

## Adsorptive removal of 2,4-dichlorophenol from water utilizing *Punica granatum* peel waste and stabilization with cement

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### ABSTRACT

The present study investigates the adsorption potential of *Punica granatum* (pomegranate) peel as an adsorbent for the removal of 2,4-dichlorophenol (2,4-DCP) from aqueous solutions. The adsorption was studied as a function of contact time, initial concentration and temperature by batch method. The adsorption capacity of pomegranate peel adsorbent for 2,4-DCP was found to be 65.7 mg g<sup>-1</sup>. The equilibrium adsorption data was well described by the Langmuir model. Kinetic studies suggest that the present system of phenol adsorption on pomegranate peel adsorbent could be described more favorably by pseudo-first-order kinetic model. Column studies were also undertaken in order to test the practical utility of prepared adsorbent and found promising. After the adsorption studies, the phenol-laden adsorbent was stabilized in cement for its ultimate disposal. The results of the present study clearly reveal that prepared adsorbent can be used beneficially in treating industrial effluents containing phenols and safely disposed of by stabilizing into cement.

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### 1. Introduction

Phenol and substituted phenols are one of the important categories of aquatic pollutants, which are toxic to human beings and are considered as priority pollutants [1]. Phenols are being discharged into natural water bodies through different industrial activities, constituting one of the major causes of environmental pollution. The presence of even small concentrations of phenols in water is of great concern as this can impart objectionable taste and odor. Phenol is a basic structural unit for a variety of synthetic organic compounds and therefore, wastewater originating from many chemical plants, pesticide and dye manufacturing industries contain phenols. Besides this, wastewater originating from other industries like pulp and paper, resin manufacturing, gas and coke manufacturing, tanning, textile, plastics, rubber, pharmaceutical and petroleum also contain different types of phenols [2]. In addition to phenols generated as a result of industrial activity, wastewaters also contain phenols formed as a result of decay of vegetation.

The ubiquitous nature of phenols, their toxicity even in trace amounts and the stricter environmental regulations make it nec-

essary to develop processes for the removal of phenols from wastewaters. Methods used for the removal of phenols include biological methods [3], membrane filtration [4], ion exchange [5], photocatalytic degradation [6], oxidation with ozone/hydrogen peroxide [7], reverse osmosis [8], electrochemical oxidation [9] and adsorption [10–12]. Among the various available methods for phenol removal, adsorption process is considered to be the best as it has wider applicability and generally removes all types of phenols and effluent treatment is convenient because of simple design and easy operation of the process. The activated carbon is mainly used as adsorbent in the adsorption processes currently in use. However, its widespread applications in wastewater treatment are restricted due to higher cost. In view of the importance of pollution control, efforts have been directed toward developing low cost alternative adsorbents.

The utilization of waste materials is increasingly becoming of vital concern because these wastes represent unused resources and, in many cases, cause serious disposal problems. Large amount of solid wastes are produced in the agricultural sector in most countries of the world. A major part of this waste is normally used as domestic fuel. However, for better utilization of this cheap and abundant agricultural wastes, it can be explored as low cost alternative adsorbent owing to relatively high fixed carbon content and presence of porous structure as reported by various researchers [13–16]. However, the prepared adsorbents have not been found to be as promising as activated carbon in water pollution control. Therefore, the search for efficient low-

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cost adsorbents is ongoing. Additionally, most adsorption studies do not suggest any environmentally safe disposal methods for the pollutants-laden adsorbent generated as a result of the adsorption process.

The present study was undertaken with two main objectives: (i) to utilize pomegranate (*Punica granatum*) peel as an adsorbent after proper treatment for the removal of phenols with a model system of 2,4-dichlorophenol (2,4-DCP) from water and, (ii) to dispose of this phenol-laden adsorbent in cement by solidification/stabilization (S/S) technology, which is a widely accepted technology to control the release of hazardous waste (especially metal ions and radioactive wastes) directly into the environment. Stabilization of metals in S/S processes consists mainly of converting the heavy metals into insoluble precipitates. However, binding mechanisms and leaching of organics in cement are largely unknown till date.

## 2. Materials and methods

### 2.1. Materials

2,4-DCP was purchased from Merck. Some of the important characteristics of 2,4-DCP are shown in Table 1. Stock solutions of 2,4-DCP were prepared by dissolving it in double-distilled water and were diluted further to obtain the lower concentration solutions. Commercial Ordinary Portland cement 43 grade was used to immobilize phenol-laden adsorbent. All reagents used were of analytical reagent grade.

### 2.2. Preparation of adsorbent using pomegranate peel waste

The pomegranate peels were collected from the local fruit market. These were first washed with double-distilled water and dried in an oven at  $80 \pm 2^\circ\text{C}$  overnight. The dried pomegranate peels were ground and this material was then thermally activated at  $600 \pm 5^\circ\text{C}$  in a muffle furnace for 1 h in the presence of air. After activation, the ash content was removed by washing it with distilled water and dried in an oven at  $110 \pm 5^\circ\text{C}$  overnight. Different mesh sizes (BSS 100–250) were obtained after sieving and kept in a desiccator for further use. The particle size of BSS 150–200 mesh was used in the present study.

### 2.3. Adsorption studies

The adsorption of 2,4-DCP on the prepared adsorbent was studied at room temperature ( $25 \pm 2^\circ\text{C}$ ) by batch experiments. Ten millilitre of 2,4-DCP solution of varying initial concentrations in 50 mL capped tubes was shaken with 0.1 g of adsorbent for a specified period of contact time in a temperature controlled shaking assembly. After equilibrium, samples were filtered using 0.45  $\mu\text{m}$  filters (Whatman) and the concentration of the 2,4-DCP was determined spectrophotometrically at  $\lambda_{\text{max}}$  of 282 nm. Reproducibility of the measurements was determined in triplicates and the average

**Table 1**  
Some characteristics of 2,4-dichlorophenol.

CAS number	000120-83-2
Chemical formula	$\text{C}_6\text{H}_4\text{Cl}_2\text{O}$
F.W.	163.00
Melting point	$45^\circ\text{C}$
Boiling point	$210^\circ\text{C}$
Water solubility	4500 mg/L ( $20^\circ\text{C}$ )
Log <i>P</i> (octanol–water)	3.06
<i>pK</i> <sub>a</sub>	7.89
Henry's law constant	$4.29\text{E}-006 \text{ atm}\cdot\text{m}^3/\text{mol}$ ( $25^\circ\text{C}$ )
Atmospheric OH rate constant	$1.06\text{E}-012 \text{ cm}^3/\text{molecule}\cdot\text{s}$ ( $25^\circ\text{C}$ )

values are reported. Relative standard deviations were found to be within  $\pm 5.0\%$ .

The amount of 2,4-DCP adsorbed ( $q_e$  in  $\text{mg g}^{-1}$ ) was determined as follows:

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

where  $C_0$  and  $C_f$  are the initial and final concentrations of the 2,4-DCP in solution (in  $\text{mol L}^{-1}$ ),  $V$  is the volume of solution (in L) and  $m$  is the mass of the adsorbent (in g). The pH of all solutions in contact with adsorbent was found to be in the range 5.5–6.5. Kinetic studies of adsorption were also carried out at two initial 2,4-DCP concentrations, where the extent of adsorption was investigated as a function of time.

### 2.4. Column studies

In the present study, a glass column ( $50 \text{ cm} \times 1.05 \text{ cm}$ ) was fully loaded with adsorbent on a glass wool support. Double-distilled water was used to rinse the adsorbent and to remove any bubbles present. 2,4-DCP solution was poured over the column and the column effluent was allowed at a flow rate of  $2.5 \text{ mL min}^{-1}$ . A definite amount of the column effluent (10 mL) was taken and the concentration of 2,4-DCP determined from time to time by UV-vis. This process has continued until the concentration in the column effluent started increasing and finally becomes constant. The plots of concentration of the adsorbate in the column effluent and volume of the effluent provide breakthrough curves.

### 2.5. Preparation and curing of cement pastes and mortars

A separate batch adsorption experiment similar to that described previously (under similar conditions) but with a larger volume (1 L) of adsorbate solution with a larger quantity of adsorbent (10 g) was conducted to produce the phenol-laden adsorbent for preparation of the solidified specimens. After the equilibration time, the solid was separated from the liquid. The phenol-laden adsorbent was then dried in an oven at  $110^\circ\text{C}$  for 24 h. After drying, the phenol-laden adsorbent was added in different proportions to cement and sand to produce a cementitious system. Well-mixed mortar pastes were cast in 2.78 in. cubic iron molds. The cubes were demolded after 24 h and were kept dipped in water for curing. These cubes were tested for compressive strength on 3, 7, 28, 60 and 90 days of curing. Three replicates were tested for each time and the average value was compared with the values obtained for the blank sample (without the addition of phenol-laden adsorbent). All the cement pastes and mortars were prepared by the methods described in the IS: 4031-1968 guidelines [17].

### 2.6. Leaching studies

An appropriate way to examine the effectiveness of the immobilization of contaminants after the solidification process is to perform the leaching test. These tests are commonly used to determine the leachability under the selected leach testing conditions. This study has been carried out by following the standard method No. 1311 as recommended by United States Environmental Protection Agency (USEPA) [18]. Crushed solid material was placed in hazardous waste filtration system with zero head space extractor. A known volume of water was added and this assembly has been agitated for 24 h continuously in the agitator. A filtered extract was collected in a closed vessel and was analyzed for phenol concentration by using the UV-vis.

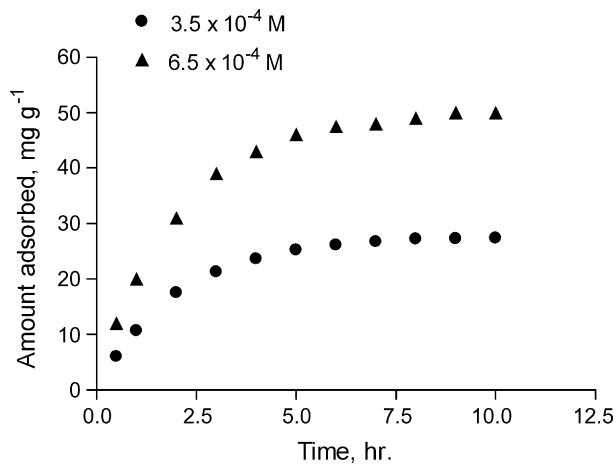


Fig. 1. Effect of contact time and concentration on adsorption of 2,4-DCP on pomegranate peel adsorbent [temperature = 25 °C, adsorbent dosage = 10 g L<sup>-1</sup>, pH = 5.5–6.5].

### 3. Results and discussion

#### 3.1. Effect of contact time and initial phenol concentration

In order to establish the equilibration time for maximum uptake of 2,4-DCP and to know the kinetics, adsorption of 2,4-DCP on prepared adsorbent was studied as a function of contact time and concentration and results are shown in Fig. 1. It is seen from the figure that the rate of uptake of 2,4-DCP is rapid in the beginning and 50% adsorption is completed in 2 h and become constant after 9 h, which indicates that equilibrium has been achieved. Thus, 10 h equilibration time was selected in subsequent batch experiments.

The effect of concentration on equilibrium time was also investigated at two different initial 2,4-DCP concentrations and results are also shown in Fig. 1. It was found that adsorption capacity at equilibrium increases from 27.4 mg g<sup>-1</sup> to 50.0 mg g<sup>-1</sup> with an increase in the initial 2,4-DCP concentration from 3.5 × 10<sup>-4</sup> M to 6.5 × 10<sup>-4</sup> M. This indicates that initial concentration plays an important role in the adsorption of 2,4-DCP on prepared adsorbent.

#### 3.2. Kinetic modeling

In the present study, we applied three important kinetic models viz. pseudo-first-order, pseudo-second-order and Weber and Morris intraparticle diffusion model in order to investigate the mechanism of adsorption of 2,4-DCP on pomegranate peel adsorbent.

##### 3.2.1. Pseudo-first-order model

Various reports [19,20] exist where adsorption has been considered as pseudo-first-order. The Lagergren's rate equation [21] is the most widely used [22–24] for the sorption of a solute from a liquid solution. Thus this first-order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \quad (2)$$

where ' $q_e$ ' and ' $q_t$ ' are the amount of 2,4-DCP adsorbed (mg g<sup>-1</sup>) at equilibrium and at time  $t$ , respectively, and  $k_f$  is the pseudo-first-order rate constant, was applied to the present study of 2,4-DCP adsorption. Fig. 2(A) shows a plot of linear form of pseudo-first-order model at two concentrations studied. The plots were found linear with good correlation coefficients ( $R^2$ ) for the pseudo-first-order kinetic model varying from 0.9923 to 0.9996 confirming that present adsorption system follows pseudo-first-order kinetics. Further, the theoretical  $q_{e(cal)}$  values were also found in accordance

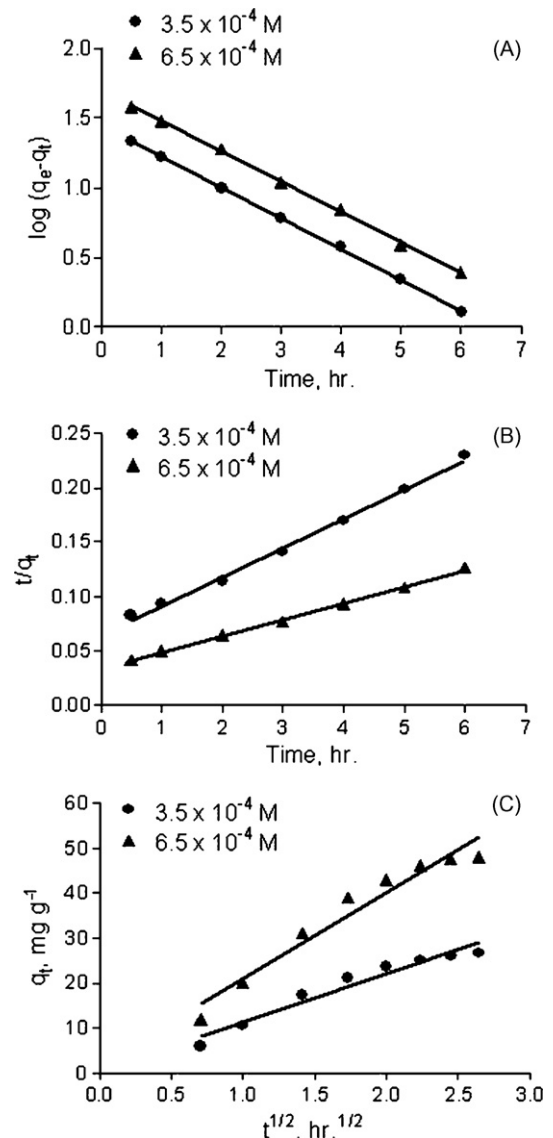


Fig. 2. Kinetic modeling of 2,4-DCP adsorption on pomegranate peel adsorbent. (A) Pseudo-first-order kinetic model plots; (B) pseudo-second-order kinetic model plots; (C) Weber and Morris intraparticle diffusion model plots.

with the experimental uptake values  $q_{e(exp)}$  (Table 2). This suggests that present adsorption system follows pseudo-first-order kinetics.

##### 3.2.2. Pseudo-second-order model

The adsorption kinetics was also described as pseudo-second-order process [25–27]:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $k_s$  is the pseudo-second-order rate constant. The present data was also tested in the light of pseudo-second-order kinetic model. The plots between  $t/q_t$  versus  $t$  were drawn and are shown in Fig. 2(B). Although correlation coefficients ( $R^2$ ) for the pseudo-second-order kinetic model were 0.9950 and 0.9979 at both concentrations studied, but the theoretical  $q_{e(cal)}$  values calculated for the pseudo-second-order model did not give reasonable values with regard to the experimental uptake values,  $q_{e(exp)}$  (Table 2). This suggests that the present adsorption system cannot be well described by pseudo-second-order process.

It is well known that adsorption kinetics is generally controlled by three consecutive mass transport steps associated with the

**Table 2**  
Comparison of calculated amount adsorbed,  $q_{e(cal)}$  and experimental amount adsorbed,  $q_{e(exp)}$  values for different initial 2,4-DCP concentrations for different models.

Phenol	$C_0$ (M)	$q_{e(exp)}$ ( $\text{mg g}^{-1}$ )	Pseudo-first-order		Pseudo-second-order	
			$q_{e(cal)}$ ( $\text{mg g}^{-1}$ )	$R^2$	$q_{e(cal)}$ ( $\text{mg g}^{-1}$ )	$R^2$
2,4-DCP	$3.5 \times 10^{-4}$	27.4	27.7	0.9996	37.5	0.9950
	$6.5 \times 10^{-4}$	50.0	54.2	0.9923	66.3	0.9979

adsorption of solute from the solution by an adsorbent. These are (i) film diffusion, (ii) intraparticle or pore diffusion, and (iii) sorption into interior sites. The third step is very rapid and hence film and pore transports are the major steps controlling the rate of adsorption. In order to understand the diffusion mechanism, intraparticle diffusion model was tested for the present 2,4-DCP adsorption study.

### 3.2.3. Weber and Morris model

Kinetic data (Fig. 1) was analyzed in the light of intraparticle diffusion model proposed by Weber and Morris [28]:

$$q_t = k_{ip}t^{1/2} + C \quad (4)$$

where,  $C$  is the intercept and  $k_{ip}$  is the intraparticle diffusion rate constant. According to this equation, a plot of uptake ( $q_t$ ) versus the square root of time, ( $t^{1/2}$ ) should be linear when adsorption mechanism follows the intraparticle diffusion process. Fig. 2(C) shows a plot of linear form of intraparticle diffusion model. As can be seen from Fig. 2(C), the intercept of the line do not pass through the origin and the correlation coefficients ( $R^2$ ) are less also than 0.99 at two concentrations studied suggesting that the mechanism of phenol (2,4-DCP) adsorption onto prepared adsorbent is not solely governed by intraparticle diffusion process.

### 3.3. Adsorption isotherms

In order to determine the efficacy of prepared adsorbent, the equilibrium adsorption studies were carried out with varying concentrations of the 2,4-DCP and adsorption isotherms are shown in Fig. 3. It is clear from figure that initially isotherms rise sharply indicating that plenty of readily accessible sites are available in the beginning for adsorption. However, after achieving equilibration, when adsorbent becomes saturated, a plateau is reached indicating that no more sites are available for further adsorption. The adsorption capacity of pomegranate peel adsorbent for 2,4-DCP was found  $65.7 \text{ mg g}^{-1}$  at  $25^\circ\text{C}$ . The adsorption of phenol on prepared carbonaceous adsorbent is purely a surface phenomenon where van der Waals forces operate to some extent. The adsorption of phe-

nol could also be occurring to some extent due to the interaction through hydrogen bonding with hydrophilic sites or groups formed on carbon surface at the time of activation. It has been reported that in the adsorption of phenols on carbon surface, the role of donor–acceptor complex mechanism involving carbonyl oxygen groups of the carbon surface acting as electron donor and the aromatic ring of the adsorbate as acceptor is important [29]. Thus, it is expected that electron withdrawing groups, which deactivate the ring, would promote adsorption through complex formation occurring via donor–acceptor mechanism. As a result of higher deactivation of the ring in 2,4-DCP, there would be higher tendency of adsorption through a donor–acceptor complex mechanism resulting in maximum adsorption.

Besides this, the solubility and  $\text{pK}_a$  of solute is also expected to affect adsorption to a great extent. A decrease in both aqueous solubility and  $\text{pK}_a$  of the solute is associated with an increase in adsorption capacity [30], 2,4-DCP having lower solubility ( $4.5 \text{ g L}^{-1}$ ) and lower  $\text{pK}_a$  (7.9) is adsorbed to higher extent. Thus, all these factors, i.e. the tendency to form more donor–acceptor complex at carbon surface, lower  $\text{pK}_a$  and lower aqueous solubility lead to same order of adsorption and it is reasonable to believe that a combined effect of these factors is observed.

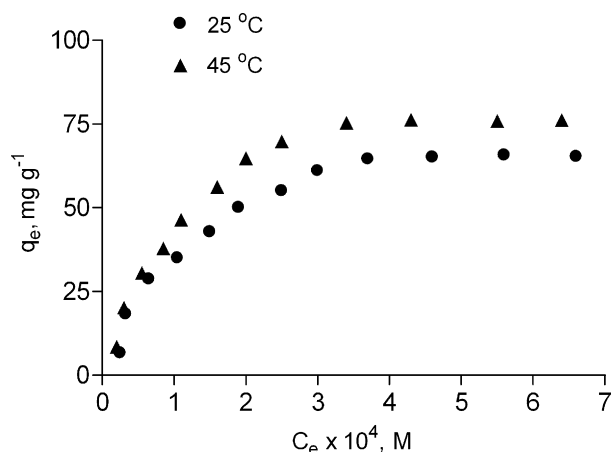
### 3.4. Effect of temperature on phenol adsorption

In order to understand the effect of temperature on the adsorption of 2,4-DCP, experiments were also conducted at  $45^\circ\text{C}$  and results are shown in Fig. 3. A comparison of adsorption isotherms at  $25^\circ\text{C}$  and  $45^\circ\text{C}$  shows that adsorption increases with increase in temperature indicating that the process is endothermic in nature. Similar results were also obtained by other workers [19,23]. It seems that at higher temperatures, dissociation of phenol molecule occurs. However, the effect of temperature can mainly be explained on the basis of hydrogen bonding [31]. In aqueous solutions of phenols, there exists extensive hydrogen bonding between the phenol molecule and water resulting in appreciable solubility. These hydrogen bonds get broken at higher temperatures and this would cause phenols to be less soluble and therefore, exhibit higher tendency to go to the adsorbent surface and get adsorbed rather remaining in the solution. This would result in more adsorption at higher temperature [31]. Few researchers [32] also described this phenomenon (more adsorption at higher temperatures) on the basis of “active surface centers” (presence of free hydroquinone and quinone groups on the carbon surface which could constitute the active surface centers for the adsorption of phenols by hydrogen bonding). They suggested that number of active surface centers available for sorption increase with increasing temperatures resulting higher adsorption of phenols.

The most widely used isotherm equation, Langmuir model was used to describe the experimental data of adsorption isotherms and for the equilibrium modeling. The linear Langmuir equation has the following form:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (5)$$

where ‘ $q_e$ ’ is the amount adsorbed at equilibrium concentration ‘ $C_e$ ’, ‘ $q_m$ ’ is the Langmuir constant representing maximum monolayer capacity and ‘ $b$ ’ is the Langmuir constant related to energy



**Fig. 3.** Adsorption isotherms of 2,4-DCP on pomegranate peel adsorbent at different temperatures [adsorbent dosage =  $10 \text{ g L}^{-1}$ ,  $\text{pH} = 5.5\text{--}6.5$ ].

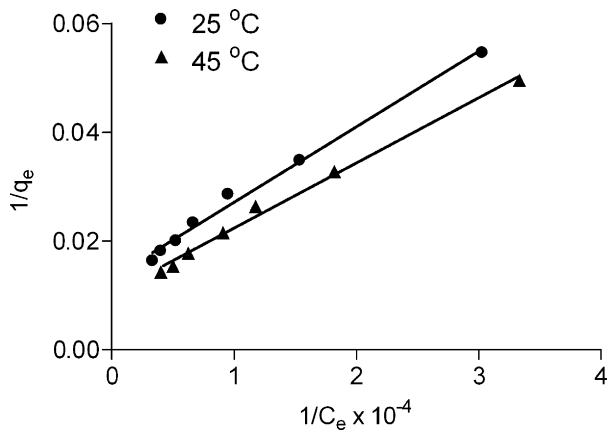


Fig. 4. Langmuir plots of 2,4-DCP adsorption on pomegranate peel adsorbent.

of adsorption. The plots between  $1/q_e$  and  $1/C_e$  for the adsorption of 2,4-DCP are drawn in Fig. 4. The values of monolayer capacity ( $q_m$ ) and Langmuir constant ( $b$ ) have been evaluated from the intercept and slope of these plots and given in Table 3. A perusal of Table 3 shows that monolayer capacity ( $q_m$ ) of the adsorbent for the 2,4-DCP is comparable to the maximum adsorption obtained from adsorption isotherms.

The effect of isotherm shape has been discussed [33] with a view to predict whether an adsorption system is 'favorable' or 'unfavorable'. The essential feature of the Langmuir isotherm can be expressed in terms of ' $R_L$ ', a dimensionless constant referred to as separation factor or equilibrium parameter. ' $R_L$ ' is calculated using the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

The values of ' $R_L$ ' calculated as per above equation are incorporated in Table 3. As the ' $R_L$ ' values lie between 0 and 1, the adsorption isotherm is favorable.

### 3.5. Thermodynamic parameters

Thermodynamic parameters were calculated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. Thermodynamic parameters were calculated using Eqs. (7)–(9):

$$\Delta G = -RT \ln K \quad (7)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Table 3

Langmuir constants and separation factor for the adsorption of 2,4-DCP on pomegranate peel adsorbent at different temperatures.

Phenol	Temperature (°C)	$q_m$ (mg g <sup>-1</sup> )	$b$ (L mol <sup>-1</sup> )	$R^2$	$R_L$
2,4-DCP	25	75.8	$6.8 \times 10^3$	0.9920	$1.3 \times 10^{-1}$
	45	96.2	$8.3 \times 10^3$	0.9932	$1.1 \times 10^{-1}$

Table 4

Thermodynamic parameters for adsorption of 2,4-DCP on pomegranate peel adsorbent at different temperatures.

Phenol	Temperature (°C)	$K$	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )
2,4-DCP	25	$3.77 \times 10^5$	-31.8	133.6	7.9
	45	$4.62 \times 10^5$	-34.5	133.5	

where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature in Kelvin and  $K$  is the equilibrium constant, related to the Langmuir constant ' $b$ ' via Eq. (10), where the value 55.5 corresponds to the molar concentration of the solvent (in this case water) with units of  $\text{mol L}^{-1}$  [34–36].

$$K = b \times 55.5 \quad (10)$$

The values of the above stated parameters are summarized in Table 4. The  $\Delta H$  values are positive due to the effect of temperature on breaking of hydrogen bonds which resulted in increased adsorption. Thus, the pre-adsorption step (breaking of hydrogen bonds between phenol and water molecules at higher temperatures) gives rise to positive  $\Delta H$ . These positive  $\Delta H$  values are only apparent heat of adsorption. As a matter of fact,  $\Delta H$  values reflect the combined effect of endothermic hydrogen bond breaking process and exothermic adsorption process. The endothermic process predominates the exothermic adsorption process giving rise to positive  $\Delta H$ . The negative  $\Delta G$  values indicate the spontaneous nature of the adsorption process. Additionally, the decrease in free energy change with the rise in temperature shows an increase in feasibility of adsorption at higher temperatures [22,37]. Further positive  $\Delta S$  values indicate the affinity of the adsorbent for 2,4-DCP and suggests an increased randomness at the solid–solution interface during adsorption process.

### 3.6. Column studies

The column operations were carried out by passing 2,4-DCP solution with a flow rate of  $2.5 \text{ mL min}^{-1}$  through column (cross-sectional area:  $0.9 \text{ cm}^2$ ; height:  $3.1 \text{ cm}$ ; mass:  $1.0 \text{ g}$  of adsorbent). Particle size of 50–200 mesh were used for column operations. The column did not get clogged due to mixing of particles of larger size with smaller ones and influent flowed freely over a period of 6–8 h involving a total outflow of ca. 700 mL of 2,4-DCP solution. Column operation was continued till concentration of 2,4-DCP in the aliquot of effluent collected reached nearly 90% of the influent concentration, i.e.  $C/C_0 \sim 0.9$ . In a traditional S-shape breakthrough curve, the concentration ratio ( $C/C_0$ ) of a given species in the effluent was plotted against the effluent volume of the target solution. The breakthrough curve was obtained (Fig. 5) by plotting  $C/C_0$  against volume of the effluent. Those points on the breakthrough curve have been considered as breakpoints at which  $C/C_0$  attains a value of 0.02. The breakthrough capacity, exhaustion capacity and degree of column utilization have been evaluated from the figure (Fig. 5). The breakthrough capacity was found lower than batch capacity which may be due to (i) lesser contact time/equilibration time of the solute with adsorbent and (ii) larger size of particles (50–200 mesh), which require longer time for equilibration and thus, inhibiting the utilization of column capacity. Similar results were also obtained by other workers [19] for the removal of chlorophenols by bituminous shale. The exhaustion capacity of column was observed relatively higher than the batch capacity. This appears due to the establishment of

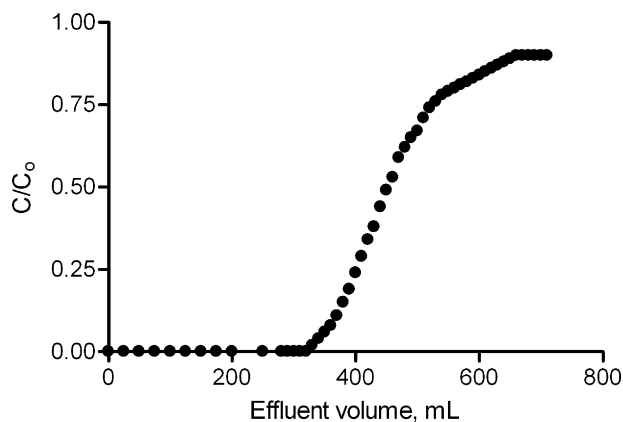


Fig. 5. Breakthrough curve of 2,4-DCP adsorption on pomegranate peel adsorbent.

continuously larger concentration gradient at the interface zone as the influent passes through the column. The concentration gradient generally remains maintained because of fresh inflow of influent, whereas, in case of batch experiments, the concentration gradient continuously decreases with time resulting in smaller adsorption capacity. Thus, these results have shown that the columns of prepared adsorbent can be used to remove 2,4-DCP from wastewaters.

### 3.7. Stabilization studies of phenol-laden adsorbent with cement

The phenol-laden adsorbent was added in different proportions to cement and sand to produce a cementitious system as described in Section 2.5 and the prepared cubes were tested further to monitor the change in different properties of the cement.

Initial and final setting time (IST and FST) were determined following the method described in Indian standard method IS: 8112-1989 [38]. Both of these parameters were determined for the blank samples as well as after the addition of 1–5% phenol-laden adsorbent in cement. All the experiments were carried out in triplicate to assure accuracy and reproducibility. It is evident from the results (Fig. 6) that there was no significant change in the IST and FST on the addition of 1–5% phenol-laden adsorbent in cement.

Further, preliminary results of the leaching study show that 2,4-DCP did not significantly leach from the mortar samples with 1–5% adsorbent composition. Leachates from the fixed phenol-laden adsorbent exhibit phenol concentration lower than the drinking water standards. These results are in consistent with the previ-

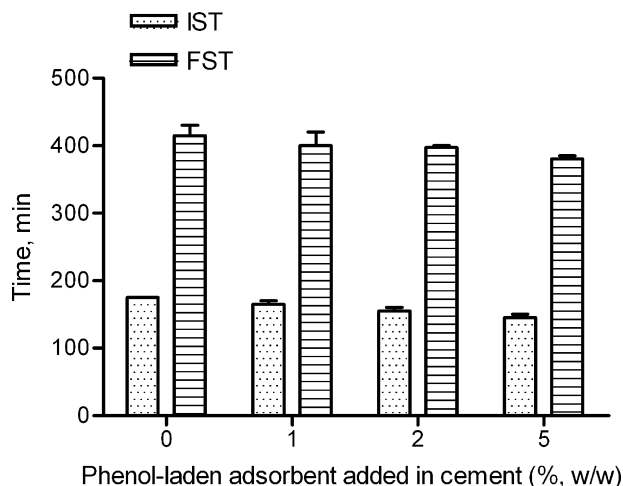


Fig. 6. Effect of addition of 1–5% phenol-laden adsorbent on the initial (IST) and final setting time (FST) of cement.

ous observation [39] where it has been reported that the use of regenerated powdered activated carbon in the S/S process reduced the leaching potential of phenol by ca. 600% compared to when no reactivated carbon was used. Further research regarding the role of several other factors influencing the leaching studies is in progress. These studies might be useful in identifying and elucidating the binding mechanism of phenol and other organic contaminants in cement.

## 4. Conclusions

The results of present study reveal that the pomegranate peel waste can be utilized as an effective adsorbent for the removal of 2,4-DCP from aqueous solutions. The adsorption potential of pomegranate peel adsorbent was found  $65.7 \text{ mg g}^{-1}$  for 2,4-DCP at  $25^\circ\text{C}$ . The adsorption data conformed best to the Langmuir model. The kinetic data were analyzed in the light of three simplified kinetic models viz. pseudo-first-order, pseudo-second-order and intraparticle diffusion models. It was found that theoretical  $q_{e(\text{cal})}$  values agreed well with the  $q_{e(\text{exp})}$  ones in case of pseudo-first-order kinetics suggesting that present study of 2,4-DCP adsorption on pomegranate peel adsorbent can be defined more favorably by pseudo-first-order kinetic model. Results of column operations have shown that the column of prepared adsorbent can be fruitfully used to remove 2,4-DCP from wastewaters. The phenol-laden adsorbent was then stabilized into the cement for ultimate disposal. The proposed technology (utilization of industrial wastes for effluent treatment and ultimate disposal of adsorbents laden with pollutants in cementitious materials by stabilization) provides a twofold benefit of wastewater treatment and solid waste management.

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