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Adsorption of Phenol and Substituted Chlorophenols from Aqueous Solution by Activated Carbon Prepared from Jackfruit (artocarpus heterophyllus) Peel-Kinetics and Equilibrium Studies

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Abstract: This study is aimed at the effectiveness of an adsorbent prepared from jackfruit peel (artocarpus heterophyllus), an agricultural waste, for the removal of phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol from aqueous solutions. Batch adsorption experiments were carried out as a function of solution pH, contact time, phenol concentration, adsorbent dose, and temperature. The adsorption equilibrium was reached in 5 h. The order of removal was found to be 2,4-dichlorophenol > 4-chlorophenol > 2-chlorophenol > phenol. The Freundlich and Langmuir isotherm models were applied to the equilibrium data. The maximum sorption capacities for phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol were found to be 144.9 mg/g, 243.9 mg/g, 277.7 mg/g, and 400.0 mg/g respectively. The removal of phenols was found to be most effective at lower pH. Kinetic data of the adsorption process could fit a pseudo second order rate equation. An attempt was also made to understand the mechanism of phenol adsorption. The results reveal that the activated carbon prepared can be economical for the removal of phenols compared to many other reported adsorbents.

Keywords: Carbon black, adsorption isotherm, phenol, chlorophenols

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INTRODUCTION

Phenols are generally prevalent in refinery and petrochemical wastewaters and potentially toxic (1). They create an oxygen demand in receiving waters and impart a taste to drinking water with minute concentrations of their chlorinated derivatives. The primary source of phenolic compounds in wastewater arise from refining plants, oil, coke plants, chemical operation, and plants, which process, phenols to plastics. Several methods such as oxidation with ozone/hydrogen peroxide, biological degradation, membrane filtration, ion exchange, electrochemical oxidation, reverse osmosis, photocatalytical degradation, and adsorption have been used for the removal of phenols (2–9). However, most of the methods have low efficiency at trace levels. The adsorption process still remains the best choice as it can generally remove all types of phenols and the effluent treatment is convenient in terms of design and operation.

Activated carbon is widely employed to treat wastewater-containing phenols and can be produced by thermal and chemical activation. However, recognizing the economics of commerically available activated carbon, many researchers have studied the feasibility of using inexpensive alternative materials like almond shells, date pits, saw dust, buffing dust of leather industry, coir pith, wool waste, coconut shell, water hyacinth (10–17) as carbonaceous precursors for waste water treatment. The high adsorption capacity in these cases is related to the surface area, the pore structure, and the surface chemistry. The amount and the chemical forms of heteroatoms on these materials depend on the origin of the carbon, the history of preparation, and the conditions of treatment (18).

Jackfruit (artocarpus heterophyllus) is a popular fruit of south India, where its per hectare production is higher than that of any other fruit. A jackfruit tree produces about 200–500 fruits annually, with each fruit weighing about 23–40 kg. The fibrous outer peel constitutes about 60% of the ripe fruit. Apart from its use as a table fruit, jack fruit is also used in several culinary preparations. Hence, a significant amount of peel is discarded as waste. The present study is undertaken to evaluate the efficiency of carbon black adsorbent prepared from jackfruit peel, an agricultural waste, for the removal of phenols from aqueous solutions. Batch adsorption studies were carried out systematically in terms of process parameters such as agitation time, initial concentration, adsorbent dose, and pH.

EXPERIMENTAL

Materials

Preparation of the Adsorbent

Jackfruit peel was cut into small pieces and dried under sunlight until the moisture was partially evaporated. Sun-dried jackfruit peel was treated with concentrated sulphuric acid in a weight ratio of 1:1.8 (peel: acid) and after carbonization the sulphuric acid was leached out and reused. The resulting black product was heated in an air-oven at 160°C for 6 h followed by repeated washing with water and drying at 200°C to remove residual acid (19). The carbon product obtained from jackfruit peel, (JPC) was ground and passed through British Standard Sieves (BSS) of 240-mesh size.

Instrumentation

The concentration of phenols in solution was determined spectrophotometrically on a Shimadzu 1650PC UV-Visible spectrophotometer. The pH of the solution was measured with an Elico (India) pH meter. IR spectra were recorded on a Perkin-Elmer FTIR instrument. X-ray measurements were done on a Phillips X-ray diffractometer using Ni–filtered Cu Kα radiation. Electrophoretic mobility was measured using a Zeta-Meter.

Methods

Adsorption Studies

In the batch method, a fixed amount of the adsorbent (0.1 g) was added to 100 ml of phenol solutions of suitable concentration. The solution was agitated continuously (140 rpm) at constant temperature for 5 h to achieve equilibration. The concentration of the phenol in the solution after equilibrium adsorption was determined spectrophotometrically at λ_{max} value of 269, 273, 279, and 284 nm for phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol, respectively. The pH of the adsorbate solution was adjusted using 0.1M aqueous solution of either HCl or NaOH.

The adsorbate uptake by JPC (jackfruit carbon), q_e (mg/g), was calculated as

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where C_o is the initial adsorbate concentration (mg/L), C_e is the equilibrium adsobate concentration (mg/L), V is the volume of the solution, and W is the mass of the adsorbent (g) and q_e is the amount adsorbed.

Kinetic Studies

Samples of JPC were agitated at 400 rpm with a fixed concentration of adsorbate solution at 32°C in a thermostatted bath. 5 ml aliquots of the solution phase were withdrawn at regular time intervals, centrifuged to remove particulates and analyzed for the phenols.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

1 g of the JPC sample was stirred with deionized water for 2 h and left to stand for 24 h. The pH of the resulting solution decreased, indicating that carbon adsorbent is of 'L' type (20).

The absence of sharp peaks in x-ray diffractrogram of the material of JPC indicated its amorphous nature (Figs. 1 and 2).

Scanning electron micrographs (SEM) of JPC clearly indicates its surface texture and porosity. (Fig. 3 and Table 1).

Effect of contact time

The adsorption results (Fig. 4) reveal that the uptake of adsorbate species is fast at initial stages of and becomes slower near the equilibrium. The equilibration time for the adsorption of various phenols is about 3 h. All the batch experiments were conducted for 5 h under vigorous agitation.

Effect of pH

The hydrogen ion concentration (pH) primarily affects the degree of ionization of the phenolic adsorbate and the surface properties of the adsorbent. The removal rate of phenols varies with pH. Lower pH values produce higher removal rates and vice versa (Fig. 5). The degree of ionization of phenols depends on the pH of the medium. Based on the relationship (23).

$$CP_o = CP_T/1 + 10^{(pH-pKa)} \tag{2}$$

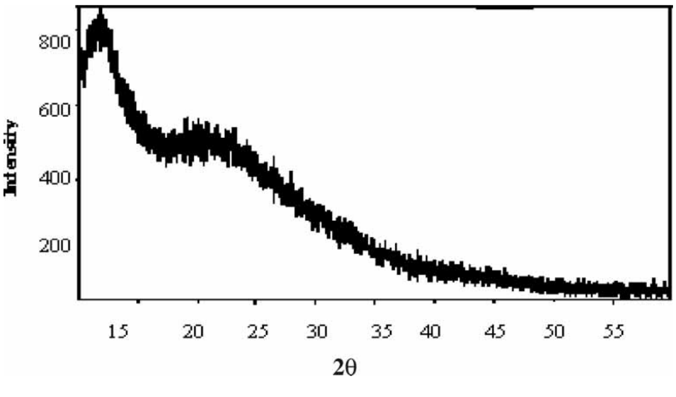

Figure 1. X-ray diffraction pattern of JPC.

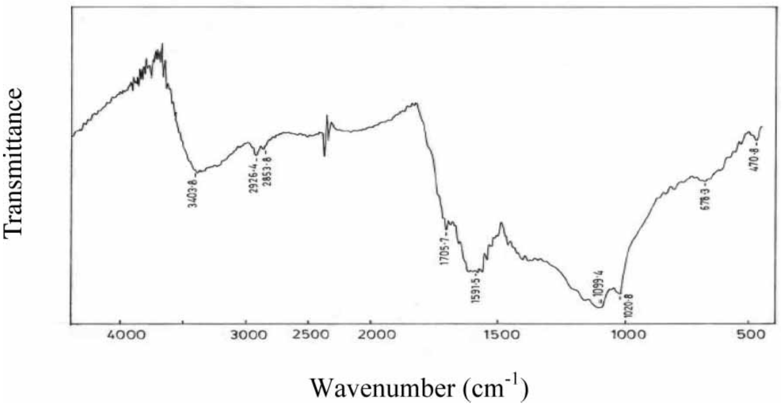

Figure 2. FTIR spectrum of JPC. (3403 cm^{-1}; O-H stretch, 2926 cm^{-1}; C-H stretch in aliphatic, 1705 cm^{-1}; C═O stretch ketones, 1591 cm^{-1}; C═C stretch in an aromatic ring and 1020 cm^{-1}; C-O stretch in ether.)

Where, CP_o is the concentration of unionized phenols species, CP_T the total concentration of phenols, and the pH is the equilibrium pH after adsorption. The concentrations of ionized phenols were calculated and the ionized phenols concentration was found to increase with the pH.

The electrophoretic mobility measurements of JPC as a function of pH show a negative charge on JPC. The negative charge increases with pH.

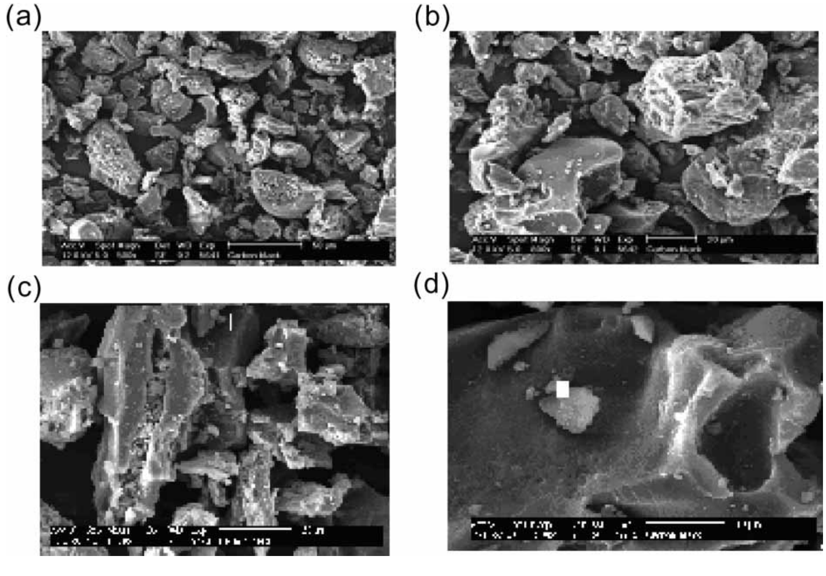

Figure 3. Scanning electron micrograph of JPC (a) 500x (b) 800x (c) 1200x (d) 2500x magnification.

Table 1. Physical characteristics of JPC

Characteristics		Method employed
Carbon	80.23%	ICP-AES
Hydrogen	3.2%	ICP-AES
Nitrogen	0.98%	ICP-AES
Sulphur	0.24%	ICP-AES
Moisture	5.3%	(21)
Ash	4.5%	(21)
Activation yield	80.6 (%)	(22)
Cation-exchange capacity	16.75 meq100 g^{-1}	Methylene blue adsorption method
Bulk density	0.71 g cm^{-3}	(21)
Total acidity	2.249 meq/100 g	Boehm's titration
Total basicity	0.0098 meq/100 g	Boehm's titration
Surface area	115.25 m^2g^{-1}	N_2 adsorption

At acidic pH, a negative charge on the surface of the adsorbent is lowered and there is no electrostatic repulsion between the adsorbate and the adsorbent. In effect, the removal of phenol is higher at lower pH values. But at higher pH, the dissociated phenoxide ion ($C_6H_5O^-$) is repelled by the highly negatively charged surface and hence there is a decrease in adsorption.

Effect of Adsorbent Dose (m)

The effect of the adsorbent dose (m) on the uptake of phenols on JPC was studied and is shown in Fig. 6. This figure reveals that removal of phenols increases with increase in carbon content. At 14 g/1000 mL of the carbon dose for phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol were found to be removed to the extent of 46%, 65%, 75%, and 96% respectively.

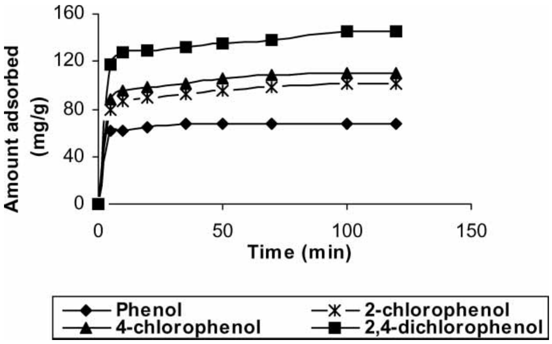

Figure 4. Effect of contact time on the adsorption of phenols on JPC. C_0; 300 mg/L, T; 305 K, carbon dosage; 1 g/L.

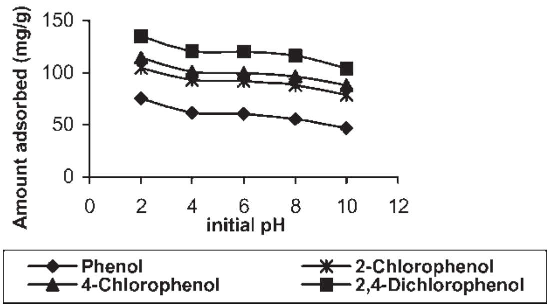

Figure 5. Effect of pH on the adsorption of phenols on JPC. C_0; 300 mg/L, T; 305 K, carbon dosage; 1 g/L.

Adsorption Isotherms

The adsorption isotherms for aqueous phenol and chlorophenols solutions are shown in Fig. 7. They are of type "L" according to Giles's classification (24) and have no plateau. This indicates that there is no formation of a monolayer on the surface over the concentration range studied. The Langmuir and Freundlich models are the most frequently employed models that describe the adsorption isotherms.

The Langmuir adsorption model serves to estimate the maximum uptake values where they cannot be reached by the experiments. It is based on the physical hypothesis that the maximum adsorption capacity is of a monolayer and there is no interaction between the adsorbed molecules.

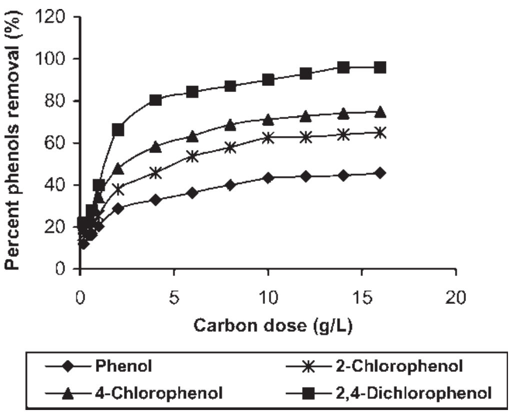

Figure 6. Effect of the adsorbent dose on the adsorption of phenols on JPC C_0; 300 mg/L, T; 305 K.

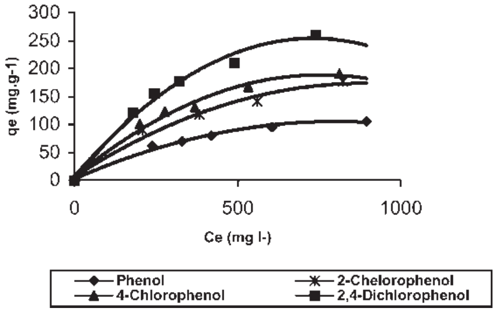

Figure 7. Adsorption isotherms (305 K) of various phenols.

The Langmuir isotherm (25) is represented by the following equations

$$q_e = Q_0bC_e/1 + bC_e \tag{3}$$

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \tag{4}$$

Where, b is the equilibrium adsorption coefficient (L/mg) and Ce the equilibrium concentration (mg/L), qe is the amount adsorbed at equilibrium concentration (mg/g), and Q_o is the maximum adsorption capacity (mg/g). The plots of C_e/q_e vs C_e are linear for JPC which show that the adsorption follows the Langmuir isotherm model. (Fig. 8). The values Q_o and b have been evaluated from the intercept and slope of these plots (Table 3).

For a Langmuir-type adsorption, the isotherm shape can be classified by a term, r a dimensionless constant separation factor (26)

$$r = 1/1 + bC_{ref} \tag{5}$$

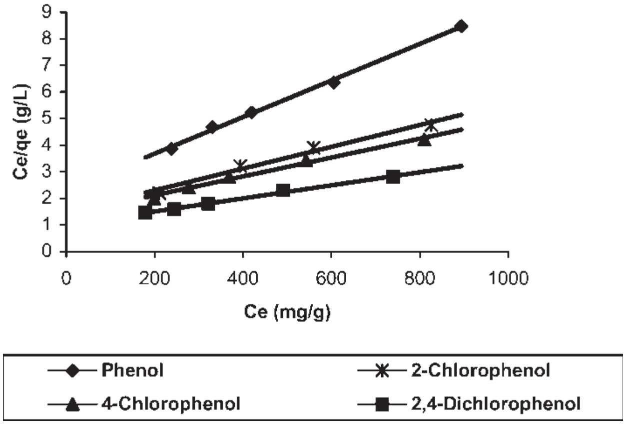

Figure 8. Langmuir plots for the adsorption of phenols on JPC Carbon dose; 1 g/L, Temperature; 305 K.

Table 2. Separation factors of various phenols adsorbed on JPCs

Separation factor, r	Isotherm type	Phenols	Separation factor
>1	Unfavorable	Phenol	0.333
1	Linear	2-Chlorophenol	0.357
$0 < r < 1$	Favorable	4-Chlorophenol	0.384
0	Irreversible	2,4-Dichlorophenol	0.400

where, C_{ref} is the highest fluid-phase concentration ($mg\,L^{-1}$) and b is the Langmuir constant ($L\,mg^{-1}$). The r-value indicates the isotherm shape according (Table 2). The obtained r-values between 0 and 1 indicate favorable adsorption.

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

$$\log q_e = \log K_f + 1/n \log C_e \tag{6}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively (Fig. 9). A linear plot of log C_e vs logq_e shows that the adsorption of phenols on JPC fits the Freundlich isotherm model. The value of K_f and n were calculated from the intercept and slope of the plots (Table 3). The values of n lie between 1 and 10 indicating favorable adsorption (27).

A comparison was made with the results obtained for other activated carbon adsorbents (Table 4). The maximum adsorption capacity (Q_0) for JPC, activated carbon (apricot stone shells-H_3PO_4 impregnated), coir pith carbon, and paper mill sludge were found to be 400, 339, 19.12, 4.49 mg/g respectively for the adsorption of 2,4-dichlorophenol. The present study shows that the JPC is an effective adsorbent for the removal of phenol and substituted phenols from aqueous solutions. As jackfruit peel is a discarded waste

Table 3. Langmuir and Freundlich constants for the adsorption of phenols on JPCws

	Langmuir constants			Freundlich constants		
Adsorbate	Q_o ($mg\,g^{-1}$)	b ($L\,mg^{-1}$)	R^2	K_f	n	R^2
Phenol	144.9	0.0029	0.9975	6.04	2.36	0.9901
2-Chlorophenol	243.9	0.0027	0.9801	8.64	2.25	0.9872
4-Chlorophenol	277.7	0.0025	0.9856	8.72	2.17	0.9897
2,4-Dichlorophenol	400.0	0.0024	0.9925	9.00	1.96	0.9770

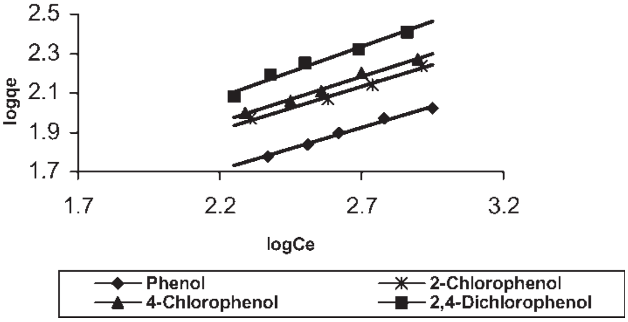

Figure 9. Freundlich isotherm of phenols on JPC Carbon dose; 1 g/L, Temperature; 305 K.

material and available relatively in abundance, the treatment is expected to be economical.

A donor-acceptor complex mechanism was reported earlier (30) for the adsorption of phenol on activated carbon. In this mechanism, carbonyl oxygen group on the carbon surface acts as the electron donor whereas the aromatic ring of the phenol acts as the acceptor. The above donor-acceptor complex mechanism is more pronounced in the case of 2,4-dichlorophenol as the presence of -cl groups is in favor of the formation of a bond between the surface carbonyl groups and the electron–deficient aromatic ring of the phenol. This hypothesis is supported by the FTIR spectra of JPC and JPC adsorbed with phenols (Fig. 10). A slight decrease in the wave number of the C═O stretching vibration in the adduct was observed compared to that of JPC.

Kinetics of Adsorption

The rate constants for the adsorption of phenols from solution on JPC were determined using a pseudo-first-order equation as well as pseudo-second-order equation

Table 4. Comparison of adsorption capacity of JPC with other activated carbon adsorbents for the adsorption of 2,4-dichlorophenol

Adsorbent	Q_o (mg g $^{-}$)	Reference
JPC	400	This work
Activated carbon (apricot stone shells-H_3Po_4 impregnated)	339	(10)
Industrial Waste carbon	132.5	(28)
Coir pith carbon	19.12	(23)
Paper mill sludge	4.49	(29)

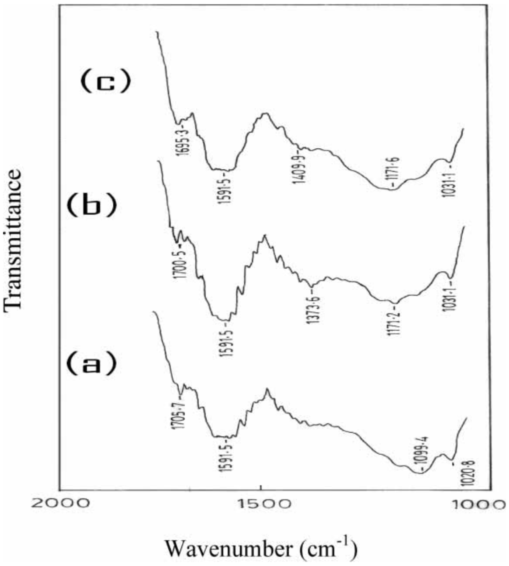

Figure 10. FTIR spectra of (a) JPC, (b) JPC after adsorption of phenol, (c) JPC after adsorption of 2,4-dichlorophenol.

The pseudo-first-order rate equation can be written as

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

where k_1 is the rate constant of pseudo-first-order adsorption and q_e and q_t are the amounts of adsorption at equilibrium and at time t, respectively. The adsorption data however did not fit well this rate equation.

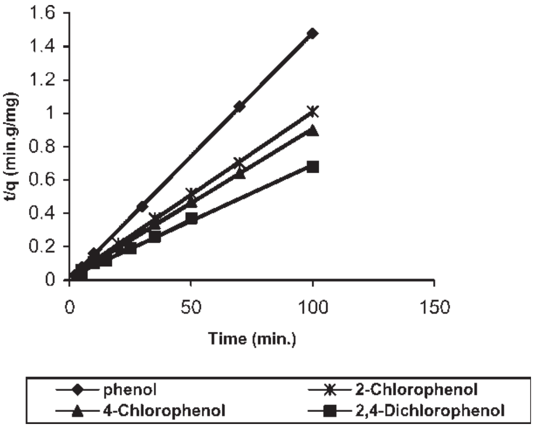

Figure 11. Pseudo-second order plots for removal of phenols on JPC C_0; 300 mg/L, Carbon dose; 1 g/L, Temperature; 305 K

Table 5. Kinetic parameters for the adsorption of phenols on JPC.

	Pseudo-first-order				Pseudo-second-order		
Phenols (Con.) (300 mg L^{-1})	q_e, exp (mg g^{-1})	k_1 (min^{-1})	q_e, calc (mg g^{-1})	R^2	$K_2 \times 10^{-3}$ (g mg $^{-1}$ min^{-1})	q_e, calc (mg g^{-1})	R^{2s}
Phenol	67.2	0.044	7.5	0.9543	46.6	67.6	0.9999
2-Chlorophenol	101.4	0.033	22.9	0.9791	6.0	101.0	0.9996
4-Chlorophenol	110.2	0.032	23.9	0.9863	4.8	112.3	0.9992
2,4-Dichlorophenol	145	0.011	31.8	0.9476	2.3	149.2	0.9979

The rate equation

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

where k_2 is the rate constant for pseudo-second-order adsorption corresponds to a pseudo second order equation.

The rate parameters k and qe can be directly obtained from the intercept and slope of the plot of t/qt Vs t (Fig. 11). Values of k and q_e computed from Fig.11 are listed in Table 5. The calculated q_e value agrees with experimental and the regression coefficients were above 0.99. These results suggest the pseudo-second-order kinetics of the adsorption process.

CONCLUSION

The aim of this work was to study the adsorption of phenol and substituted phenols on JPC. A comparison was made with results obtained with other activated carbon adsorbents. The present study shows that JPC is an effective adsorbent for the removal of phenol and substituted phenols from aqueous solutions. Adsorption of phenols onto JPC followed both the Langmuir and the Freundlich isotherm models. The order of removal was found to be 2,4-dichlorophenol > 4-chlorophenol > 2-chlorophenol > phenol. JPC is an inexpensive adsorbent and therefore will have the advantage of economic viability.

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