

# Removal of phenol from aqueous solution by adsorption onto seashells: equilibrium, kinetic and thermodynamic studies

Papita Das Saha, Jaya Srivastava and Shamik Chowdhury

## ABSTRACT

The efficacy of seashells as a new adsorbent for removal of phenol from aqueous solutions was studied by performing batch equilibrium tests under different operating parameters such as solution pH, adsorbent dose, initial phenol concentration, and temperature. The phenol removal efficiency remained unaffected when the initial pH of the phenol solution was in the range of 3–8. The amount of phenol adsorbed increased with increasing initial phenol concentration while it decreased with increasing temperature. The adsorption equilibrium data showed excellent fit to the Langmuir isotherm model with maximum monolayer adsorption capacity of  $175.27 \text{ mg g}^{-1}$  at pH 4.0, initial phenol concentration =  $50 \text{ mg L}^{-1}$ , adsorbent dose = 2 g and temperature = 293 K. Analysis of kinetic data showed that the adsorption process followed pseudo-second-order kinetics. Activation energy of the adsorption process, calculated using the Arrhenius equation, was found to be  $51.38 \text{ kJ mol}^{-1}$ , suggesting that adsorption of phenol onto seashells involved chemical ion-exchange. The numerical value of the thermodynamic parameters ( $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ ) indicated that adsorption of phenol onto seashells was feasible, spontaneous and endothermic under the examined conditions. The study shows that seashells can be used as an economic adsorbent for removal of phenol from aqueous solution.

**Key words** | adsorption, equilibrium, kinetics, phenol, seashell, thermodynamics

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## INTRODUCTION

In the past few decades, the rapid pace of industrialization, population expansion, and unplanned urbanization have contributed greatly to the severe pollution of water bodies and surrounding soils (Bhatnagar & Sillanpaa 2010). The main sources of freshwater pollution can be attributed to discharge of untreated toxic industrial wastes and dumping of industrial effluents (Ahmaruzzaman & Gupta 2011). Phenol released from the wastewater streams of paint, pesticide, coal conversion, polymeric resin, gasoline, rubber proofing, steel, petroleum and petrochemical industries is considered as a priority pollutant due to its toxic and carcinogenic properties (Mohd Din *et al.* 2009; Kilic *et al.* 2011; Yousef *et al.* 2011). Acute exposure to phenol can have

detrimental effects on the brain, digestive system, eye, heart, liver, lung and skin (Kilic *et al.* 2011). Therefore, removal of phenol from industrial effluents is essential before discharging into water bodies. Accordingly, various techniques, such as advanced oxidation, membrane filtration, biological degradation, electrochemical oxidation, photocatalytic degradation and adsorption, have been employed for the removal of phenol from aqueous media, among which adsorption has been found to be the most effective treatment technology due to its high efficiency and low operating costs (Kilic *et al.* 2011; Yousef *et al.* 2011). Activated carbon is the most widely used adsorbent for removal of phenol from industrial wastewaters because

of its large surface area, micro-porous nature, high adsorption capacity, high purity and easy availability (Hameed & Rahman 2008). However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. It is therefore important to search for a low cost and easily available adsorbent for removal of phenol from aqueous media.

Seashells have fascinated people ever since they first washed up on the shore. They are still popular with beachgoers even today. A seashell is the hard, protective, outer layer of a marine mollusc. A shell is usually made of outer layers of proteins, followed by an intermediate layer of calcite and a smooth inner layer of platy calcium carbonate crystals (Narayanan *et al.* 2006). Shells very often wash up onto a beach empty and clean, the animal having already died, and the soft parts having rotted away or having been eaten by predators or scavengers (Chowdhury & Saha 2010). With hundreds of miles of shorelines throughout the world, it is not difficult to find seashells accumulated on beaches. Seashells have important functional groups such as  $-\text{CH}_2$ ,  $-\text{OH}$ ,  $-\text{CO}_3$ , and  $-\text{PO}_4$  which make them effective adsorbents for removal of organic and inorganic pollutants from wastewater streams of industries (Chowdhury & Saha 2010). In our previous study, seashells showed remarkable efficiency for the removal of basic dye from aqueous solution (Chowdhury & Saha 2010). In this work, the suitability of seashells for phenol adsorption was assessed employing a batch experimental setup. The effect of parameters like solution pH, adsorbent dose, adsorbate concentration and temperature was studied. The Langmuir and Freundlich isotherm models were used to describe the equilibrium data. The adsorption mechanism was also evaluated in terms of kinetics and thermodynamics.

## MATERIALS AND METHODS

### Adsorbent

Shells from bivalve molluscs that most commonly wash up on large sandy beaches were used in this study. The seashells were collected from the beaches of Puri, Orissa, India. The shells were thoroughly washed with distilled water to

remove sand, dirt and any unwanted particles. The wet shells were then spread on a stainless steel tray and dried in an oven at  $383 \pm 1$  K for 24 h. The shells were then crushed and ground using a ball mill and sieved to retain the  $<250$   $\mu\text{m}$  mesh size for adsorption studies.

### Chemicals

Phenol ( $\text{C}_6\text{H}_5\text{OH}$ ;  $\lambda_{\text{max}}$ : 270 nm) used in this study was of analytical reagent grade and was obtained from Sigma-Aldrich (India). Double-distilled water was used in all the experiments.

### Batch adsorption studies

Batch adsorption experiments were conducted in 250 mL glass-stoppered, Erlenmeyer flasks with 100 mL phenol solution (of desired concentration and pH). A weighed amount of adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm and at a constant temperature in an incubator shaker (Innova 42, New Brunswick Scientific, Canada) until they reached equilibrium. The residual phenol concentration was determined using UV/VIS spectrophotometer (U-2800, Hitachi, Japan). The effects of pH (3–10), adsorbent dose (0.5–5 g), initial phenol concentration (20–100  $\text{mg L}^{-1}$ ) and temperature (293–303 K) were investigated during the present study. In order to ensure the accuracy, reliability and reproducibility of the collected data, all adsorption experiments were performed in triplicate, and the mean values were used in data analysis. Relative standard deviations were found to be within  $\pm 3\%$ .

The amount of phenol adsorbed per unit adsorbent (mg phenol per g adsorbent) was calculated according to a mass balance on the phenol concentration using Equation (1):

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

where  $C_0$  is the initial phenol concentration ( $\text{mg L}^{-1}$ ),  $C_e$  is the equilibrium phenol concentration in solution ( $\text{mg L}^{-1}$ ),  $V$  is the volume of the solution (litres), and  $m$  is the mass of the adsorbent in grams.

The percentage phenol removal was calculated using the following equation:

$$\% \text{ removal} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (2)$$

## RESULTS AND DISCUSSION

### Adsorbent characterization

The BET (Brunauer, Emmett and Teller) surface area, total pore volume and average pore diameter of the adsorbent were determined by N<sub>2</sub> adsorption/desorption measurements (NOVA 2200, Quantachrome Corporation, USA) and were found to be 3.6 m<sup>2</sup> g<sup>-1</sup>, 0.0065 cm<sup>3</sup> g<sup>-1</sup> and 38 Å, respectively. The Fourier transform infrared spectroscopy and scanning electron microscopy analysis of the adsorbent has been previously reported (Chowdhury & Saha 2010).

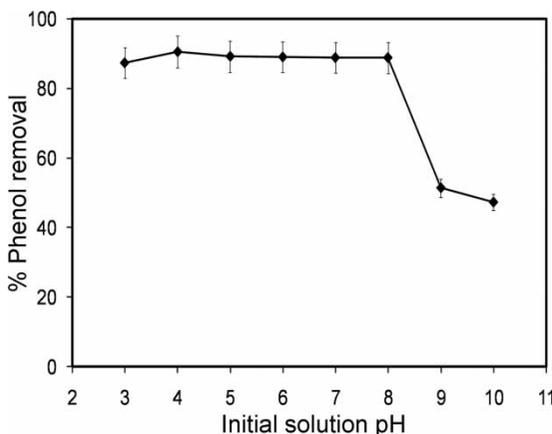
### Effect of pH

To investigate the effect of solution pH on the adsorption of phenol by seashells, a series of batch adsorption experiments as described above was carried out over a pH range of 3–10. The results thus obtained are shown in Figure 1. The phenol removal efficiency was nearly

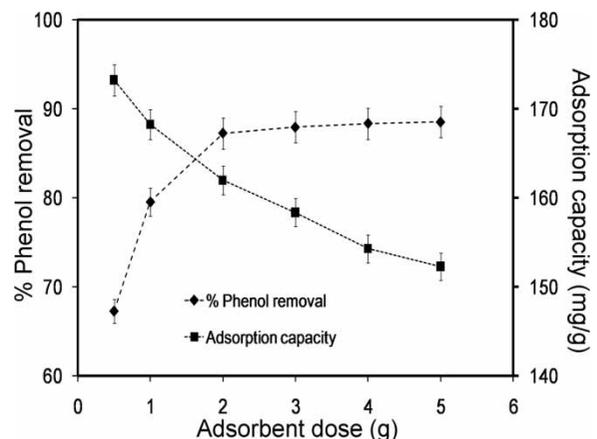
unaffected in the pH range of 3–8. With further increase in pH, a significant decrease in adsorption efficiency was observed. Maximum adsorption was observed at pH 4. A similar effect of pH was observed on the adsorption of phenol by activated carbon derived from rattan sawdust (Hameed & Rahman 2008). Phenol is a weak acid with  $pK_a \approx 9.89$  and is dissociated at  $pH > pK_a$  (Hameed & Rahman 2008). The adsorption thus decreases at high pH values due to ionization of phenol molecules. The decrease in phenol uptake capacity at higher pH could also be due to the electrostatic repulsions between the negatively charged adsorbent surface and the phenolate–phenolate anions in solution (Hameed & Rahman 2008). All further experiments were performed at pH 4.

### Effect of adsorbent dose

The influence of different adsorbent concentration on the phenol removal efficiency was investigated in the range of 0.5 to 5 g. Data obtained from the experiments are presented in Figure 2. The percentage phenol removal increases with increasing adsorbent dose from 0.5 to 2 g. Such a trend is mostly attributed to increase in the adsorptive surface area and the availability of more active adsorption sites (Saha *et al.* 2010). On the other hand, the equilibrium adsorption capacity decreases with increasing amount of adsorbent. This may be due to the decrease in total adsorption surface area available to phenol molecules resulting from



**Figure 1** | Effect of pH on adsorption of phenol by seashells; experimental conditions: initial phenol concentration = 50 mg L<sup>-1</sup>, adsorbent dose = 2 g/0.1 L, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K.

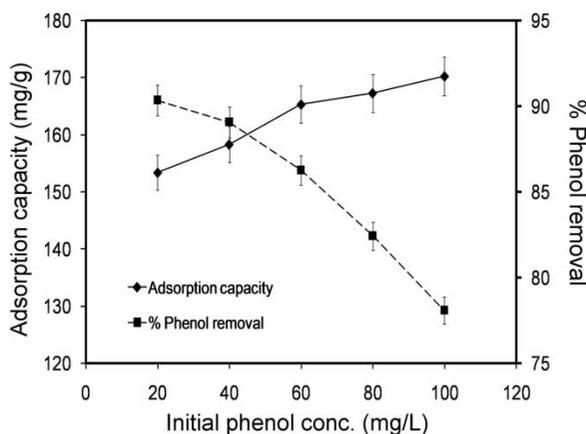


**Figure 2** | Effect of adsorbent dose on adsorption of phenol by seashells; experimental conditions: initial phenol concentration = 50 mg L<sup>-1</sup>, pH = 4, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K.

overlapping or aggregation of adsorption sites (Saha *et al.* 2010). Thus, with increasing adsorbent mass, the amount of phenol adsorbed onto unit mass of adsorbent gets reduced, thus causing a decrease in  $q_e$  value with increasing adsorbent mass concentration. Maximum phenol removal is observed at 2 g and further increase in adsorbent dose does not significantly change the adsorption yield. This is due to the binding of almost all phenol molecules to the adsorbent surface and establishment of equilibrium between the phenol molecules on the adsorbent and in the solution (Saha *et al.* 2010). These observations are in agreement with those reported previously by Su *et al.* (2011) for adsorption of phenol by organomontmorillonite. An optimum adsorbent dose of 2 g was used for the successive experiments.

### Effect of initial phenol concentration

Figure 3 shows the adsorption performance of seashells at different initial concentrations of phenol in the range of 20 to 100 mg L<sup>-1</sup>. The adsorption capacity increases from 153.38 to 170.27 mg g<sup>-1</sup> with increase in initial phenol concentration from 20 to 100 mg L<sup>-1</sup>. The increase in phenol uptake capacity can be attributed to the fact that increasing concentration gradient provides an increasing driving force to overcome all mass transfer resistances of the phenol molecules between the aqueous and solid phases, leading to an increased equilibrium uptake capacity until adsorbent saturation is achieved (Chowdhury *et al.* 2011). On the contrary,

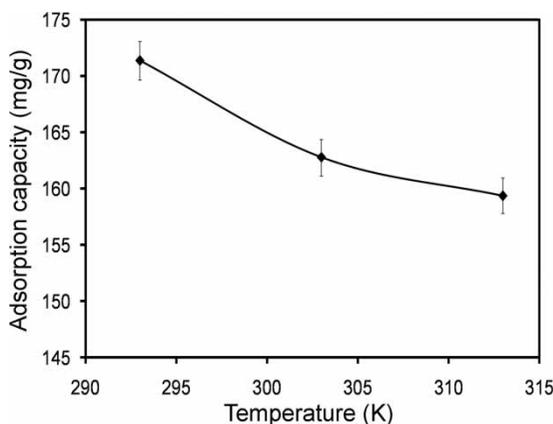


**Figure 3** | Effect of initial phenol concentration on adsorption of phenol by seashells; experimental conditions: pH = 4, adsorbent dose = 2 g/0.1 L, agitation speed = 150 rpm, contact time = 3 h, temp. = 303 K.

the adsorption efficiency decreases with increase in initial phenol concentration. This may be due to the saturation of the adsorption sites on the adsorbent with increase in phenol concentration (Chowdhury *et al.* 2011). For a given adsorbent dose the total number of available adsorption sites is fixed, thereby adsorbing almost the same amount of phenol, thus resulting in a decrease in the percentage removal of phenol with increasing initial phenol concentration. Similar results have been reported for adsorption of phenol by physiochemical-activated coconut shell (Mohd Din *et al.* 2009).

### Effect of temperature

Figure 4 illustrates the adsorption profile of phenol by seashells at different temperatures. The adsorption capacity decreases with increase in temperature over the range of 293–313 K. The observed trend suggests that adsorption of phenol by seashells is kinetically controlled by an exothermic process. Such behaviour may be due to the increasing tendency to desorb phenol from the interface to the solution at higher temperatures (Kilic *et al.* 2011). Also, increase in temperature results in weakening of the bonds between the adsorbate and the binding sites of the adsorbent, leading to low phenol adsorption capacity (Chakraborty *et al.* 2011). A similar phenomenon was also observed for adsorption of phenol by activated carbon prepared from tobacco residues (Kilic *et al.* 2011).



**Figure 4** | Effect of temperature on adsorption of phenol by seashells; experimental conditions: initial phenol concentration = 50 mg L<sup>-1</sup>, pH = 4, adsorbent dose = 2 g/0.1 L, agitation speed = 150 rpm, contact time = 3 h.

## Adsorption isotherms

Equilibrium adsorption isotherms provide the most important information in understanding an adsorption process. Therefore, in the present study, the experimental equilibrium data obtained by performing batch adsorption tests at different temperatures were fitted to the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) adsorption isotherms.

The Freundlich model is described as (Freundlich 1906):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorbate concentration on the adsorbent,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium adsorbate concentration in solution,  $K_F$  ( $\text{mg g}^{-1}$ ) ( $\text{L g}^{-1}$ ) $^{1/n}$  is the Freundlich constant related to adsorption capacity and  $n$  is the heterogeneity factor.

The Langmuir isotherm can be written as (Langmuir 1916):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (4)$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum adsorption capacity and  $K_L$  ( $\text{L mg}^{-1}$ ) is the adsorption equilibrium constant.

The D–R isotherm model has the following formulation (Dubinin & Radushkevich 1947):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad (6)$$

where  $\beta$  is a coefficient related to the mean free energy of adsorption ( $\text{mmol}^2 \text{J}^{-2}$ ),  $\varepsilon$  is the Polanyi potential ( $\text{J mmol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ ) and  $T$  is the temperature (K).

The Freundlich model constants  $K_F$  and  $n$  were determined from the intercept and slope of the plots between  $\log q_e$  and  $\log C_e$  while the Langmuir model parameters  $q_m$  and  $K_L$  were calculated from the intercept and slope of the plots between  $1/q_e$  and  $1/C_e$ . The model parameters and constants thus obtained along with the correlation coefficients ( $R^2$ ) are listed in Table 1. The low  $R^2$  values for the Freundlich model suggest that this model was not suitable for

**Table 1** | Isotherm constants and kinetic parameters for adsorption of phenol by seashells

Model	Parameter	Temperature (K)		
		293	303	313
<b>Isotherm model</b>				
Langmuir	$q_m$ ( $\text{mg g}^{-1}$ )	175.27	170.83	167.44
	$K_L$ ( $\text{L mg}^{-1}$ )	2.28	1.97	1.45
	$R^2$	0.99	0.99	0.99
Freundlich	$K_F$ ( $\text{mg g}^{-1}$ ) ( $\text{L mg}^{-1}$ ) $^{1/n}$	7.26	6.15	5.43
	$N$	3.92	3.21	2.69
	$R^2$	0.93	0.92	0.92
Dubinin–Radushkevich	$q_m$ ( $\text{mg g}^{-1}$ )	131.88	127.15	121.63
	$\beta$ ( $\text{mmol}^2 \text{J}^{-2}$ )	$5.48 \times 10^{-9}$	$5.96 \times 10^{-9}$	$6.23 \times 10^{-9}$
	$E$ ( $\text{kJ mol}^{-1}$ )	9.54	9.15	8.95
	$R^2$	0.88	0.87	0.87
<b>Kinetic model</b>				
Pseudo-first-order	$q_{e,\text{exp}}$ ( $\text{mg g}^{-1}$ )	171.36	162.77	159.59
	$q_{e,\text{cal}}$ ( $\text{mg g}^{-1}$ )	145.07	139.63	133.87
	$k_1$ ( $\text{min}^{-1}$ )	0.56	0.31	0.12
	$R^2$	0.89	0.88	0.89
Pseudo-second-order	$q_{e,\text{cal}}$ ( $\text{mg g}^{-1}$ )	172.238	163.59	160.17
	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.07	0.04	0.01
	$R^2$	0.99	0.99	0.99

describing the equilibrium adsorption data of phenol onto seashells. The Freundlich model constant  $n$  gives a measure of favourability of adsorption, with the value of  $n$  between 1 and 10 representing a favourable adsorption (Chowdhury et al. 2011). In the current investigation, the values of  $n$  obtained for adsorption of phenol are  $1 < n < 10$ , suggesting that adsorption of phenol onto seashells can be considered as favourable. Unlike the Freundlich model, the comparatively high  $R^2$  values for the Langmuir model establish the fact that adsorption took place at specific homogeneous sites within the adsorbent and that, once a phenol molecule occupied a site, no further adsorption could take place at that site, thereby forming a monolayer (Chakraborty et al. 2011).

The value of the D-R model constants  $q_m$  and  $\beta$ , as determined from the intercept and slope of the plots between  $\ln q_e$  and  $\varepsilon^2$ , together with the  $R^2$  values are given in Table 1. The  $R^2$  values are considerably lower than in the Freundlich and Langmuir isotherm models, implying that the D-R isotherm was not suitable for describing the adsorption equilibrium of phenol onto seashells.

The D-R isotherm model constant  $\beta$  can be used to measure the mean free energy of adsorption  $E$  ( $\text{kJ mol}^{-1}$ ), which in turn gives an idea about the type of adsorption mechanism.  $E$  can be computed using the following relationship (Chowdhury & Saha 2010):

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)$$

The magnitude of  $E$  may characterize the adsorption process as chemical ion-exchange ( $E = 8\text{--}16 \text{ kJ mol}^{-1}$ ) or physisorption ( $E < 8 \text{ kJ mol}^{-1}$ ) (Chowdhury & Saha 2010). In the present study, the values of  $E$  are  $>8 \text{ kJ mol}^{-1}$  at all temperatures (Table 1), implying that adsorption of phenol by seashells involves chemical ion-exchange.

Table 2 outlines the comparison of  $q_m$  values of various adsorbents including seashell for adsorption of phenol. It is to be noted that the maximum adsorption uptake capacity varies as a function of experimental conditions. In particular, the solution pH and temperature have a very important effect on the estimation of the maximum amount of phenol uptake per unit adsorbent. Therefore, for a direct and meaningful comparison, the

**Table 2** | Comparison of maximum phenol adsorption capacity of seashells with other reported adsorbents

Adsorbent	pH	Temperature (K)	Maximum adsorption capacity ( $\text{mg g}^{-1}$ )	Reference
Sugarcane bagasse fly ash	6.5	303	23.83	Srivastava et al. (2006)
Activated carbon (laboratory grade)	6.5	303	24.64	Srivastava et al. (2006)
Activated carbon (commercial grade)	6.5	303	30.21	Srivastava et al. (2006)
Clay	6.5	303	30.3	Nayak & Singh (2007)
Natural zeolite	4	298	34.5	Yousef et al. (2011)
Dried activated sludge	1.0	298	86.1	Aksu & Gonen (2004)
Carbonized beet pulp	6	333	89.5	Dursun et al. (2005)
Rattan sawdust based activated carbon	–	$303 \pm 1$	149.25	Hameed & Rahman (2008)
Coconut shell based activated carbon	7	303	205.84	Mohd Din et al. (2009)
Seashell	8	293	175.27	This study

maximum amount of phenol adsorbed by seashells has been compared to the maximum phenol adsorption capacity of other reported adsorbents under different experimental conditions. From Table 2, it is evident that seashell has higher phenol adsorption capacity than many of the other reported adsorbents. Thus, it seems that seashells can be considered as an efficient and low-cost alternative adsorbent for removal of phenol from wastewater streams of industries.

### Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were applied in this study to investigate the reaction pathway and potential rate-limiting step of adsorption of phenol onto seashells.

The pseudo-first-order kinetic model has the following formulation (Ho 2004):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorbate concentration on the adsorbent,  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount of adsorbate adsorbed at time  $t$  and  $k_1$  ( $\text{h}^{-1}$ ) is the pseudo-first-order rate constant. A plot of  $\ln(q_e - q_t)$  versus  $t$  gives a straight line, with the slope and intercept giving the values of  $k_1$  and  $q_e$ , respectively.

The pseudo-second-order kinetic model is expressed by the following equation (Ho & McKay 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{h}^{-1}$ ) is the pseudo-second-order rate constant. The constants  $k_2$  and  $q_e$  can be calculated from the intercept and slope of the linear plot of  $t/q_t$  versus  $t$ .

Table 1 presents the value of the pseudo-first-order and pseudo-second-order model constants together with the correlation coefficients ( $R^2$ ) for adsorption of phenol by seashells. The kinetic data obtained at different temperatures show excellent correlation with the pseudo-second-order kinetic model. The  $R^2$  values from the pseudo-second-order kinetic equation are significantly higher than those from the pseudo-first-order kinetic model. The calculated equilibrium uptake ( $q_{e,\text{cal}}$ ) values from the pseudo-second-order model also show good agreement with the experimental values ( $q_{e,\text{exp}}$ ). These findings suggest that the adsorption of phenol by seashells was in accordance with pseudo-second-order kinetics and that the overall rate of phenol adsorption was controlled by a chemical process (Ho & McKay 1999).

In a well-agitated batch adsorption system, there is a possibility of intraparticle pore diffusion of adsorbate ions, which may be the rate-limiting step. Therefore, the possibility of intra-particle diffusion resistance affecting the adsorption process was explored by using the intra-particle diffusion model (Weber & Morris 1963).

$$q_t = k_i t^{0.5} \quad (10)$$

where  $k_i$  ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ) is the intraparticle diffusion rate constant.

According to Equation (9), if a plot of  $q_t$  versus  $t^{0.5}$  is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, if the data exhibit multi-linear plots, then the process is governed by two or more steps. In the current investigation, the plots of  $q_t$  versus  $t^{0.5}$  for adsorption of phenol onto seashells at different temperatures were multimodal with three distinct regions representing the different stages in adsorption: an initial curve portion followed by a linear portion and then a plateau. The initial curved region is attributed to the external surface adsorption in which the adsorbate diffuses through the solution to the external surface of the adsorbent. The second stage relates the gradual uptake reflecting intraparticle diffusion as the rate-limiting step. The final plateau region refers to the gradual adsorption stage and the final equilibrium stage, in which the intraparticle diffusion starts to slow down and level out. The present finding implies that, although intraparticle diffusion is involved in the adsorption process, it is not the sole rate-limiting step and that some other mechanisms also play an important role.

### Activation energy and thermodynamic parameters

The activation energy,  $E_a$ , for adsorption of phenol onto seashells was calculated by using the Arrhenius equation (Saha et al. 2010):

$$\ln k = \ln A - \frac{E_a}{RT} \quad (11)$$

where  $k$  is the rate constant,  $A$  is the Arrhenius constant,  $E_a$  is the activation energy ( $\text{kJ mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature (K).

By plotting  $\ln k_2$  versus  $1/T$ ,  $E_a$  was determined from the slope of the linear plot and was found to be  $51.38 \text{ kJ mol}^{-1}$ . The magnitude of  $E_a$  may give an idea about the type of adsorption. There are two main types of adsorption: physical and chemical.  $E_a$  for physical adsorption is usually less than  $40 \text{ kJ mol}^{-1}$ , since the forces involved in physical adsorption are weak. Higher values represent chemical reaction processes as chemical adsorption is specific and involves forces much stronger than those in physical adsorption (Saha et al. 2010). The value of  $E_a$  in the present study

**Table 3** | Thermodynamic parameters for adsorption of phenol onto seashells

$\Delta G^0$ (kJ mol <sup>-1</sup> )				
293 K	303 K	313 K	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )
-21.65	-18.32	-15.97	-107.63	-284.19

suggests that adsorption of phenol by seashells is a chemical adsorption process.

The thermodynamic parameters such as Gibbs free energy change ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were calculated using the following equations (Chowdhury & Saha 2010):

$$\Delta G^0 = -RT \ln K_C \quad (12)$$

$$K_C = \frac{C_a}{C_e} \quad (13)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (14)$$

where  $R$  is the universal gas constant (8.314 kJ mol<sup>-1</sup>),  $T$  is the temperature in  $K$ ,  $K_C$  is the distribution coefficient for adsorption,  $C_a$  is the equilibrium adsorbate concentration on the adsorbent (mg L<sup>-1</sup>) and  $C_e$  is the equilibrium adsorbate concentration in solution (mg L<sup>-1</sup>). The values of  $\Delta G^0$  for adsorption of phenol by seashells are listed in Table 3. The values of  $\Delta H^0$  and  $\Delta S^0$  obtained from the slope and intercept of the plot of  $\Delta G^0$  as a function of  $T$  are also summarized in Table 3. The  $\Delta G^0$  values are negative, suggesting that the adsorption process is feasible and spontaneous in nature. The negative value of  $\Delta H^0$  implies that the adsorption phenomenon is exothermic. The negative value of  $\Delta S^0$  suggests that the process is enthalpy driven.

## CONCLUSION

In this study, powdered seashell was tested as an alternative adsorbent for removal of phenol from aqueous solution by performing batch equilibrium tests. The following conclusions are made based on the results of the present study:

- The adsorption capacity decreases with increasing temperature while it increases with increasing initial phenol concentration.

- The adsorption efficiency remains unaffected when the initial pH of the phenol solution is in the range of 3–8.
- The Langmuir isotherm adequately describes the adsorption equilibrium data, suggesting monolayer adsorption on a homogeneous surface.
- The results of kinetic study show that the pseudo-second-order model fits well to the experimental adsorption data.
- Thermodynamic studies demonstrate the feasible, spontaneous and endothermic nature of adsorption of phenol by seashells.
- The results suggest that seashells can be used as an efficient low-cost adsorbent for removal of phenol from wastewater.
- To date, it is the first report on utilization of seashells as adsorbent for removal of phenol from aqueous medium.

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