radius of the adsorbent particle (cm) and D_p is the diffusion coefficient (cm^2/s). The values of D_p were calculated for different temperatures and different

concentrations of phenol. The removal of phenol follows pore diffusion process since the coefficient values were in the range of 10^{-11} - 10^{-13} cm^2/s . The values of D_p for phenol were 0.442 and 0.353×10^{-12} cm^2/sec for 10 and 20 mg/L and 0.295×10^{-12} cm^2/sec for 30 and 40 mg/L and 0.884×10^{-12} cm^2/sec for 10 mg/L of phenol in the range of temperature 35-60 °C have been observed.

3.5. Effect of pH and desorption studies

The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization and speciation of different pollutants (Srivastava et al., 2006). Effect of pH on the removal of phenol is shown in Figure 5. The percent removal decreased with increase in pH. Based on the relationship (Arcand et al., 1995):

$$CP_0 = \frac{CP_T}{\left\{1 + 10^{(pH - pK_a)}\right\}} \quad (21)$$

where CP_0 is the concentration of unionized phenol species, CP_T is the total concentration of phenol taken, pH is the final pH (equilibrium pH) after adsorption and pK_a is 9.89 for phenol. The concentration of ionized phenol species (phenolate) were calculated at different final pH values and plots of the percent ionized phenol versus final pH are shown in Figure 6. Increase of ionized phenol concentration was observed with increase in pH. Since there is no electrostatic repulsion between the unionized phenol species and the positively charged adsorbent surface at pH 2.0, the removal is higher. As the initial pH is increased, the percent of unionized species decreases and that of the ionized species increases. At the same time the number of negatively charged sites on the adsorbent surface also increases. At the initial pH of 11 (final pH 10.8 for 10 mg/L and 10.4 for 20 mg/L) the per cent ionized species were 87.9 and 75.6 for 10 and 20 mg/L, respectively, and the per cent removal observed by the highly negatively charged adsorbent surface was the least i.e. 50 and 44% for 10 and 20 mg/L of phenol, respectively. At alkaline pH ($pH_{zpc} = 8.0$), the adsorbent surface was negatively charged. Hence decrease in adsorption was observed due to electrostatic repulsion between the negatively charged adsorbent surface and phenolate species. Despite the electrostatic repulsion at the initial pH 11, a significant removal was observed. When the electron density of the aromatic ring of a solute is higher, its affinity for the carbon surface is also higher (Furuya, 1997). Similar result was observed during removal of

phenol, m-chlorophenol, p-chlorophenol and 2,4,6-trichlorophenol from aquatic systems by dye laden microbeads (cibacron blue F3GA carrying polymerized hydroxyethylmethacrylate (pHEMA) microbeads) (Denizli et al., 2001). Furuya (1997) also found that increase in the electron density of the adsorbate led to an increase in its uptake by activated carbon. Comparison of initial pH with final pH in the presence and absence of phenol showed that the final pH was generally higher than the initial pH in the blank, i.e. in the absence of phenol. This is due to the leaching of cations like Na and K from the carbon and subsequent replacement with the protons from the bulk solution on the adsorbent surface. Generally, adsorption of phenols by coir pith carbon showed slightly higher final pH compared to the blank. Adsorption of phenolate ion release OH^- ions by the adsorbent into the bulk solution leading to an increase in final pH compared to the blank. This shows that ion exchange mechanism is operative in the removal process. At basic pH, where high concentration of phenolate ion was present, adsorption occurs, though small, but significant. This shows that chemisorption also plays a role in the adsorption process.

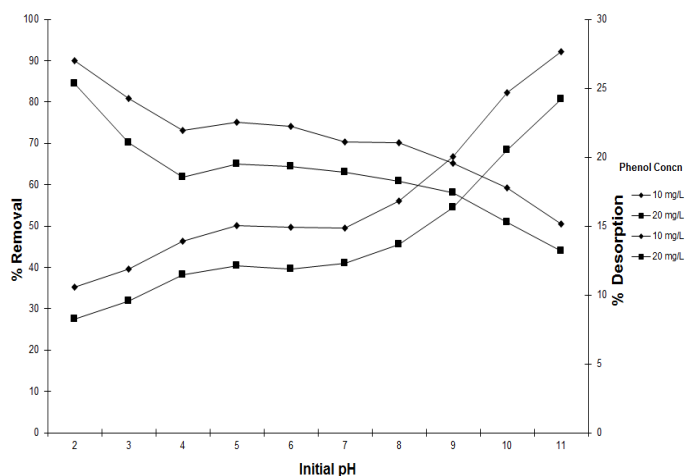


Figure 5. Effect of pH on adsorption and desorption of phenol: Adsorbent dose, 100 mg/50 mL; 10 mg/L agitation time 80 min; 20 mg/L agitation time 100 min (B) Effect of pH on desorption of phenol from phenol-loaded adsorbent. Adsorbent dose, 100 mg/50 mL; 10 mg/L agitation time 80 min; 20 mg/L agitation time 100 min.

Desorption studies shows that regeneration of spent carbon and recovery of the phenol would make the treatment process economical. Also desorption studies help to elucidate the mechanism of adsorption. From the graph between the pH and percentage of

desorption, the maximum desorption efficiency was determined. The graph is represented in Figure 5. This indicates that chemisorption plays a major role in adsorption process.

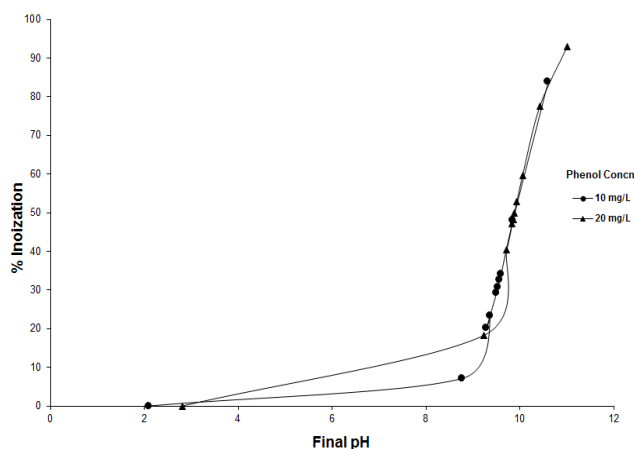


Figure 6. Effect of final pH on ionization of phenol; Temp, 35°C.

3.5. Effect of temperature

Temperature has a pronounced effect on the adsorption capacity of the adsorbent. Increase in temperature increased the percent removal. The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equations:

$$\Delta G^0 = -RT \ln K_c \quad (22)$$

where R is gas constant and K_c is the equilibrium constant and T is the temperature in K. According to van't Hoff equation,

$$\log_{10} K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (23)$$

Plot of $\log K_c$ versus $1/T$ was linear. Positive values of ΔH^0 (24.99 kJ/mol) confirmed the endothermic nature of adsorption and reversible process (Neetu and Chandrajit, 2016). The negative values (-1.364, -1.915, -2.703 and -3.548) of ΔG^0 indicated the spontaneous nature of adsorption for phenol at 35, 40, 50 and 60 °C. Entropy of activation can be regarded as a measure of the "saddle point of energy" over which reactant molecules must pass as activated complexes. The positive values of ΔS^0 (85.76 J/mol/K) suggest that an increased randomness at the solid/solution interface during the adsorption of phenol on coir pith carbon.

Kinetic models were also applied for temperature studies and it showed perfect linear curves for phenol at different temperature studies and the equilibrium data obtained for all the kinetics are presented in Table 1. It has been observed that increasing the temperature enhanced the adsorption capacity of phenol for some adsorbents while the opposite phenomenon occurred for other adsorbents. Adsorptive capacity of phenol onto granular activated carbon increased with decreasing temperature (Zogorski and Faust, 1978). The effect of dissolved oxygen on the capacity of phenol adsorption by granular activated carbon at 21 and 35°C also reported the same phenomenon (Vidic and Suidan, 1991). Adsorption of phenol by fly ash increased as the temperature increased in the range of 30–50°C (Singh and Rawat, 1994). The effect of temperature on rate of adsorption always showed that kinetic rate increased with increasing temperature. As a diffusion-limited process, the rate of adsorption of the organics from solution increases as the temperature of the system is increased. Increasing the temperature from 10 to 30°C increases the removal rate of phenol by 21 % (Zogorski et al., 1976).

4. CONCLUSIONS

The present study shows that coir pith carbon is an effective adsorbent for the removal of phenol from aqueous solution. Owing to excess of positive charge on the surface, coir pith carbon exhibited high adsorption capacity to remove phenol. Equilibrium adsorption was achieved in about 80 min. With respect to the suitability of the first-order and second-order kinetic models for phenol adsorption onto carbon, it has been determined that the adsorption kinetics of phenol followed the second-order kinetics which provides the best correlation of the data. Also, the calculated q_e values, agreed well with the experimental values, supporting the chemisorption. By comparing the correlation coefficients determined for each linear transformation of isotherm equations, the Langmuir and Tempkin isotherm model described the experimental data reasonably well. The effective diffusion coefficient of phenol was in the order of 10-12 cm²/s. Considering that the raw material (coir pith) is freely available in large quantities from coir industries, the treatment method seems to be economical. Based on the above positive results and low-cost nature, coir pith is recommended as effective and practical adsorbent for removal of phenol from wastewater.

REFERENCES

- Aharoni, C. and Ungarish, M. (1977) Kinetics of activated chemisorption. Part 2. Theoretical Models. *Journal of Chemical Society, Faraday Transactions*, 73, 456.
- Aharoni, C., Sideman, S. and Hoffer, E. (1979) Adsorption of phosphate ions by colloid ion-coated alumina. *Journal of Chemical Technology and Biotechnology*, 29, 404-412.
- Ahmaruzzaman, M. and Sharma, D.K. (2005) Adsorption of phenols from wastewater. *Journal of Colloidal Interface Science*, 287, 14-24.
- Ajmal, M., Rao, R.A.K., Ahmad, R. and Ahmad, J. (2000) Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater. *Journal of Hazardous Materials*, 79, 17-131.
- Allen, S.J., McKay, G. and Khader, K.Y.H. (1989) Intraparticle diffusion of a basic dye during adsorption onto sphagnum peat. *Environmental Pollution*, 56, 39-50.
- Alves, M.G., Sabio, M.M. and Reinoso, F.R. (2010) Modification of activated carbon hydrophobicity by pyrolysis of propene. *Journal of Analytical and Applied Pyrolysis*, 89, 17-21.
- Arcand, Y., Hawari, J. and Guiot, S.R. (1995) Solubility of pentachlorophenol in aqueous solutions. *Water Research*, 29, 131-136.
- Asfour, H.M., Nassar, M.M., Fadali, O.A. and El-Geundi, M.S. (1985) Colour removal from textile effluents using hardwood sawdust as an adsorbent. *Journal of Chemical Technology and Biotechnology*, A35, 28.
- Basim, A., Hamza, A.A., Ihsanullah, B.A., Tawfik A.S., Vinod Kumar G., Tahar, I. and Muataz, A.A. (2016) Sorption of phenol from waters on activated carbon impregnated with iron oxide, aluminum oxide and titanium oxide. *Journal of Molecular Liquids*, 213, 351-359.
- Cermola, F., DellaGreca, M., Iesce, R., Montelrla, S. Pollio, A. and Temussi, F. (2004) A mild photochemical approach to the degradation of phenols from olive oil mill wastewater. *Chemosphere*, 55, 1035-1041.
- Chenug, C.W., Porter, J.F. and McKay, G. (2000) Sorption kinetics for the removal of copper and zinc from effluents using bone char. *Separation and Purification Technology*, 19, 55-64.
- Chonticha, M., Piyapong, T., Adilan, H., Poonsul, P., Tsuyoshi, I. and Sompong, O, T. (2016) Simultaneous thermophilic hydrogen production and phenol removal from palm oil mill effluent by Thermoanaerobacterium-rich sludge. *International Journal of Hydrogen Energy*, 37, 15598-15606.
- Crank, J. (1965) *The mathematics of diffusion*, Vol. 84, 1st Edition, Oxford Clarendon Press, London.
- Dabrowski, A., Podkoscielny, P., Hubicki, Z. and Barczak, M. (2005) Adsorption of phenolic compounds by activated carbon—a critical review. *Chemosphere*, 58, 1049-1070.
- Denizli, A., Ozkan, G. and Ucar, M. (2001) Removal of chlorophenols from aquatic systems with dye-affinity microbeads. *Separation and Purification Technology*, 24, 255-262.
- Dubin, M.M. and Radushkevich, L.V. (1947) Equation of the characteristic curve of activated charcoal. *Chemisches Zentralblatt* 1, 875
- Freundlich, H. (1907) Ueber die adsorption in loesungen. *Zeitschrift für Physikalische Chemie*, 57, 385-470.
- Furuya, E.G., (1997) A fundamental analysis of the isotherm for the adsorption of phenolic compounds on activated carbon. *Separation and Purification Technology*, 11, 69-78.
- Gong, R., Ding, Y., Li, M., Yang, C., Liu, H. and Sun, Y. (2005) Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. *Dyes and Pigments*, 64, 187-192
- Ho, Y.S. and McKay, G. (1998) A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Transactions of the Institute of Chemical Engineers*, 76, 332-340.
- Ho, Y.S. and McKay, G. (1999) Batch lead(II) removal from aqueous solution by peat: equilibrium and kinetics. *Transactions of the Institute of Chemical Engineers*, 77, 165-173.
- Ho, Y.S. and McKay, G. (1999) Pseudo-second order model for sorption processes. *Process Biochemistry*, 34, 451-465.
- Jaramillo, J., Alvarez, P.M. and Serrano, V.G. (2010) Oxidation of activated carbon by dry and wet methods surface chemistry and textural modification. *Fuel Processing Technology*, 91, 1768-1775.
- Kannan, N. and Sundaram, M. M. (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons comparative study. *Dyes and Pigments*, 51, 25-40.
- Kent, J. A. and Riegel's (1992) *Handbook of Industrial Chemistry*, 9th Edition, Van Nostrand Reinhold Publications, p.50.
- Lagergren, S. and Svenska, B. K. (1898) Zur theorie der sogenannten adsorption gelöster stoffe. *Vetenskapsakad. Handl*, 24, 1-39.
- Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, 40, 1361-1403.
- Luis, A.R.C., Linda, V.G.G. and Leonardo, A.B.P. (2016) Biosorbents prepared from orange peels using instant controlled pressure drop for Cu(II) and phenol removal. *Industrial Crops and Products*, 84, 344-349.
- McKay, G., Otterburn, M.S. and Sweeney, A.G. (1980) The removal of colour from effluent using various adsorbents—III. Silica: Rate processes. *Water Research*, 14, 15-20.
- Michelson, L.D., Gideon, P.G., Pace, E.G. and Kutal, L.H. (1975) Removal of soluble mercury from wastewater by complexing technique. *US Dept. Industry, Office of Water Research and Technology, Bull. No. 74.*
- Monahan, E.S., 1998. *Environmental Chemistry*. Lewis Publisher Press, p. 241.
- Neetu, S. and Chandrajit. B. (2016) Simultaneous removal of phenol and cyanide from aqueous Solution by adsorption onto surface modified activated carbon prepares from coconut shell. *Journal of Water Process Engineering*, 9, 233-245.
- Poots, V.J.P., McKay, G. and Healy, J.J. (1978) Removal of basic dye from effluent using wood as an adsorbent. *Journal of Water Pollution Control Federation*, 50, 926-935.
- Reddad, Z., Gerente, C., Andres, Y. and Cloirec, P.L. (2002) Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental Science and Technology*, 36, 2067-2073.
- Rengaraj, S., Moon, S.H., Sivabalan, R., Arabindoo, B. and Murugesan, V. (2002) Agricultural solid waste for the removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon. *Waste Management*, 22, 543-548.
- Saad, M. A., Mu, N., Tansir, A., Zeid, A.A. and Ali A. (2014) Synthesis, characterization of curcumin based ecofriendly antimicrobial bio-adsorbent for the removal of phenol from aqueous medium. *Chemical Engineering Journal*, 254, 181-189

- Singh, K.B. and Rawat, N.S. (1994) Comparative sorption equilibrium studies of toxic phenols on fly ash and impregnated fly ash. *Journal of Chemical Technology Biotechnology*, 61, 307–313.
- Srivastava, V.C., Swamy, M.M., Mall, I.D., Prasad, B. and Mishra, I.M. (2006) Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics. *Colloidal Surface A: Physicochemical Engineering Aspects*, 272, 89-104.
- Tchobanoglous, G., Burton, F.L. and Stensel, H.D. (2002) *Wastewater Engineering: Treatment and reuse*, 4th Edition, McGraw Hill International.
- Tong, Z., Qingxiang, Z., Hui, H., Qin, L., Yi, Z. and Min, Q. (1998) Kinetic study on the removal of toxic phenol and chlorophenol from waste water by horseradish peroxidase. *Chemosphere*, 37, 1571–1577.
- Tutem, E., Apak, R. and Unal, C.F. (1998) Adsorptive removal of chlorophenols from water by bituminous shale. *Water Research*, 32, 2315-2324.
- Victor-Ortega, M. D. and Ochando-Pulido, J.M. (2016) Phenols removal from industrial effluents through novel polymeric resins: Kinetics and equilibrium studies. *Separation and Purification and Technology*, 160, 136-144.
- Vidic, R.D. and Suidan, M.T. (1991) Role of dissolved oxygen on the adsorptive capacity of activated carbon for synthetic and natural organic matter. *Environmental Science and Technology*, 25, 1612–1618.
- Weber Jr. W.J. and Morris, J.C. (1963) Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division ASCE*, 89, 31-59.
- Weber, T.W. and Chakravorti, R.K. (1974) Pore and solid diffusion models for fixed-bed adsorbers. *American Institute of Chemical Engineers Journal*, 20, 228-238.
- Zogorski, J.S. and Faust, S.D. (1978) Equilibria of adsorption of phenols by granular activated carbon. In: Rubin, A.J., (Ed.), *Chemistry of Wastewater Technology*, Ann Arbor Science Publishers, Ann Arbor, Michigan, Chapter 9.
- Zogorski, J.S.M., Faust, S.D. and Haas Jr., J.H. (1976) The kinetics of adsorption of phenols by granular activated carbon. *Journal of Colloidal and Interface Science*, 55, 329–341.