Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent—Kinetics and isotherm analysis

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Abstract

Adsorptive removal of parachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP) from aqueous solutions by activated carbon prepared from coconut shell was studied and compared with activated carbon of commercial grade (CAC). Various chemical agents in different concentrations were used (KOH, NaOH, $CaCO_3$, H_3PO_4 and $ZnCl_2$) for the preparation of coconut shell activated carbon. The coconut shell activated carbon (CSAC) prepared using KOH as chemical agent showed high surface area and best adsorption capacity and was chosen for further studies. Batch adsorption studies were conducted to evaluate the effect of various parameters such as pH, adsorbent dose, contact time and initial PCP and TCP concentration. Adsorption equilibrium reached earlier for CSAC than CAC for both PCP and TCP concentrations. Under optimized conditions the prepared activated carbon showed 99.9% and 99.8% removal efficiency for PCP and TCP, respectively, where as the commercially activated carbon had 97.7% and 95.5% removal for PCP and TCP, respectively, for a solution concentration of 50 mg/L. Adsorption followed pseudo-second-order kinetics. The equilibrium adsorption data were analysed by Langmuir, Freundlich, Redlich–Peterson and Sips model using non-linear regression technique. Freundlich isotherms best fitted the data for adsorption equilibrium for both the compounds (PCP and TCP). Similarly, acidic pH was favorable for the adsorption of both PCP and TCP. Studies on pH effect and desorption revealed that chemisorption was involved in the adsorption process. The efficiency of the activated carbon prepared was also tested with real pulp and paper mill effluent. The removal efficiency using both the carbons were found highly satisfactory and was about 98.7% and 96.9% as phenol removal and 97.9% and 93.5% as AOX using CSAC and CAC, respectively.

1. Introduction

Chlorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. They have been used in number of industries. Chlorophenols with at least two chlorines are used as pesticides, and 4-chlorophenols are used in antiseptics. Small amount are produced when water is disinfected with chlorine. They are also produced while bleaching wood pulp with chlorine to make paper [1]. They are weak acids and permeate human skin by in vitro and are readily absorbed by gastro-intestinal tract. The acute toxicity of chlorophenols include increased respiratory rate, vomiting, and nausea [2]. They create complicated problems to water bodies such as bad odour and taste in drinking water, death of aquatic life in inland water bodies, inhibition of the normal activities of microbial population in wastewater treatment plant, etc. Chlorophenols display a pronounced undesirable effect in potable water at concentration as low as 0.1 mg/L. A perceptible odour is imparted to fish flesh at this concentration [3].

Several methods for the treatment of phenolic wastewaters have been proposed in the literature. These include physico-chemical treatment processes, chemical oxidation and biological degradation. The physico-chemical processes include adsorption and ion exchange. Various oxidizing agents (oxygen, hydrogen peroxide, ozone, etc.) have been used for wet oxidation of phenolic wastewaters. For high strength and low volume of phenolic wastewaters, phenol removal by adsorption using granular/powdered activated carbon has been widely used [4–10]. Many studies on the preparation of 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

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hulls, rice straw, soya bean hulls and many more [11] have been reported. Many materials like coir pith [12], dried activated sludge, fly ash [13], palm seed coat [14], bituminous coal [15] and red mud [16] have been reported in the removal of chlorophenols. Waste coconut shells which are discarded from the coconut processing units can be used in the removal of chlorophenols. Carbonized coconut shell has been investigated in the wastewater treatment [17] and in the removal of heavy metals [18], dyes [19], etc. Various chemical agents like KOH [20], NaOH [21], ZnCl$_2$ [22], H$_3$PO$_4$ [23], CaCO$_3$ [24] have been reported to be used for effective preparation of carbon used in adsorption.

In the present investigation, coconut shell activated carbon was prepared using various chemical agents in different concentrations and the carbon with best surface area and adsorptive capacity was screened and used. The aim of the present work is to explore the possibility of coconut shell being utilized as an adsorbent in the removal of parachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP) from wastewater, compare the removal efficiency of the prepared carbon with commercial activated carbon and to obtain suitable kinetic and isotherm model.

2. Experimental

Waste coconut shells were collected from coconut processing industries located in Karur, Karur district, Tamilnadu state, India. The shells were broken to small pieces of 1–2 mm and dried in sunlight. All the chemicals used were of analytical reagent grade. All the reagents and stock solutions were prepared with double-distilled water. Coconut shell based commercial activated carbon (particle size 125–250 μm) was purchased from Anand Carbons, Tuticorin, India.

2.1. Adsorbent preparation

The sun dried coconut shells were impregnated with different chemical agents of various concentrations [KOH (10% and 50%), NaOH (10% and 50%), ZnCl$_2$ (10% and 50%), H$_3$PO$_4$ (50%), CaCO$_3$ (50%)] in separate jars and left overnight at room temperature. The impregnated samples were carbonized at 600 °C for 2 h and activated with nitrogen gas flow at 800 °C for 1 h. The material was thoroughly washed with distilled water and soaked in dilute HNO$_3$ overnight to eliminate the residual alkali content from the pores of the carbon except the material treated with H$_3$PO$_4$ which was soaked in NaOH to eliminate the residual acid. The material was again washed with distilled water until pH of the carbon reached 7 ± 0.5. The carbon was then dried in oven at 60 °C for 12 h, ground and sieved to desired particle size (125–250 μm). The prepared carbons and commercial carbon were characterized as per the standard methods and procedures [25–27].

2.2. Adsorption studies

To study the effect of important parameters like pH, carbon dosage, initial concentration and contact time, batch experiments were conducted at room temperature (30 ± 2 °C). For each experimental run 100 mL of PCP/TCP of known concen-

tration, pH and a known amount of the absorbent were taken in 250 mL stoppered conical flask and agitated at 200 rpm. The samples were withdrawn at appropriate time intervals. As some of the carbon particles remained suspended and did not settle down easily, all the samples were centrifuged at 500 rpm for 15 min and analysed for residual PCP/TCP concentration by 4-aminoantipyrine method [28] using Spekol 1200 spectrophotometer at 500 nm. The amount of chlorophenols (PCP and TCP) adsorbed by the carbon was calculated from the differences between the chlorophenol quantity added to the carbon and the chlorophenol content of the supernatant using the following equation:

$$Q = V(C_0 - C_f)/M \qquad (1)$$

where Q is the chlorophenol uptake (mg/g), C_0 and C_f the initial and final chlorophenol concentrations in the solution (mg/L), respectively, V the solution volume (L) and M is the mass of activated carbon (g). Chlorophenol and carbon-free blanks were used as control. The effect of pH on the chlorophenol removal was studied over a pH range of 1–12. pH was adjusted by the addition of dilute aqueous solutions of H$_2$SO$_4$ or NaOH (0.1N). For the optimum amount of adsorbent per unit mass of adsorbate, chlorophenol solution was contacted with different amounts of adsorbents till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the chlorophenols from the aqueous solution at different time intervals. For adsorption isotherms, chlorophenol solutions of different concentrations were agitated with the known amount of adsorbent till the equilibrium was achieved. The residual chlorophenol concentration (C) of the solution was then determined. Thus, the batch tests were carried out to compare the adsorptive capacity and intensity of the adsorbents. Four non-linear isotherms namely Langmuir [29], Freundlich [29], Redlich–Peterson [30] and Sips isotherms [31] were employed to study the equilibrium adsorption.

2.3. Desorption studies

After adsorption experiments with 50 mg/L solution of PCP/TCP and 500 mg of carbon, the chlorophenol laden carbon was separated out by filtration using Whattman filter paper no. 42 and the filtrate was discarded. The chlorophenol loaded carbon was given a gentle wash with double-distilled water to remove the unadsorbed chlorophenols if present. Desorption studies were carried out using several such carbon samples. They were agitated with 50 mL of distilled water of various pH (4–11). Desorption studies were also carried out with NaOH solutions of various concentrations (0.1–1N). The desorbed chlorophenols in the solution were separated by centrifugation and analysed as before.

3. Results and discussion

3.1. Adsorption characteristics

The results of the sorbants characterization experiments are summarized in Table 1. The specific surface area (by acetic acid

Table 1
Characteristics of activated carbons prepared using different chemical agents and CAC

| Characteristics	Methods employed	Activated carbons								Commercial AC
		10% KOH	50% KOH	10% NaOH	50% NaOH	10% ZnCl$_2$	50% ZnCl$_2$	50% H$_3$PO$_4$	50% CaCO$_3$	
pH [25]	pH meter	8.09	8.02	7.40	8.97	6.01	6.65	6.32	9.01	8.52
Moisture content (%) [25]	Moisture balance	5.78	8.82	7.57	7.34	7.44	7.57	7.68	5.98	5.36
Ash content (%) [25]	Gravimetric method	3.19	1.71	2.16	1.08	3.24	2.13	3.24	3.07	1.06
Decolourising power (mg/g) [25]	Methylene blue	27.00	75.00	24.00	67.50	25.50	28.50	15.00	33.00	63.00
Ion exchange capacity (%) [25]	Titrimetric method	Nil	0.15	Nil	0.2	Nil	Nil	Nil	Nil	Nil
Specific surface area (m^2/g) [25]	Acetic acid method	647.0	1195	525	970	328	586	245	424	980
Apparent density (g/cm^3) [25]	Gravimetric method	0.58	0.76	0.54	0.30	0.021	0.67	0.14	0.71	0.54
Water soluble matter (%) [25]	Gravimetric method	0.87	0.44	0.7	3.45	2.96	4.327	8.54	3.39	0.72
Acid soluble matter (%) [25]	Gravimetric method	4.39	4.36	20.29	18.52	18.60	12.98	13.52	15.20	14.30
Iodine number (mg/g) [26]	Titrimetric method	625.30	1253.78	493.90	650.50	217.00	293.90	151.30	412.20	820.50
Phenol number (mg) [26]	Spectrophotometer method	256	556	126	335	132	95	82	80	240
Iron content (mg/g) [25]	Spectrophotometer (1–10 phenonthroline)	0.038	0.05	0.15	0.21	0.12	0.11	0.34	0.42	0.10
BET surface area (m^2/g) [27]	Liquid nitrogen (Sorptomatic 1990)	–	935.24	–	746.32	–	–	–	–	838.45
Pore specific volume (cm^3/g) [27]	Sorptomatic 1990	–	0.49	–	0.22	–	–	–	–	0.39
Micropore volume (cm^3/g) [27]	Sorptomatic 1990	–	0.098	–	0.036	–	–	–	–	0.032
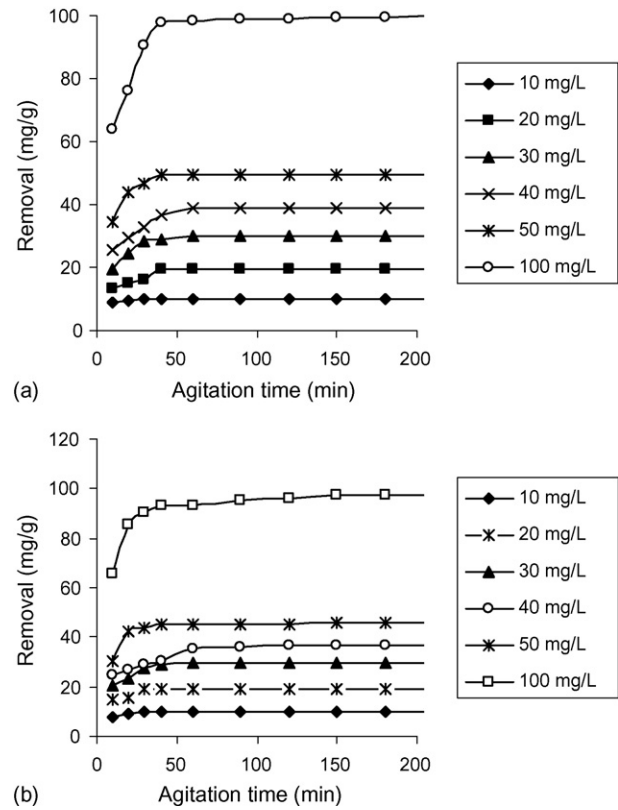
Fig. 1. Effect of agitation time and initial concentration on PCP adsorption by CSAC and CAC. (a) CSAC: conditions—pH 2; PCP concentration, 10–100 mg/L; carbon dosage, 500 mg of CSAC/100 mL. (b) CAC: conditions—pH 2; PCP concentration, 10–100 mg/L; carbon dosage, 500 mg of CAC/100 mL.

method) was higher for the carbon prepared using 50% KOH as chemical agent (CSAC) (1195 m^2/g) than those of the other carbons prepared. The BET surface area (935.24 m^2/g) was also higher.

Many works have been carried out in the area of chemical activation. The mechanism of chemical activation by KOH is not very clear; however the possible reactions during chemical activation of pistachio-nutshells using KOH are reported by Yang and Lua [32]. Some mechanisms have also been proposed [33–35].

Preliminary adsorption test using 50 mg/L of PCP and TCP showed that CSAC had high adsorptive capacity than others. Thus, this carbon was screened for further studies and for comparison with the commercially available carbon (CAC).

3.2. Effects of agitation time and initial concentration of PCP and TCP on adsorption by CSAC and CAC

The effect of agitation time and initial concentration on the removal of the PCP by CSAC and CAC is shown in Fig. 1 and TCP by CSAC and CAC is shown in Fig. 2. Here, all the other parameters like pH (2), carbon dosage (500 mg) were kept constant. The plots show that the adsorption of PCP/TCP increases with an increase in agitation time and attains equilibrium earlier using CSAC than CAC for all the concentrations for PCP. While there was very less difference in equilibrium time for TCP using
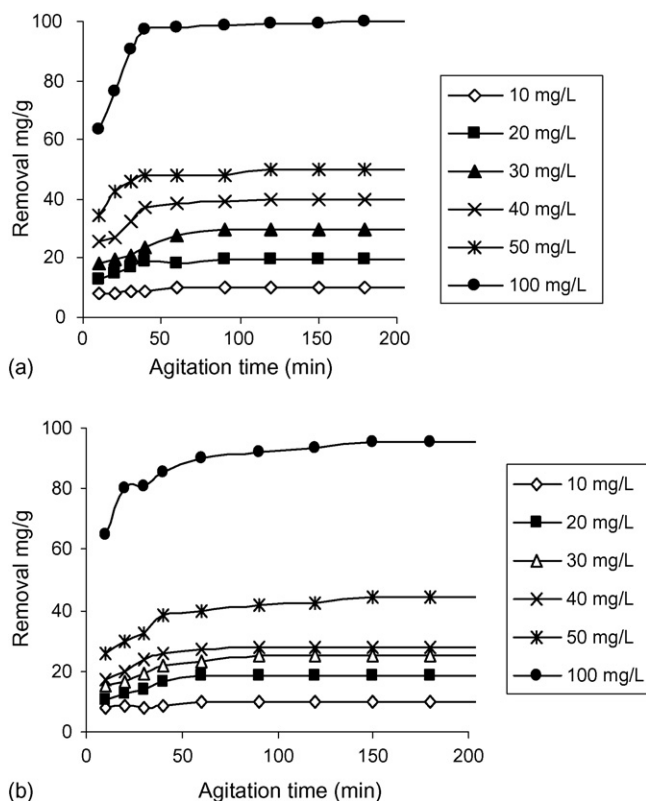
Fig. 2. Effect of agitation time and initial concentration on TCP adsorption by CSAC and CAC. (a) CSAC: conditions—pH 2; TCP concentration, 10–100 mg/L; carbon dosage, 500 mg of CSAC/100 mL. (b) CAC: conditions—pH 2; TCP concentration, 10–100 mg/L; carbon dosage, 500 mg of CAC/100 mL.

both the carbons. The contact time required for the removal of PCP/TCP by CSAC was very short. This result is interesting because equilibrium time is one of the important parameters for economical wastewater treatment applications. The equilibrium time for 10, 20, 30, 40, 50 and 100 mg/L was found to be 40, 40, 60, 90, 150 and 180 min for PCP by CSAC; 60, 90, 120, 120, 150 and 180 min for PCP by CAC; 60, 90, 90, 150 and 210 for TCP by CSAC; 60, 60, 90, 120, 150 and 210 min for TCP by CAC, respectively. It is clear that the removal depends on its concentration. The removal curves are single, smooth and continuous leading to saturation. Based on this result, the contact time was fixed at 210 min for the rest of the batch experiments to make sure that equilibrium was reached in all cases. It is also clear that the removal depends on its initial concentration. Depending on the concentration of the solution, the carbon dosage and time also varies for effective removal of chlorophenols.

3.3. Effect of pH

Effect of pH on the removal of PCP and TCP by CSAC and CAC is shown in Fig. 3. Here, all the other parameters like agitation time (210 min), initial concentration (50 mg/L) and carbon dosage (500 mg) were kept constant. The removal (mg/g) decreased with increase in pH for both PCP and TCP using CSAC. CAC also showed comparatively high removal with pH
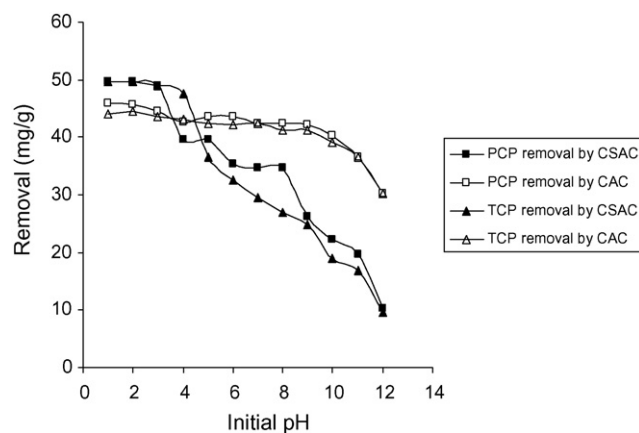

Fig. 3. Effect of pH on the removal of PCP and TCP. Conditions—carbon dosage, 500 mg/100 mL; agitation time, 210 min; CP concentration, 50 mg/L.

2 for both the carbons. This is because as the pH is increased, the percentage of the unionized species of the compounds decreases and of the ionized species increases. At pH 2, the adsorbent surface has more positively charged sites where unionized species of halogenated organic compounds are high. This does not favor any repulsion between the adsorbent surface and adsorbate. But with the increase in pH, the case is vice versa and the adsorption of the ionized organic halide decreases [12]. This occurs based on the relationship [36]:

$$CP_0 = CP_T / \{1 + 10^{pH - pK_a}\} \qquad (2)$$

where CP_0 is the concentration of unionized chlorophenol species, CP_T the total concentration of chlorophenol taken, pH the final pH (equilibrium pH) after adsorption and pK_a is 9.38 and 7.09 [37] for PCP and TCP, respectively, the concentrations of the ionized chlorophenol species were calculated and the ionized chlorophenol concentration was found to increase with pH.

Thus, the optimum pH for the removal of PCP and TCP by both the carbons was chosen as pH 2 ± 0.5 as it showed the maximum removal of the chlorophenols than others. Despite the electrostatic repulsion at above pH 11, removal was observed. This indicates that chemisorption might be involved in the removal process. Similar results were reported in the adsorption of phenol, 2,4,6-trichlorophenol and pentachlorophenol on coir pith carbon [38].

The functional group of the CSAC carbon was estimated using FTIR spectrum and the sample displayed 1760 cm^{-1}, C–O stretch in ketones; 1485 cm^{-1}, C–C stretch in aromatic rings; 823 cm^{-1}, C–H out-of-plane bending in benzene derivatives. These bands were presumed to be basic functional groups of pyrones (cyclic ketone) and other keto-derivatives of pyran, which was also observed by Jankowska et al. [39]. Thus, PCP and TCP adsorption can be explained in terms of dispersive interactions between the aromatic ring of phenol and the basic groups of the surface of the carbon.

Change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. Adsorption of various anionic and cationic species on such adsorbents has been
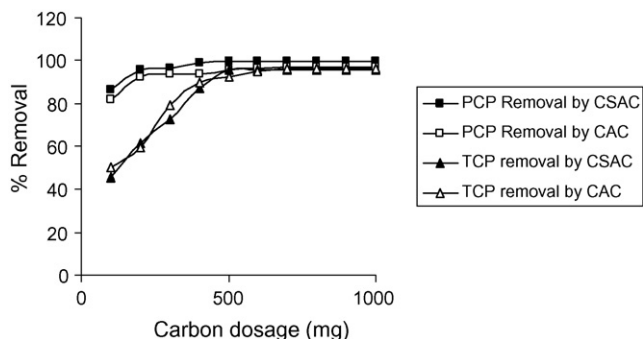
Fig. 4. Effect of carbon dosage on the removal of PCP and TCP. Conditions—carbon dosage, 100–1000 mg/100 mL; pH 2; agitation time, 210 min; CP concentration, 50 mg/L.

explained on the basis of the competitive adsorption of H$^+$ and OH$^-$ ions with the adsorbates [40].

3.4. Effect of adsorbent dosage

The effect of adsorbent dosage on the uptake of PCP/TCP on CSAC and CAC was studied at different adsorbent doses (100–1000 mg/100 mL) for the concentrations of 50 mg/L and the result is shown in Fig. 4. This figure reveals that the % removal of PCP/TCP increases with increase in adsorbent dosage. The removal of PCP/TCP at adsorbent dosage larger than 0.5 g/100 mL remained almost unchanged using CSAC, while for CAC saturation occurred at 0.7 g/100 mL for PCP and 0.6 g/100 mL for TCP. An increase in the adsorption with the adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites. Thus, 0.5 g/100 mL was used as the optimum dosage for CSAC and 0.7 g/100 mL for CAC for the removal of PCP and TCP.

Under optimized conditions (pH, carbon dosage, equilibrium time) the prepared activated carbon obtained 99.9% and 99.8% removal efficiency for PCP and TCP, respectively, where as the commercially activated carbon had 97.7% and 95.5% removal for PCP and TCP for a solution concentration of 50 mg/L, respectively.

3.5. Adsorption dynamics

3.5.1. Adsorption rate constant

The rate constant of adsorption was determined from the first-order rate expression given by (Eq. (3)) Lagergren et al. [41]:

$$\log(q_e - q) = \log q_e - k_1 t/2.303 \tag{3}$$

where q_e and q are the amounts of PCP/TCP adsorbed (mg/g) at equilibrium and at time t (min), respectively and k_1 is the rate constant of adsorption (min). Values of k_1 were calculated from the plots of $\log(q_e - q)$ versus t for different concentrations of PCP/TCP. The experimental q_e values did not agree with the calculated ones, obtained from the linear plots (using EXCEL software) and also the correlation coefficients are lesser (Table 2). This shows that the adsorption of PCP/TCP onto CSAC and CAC is not a first-order reaction. Thus, it may obey

the second-order kinetic model [42] which is expressed as

$$t/q = 1/k_2 q_e^2 + t/q_e \tag{4}$$

where k_2 is the rate constant of second-order adsorption (g/mg min). If the second-order kinetics is applicable, then the plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand and the equilibrium adsorption capacity q_e can be calculated from Eq. (2). Also, it is more likely to predict the behavior over the whole range of adsorption [42]. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q versus t. The linear plots of t/q versus t show a good agreement for both the compounds using the two carbons (CSAC and CAC) and also there was a good agreement between experimental and calculated q_e values (Table 2). The correlation coefficients for the second-order kinetic model are greater than 0.977. These indicate that the adsorption system belongs to the second-order kinetic model. Similar observations have been reported in the adsorption of 2-chlorophenol by coir pith carbon [12], 2,4,6-chlorophenol and pentachlorophenol on coir pith carbon [38].

3.5.2. Modeling of isotherm curves

The different experimental isotherms were modeled according to four equations: the Langmuir, Freundlich, Redlich–Peterson and Sips isotherm models using EXCEL software and solver tool.

Langmuir sorption model serves to estimate the maximum uptake values where they cannot be reached in the experiments. Langmuir's model does not take into account the variation in adsorption energy, but it is the simplest description of the adsorption process. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface. Langmuir's equation [29] is

$$Q = Q_{max} b C_e/1 + b C_e \tag{5}$$

where b is the equilibrium adsorption coefficient (L/mg) and Q_{max} the maximum adsorption capacity (mg/g), C_e the equilibrium concentration (mg/L), Q is the amount adsorbed at equilibrium (mg/g).

The Freundlich equation is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface [29]:

$$Q = k_f C^{1/n} \tag{6}$$

where k_f (L/g)$^{1/n}$ and n are Freundlich constant.

The Redlich–Peterson equation [30] is widely used as a compromise between Langmuir and Freundlich systems. This model incorporates the advantageous significance of both Freundlich and Langmuir model. Redlich–Peterson isotherms equation represents the equilibrium curve to follow Henrys law and the curve behavior follows Freundlich isotherm equation at higher initial solute concentration and it can be represented as follows:

$$Q = K_{RP} C_e/[1 + (\alpha_{RP} C_e)^\beta] \tag{7}$$

Table 2

Comparison of the first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial concentrations

Initial concentration (mg/L)	First-order kinetics				Second-order kinetics			
	q_e (experimental values) (mg/g)	K_1 (g/mg/min)	q_e (calculated values) (mg/g)	R^2 (I order)	q_e (experimental values) (mg/g)	K_2 (g/mg/min)	q_e (calculated values) (mg/g)	R^2 (II order)
PCP								
CSAC								
10	1.862	0.071	1.449	0.947	1.862	0.459	1.877	0.998
20	3.651	0.022	1.711	0.989	3.651	0.079	3.716	0.998
30	5.385	0.043	4.360	0.956	5.385	0.016	5.868	0.989
40	6.312	0.096	3.042	0.908	6.312	0.017	6.600	0.997
50	9.982	0.052	6.423	0.956	9.982	0.020	10.091	0.999
100	19.101	0.024	8.562	0.856	19.101	0.040	19.082	0.998
CAC								
10	1.978	0.256	1.231	0.982	1.978	0.337	1.996	0.998
20	3.877	0.156	1.632	0.705	3.877	0.102	3.929	0.977
30	5.899	0.025	2.365	0.845	5.899	0.051	6.060	0.989
40	7.392	0.036	4.569	0.873	7.392	0.062	7.716	0.997
50	9.106	0.027	5.698	0.746	9.106	0.016	9.041	0.999
100	19.93	0.044	6.539	0.850	19.93	0.014	19.840	0.999
TCP								
CS-AC								
10	1.899	0.089	1.203	0.972	1.899	0.198	1.931	0.999
20	3.678	0.063	2.456	0.787	3.678	0.034	3.888	0.999
30	5.576	0.023	2.589	0.920	5.576	0.031	5.273	0.998
40	6.321	0.024	3.231	0.893	6.321	0.023	6.801	0.988
50	9.946	0.016	4.269	0.956	9.946	0.029	10.117	0.998
100	19.938	0.023	7.582	0.756	19.938	0.012	20.442	0.997
CAC								
10	1.978	0.189	1.568	0.952	1.978	0.189	1.946	0.989
20	3.876	0.068	1.999	0.863	3.876	0.068	3.596	0.979
30	5.676	0.046	2.589	0.854	5.676	0.046	5.632	0.999
40	7.392	0.023	4.562	0.726	7.392	0.023	7.456	0.989
50	9.166	0.019	6.256	0.759	9.166	0.019	10.231	0.998
100	19.532	0.010	9.632	0.869	19.532	0.010	19.623	0.989

where K_{RP} (L/g) and α_{RP} (L/mg)$^\beta$ are Redlich–Peterson isotherm constants and β is the exponent which lies between 1 and 0.

Sips model suggests that the equilibrium data follow Freundlich curve at lower solute concentration and follows Langmuir pattern at higher solute concentration. The equation [31] can be represented as follows:

$$Q = (K_s C_e)^\beta / [1 + (\alpha_s C_e)^\beta] \tag{8}$$

where K_s (L/g) and α_s (L/mg)$^\beta$ are Sips isotherm constants and β is the exponent which lies between 1 and 0.

The four non-linear models were applied to experimental data. The R^2 values for all the isotherms used are shown in Table 3. The plots between concentration of the PCP/TCP and the uptake drawn by Freundlich isotherm showed higher R^2 values (above 0.983) than the other models used. This shows that adsorption follows Freundlich isotherm for both PCP and TCP for both the carbons (Figs. 5 and 6). In general, as the k_f value increases, the adsorption capacity also increases. The Freundlich

Table 3

Langmuir, Freundlich, Redlich–Peterson and Sips model parameters for PCP/TCP

| Compounds	Langmuir			Freundlich			Redlich–Peterson				Sips			
	Q_{max} (mg/g)	b (L/mg)	R^2	K_f (L/g)$^{1/n}$	n	R^2	K_{RP} (L/g)	α_{RP} (L/mg)$^\beta$	β	R^2	K_s (L/g)	α_s (L/mg)$^\beta$	β	R^2
PCP														
CSAC	72.769	0.019	0.937	9.211	3.121	0.983	1.900	0.025	1.005	0.937	2.638	0.038	0.496	0.958
CAC	134.096	0.025	0.887	9.105	2.648	0.980	2.362	0.011	1.052	0.929	2.426	0.014	0.924	0.965
TCP														
CSAC	122.336	0.048	0.842	2.045	1.468	0.996	0.903	0.004	0.996	0.979	0.986	0.002	0.890	0.956
CAC	112.350	0.014	0.829	2.944	1.661	0.989	1.224	0.009	0.995	0.966	1.645	0.009	0.844	0.976
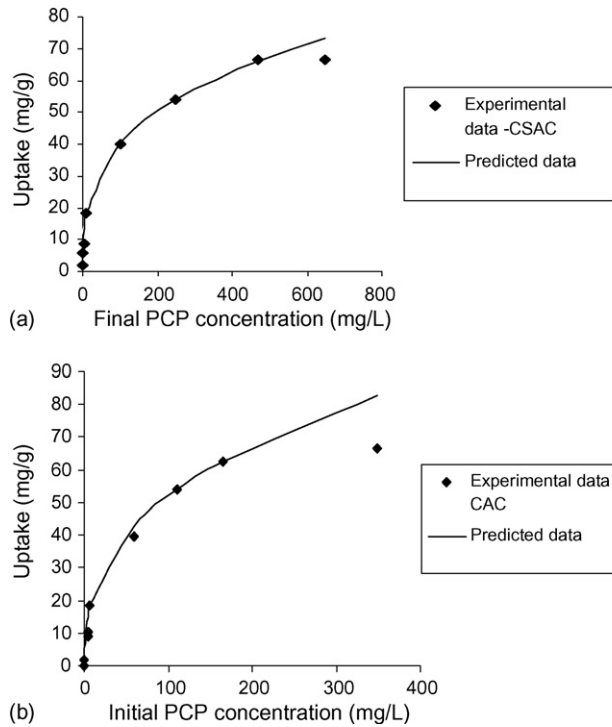
Fig. 5. Freundlich isotherm for PCP by CSAC and CAC. (a) Conditions—carbon used, CSAC; PCP concentration, 10–1000 mg/L. (b) Conditions—carbon used, CAC; PCP concentration, 10–1000 mg/L.
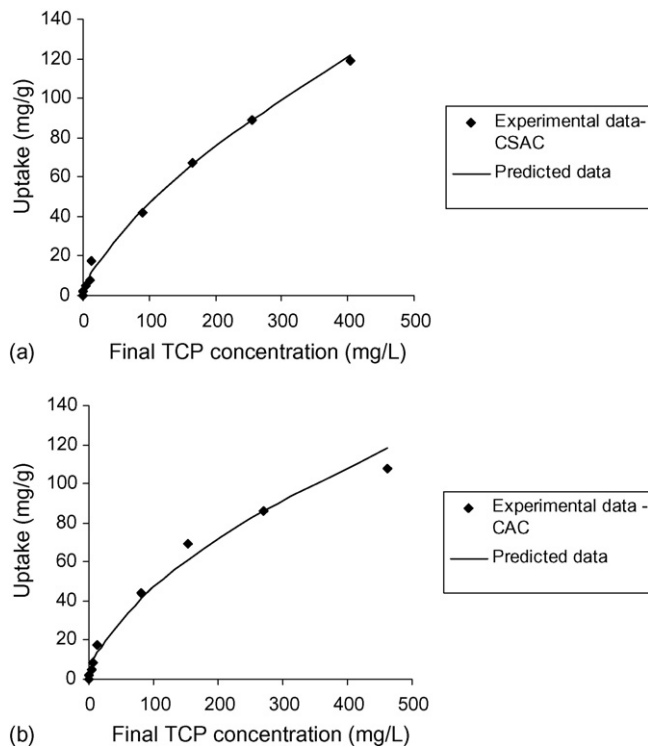

Fig. 6. Freundlich isotherm for TCP by CSAC and CAC. (a) Conditions—carbon used, CSAC; TCP concentration, 10–1000 mg/L. (b) Conditions—carbon used, CAC; TCP concentration, 10–1000 mg/L.
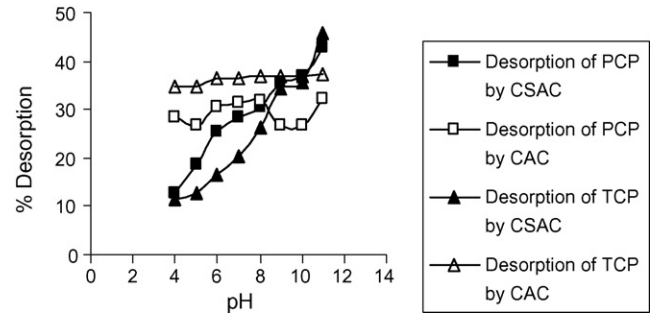

Fig. 7. Desorption studies for PCP and TCP by CSAC and CAC. Conditions—pH 4–11; agitation time, 60 min; PCP and TCP concentration, 50 mg/L.

Table 4
Effect of different concentrations of NaOH on desorption of PCP/TCP

Desorption reagent	PCP (% desorption)		TCP (% desorption)	
	CSAC	CAC	CSAC	CAC
0.1N NaOH	27.2	32.5	21.6	19.5
0.2N NaOH	33.5	36.9	34.1	25.9
0.5N NaOH	66.5	65.2	53.7	51.6
1N NaOH	99.9	78.0	99.9	85.4

constant, n should have values lying in the range of 1–10 for classification as favorable adsorption [43]. Values of k_f and n are also presented in Table 3. The n values reveal that adsorption is favorable for both the compounds using both the carbons.

3.6. Desorption studies

Regeneration of spent carbon and recovery of the chlorophenols would make the treatment process economical. Also desorption studies help elucidate the mechanism of adsorption. From the graph between the pH and percentage of desorption, the maximum desorption efficiency was determined [12]. The desorption efficiency by varying the pH of distilled water from 4 to 11 for both the carbons for PCP and TCP was found to be low. The graph is represented in Fig. 7. This indicates that chemisorption plays a major role in adsorption process [38].

Thus, attempts were next made to desorb chlorophenols from the carbon sources using different concentrations of NaOH. The results obtained are presented in Table 4. The maximum percentage recovery of the PCP by CSAC and CAC was 99.8% and 78.0% and TCP was 99.9% and 85.4%, respectively with 1N NaOH solution.

4. Studies with the real effluent

The efficiency of the prepared activated carbon and the commercial carbon was tested with real bleaching pulp and paper mill effluent obtained from Karur, India. The pulp and the paper mill industries are known to be one of the largest polluting industries. Conventional pulp bleaching uses a variety of chlorine species as bleaching agents. The advantage of using chlorine is simply that it is cheap and effective [44]. Chlorophenol is a toxic substance present in major amount in the

Table 5
Characteristics of pulp and paper mill effluent

Parameter	Values
pH	6.98
Turbidity (NTU)	300
Total solids (mg/L)	1200
Chloride (mg/L)	11.7
TDS (mg/L)	4000
TOC (mg/L)	55
AOX (mg/L)	145
Phenols (4-aminantipyrine method) (mg/L)	40

effluent. The characteristic of the effluent is shown in Table 5. The chlorophenol content as adsorbable organic halides (AOX) was also analysed using AOX analyzer (Analytical Jena) and was found to be 145 mg/L and the phenol content was analysed by 4-amino-anti pyrine method and was found to be 40 mg/L. The pH of the effluent was adjusted to 2 and a carbon dosage of 500 mg/100 mL was taken and agitated for 210 min. The removal efficiency using both the carbons were found highly satisfactory and was about 98.7% and 96.9% as phenol removal and 97.9% and 93.5% as AOX removal using CSAC and CAC, respectively.

5. Conclusions

From the study it can be clearly seen that CSAC has a good efficiency when compared to the high cost commercially available carbon (CAC). The effectiveness of the prepared activated carbon was analysed by optimizing the conditions of pH, carbon dosage, and concentration of chlorophenol solution using PCP and TCP as the standard compounds. Under optimized conditions the prepared activated carbon obtained 99.9% and 99.8% removal efficiency for PCP and TCP, respectively where as the commercially activated carbon had 97.7% and 95.5% removal, respectively for PCP and TCP. The kinetic and the isotherm analysis revealed that adsorption followed second-order kinetics for both the carbons and the adsorption equilibrium data obeyed the Freundlich isotherm. Both pH and desorption studies showed that chemisorption is involved in the process. The studies with real pulp and paper mill effluent revealed that the prepared coconut shell carbon is more effective than the high cost commercial activated carbon in the removal of chlorophenols. The approximate cost for the preparation of activated carbon in the laboratory was estimated as Rs. 217 kg^{-1} which is very much lesser than the commercial activated carbon (Rs. 550 kg^{-1}).

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