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Removal of phenols from water and petroleum industry refinery effluents by activated carbon obtained from coconut coir pith

T.S. Anirudhan · S.S. Sreekumari · C.D. Bringle

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Abstract Coir pith obtained from the coir industry as waste biomass was used to prepare activated carbon by chemical activation using phosphoric acid (H_3PO_4). The influences of activation temperature and lasting time of activation on specific surface areas (SSA) of the activated carbons were observed. Physical characteristics of the activated carbon were investigated using X-ray diffraction (XRD), infrared spectroscopy (IR), surface area analyzer, scanning electron microscopy (SEM), thermal analysis and potentiometric titration. The feasibility of using activated carbon for the removal of phenol (P), *p*-chlorophenol (PCP) and *p*-nitrophenol (PNP) from water and petroleum refinery industry effluents was investigated. The effects of contact time, adsorbent dose, ionic strength and initial concentration on the adsorption of phenols onto the activated carbon were investigated. The optimum pH for the maximum removal of phenols was 6.0. The equilibrium adsorption data of phenols were correlated to Langmuir and Freundlich isotherm models, the latter being the best fit of the experimental data. Dynamics of the sorption process and mass transfer were investigated using McKay and Urano-Tachikawa models. Adsorption kinetic data fits the Urano-Tachikawa kinetic model. The utility of the adsorbent was tested by using petroleum refinery industry effluent. The adsorbed phenols can be recovered by treatment with 0.1 M NaOH solution.

Keywords Coir pith · Activated carbon · Adsorption isotherm · Phenols · Mass transfer studies · Desorption

1 Introduction

Phenols and substituted phenols are common pollutants in wastewaters. Major sources of water pollution with phenolic compounds are industries like oil refineries, petrochemicals, leather and textile manufacturing, plastic, rubber, pesticides, insecticides and pharmaceuticals (Kujawski et al. 2004; Srivastava et al. 2006). Discharge of phenolic wastes imparts a carbolic odour to water bodies and cause toxic effect on aquatic life, plants and human beings. They have been found to accelerate tumour formation, cancer and mutation. The permissible limit for phenolic concentrations in industrial effluents before discharging into municipal sewers and surface waters are 1–5 $\mathrm{mg\,L^{-1}}$ (IS 3306 1974; Central Bureau of Water Pollution Control 1981) and the WHO recommends the permissible phenolic concentration of 0.001 $\mathrm{mg\,L^{-1}}$ in potable waters (World Health Organization 1963). Compared to other methods, adsorption technique is widely used for water treatment due to its sludge-free clean operation, economical, availability of wide range of adsorbents and complete removal of phenols from wastewaters. Activated carbons are often used for the removal of organic contaminants from water (Furuya et al. 1997). Activated carbons with desired internal surface area, porosity and sorption characteristics can be manufactured by choosing a right kind of precursor or controlling the process conditions. Agricultural waste materials such as waste apple pulp, straw, coconut shell, coir pith, saw dust, apricot stone shell, olive stones, sugarcane bagasse and peanut hull have been employed to produce activated carbons with high surface area.

Two main processes are involved in the production of activated carbons:

(i) carbonization of precursor material (ii) activation of resulting carbonized substances. Activation process in-

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T.S. Anirudhan (✉) · S.S. Sreekumari · C.D. Bringle
Department of Chemistry, University of Kerala, Kariavattom,
Trivandrum 695 581, India
e-mail: tsani@rediffmail.com

creases the pore volume and enlarges the diameter of the pores that are formed during carbonization. The most commonly used activation techniques are the physical activation and chemical activation. The physical activation involves oxidation and gasification of the char at high temperatures (>800 °C). In chemical activation process the carbonization and activation are carried out in a single step by the thermal decomposition of the raw material impregnated with certain chemicals such as $ZnCl_2$, NH_4Cl, $BaCl_2$, $MgCl_2$, NaOH, KOH, K_2CO_3, K_2HPO_4 and H_3PO_4. The temperatures used in chemical activation are lower than that used in the physical activation process. Although physical activation permits better control over the creation of a desired micro porous structure, chemical activation is an adequate procedure to develop large pores in activated carbons.

As a by-product coir fibre extraction from coconut husk, large quantities of coir pith (CP) are obtained, which have been accumulating at production sites over the years. The extraction of 1 kg of fibre generates more than 2 kg of CP. India is the market leader in the production of coir fibre, producing 7.5 million tons of CP annually. Its main chemical constituents are cellulose, hemicellulose, lignin, polysaccharides and tannin. Any attempt to reutilize the CP will be worthwhile. The CP can be converted into good manure after 30 to 40 days, and can be applied to a wide variety of crops, used to prepare potting mixture and used as organic manure in kitchen gardens. The ability of CP to remove uranium from aqueous solutions has been demonstrated (Parab et al. 2005). Anion exchangers with different functionalities have been prepared from CP, which are effectively and inexpensively decontaminates wastewaters rich in heavy metals (Anirudhan and Unnithan 2007). Only one report is available in the use of CP as a precursor material in the production of activated carbon. In this work Namasivayam and Sangeetha (2006) used chemical activation by $ZnCl_2$ for the production of activated carbon in removing organic substances from solutions. However, the use of other activating agents such as H_3PO_4 may be preferred, not only because of the simplicity of the extraction process after carbonization and impregnant recovery, but also because of the decline of the $ZnCl_2$ process due to problems of environmental contamination with Zn compounds. The chemical activation by H_3PO_4 has been applied to different cellulosic and lignocellulosic materials to prepare high surface area activated carbons and has been reviewed by Molina-Sabio et al. (1995). In the present work, chemical activation by H_3PO_4 was employed to convert CP to a useful activated carbon for the removal of phenol and substituted phenols from wastewater. The adsorption of phenol, *p*-chlorophenol and *p*-nitrophenol was studied in batch system with respect to the initial pH, contact time, initial phenol concentration, ionic strength, adsorbent dose and temperature.

2 Materials and methods

2.1 Materials

The raw material, CP obtained from a local coir industry was used for the preparation of activated carbon. The amount of main composition such as α-cellulose, hemicellulose, lignin and moisture in the CP was determined using standard method described by Ott (1946) and was found to be 48.4, 16.7, 24.3 and 4.2% respectively. All chemicals were of analytical grade. H_3PO_4, P, PCP and PNP were obtained from Fluka, Switzerland, while H_2SO_4, methylene blue (MB), NaCl, and NaOH were purchased from E.Merck, India. The adsorbate solutions of various concentrations from 0.1 to 1.4 $\text{mmol}\,\text{L}^{-1}$ were prepared with distilled water from a stock solution of 10 $\text{mmol}\,\text{L}^{-1}$.

2.2 Preparation of adsorbent

CP was washed with dilute sulphuric acid (5%) to remove adhered dirt such as oil and grease. It was then washed with distilled water to remove water-soluble materials until washings are nearly of neutral effect and dried at 80 °C for 4 h. The CP was impregnated with the H_3PO_4 solution. For this, 25 g of the dried CP were added to a 100 mL of phosphoric acid (75%) and stirred at 80 °C in a water bath for 2 h. Evaporation was minimized during this 2 h of impregnation. After impregnation, the solution was completely evaporated to dryness. The H_3PO_4 impregnated CP was subjected to carbonization in a Matri (India) made muffle furnace at a heating rate of $10\,^{\circ}\text{C}\,\text{min}^{-1}$ for different temperatures under a flow of nitrogen (flow rate 60 $\text{mL}\,\text{min}^{-1}$) for 2 h. After cooling to room temperature, the carbonized material was washed with distilled water, dried in an air oven at 80 °C until constant weight and cooled. The activated carbon was ground and sieved between particle size 80 and 230 mesh (average particle diameter 0.096 mm).

2.3 Equipments and method of characterization

The surface area of the activated carbon was measured using N_2 adsorption data at 77 K with a Quantasorb surface area analyzer (model $Q_{s/7}$). The Dubinin–Radushkevich (DR) equation was used to calculate the macropore volume. The total pore volume was determined from the amount of N_2 adsorbed at a relative pressure of 0.95. The specific surface area (SSA) was calculated using BET isotherm equation. The functional groups associated with surface of the activated carbon was identified using a Nicolet 400 D FTIR spectrophotometer with KBr background. A scanning electron microscope (Philips XL-3 CP) operated at 12 kV was used to study the surface morphology. X-ray powder diffraction analysis of the adsorbent was carried out using a Rigaku diffractometer with Ni filtered CuKα radiation. The thermal characteristics of the original CP was examined by Metler Toledo Star thermogravimetric analyzer. The potentiometric method (Schwarz et al. 1984) was used for the determination of the pH of point of zero charge (pH_{PZC}). The apparent density of the adsorbent was determined by specific-gravity bottle using nitrobenzene as displacing liquid. The concentrations of phenols were measured by UV-visible spectrophotometer (Jasco V-530). All pH measurements were made on a micro processor pH meter (Systronic µ362 Model). A temperature controlled water bath shaker (Labline, India) with a temperature variation of $\pm 1\,^\circ$C was used for equilibrium studies.

2.4 Batch adsorption studies

The phenol adsorption on activated carbon was determined from batch experiments as a function of pH, contact time, initial phenol concentration, temperature and adsorbent dose. Experiments were carried out using 100 mL Erlenmeyer flasks. A fixed amount of carbon (0.1 g) was added to 50 mL of phenols of different concentrations ranging from 0.1 to 1.4 $\text{mmol}\,L^{-1}$. Initial pH of the solution was adjusted with 0.1 M HCl and NaOH using pH meter. The mixture was agitated in a temperature controlled water bath shaker for 4 h at a constant agitation speed of 200 rpm to achieve equilibrium. After equilibrium, the solutions were filtered and the concentration of the phenols in the solution was determined spectrophotometrically by monitoring the absorbances at 270 nm for P, 274 nm for PCP and 318 nm for PNP. The adsorbed phenol was obtained from the difference between the initial phenol concentration and final detected phenol concentration. Kinetic studies were conducted at four different concentrations (0.1, 0.2, 0.3 and 0.4 $\text{mmol}\,L^{-1}$) of the phenols at 30 °C. Samples were withdrawn at regular intervals to plot the amount adsorbed versus time. Kinetic studies were also conducted at four different temperatures ranging from 10 to 40 °C using an initial concentration of 0.4 $\text{mmol}\,L^{-1}$. Isotherm experiments were performed using different initial concentrations ranging between 0.1 and 1.4 $\text{mmol}\,L^{-1}$ at 30 °C.

2.5 Desorption and regeneration studies

Desorption studies help to elucidate the mechanism of adsorption as to recover the pollutants from the spent adsorbent apart from protecting the environment from solid waste disposal problem. After adsorption, the phenol loaded carbon was washed with distilled water to remove the unadsorbed adsorbates. Several such carbon samples were prepared. The loaded carbon was resuspended in 50 mL of 0.1 M NaOH and was equilibrated for 4 h. It was centrifuged and the concentration of phenol in supernatant solution was determined as described above. The percentage desorption from the spent adsorbent was calculated from the amount of phenol adsorbed on activated carbon and the final concentration of phenol in the desorption medium.

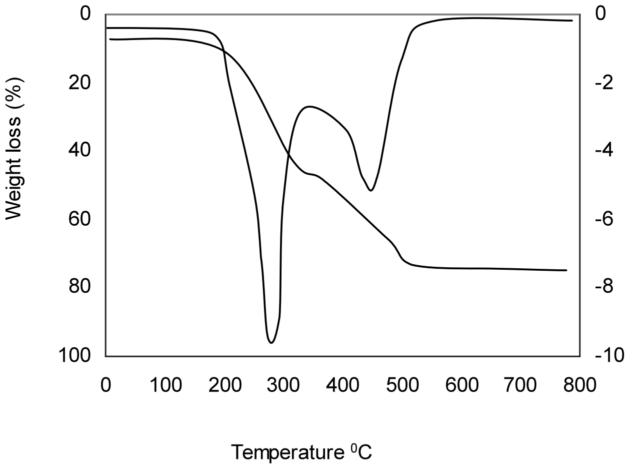

Fig. 1 TG and DTG curves of CP

3 Results and discussion

3.1 Adsorbent characterization

Figure 1 illustrates the sequential thermal decomposition processes occurring in pure CP during carbonization by means of the experimental and differential thermograms (TG, DTG). The TG and DTG curves of CP show the weight loss at two different temperature ranges: (i) 240–380 °C and (ii) 380–620 °C. In the initial stage of decomposition ($T_1 = 320\,^\circ$C) almost 58% of the dry weight loss was observed due to the release of water, CO and CO_2 by the pyrolitic decomposition of cellulose unit leaving behind a rigid carbon skeleton. In the second stage ($T_2 = 560\,^\circ$C) a weight loss of 64% of the initial dry weight was observed. This transition is the characteristic of pyrolitic depolymerization process in lignin and internal thermal rearrangement of the carbohydrate anhydride residues resulting in char formation, eventually provide pseudo-graphitic layers with microporous interstices (Pollard et al. 1995).

The influences of activation temperature and lasting time of activation temperature were observed in the experiment. The activation of H_3PO_4 impregnated CP was performed at various temperatures (500–900 °C) for fixed time (2 h). The values of SSA of carbon obtained at 500, 550, 600, 650, 700 and 900 °C were 308, 428, 493, 470, 488 and 474 $m^2\,g^{-1}$ respectively; the corresponding pore volumes were 0.31, 0.36, 0.47, 0.41, 0.36 and 0.44 $mL\,g^{-1}$. Based on these results, the optimal activation temperature for carbonized material from CP was chosen as 600 °C. The SSA of activated carbon may also be influenced by the lasting time of activation

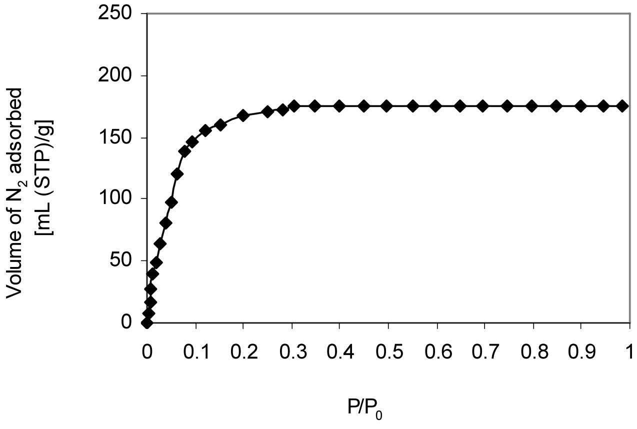

Fig. 2 N_2 adsorption isotherm onto activated carbon

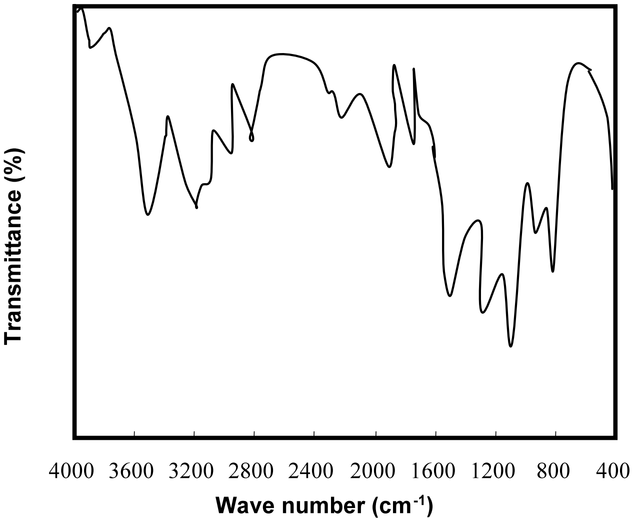

Fig. 3 FT-IR spectra of CP activated carbon

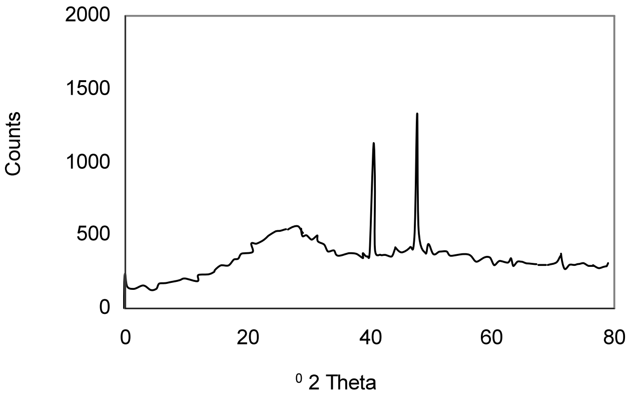

Fig. 4 X-ray diffraction patterns of the activated carbon

temperature. The influence of lasting time of activation temperature on SSA was also investigated for different lasting time at 600 °C. The values of SSA was found to be 362, 406, 493, 469 and 474 $m^2\,g^{-1}$ for the lasting time of 1.0, 1.5, 2.0, 2.5 and 3.0 h respectively. The corresponding total pore volume was found to be 0.28, 0.37, 0.46, 0.41 and 0.39 $mL\,g^{-1}$. Based on these results, an optimal lasting time of 2 h was recommended for an activation temperature of 600 °C. The characterization and phenols adsorption experiments were performed using activated carbon prepared from CP with an activation temperature of 600 °C and a lasting time of 2 h.

The elemental analysis of activated carbon used in the present investigation indicated the presence of 69.9% total C, 2.3% H, 2.9% N and 25.1% O_2. The nitrogen adsorption isotherm for the carbon (Fig. 2) is of type I indicating the micropores. The isotherm is characterized of a molecular sieve material; that is, they possess a rectangular 'knee' indicative to the presence of wider micropores and negligible mesoporosity (Freeman et al. 1995). The values of SSA, the micropore volume and total volume were calculated using the isotherm data as described earlier and were 493 $m^2\,g^{-1}$, 0.32 $mL\,g^{-1}$ and 0.46 $mL\,g^{-1}$ respectively. Boehm titrations (Dargaville et al. 1996) were performed to determine the amount of carboxyl, phenolic, total acid and total basic groups in the activated carbon and were found to be 0.12, 0.05, 0.31 and 0.27 $meq\,g^{-1}$ respectively.

The FTIR spectrum of activated carbon is shown in Fig. 3. The spectrum shows a broad band near 3630 cm^{-1} which indicates the presence of hydroxyl groups on the carbon surface. The stretching was attributed to the absorbed water on the surface of activated carbon. The stretching frequencies of the aromatic C=C and aromatic C–H groups give rise to peaks at 3032 and 2874 cm^{-1} respectively, which are originally existed as the support for the activated carbon. The peak at 1759 cm^{-1} ($\nu_{C=O}$) along with another peak at 1436 cm^{-1} ($\nu_{C\text{–}O}$) indicate the presence of carboxylic acid groups. The peak at 1596 cm^{-1} is assigned to a conjugated hydrogen bonded carboxyl group, assigned by several authors on activated carbon. The peak at 2985 cm^{-1} is due to C–H stretching of CH_2 groups. The two peaks at 1165 cm^{-1} (P=O) and 993 cm^{-1} (P–OH) was characteristic of PO_2 stretching. The bands near 1600 cm^{-1} indicates the fingerprint region of C=O, C–O and O–H groups that exist as functional groups of activated carbon. The band at 887 cm^{-1} is due to out-of-plane bending of C–H group in benzene derivatives.

The XRD pattern (Fig. 4) shows a broad peak centered at $2\theta = 26^\circ$ corresponding to the disordered graphitic 002 plane, assigned by several authors also as characteristic peak created by general activated carbons (Lee et al. 2002).The carbon also shows a sharp peak at $2\theta = 36.8^\circ$ indicates the presence of phosphate and peak at $2\theta = 43.2^\circ$ is due to the presence of SiO_2.

The SEM image of activated carbon (Fig. 5) shows that adsorbent has abundant porous structure, and the size of the pores on the surface is about 3 to 10 µm. Its porous structure provides new adsorption sites from inner cavities to accom-

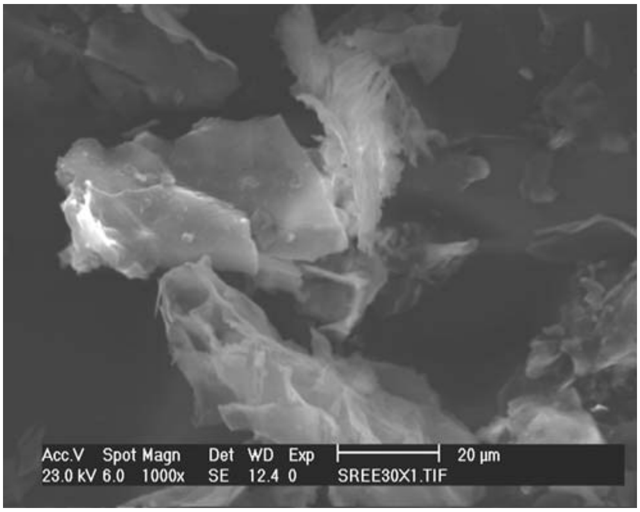

Fig. 5 Scanning electron micrograph of the activated carbon

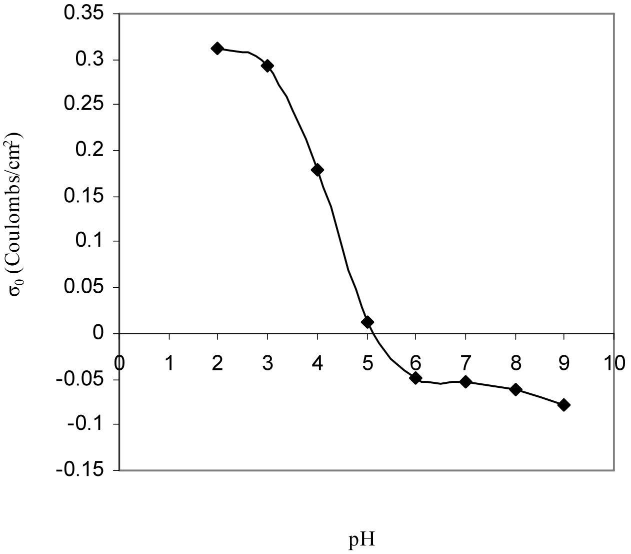

Fig. 6 Surface charge density as a function of pH in aqueous solution of NaCl

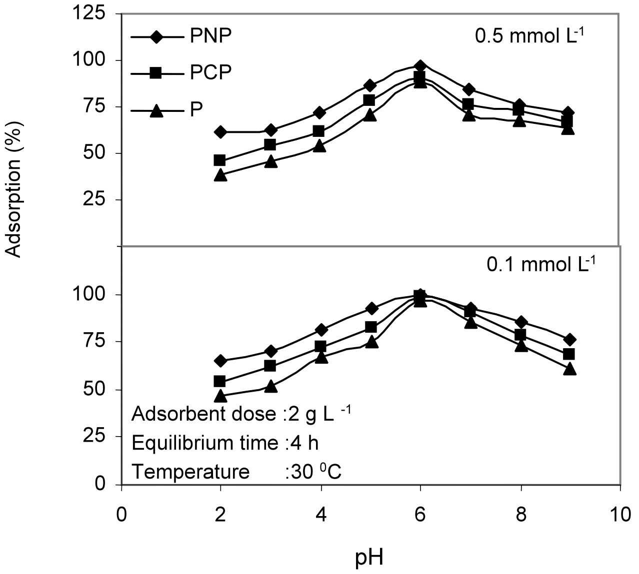

Fig. 7 Effect of pH on the adsorption of phenols onto activated carbon

modate phenols. During the carbonization of CP, the volatile matter produces a high pressure which breaks the cellular structure of the particle and creates pores seen on the surface of the activated carbon. During activation, the gas released on thermal decomposition produces hollows in the carbon particles from which gas escapes through small channels and forms bottle shaped pores.

The pH dependent surface charge is very much used in predicting the adsorption characteristics of adsorbents. The potentiometric titration method was used to determine the surface charge density σ_0 as the function of pH and ionic strength and it was calculated using equation (1).

$$\sigma_0 = \frac{F(C_A - C_B) + ([\mathrm{OH}^-] - [\mathrm{H}^+])}{A} \tag{1}$$

where F is the Faraday's constant, C_A and C_B are the concentrations of the acid (HCl) and base (NaOH) after each addition, $[\mathrm{OH}^-]$ and $[\mathrm{H}^+]$ are the concentration of free hydroxide and hydronium ion bound to suspension surface and A is the specific surface area of the suspension surface ($\mathrm{cm}^2\,\mathrm{L}^{-1}$). The plot of σ_0 versus pH is given in Fig. 6. The point of intersection of σ_0 with the pH curve gives the $\mathrm{pH}_{\mathrm{PZC}}$ and it was found to be 5.0.

3.2 Effect of pH on the adsorption of phenols

The effect of pH on the adsorption of phenols on activated carbon was studied by changing the pH of the solution from 2.0 to 9.0 and the results are shown in Fig. 7. It can be observed that the removal of different phenols increased with increasing pH from its minimum at lower pH 2.0 to its maximum at a pH of 6.0 where the maximum removal was observed. An increase in pH above 6.0 shows a decreasing trend in adsorption. At an initial concentration of 0.1 and 0.5 $\mathrm{mmol\,L}^{-1}$, the maximum adsorption of 99.3 and 96.4% for PNP, 98.1 and 90.3% for PCP and 96.7 and 88.7% for phenol was observed at pH 6.0. Phenols are hydrophobic ionisable organic compounds that can exist as either the protonated species depending on the solution pH. The adsorption of phenols on activated carbon increases in the order P < PCP < PNP. The $\mathrm{pK_a}$ of P, PCP and PNP was found to be 9.9, 8.2 and 7.1 respectively and thus at optimum conditions of pH 6.0 the protonated species appears to be more readily adsorbed on the negative surface of the carbon. A donor–acceptor complex mechanism was reported by the earlier workers for the adsorption of phenol on activated carbon. In this mechanism carbonyl oxygen group on to carbon surface acts as the electron donor whereas the aromatic ring of the phenol act as the acceptor. An electron withdrawing nitro group in phenol lowers the electron density in the ring in comparison with phenol, and as a result the interaction of the adsorbate and the carbon is enhanced. PCP is also adsorbed more than P because of the electron withdrawing inductive effect of chlorine, i.e., electronegative chlorine atom attracts electron towards the benzene ring thus enhancing the activation of the molecules. The decrease in adsorption capacity as the solution pH increased from 6.0 to 9.0 can be attributed to the electrostatic repulsion existing between carbon surface and the phenolate anions in solution. Since the $\mathrm{pH_{ZPC}}$ for activated carbon was found to be 5.0, the surface of carbon is positively charged when $\mathrm{pH} < \mathrm{pH_{ZPC}}$. Therefore, in the lower pH range the protonated species will be repelled by the carbon. In all cases there is a reduction in the adsorption at a higher pH which is possibly due to the increased solubility of phenols and the abundance of $\mathrm{OH^-}$ ions thereby increasing hindrance to diffusion of phenolate anions.

The adsorption of phenols on activated carbon in the pH range 6.0 to 9.0 can be attributed to π–π interactions which involve dispersive forces between π interaction in the aromatic ring of the phenol and π electrons in the aromatic rings of the graphitic layer. The activated carbon used in the present study has both basic and acidic sites on the edge of the graphitic layer of the activated carbon would increase the π electron density so that π–π interaction would become stronger. The π–π interactions are weak attractive forces and hence the adsorption phenols on activated carbon is reversible.

3.3 Adsorption isotherm

Several equilibrium models have been used to describe the equilibrium nature of adsorption. The Langmuir and Freundlich isotherm are the most frequently used models to describe the adsorption data. The equilibrium sorption of P, PCP and PNP by CPAC was measured at 30 °C using different initial concentrations ranging between 0.1 and 1.4 $\mathrm{mmol\,L^{-1}}$ at pH 6.0. These isotherms were classified as H-type of Giles et al.'s classification (Giles et al. 1960). The experimental isotherm data have been modeled by the well-known Langmuir and Freundlich models given respectively by

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}, \tag{2}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \tag{3}$$

where Q^0 and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption respectively, and K_F and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity respectively. The isotherm constants at different temperatures were computed according with the least squares fitting method using experimental q_e and C_e values (Table 1). The validity of the isotherm models was tested by comparing the experimental and calculated data at 30 °C (Fig. 8). The fitness of the isotherm model is quantitatively determined from the nor-

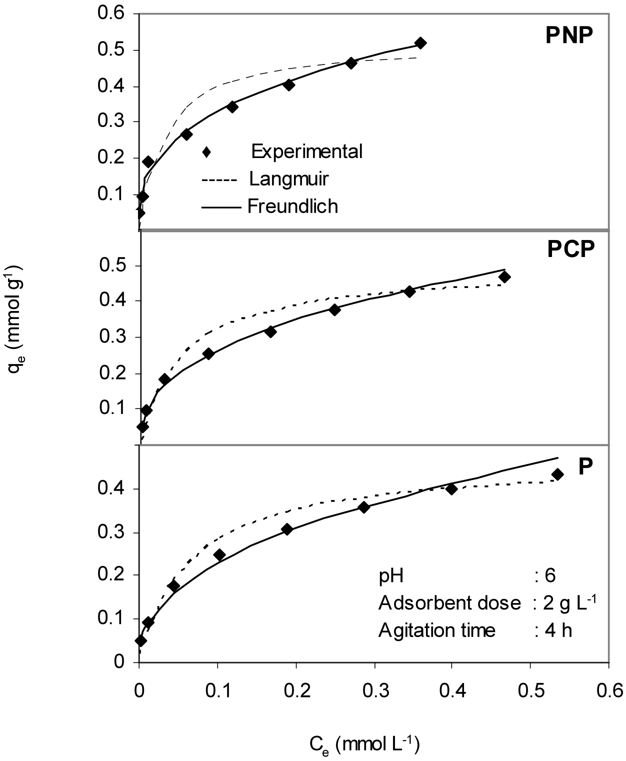

Fig. 8 Adsorption isotherm of phenols onto activated carbon

Table 1 Langmuir and Freundlich isotherm parameters for the adsorption of phenols

Phenols	Langmuir				Freundlich			
	Q^0 ($\mathrm{mmol\,g^{-1}}$)	b ($\mathrm{L\,mmol^{-1}}$)	R^2	Δq (%)	K_F	$1/n$	R^2	Δq (%)
P	0.46	15.23	0.983	23.9	0.61	0.429	0.993	6.7
PCP	0.49	19.34	0.974	30.9	0.66	0.399	0.994	6.3
PNP	0.52	31.34	0.967	40.6	0.73	0.342	0.991	7.2

malized standard deviation, defined as

$$\Delta q\ (\%) = 100\sqrt{\frac{\sum[(q_{e,\mathrm{exp}} - q_{e,\mathrm{calc}})/q_{e,\mathrm{exp}}]^2}{N-1}}. \tag{4}$$

Based on the correlation coefficients (R^2) and standard deviation (Δq) values, it is clear that the Freundlich adsorption isotherm gives a best fit for adsorption of phenols on to activated carbon for the entire range of concentrations. The ultimate adsorption capacity of the adsorbent can be obtained from isothermal data by substituting the required equilibrium concentration in the Freundlich equation. Thus for an equilibrium concentration of 1 $\mathrm{mmol\,L^{-1}}$, each gram of activated carbon can remove 0.61, 0.66 and 0.73 mmol of P, PCP and PNP respectively at 30 °C.

The reported K_F values for the adsorption of P on bentonite (Viraraghavan and Alfaro 1998), peat (Viraraghavan and Alfaro 1998), rice husk (Ahmaruzzaman and Sharma 2005) and granular activated carbon (Tancredi et al. 2004) were found to be 0.20, 0.03, 0.11 and 0.17 respectively. For PCP adsorption on petroleum coke, rice husk char, coke breeze and rice husk (Ahmaruzzaman and Sharma 2005), the values of K_F were reported to be 0.18, 0.28, 0.24, 0.37 respectively. The reported K_F value for PNP on petroleum coke, coke breeze and rice husk char (Ahmaruzzaman and Sharma 2005), were 0.10, 0.06, 0.25 respectively. The K_F values for P, PCP and PNP (0.61, 0.66 and 0.73) at room temperature reveal that this low cost adsorbent possess remarkable capacity than the non-conventional adsorbent for the removal of phenols from wastewater systems.

3.4 Effect of ionic strength

Ionic strength is an important factor in the study of aqueous phase equilibrium. When the concentration of the supporting electrolyte, NaCl solution, was varied from 0.001 M to 0.1 M the adsorption of phenols increases slightly. With the increase in ionic strength from 0.001 to 0.1 M, the percentage of adsorption increases from 92.7 to 96.7% for PNP, from 82.6 to 88.2% for PCP and 67.8 to 71.6% for P. According to Guoy and Chapman theory, when two phases such as sorbent particles and sorbate particles are in contact, they are bound to be surrounded by an electrical double layer due to electrostatic interaction (Osipow 1972). The slight increase in adsorption with increase in ionic strength is due to the compression of the electrostatic double layer.

Ionic strength can also be explained by the electrostatic interactions (Castilla 2004). These interactions can be either attractive or repulsive. The added salt can reduce these interactions by increasing the ionic strength of the solution. This is due to the screening effect of the surface charge produced by the salt. When the electrostatic interaction between the surface and the adsorptive is repulsive, or the surface concentration is sufficiently high, an increase in ionic strength will increase the adsorption. Similarly when the electrostatic interactions are attractive, or the surface concentration is sufficiently low, an increase in ionic strength will decrease the adsorption. Various weak organic electrolytes and poly electrolytes like bisphenol A and natural organic matter show these effects (Newcombe and Drikas 1997). In the case of phenols the uptake increased with ionic strength. At pH 6.0, the surface charge would be negative. The added salt screened the surface charge by the increase in electrolyte concentration.

3.5 Effect of contact time and initial concentration

The results of the experiments performed to determine the optimum contact time for phenol adsorption are summarized in Fig. 9. As it can be seen from the figure, there is a rapid uptake kinetics within 30 min and adsorption equilibrium is attained within 2 h. Therefore 2 h contact time was chosen as the optimum equilibrium time for the experimental studies. There was not much difference between the amount of phenol adsorbed on activated carbon after this time. The time necessary to reach the equilibrium is independent of initial phenol concentrations. The equilibrium time for the removal of phenols by the adsorbent was compared with the values of different adsorbents. It is observed that very low contact time is needed for the removal of phenols. The low equilibrium time observed for the adsorption of phenol on activated carbon made from coffee grounds (Namane et al. 2005), activated carbon from straw and used rubber tyres (Streat et al. 1995), burnt wood charcoal (Palanichamy et al. 1994), impregnated fly ash (Singh et al. 1994) and dual-cation organobentonites (Zhu et al. 2000) were 60 min, 2 h, 1 h, 2 h and 2 h respectively. It was reported that the contact time required to attain equilibrium for the removal of PCP by activated carbon from straw and used rubber tyres (Streat et al. 1995) and PNP by dual-cation organobentonites (Zhu et al. 2000) was 2 h. Hence the present adsorbent appears to be suitable for the removal of phenols from wastewater.

For the same amount of adsorbent, the sorption efficiencies decrease with the increase of phenol concentration in solution, while the amount of phenol adsorbed increased with increase of initial concentration. With the increase of initial concentration of phenols from 0.1 to 0.4 $\mathrm{mmol\,L^{-1}}$, the percentage uptake decrease from 96.7% (0.047 $\mathrm{mmol\,g^{-1}}$) to 88.9% (0.176 $\mathrm{mmol\,g^{-1}}$) for P, 98.1% (0.048 $\mathrm{mmol\,g^{-1}}$) to 92.1% (0.180 $\mathrm{mmol\,g^{-1}}$) for PCP and 99.6% (0.049 $\mathrm{mmol\,g^{-1}}$) to 96.9% (0.193 $\mathrm{mmol\,g^{-1}}$) for PNP. Kinetic adsorption data was analyzed in terms of pseudo-first-order and pseudo-second-order kinetic models (McKay and Ho 1999). The linear form of pseudo-first-order equation is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t, \tag{5}$$

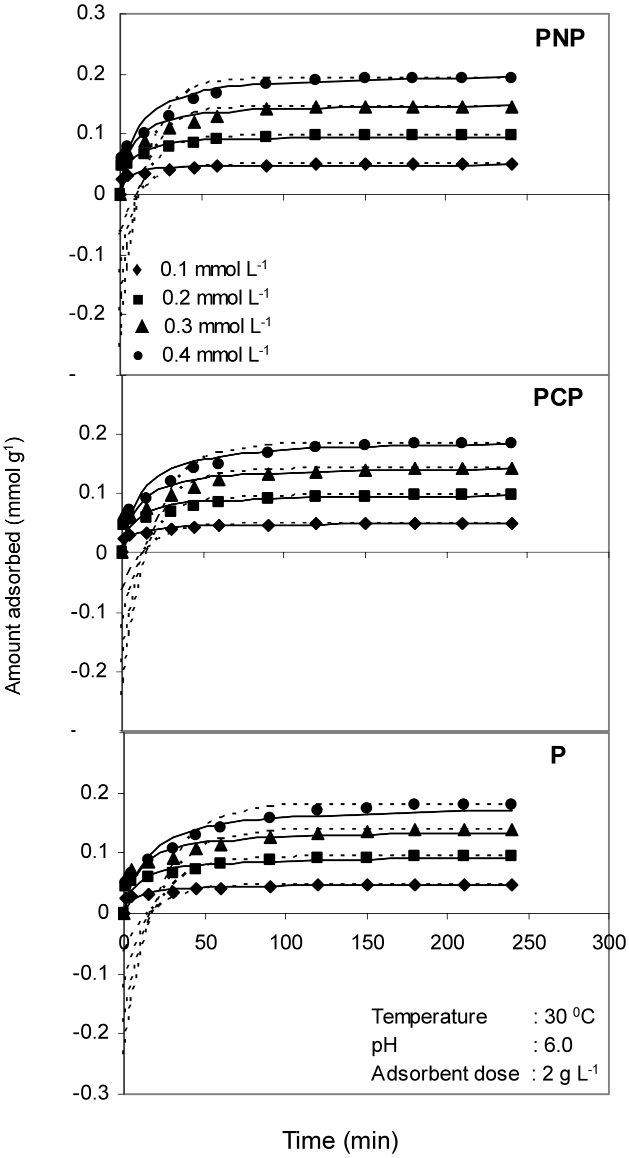

Fig. 9 Comparison between experimental contact time data and (symbols) the fittings to pseudo-first-order (- - - -) and pseudo-second-order (—) kinetic models for the adsorption of phenols onto activated carbon at different concentrations

where q_e and q_t are the amount of phenols adsorbed ($\mathrm{mmol\,g^{-1}}$) at equilibrium and at time t (min) respectively, and k_1 is the rate constant of adsorption ($\mathrm{min^{-1}}$). The values of k_1 were evaluated from the plots of $\log(q_e - q_t)$ versus t for different concentrations of phenols. The calculated q_e values do not agree with the experimental q_e values.

The pseudo-second-order equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 is the rate constant of second-order adsorption ($\mathrm{g\,mmol^{-1}\,min^{-1}}$). The straight line plots of t/q_t against t have also been analysed. The values of q_e, k_2 and the correlation coefficients R^2 for phenols at different concentrations were calculated from these plots. Comparison between the experimental results and calculated values of the contact time for different concentrations of phenols are shown in Fig. 9. The correlation coefficients of pseudo-second-order kinetic model are greater than 0.990. The calculated q_e values are in good agreement with the experimental values. Therefore the sorption reaction belongs to the pseudo-second-order kinetic model. Similar behavior has been observed in the adsorption of phenol on beet pulp (Dursun et al. 2005), plumkernel (Juang et al. 2000), bagasse fly ash and activated carbon (Srivastava et al. 2006) and activated carbon from rattan saw dust (Hameed and Rahman 2008). The presence of various functional groups like carboxylic, carbonyl, hydroxyl, ether, quinone, lactone and anhydride implies that there are many types of solute-adsorbent interactions (Figueiredo et al. 1999). The phenol uptake depend not only on the micropore volume but also on these interactions (Fierro et al. 2008).

3.6 External and internal mass transfer processes

The adsorbate transport from the solution phase to the surface of the sorbent particle occurs in several steps. It is known that the overall sorption kinetics could be mainly controlled by external or film mass transfer diffusion process and pore diffusion or intraparticular diffusion process. In order to clarify the adsorption process, several adsorption models were applied to evaluate the experimental data. The external mass transfer analysis of phenols during the adsorption process is studied using the kinetic model developed by McKay et al. (1981).

$$\ln\left[\left(\frac{C_t}{C_0}\right) - \frac{1}{(1+mK_L)}\right] = \ln\left[\frac{mK_L}{(1+mK_L)}\right] - \left[\frac{(1+mK_L)}{mK_L}\right] B_L S_S t \tag{7}$$

where C_0 is the initial concentration of the adsorbate, C_t is the adsorbate concentration after time t, m is the mass of the adsorbent per unit volume of particle free solution of solute, K_L is the Langmuir constant obtained by multiplying Q^0 and b, B_L is the mass transfer coefficient, S_S is the outer specific surface of the adsorbent per unit volume of particle free slurry. The values of S_S were determined by the following equation:

$$S_S = \frac{6m}{d_p \rho_p (1 - \varepsilon_p)} \tag{8}$$

where, d_p is the particle diameter, ρ_p is the density of the adsorbent and ε_p is the porosity of the adsorbent. The values of B_L for P, PCP and PNP were determined from the slopes and

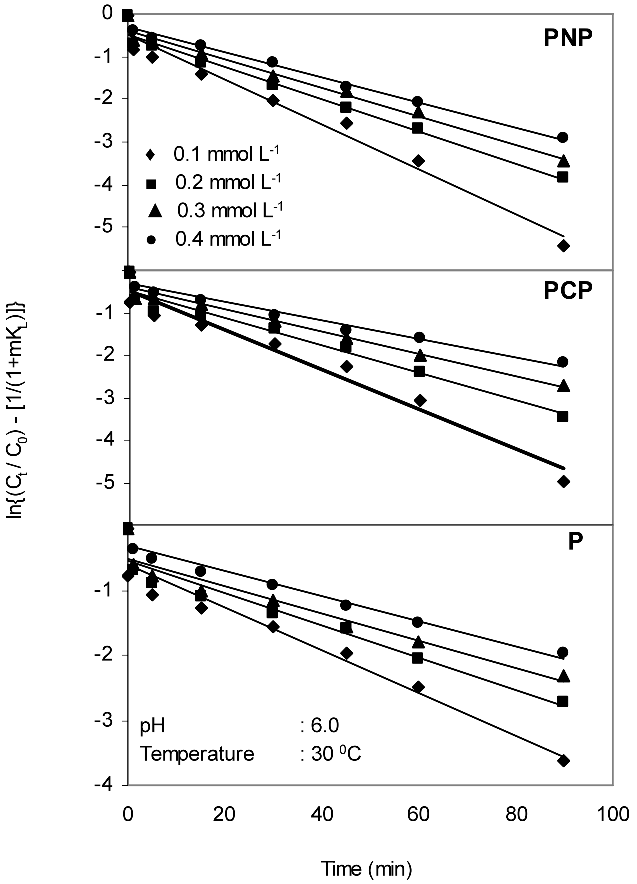

Fig. 10 The McKay et al. kinetic plots for the adsorption of phenols onto activated carbon at different concentrations

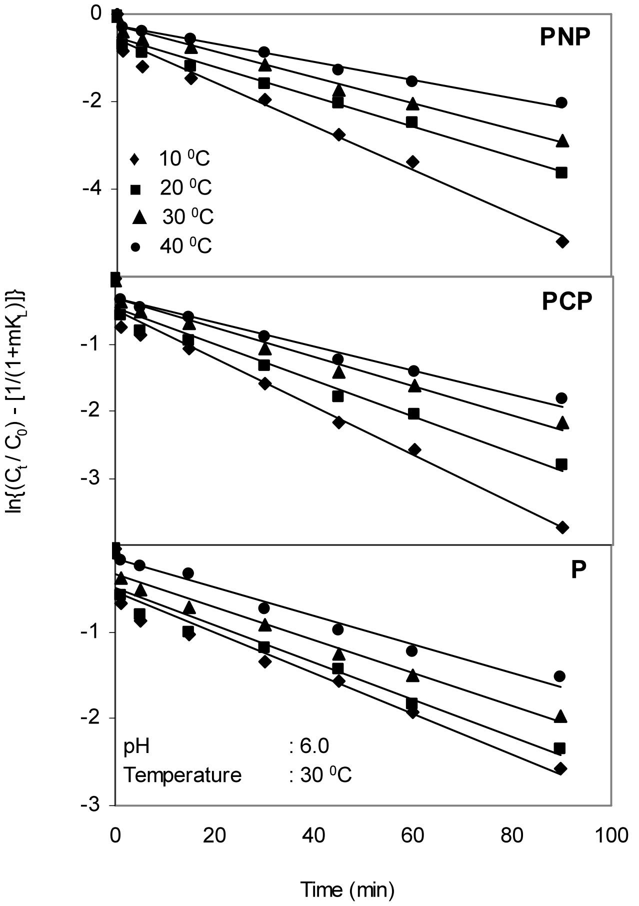

Fig. 11 The McKay et al. kinetic plots for the adsorption of phenols onto activated carbon at different temperatures

intercepts of the plots of $\ln[(C_t/C_0) - [1/(1 + mK_L)]$ versus t for different concentrations and temperatures (Figs. 10 and 11) using regression analysis. The results are presented in Tables 2 and 3. The linear nature of the plots confirms the validity of the diffusional model for the present system. The B_L values are affected by the initial concentration and temperature. It was observed that the B_L values decreased, which has been the reason for the decreasing trend of percentage of phenol adsorption by activated carbons with a gradual increase of phenol concentration. As the results in Table 2 show the values of B_L decreases with increase of temperature, suggests that the adsorption is thus faster at lower temperatures. The values of B_L also indicate that the velocity of phenol transport is rapid enough to use activated carbon for the treatment of wastewater containing phenols (Vinod et al. 2002).

The experimental data were also tested for diffusion using Urano-Tachikawa kinetic model (Urano and Tachikawa 1991). The diffusion coefficient for the adsorption of phenols by activated carbon was determined by the equation:

$$\log\left[1 - \left(\frac{q_e}{q_t}\right)^2\right] = -\frac{4\pi^2 D_i}{2.303 d^2} t \tag{9}$$

where q_t and q_e are the amounts of solute adsorbed at time t and at equilibrium respectively, d is the diameter of the adsorbent, D_i is the intraparticle diffusion coefficient. The D_i values were calculated at different concentrations and temperatures for the three phenols from the slopes of the plots shown in Figs. 12 and 13 and are presented in Tables 2 and 3. The values of D_i increased significantly with increasing initial phenol concentration. Decreasing the phenol concentration in the solution seems to reduce the diffusion of phenol molecules in the boundary layer and to enhance the diffusion into the solid. The diffusion of phenol within the pores of wider-width and electrostatic interaction at the surface of the adsorbent increases with the decrease of temperature and results in higher D_i values. It is evident from the results that intraparticular mass transfer diffusion is the rate-limiting step, since the magnitude of the coefficients is in the order of 10^{-14} $\text{m}^2\ \text{s}^{-1}$ (Vinod and Anirudhan 2002).

3.7 Test with industrial wastewater

The utility of the activated carbon was demonstrated by treating it with a real industry effluent sample. The effluent sample was collected from a petroleum refinery industry

Table 2 Kinetic parameters for the adsorption of phenols on activated carbon at different concentrations

Concentration (mmol L^{-1})	McKay et al. equation		Urano-Tachikawa equation	
	B_L (cm s^{-1})	R^2	D_i ($\text{m}^2\,\text{s}^{-1}$)	R^2
P (30 °C)				
0.1	1.26×10^{-4}	0.944	8.23×10^{-14}	0.992
0.2	9.52×10^{-5}	0.928	7.75×10^{-14}	0.992
0.3	8.14×10^{-5}	0.919	7.21×10^{-14}	0.993
0.4	7.35×10^{-5}	0.964	6.99×10^{-14}	0.993
PCP (30 °C)				
0.1	1.83×10^{-4}	0.960	1.06×10^{-13}	0.996
0.2	1.27×10^{-4}	0.956	1.01×10^{-13}	0.992
0.3	1.01×10^{-4}	0.960	9.29×10^{-14}	0.992
0.4	8.50×10^{-5}	0.965	8.22×10^{-14}	0.993
PNP (30 °C)				
0.1	2.15×10^{-4}	0.974	1.21×10^{-13}	0.995
0.2	1.51×10^{-4}	0.975	1.19×10^{-13}	0.997
0.3	1.34×10^{-4}	0.975	1.15×10^{-13}	0.992
0.4	1.18×10^{-4}	0.984	1.07×10^{-13}	0.991

Table 3 Kinetic parameters for the adsorption of phenols on activated carbon at different temperatures

Temperature (°C)	McKay et al. equation		Urano-Tachikawa equation	
	B_L (cm s^{-1})	R^2	D_i ($\text{m}^2\,\text{s}^{-1}$)	R^2
P (0.4 mmol L^{-1})				
10	9.31×10^{-5}	0.922	9.13×10^{-14}	0.992
20	8.40×10^{-5}	0.920	7.93×10^{-14}	0.993
30	7.35×10^{-5}	0.965	6.99×10^{-14}	0.993
40	6.01×10^{-5}	0.979	6.06×10^{-14}	0.994
PCP (0.4 mmol L^{-1})				
10	1.45×10^{-4}	0.968	1.30×10^{-13}	0.996
20	1.07×10^{-4}	0.949	1.13×10^{-13}	0.991
30	8.50×10^{-5}	0.965	8.22×10^{-14}	0.994
40	7.44×10^{-5}	0.959	8.17×10^{-14}	0.992
PNP (0.4 mmol L^{-1})				
10	2.02×10^{-4}	0.970	1.56×10^{-13}	0.994
20	1.38×10^{-4}	0.961	1.32×10^{-13}	0.991
30	1.26×10^{-4}	0.984	1.14×10^{-13}	0.991
40	8.20×10^{-5}	0.982	8.29×10^{-14}	0.990

Table 4 Four cycles of phenols adsorption–desorption with NaOH as the desorbing agent

No. of cycles	P		PCP		PNP	
	Adsorption (%)	Desorption (%)	Adsorption (%)	Desorption (%)	Adsorption (%)	Desorption (%)
1	94.0	97.3	96.5	96.3	99.6	94.5
2	89.7	91.6	92.3	91.1	96.2	90.1
3	88.2	89.1	89.4	88.7	92.8	86.9
4	85.1	86.4	86.3	82.6	91.2	83.7

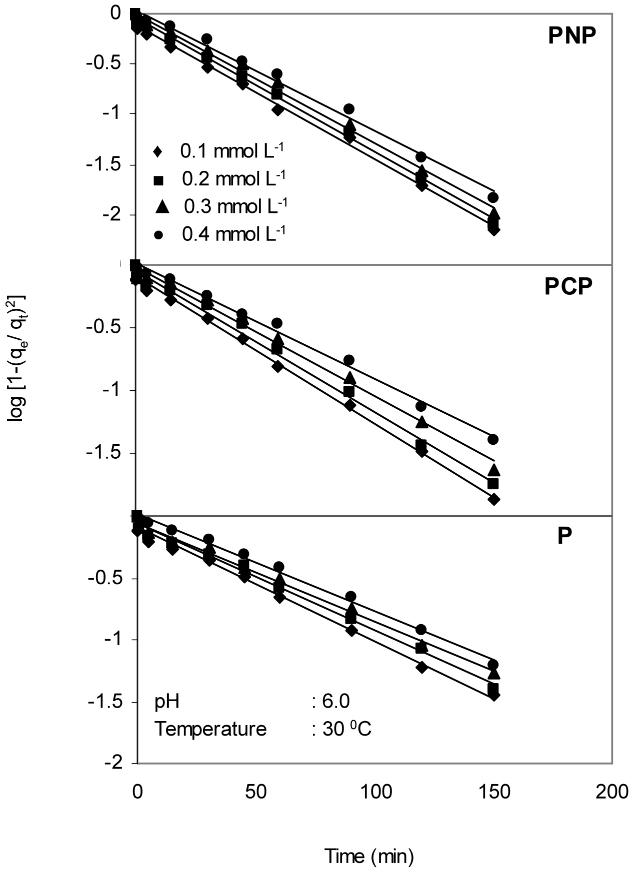

Fig. 12 The Urano-Tachikawa plots for the adsorption of phenols onto activated carbon at different concentrations

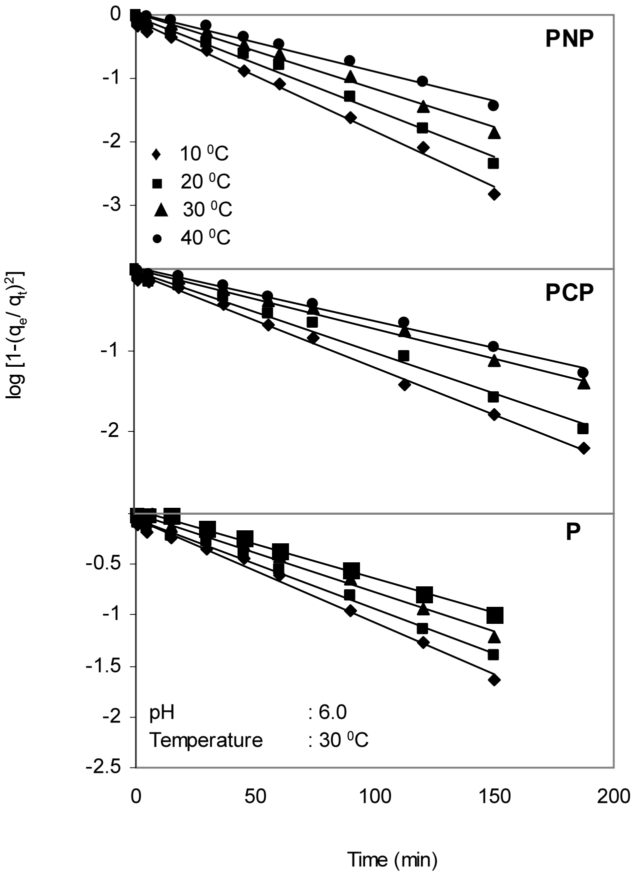

Fig. 13 The Urano-Tachikawa plots for the adsorption of phenols onto activated carbon at different temperatures

situated in Kochi city (India). The effluent sample was characterized using standard methods (APHA 1992). The composition of the effluent sample is: P (0.24 mmol L^{-1}), PCP (0.22 mmol L^{-1}), PNP (0.21 mmol L^{-1}), grease (145.5 mg L^{-1}), free oil (1412.0 mg L^{-1}), sulphide (0.95 mmol L^{-1}), sulphate (1.32 mmol L^{-1}), chloride (1.72 mmol L^{-1}), ammonia (0.22 mmol L^{-1}), BOD (106.7 mmol L^{-1}), COD (584.1 mmol L^{-1}), conductivity, 132.3 μS cm^{-1} and pH 5.7. The effect of adsorbent dose ranging from 25 to 300 mg per 50 mL of the wastewater on phenol adsorption was studied (Fig. 14). Almost complete (100%) removal of phenols from 50 mL of sample was possible with 200, 175 and 150 mg of activated carbon for P, PCP and PNP respectively. These results are in good agreement with that obtained from batch experiments which shows that the activated carbon can effectively remove the phenols even in presence of other ions.

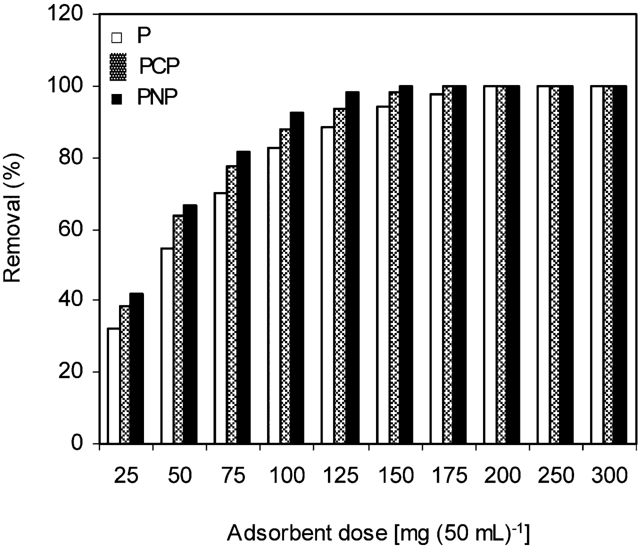

Fig. 14 Effect of adsorbent dose on the removal of phenols from petroleum refinery effluent by activated carbon

3.8 Desorption and regeneration studies

Desorption of P, PCP and PNP was tried with 0.001, 0.005, 0.01, 0.05 and 0.1 M sodium hydroxide solutions. It was found that maximum desorption occurs in the case of 0.1 M NaOH solution (Fig. 15). The phenols react with NaOH to form sodium phenates which are readily desorbed. Table 4 summarizes the results of desorption and regeneration of

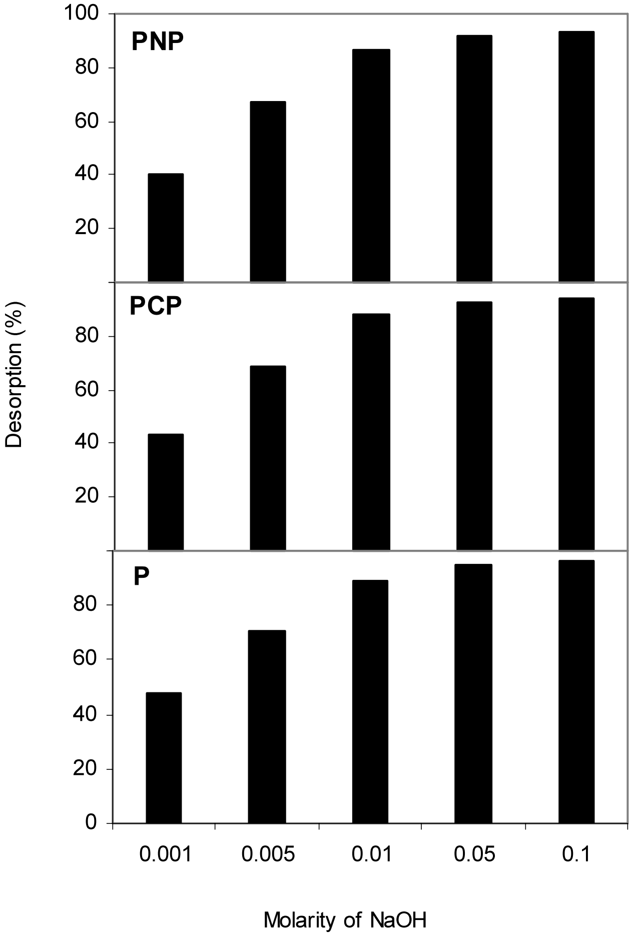

Fig. 15 Desorption of phenols with different concentrations of NaOH as desorbing agent

activated carbon. The adsorption capacity of the activated carbon decreases from the first cycle to the fourth cycle. The gradual reduction of phenols uptake in four cycles of adsorption—desorption indicates that the reaction sites on the surface of the adsorbent were either destroyed or morphologically altered. About 10–15% loss in adsorbent was also observed by the time the carbon reached to fourth cycle. The adsorption of phenols on to the activated carbon is reversible. The spent adsorbent can be regenerated and reused upon repeated treatment with 0.1 M NaOH or by heat treatments in inert atmosphere.

4 Conclusions

Coir pith, a waste biomass, obtained from coir industry was evaluated as a precursor material for the preparation of activated carbon. H_3PO_4 was used as an activating agent. The surface characteristics of the activated carbon were measured. Adsorption performance of the activated carbon was investigated for the removal of phenol, *p*-chlorophenol and *p*-nitrophenol from aqueous solutions. The optimum pH for the phenols removal was found to be 6.0. The isothermal data obey the Freundlich equation for the system. McKay and Urano-Tachikawa models were applied to investigate the kinetic data. Adsorption in the initial stage was due to the boundary layer diffusion whereas in the later stages adsorption was due to intraparticle diffusion. The adsorption efficiency of the adsorbent was evaluated using a petroleum refinery industry wastewater. The spent adsorbent can be regenerated by repeated alkali treatment or by heat treatments in inert atmosphere.

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