Introduction

Discharge of phenolic wastes imparts a carbolic odour to water body and has detrimental effects on human beings and fish. The source of phenolic pollution is from the discharge of various industries such as petroleum-refinery, pharmaceuticals, paints, steel, petrochemical, and plywood. Environmental Protection Agency (EPA) has set a limit of 0.1 mg/L of phenol in wastewater. According to the Indian Standard Institution², the permissible limit for phenol for the discharge of effluents into inland surface water is 1.0 mg/L. In the past two decades, several studies have been carried out on adsorption, as an efficient and economically feasible process, for removing phenols from aqueous industrial effluents. Many researchers have shown that activated carbons prepared from industrial and agricultural by-products or waste materials is an effective adsorbent for the removal of phenol from wastewaters. Cost-effectiveness, availability, and adsorption properties are the main criteria for choosing an adsorbent to remove pollutants. Taking these criteria into consideration, earlier workers used the activated carbon prepared from jute stick¹, sawdust¹, Sarkanda grass⁵, palm tree cobs⁶, rice husk⁷, tamarind nut⁸, Moringa oleifera husk⁹, Coconut coir¹₀, and Salvinia molesta Mitchell¹¹.

A two-stage carbonization-activation process, involving heating the precursor to a particular temperature under nitrogen, followed by exposure to a steam/nitrogen mixture at higher temperature is usually used for the production of activated carbon from various materials. This process requires nitrogen, which is not easily available in many parts of the developing countries like India, and two heating stages, involving high-energy input. Earlier workers¹¹ demonstrated that single-step steam pyrolysis activation produced high quality carbon for wastewater treatment. In the present study we use single-step steam pyrolysis for producing activated carbon because of its advantages such as: (i) It requires no chemical input, (ii) It requires less energy than traditional processes which involve two heating steps, frequently a high temperature, and (iii) Local availability of low-cost carbon by this

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The charge, electrode potential titration method was used to determine carbon. The surface area of the carbon was determined by the N$_2$ BET method, using a Quantasorb surface analyzer (model-05/7) and porosity by mercury porosimeter. The zero point charge, pH$_{ZPC}$ is defined as the pH of the suspension at which the surface charge density $\sigma_0 = 0$. A potentiometric titration method was used to determine $\sigma_0$ (C/cm$^2$) as the function of pH and ionic strength. The $\sigma_0$ was calculated from the titre value using Eq. (1)$^{15}$:

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

where $F$ is the Faraday constant, $A$ is the surface area of the suspension (cm$^2$/L), $C_A$ and $C_B$ are the concentration of acid and base (eq/L) after each addition during the titration and $[OH^-]$ and $[H^+]$ are equivalents of the OH$^-$ and H$^+$ ions bound to the suspension surface (eq/cm$^2$). The point of intersection of the $\sigma_0$ vs pH curve gives pH$_{ZPC}$. The carbon was ignited in a muffle furnace at 100°C for about 3 h to determine the moisture content. The characteristics of the activated carbon are: surface area, 421 m$^2$/g; porosity, 0.51 mL/g; pH$_{ZPC}$, 3.45; apparent density, 1.2 g/mL; anion exchange capacity, 0.83 meq/g; moisture content, 6 per cent; ash content, 2.3 per cent and iodine number 579. FTIR spectra of activated carbon were recorded on a Perkin Elmer FTIR spectrometer (model-180) between 400-4000 cm$^{-1}$. IR spectra of carbon showed the presence of conjugated hydrogen bonded carbonyl group (band at 1613 cm$^{-1}$), as suggested by Hallum and Drushel$^{15}$. The additional peaks at 1750 cm$^{-1}$ ($\omega_{\text{COOH}}$) and 1450 cm$^{-1}$ ($\delta_{\text{OH}}$) indicate the presence of carboxylic (-COOH) groups on the carbon surface$^{16}$.

The equilibrium isotherms were determined by equilibrating 2.0 g/L of activated carbon with 50 mL of phenol solution in a glass stoppered bottle of 100 mL capacity. These were shaken in a temperature controlled water bath shaker (Remi model G-16) at 200 rpm for 4 h. Aliquots of phenol solutions were withdrawn at different preselected reaction time and filtered. The filtrate was analysed for phenol content, using UV-visible spectrophotometer at 270 nm. Once the residual concentration ($C_r$, mg/L) is known, the phenol concentration in the carbon ($q_e$, mg/g) was determined using the mass balance formula $q_e = (C_r - C_0) \cdot \frac{V}{m}$, where $C_0$ is the initial concentration (mg/L), $V$ is the volume of the solution (mL) and $m$ is the mass of the adsorbent (g).

Several contact time experiments were carried out at constant pH to study the effect of the number of variables such as the effect of initial concentration of phenol, temperature, agitation speed and particle size of the adsorbent on adsorption. Effect of pH was studied by adjusting the initial pH of phenol solution to different values between 2 and 10 with dil. NaOH and HCl. The adsorption isotherms at different 10-40°C were obtained at pH 5.5 and fixed adsorbent conc. of 2 g/L, for varying concentration of phenol.
ranging from 50 to 500 mg/L. In these studies the test solutions were agitated until equilibrium had been attained. After attainment of equilibrium, the supernatant liquid was carefully filtered and desorption experiments were carried out using distilled water and hot water. To regenerate the adsorbent the adsorption and desorption process were followed for three cycles. After each desorption cycle the spent adsorbent was washed with distilled water to remove unadsorbed phenol from carbon surface and dried at room temperature. Experiments were carried out in duplicate and the percentage error was < 5.0.

Results and Discussion

Figure 1(a) presents the effect of agitation time on the adsorption of phenol for different initial concentrations. The curves shows strong adsorption during 30 min and equilibrium is established in approx. 4 h. The saturation period of the adsorption is entirely independent of the initial concentration. With an increase in initial concentration of phenol from 50 to 125 mg/L, the uptake of phenol decreases from 94.00 per cent (23.7 mg/g) to 72.16 per cent (45.1 mg/g). The results show that the percentage removal is influenced by the initial concentration. This is because at high initial concentration the ratio of the initial number of moles of phenol to the available surface area is high, hence the fractional adsorption becomes dependent on initial concentration.

Figure 1(b) shows a series of agitation time curves at 10, 20, 30 and 40 °C respectively. The percentage adsorption of phenol decreased from 98.0 per cent (24.5 mg/g) to 86.6 per cent (21.65 mg/g) with increase of temperature from 10 to 40 °C. This indicates that the lower the temperature the greater will be the adsorption. Figure 1(c) shows that the amount of phenol sorbed from solution increases with the lapse of time and reaches the saturation in 4 h. The saturation of adsorption is entirely independent of agitation rate as confirmed by the results presented in Figure 1(c). The maximum adsorption of 96.0 per cent (23.99 mg/g) is observed at an agitation rate of 400 rpm and it decreases to 80.0 per cent (20.0 mg/g) when the agitation rate decreases to 100 rpm. The results indicate that external adsorption of phenol onto carbon is controlled by the degree of agitation. As can be seen from Figure 1(d) the rate of adsorption is influenced by the particle size of carbon. The removal of phenol

Figure 1—The effect of (a) initial concentration, (b) temperature, (c) agitation rate and (d) particle size of the adsorbent on the kinetics of phenol adsorption by activated carbon.
by carbon decreases from 94.4 per cent (23.6 mg/g) to 77.96 per cent (19.49 mg/g) by increasing the particle size from $7.4 \times 10^{-3}$ to $50.8 \times 10^{-3}$ cm. The higher removal with the smaller particle has been attributed to greater access to the internal pores, i.e., shorter path lengths and to the large surface area per unit weight of carbon.

The two important aspects for parameter evaluation of the adsorption study are the kinetic and the equilibria of adsorption. The kinetic constants of phenol adsorption, which would be used to optimize the residual time of industrial wastewaters in activated carbon column, are measured at different experimental variables. For the porous adsorbent studied, sorption kinetics are mainly controlled by three stages including diffusion process\(^7\). The first stage involves the transport of the adsorbate to the external surface of the adsorbent. The second stage is the diffusion of the sorbate into the pores of the adsorbent, then proceeds and it is finally adsorbed into the internal surface of the adsorbent. The last stage is relatively rapid and non-limiting phase. First stage describes external or film mass transfer resistance and second stage is related to the intraparticle mass transfer diffusion model.

Due to the porous nature of the adsorbent, intraparticle diffusion is expected to be the rate limiting step. Hence, applying pore diffusion phenomena the sorption kinetics are modelised, according to the following intraparticle diffusion equation\(^\text{18} \text{[Eq. (2)]}$$

$$
\frac{q_t}{q_e} = 1 - \left(1 - \frac{q_t}{q_e}\right)^2 = \frac{4\pi^2 D t}{2.3 d^2}, \quad \ldots (2)
$$

where $q_t$ and $q_e$ are the adsorbate concentration of the solid at time $t$ and at equilibrium, respectively, $d$ is the particle diam. and $D_s$ is the diffusion coefficient in the solid (m$^2$/s). The diffusion coefficient of adsorption at different variables are determined from the slopes of the straight line plots of $\log[1-(q_t/q_e)^2]$ vs $t$ (Figure 2) and are given in Table 1. The values of $D$ are found to increase with the increasing initial concentration. These results are consistent with previous studies on phenol adsorption onto activated carbon\(^\text{14}\) and metal adsorption onto chitosan\(^\text{15}\). Increasing the solute concentration in the solution seems to reduce the diffusion of solute in the

Figure 2—Urano and Taichikawa plots for the adsorption of phenol on activated carbon at different (a) initial concentration, (b) temperature, (c) agitation rate and (d) particle size of the adsorbent.
boundary layer and to enhance the diffusion in the solid. If intraparticle or pore diffusion is to be the rate limiting step the pore diffusion coefficient should be in the range of \(10^{-12}\) to \(10^{-13}\) m\(^2\)/s. Here the values of \(D_i\) are in the order of \(10^{-13}\) m\(^2\)/s, indicating that the rate limiting step appears to be intraparticle diffusion for phenol-carbon system.

It is evident from the Table 1 that the values of \(D_i\) decrease with rise in solution temperature. The increase in the kinetic energy of the adsorbate species with the rise of solution temperature, due to the increased relative escaping tendency of phenol from solid phase to bulk phase and thus a decrease in adsorption is observed. The decrease in \(D_i\) with temperature indicates the exothermic nature of the adsorption. The decrease in physical force responsible for adsorption with temperature also causes the decrease in adsorption at higher temperatures. The \(D_i\) values range from \(2.820 \times 10^{-13}\) m\(^2\)/s for an agitation rate of 100 rpm to \(4.065 \times 10^{-13}\) m\(^2\)/s for 400 rpm. With change in particle size from \(50.8 \times 10^{-3}\) to 7.4 x \(10^{-3}\) cm the values of \(D_i\) increases from \(1.184 \times 10^{-13}\) to 7.932 x \(10^{-13}\). The increase in the extend of adsorption by increasing the agitation rate and decreasing the particle size further support the above view that intraparticle diffusion controls the adsorption process.

The External mass transfer analysis of phenol during the adsorption process is studied using the mass transfer diffusion model developed by McKay et al.\(^7\).

\[
\ln \left( \frac{C_t}{C_o} \right) = \ln \left( \frac{1}{1 + mk_L} \right) + \left( \frac{1 + mk_L}{mk_L} \right) B_L S_s t
\]

where \(C_t\) is the concentration of solute at time \(t\), \(C_o\) is the initial concentration of the solute, \(m\) is the mass of the adsorbent per unit volume of particle-free solution of solute, \(k_l\) is the Langmuir constant (obtained by multiplying \(Q^\circ\) with \(b\)), \(S_s\) is the specific surface per unit volume of particle-free slurry and \(B_L\) is the mass transfer coefficient. The values of \(B_L\) were determined from the slope and intercepts of the plots.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Diffusion constant</th>
<th>Mass transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D_i) (m(^2)/s)</td>
<td>(r)</td>
</tr>
<tr>
<td>Initial concentration (mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>(2.77 \times 10^{-14})</td>
<td>0.9159</td>
</tr>
<tr>
<td>75</td>
<td>(3.03 \times 10^{-14})</td>
<td>0.9643</td>
</tr>
<tr>
<td>100</td>
<td>(3.38 \times 10^{-14})</td>
<td>0.9975</td>
</tr>
<tr>
<td>125</td>
<td>(4.03 \times 10^{-14})</td>
<td>0.9896</td>
</tr>
<tr>
<td>Temperature (°C)</td>
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<td></td>
</tr>
<tr>
<td>10</td>
<td>(5.29 \times 10^{-13})</td>
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</tr>
<tr>
<td>20</td>
<td>(5.01 \times 10^{-13})</td>
<td>0.9982</td>
</tr>
<tr>
<td>30</td>
<td>(2.77 \times 10^{-13})</td>
<td>0.9159</td>
</tr>
<tr>
<td>40</td>
<td>(2.41 \times 10^{-13})</td>
<td>0.9824</td>
</tr>
<tr>
<td>Particle size (cm)</td>
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<td></td>
</tr>
<tr>
<td>7.4 x (10^{-3})</td>
<td>(7.93 \times 10^{-11})</td>
<td>0.9717</td>
</tr>
<tr>
<td>10.6 x (10^{-3})</td>
<td>(5.33 \times 10^{-11})</td>
<td>0.9642</td>
</tr>
<tr>
<td>14.9 x (10^{-3})</td>
<td>(2.47 \times 10^{-11})</td>
<td>0.9848</td>
</tr>
<tr>
<td>50.8 x (10^{-6})</td>
<td>(1.18 \times 10^{-11})</td>
<td>0.9527</td>
</tr>
<tr>
<td>Agitation rate (rpm)</td>
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<td></td>
</tr>
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<td>(2.12 \times 10^{-13})</td>
<td>0.9901</td>
</tr>
<tr>
<td>200</td>
<td>(2.77 \times 10^{-13})</td>
<td>0.9159</td>
</tr>
<tr>
<td>300</td>
<td>(3.53 \times 10^{-13})</td>
<td>0.9587</td>
</tr>
<tr>
<td>400</td>
<td>(4.07 \times 10^{-13})</td>
<td>0.9369</td>
</tr>
</tbody>
</table>
of $\ln \left( \frac{C}{C_0} \right) - \left[ \frac{1}{1 + mk_b} \right]$ vs $t$, for different experimental variables (Figure 3) using the least squares method. The values of $B_t$ are calculated and are presented in Table 1. From Table 1, it is seen that as expected, the mass transfer coefficient suggests that the velocity of phenol transport is rapid enough to use activated carbon for the treatment of water and wastewater containing phenol. The $B_t$ values range from $4.395 \times 10^6$ cm/s at 50 mg/L to $2.588 \times 10^6$ cm/s at 125 mg/L at different initial phenol concentrations. It is found that increasing the initial phenol concentration results in a decrease in the external mass transfer coefficient.

As the Table 1 shows, the value of $B_t$ decreases from $5.467 \times 10^6$ at 10°C to $3.888 \times 10^6$ cm/s at 40°C, which suggests that sorption is thus faster at lower temperatures. The energy of activation is determined from the slope of the Arrhenius plot of $\ln B_t$ vs $1/T$ (Figure not shown) and is found to be $-7.95$ kJ/mol. The negative value of activation energy suggests that a feasible process option would comprise adsorbing the phenol onto activated carbon at relatively low temperature and then desorbing it at a higher temperature to regenerate the activated carbon. The findings of the present investigation also indicate that mass transfer of phenol is one of the parameters deciding the agit ation speed and smaller particle size of the sorbent. The results are similar to those reported for the adsorption of phenol by Salvinia molesta Mitchell-based activated carbon. The effect of particle size and agitation speed on mass transfer coefficient is possibly more complex than originally suggested in Kolmogorov's theory due to the relative velocity between fluid and particle in the agitating system. According to the Kolmogorov’s theory, when the agitation speed is very high the shear force on the boundary layer is greater which effectively reduce the thickness of the boundary film. Thus the resistance to film transfer is correspondingly reduced. The trend in $B_t$ values in Table 1 supports this concept. Smaller particles have a larger external surface area available for adsorption per unit mass of adsorbent than larger particles and one could anticipate higher $B_t$ values. The assumption that large surface area presented by smaller particles results in a lower driving force per unit area, remain very plausible.

Earlier studies have indicated that solution pH is an important parameter affecting the sorption of phenol on activated carbon surface. In general, agricultural or industrial waste based activated carbons carry a

![McKay et al. plots for the adsorption of phenol on activated carbon at different initial concentration, temperature, agitation rate and particle size of the adsorbent](image-url)
surface charge, which is essentially dependent on pH of the solution. Phenol adsorption by activated carbon as a function of solution pH is studied (Figure 4). The uptake is small with low pH range and gradually increases up to pH 5.5, where maximum removal of 99 and 92 per cent is observed from an initial concentration of 25 and 50 mg/L, respectively. At pH range greater than 5.5 the adsorption capacity decreases to a minimum value at pH 10.0. Various reasons can explain the behaviour of the adsorbent in phenol adsorption relative to pH. The pH<sub>pe</sub> of the carbon is found to be 3.45. Below this pH carbon surface is positively charged and above the surface is negative. At lower pH, most of the phenol exists in protonated form and surface of the carbon is also positive. Positively charged carbon surface repel positively charged protonated phenol and results in the reduction of phenol adsorption. With increase in pH the molecular form of phenol persists in the medium, leading to the enhancement of phenol adsorption. It is also observed that phenol molecules are easily adsorbed compared to negative phenolate anions and protonated species, as shown previously by others<sup>29</sup>. Phenol adsorption on carbon usually occurs through a donor-acceptor complex mechanism involving carbonyl oxygen group on the carbon surface acting as the electron donor and aromatic ring of the phenol as the acceptor. At high pH values, the contribution of OH<sup>-</sup> ions far exceed that of the phenolate anion and hence occupied on the carbon surface leaving phenolate anion unbound. The increased solubility and increased hindrance to the diffusion of the phenol ions at higher pH may also lead to a decrease in phenol adsorption.

Adsorption isotherm experiments were carried out to evaluate the potential of the sorbent for commercial application. Since solution temperature has significant effect on adsorption equilibrium, the phenol removal capacity of activated carbon was determined by adsorption isotherms obtained at 10, 20, 30, and 40°C, respectively. The shape of the isotherm gives an indication whether the adsorption is favorable or not. The adsorption isotherms (q<sub>e</sub> vs C<sub>e</sub>) are regular, positive and concave to the concentration axis (Figure 5). Initially the adsorption is quite rapid, which is followed by a slow approach to equilibrium at high phenol concentration. These results indicate the utility of the adsorbent for the removal of phenol from wastewaters in a wide concentration range. According to the slope of the initial position of the curves, isotherm may be classified as H-type of the Giles classification<sup>21</sup>. This suggests that activated carbon has high affinity for phenol and there is no competition from the solvent for sorption sites. It is also observed from the Figure 5 that isotherms tend to define a plateau at higher equilibrium concentration. Isotherms belonging to subgroup II of the Giles classification. According to Giles <i>et al.</i><sup>23</sup>, saturation of the surface by phenol molecules seems to be reached that is to say, a complete monolayer covering of phenol on carbon is possible under used experimental conditions.
The isotherm data at different temperatures were processed using the Langmuir and Freundlich isotherm models. The Langmuir isotherm is based upon an assumption of monolayer adsorption onto a surface containing finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The linear form of the Langmuir equation is represented in Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} \frac{C_e}{q_e}$$  \hspace{1cm} (4)

where \(C_e\) and \(q_e\) are the equilibrium adsorbate concentration in liquid and solid phase, respectively, \(Q^0\) and \(b\) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The Freundlich isotherm model assumes heterogeneous surface energies, in which energy term in the Langmuir equation varies as a function of the surface coverage due to variation in the heat of adsorption. The linear form of the Freundlich isotherm equation is represented by Eq. (5):

$$\log q_e = \frac{1}{n} \log C_e + \log K_F$$  \hspace{1cm} (5)

where \(K_F\) and \(1/n\) are Freundlich constants related to adsorption capacity and intensity of adsorption respectively.

The plots of \(C_e/q_e\) vs \(C_e\) gives straight lines at each temperature showing the applicability of Langmuir isotherm (Figure 6). The Langmuir isotherm constants were computed according to the least squares fitting method, using experimental \(q_e\) and \(C_e\) values. The data are presented in Table 2. At 30°C, coconut husk based activated carbon adsorbed 146.16 mg/g phenol which is found to be better adsorbent than the adsorbent such as local activated carbon (22.0 mg/g), fibrous activated carbon (25.5 mg/g), E Merck activated carbon (35.5 mg/g), waste fertilizer carbon (35.5 mg/g), polymeric adsorbent (15.0 mg/g), bagasse fly ash (17.0 mg/g), granular activated carbon (20.0 mg/g) and salvinia molesta Mitchell-based activated carbon (115.06 mg/g). The data from the Table 2 show that the lower temperature promotes adsorption of phenol, which has stronger coulombic interaction with the adsorbent and adsorbate. As the temperature increased from 10 to 40°C, the \(Q^0\) of phenol lost more than 22 per cent of its adsorption. The essential characteristics of the Langmuir isotherm can be expressed in terms of a
dimensionless constant separation factor or equilibrium factor, \( R_L \), which is defined by
\[
R_L = \frac{I}{1 + bC_0}
\]
where \( b \) is the Langmuir constant and \( C_0 \) is the initial concentration of sorbate. \( R_L \) values obtained (data not shown) at different concentrations and temperatures are between 0 and 1 indicates favourable adsorption of phenol on activated carbon.

The linear plots of \( \log q_e \) vs \( \log C_c \) (Figure 7) show that adsorption of phenol onto carbon also follows Freundlich isotherm model. The values of \( K_F \) and \( 1/n \) (Table 2) at 30°C were found to be 8.11 and 0.5177, respectively. Values of \( 0 < 1/n < 1.0 \) show the favorability of adsorption on activated carbon\(^a\). The ultimate adsorption capacity of activated carbon can be calculated by substituting the required equilibrium concentration in the Freundlich equation. Thus for an equilibrium conc. of 1 mg/L of phenol, 1 g of the activated carbon can remove 8.11 mg phenol at 30°C. For phenol adsorption at 30°C on peat\(^b\), commercial activated carbon, coal fly ash\(^c\) and organoclay\(^d\), the values of \( K_F \) were reported to be 0.46, 0.22, 0.31 and 0.50 mg/g, respectively, which shows that adsorption capacity of coconut husk based activated carbon is very high.

To judge the fitting of the above two models the adsorption data on activated carbon, a normalized deviation (\( \Delta g \)%) was calculated by the Eq. (6).

\[
\Delta g(\text{percent}) = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{q_{e,i}^{\text{calc}} - q_{e,i}^{\text{exp}}}{q_{e,i}^{\text{exp}}} \right), \quad \text{(6)}
\]

where the superscripts 'calc' and 'exp' are the calculated and experimental values. \( N \) is the number of measurements. The values of \( \Delta g \) (per cent) are listed in Table 2. From the results it was found that \( \Delta g \) obtained from Langmuir equation is smaller (\( \Delta g = 2.1 - 5.9 \) per cent) and it is somewhat better than of the Freundlich plot (\( \Delta g = 2.4 - 18.8 \) per cent).

Thermodynamic parameters were calculated from the variations of the thermodynamic distribution coefficient, \( K_o \) with change in temperature. \( K_o \) for the phenol adsorption was determined by the procedure described by Khan and Singh\(^e\) by plotting \( \ln q/C_e \) vs \( q_e \) and extrapolating to zero \( q_e \) (Figure 8). The standard free energy change \( AG^o \) for the interaction of activated carbon with phenol was calculated as \( AG^o = -RT\ln K_o \). From the variation of \( \ln K_o \) with temperature, the standard enthalpy, \( AH^o \) and entropy \( AS^o \) changes were computed using Eq. (7).

\[
\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \text{(7)}
\]

The plot of \( \ln K_o \) vs \( 1/T \) was found to be linear. The values of \( \Delta H^o \) and \( \Delta S^o \) were obtained from the slope and intercept of the plot. The negative values of \( \Delta S^o \) for phenol removal indicate the feasibility of the process and spontaneous nature of the adsorption. The negative value of \( \Delta H^o \) (-30.73 kJ/mol) indicates that phenol-activated carbon interaction is exothermic. The negative value of \( \Delta S^o \) (-99.54 kJ/K mol) indicates that the adsorption is spontaneous process.

---

\(1\) = 20°C, 30°C, 40°C

\(2\) = 10°C, 20°C, 30°C, 40°C

\(3\) = 2 g/L, 2.5 g/L

\(4\) = 200 rpm, 250 rpm

\(5\) = pH 5.5, pH 6.5

\(6\) = Agitation time 4 h, Agitation speed 200 rpm

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**Figure 7**—Freundlich adsorption isotherm for phenol on activated carbon

**Figure 8**—Plots of \( \ln (q/C_e) \) vs \( q_e \) for the adsorption of phenol on activated carbon
J/(mol K) indicates a greater order of reaction during the adsorption of phenol onto activated carbon and also reflects the affinity of the adsorbent material for phenol.

Information concerning the magnitude of the heat of adsorption and its variation with surface coverage can provide useful information concerning the nature of the surface and the adsorbed molecules. The heat of adsorption determined at constant amount of sorbate adsorbed is known as the isosteric heat of adsorption (\( \Delta H_x \)) and is calculated using the Clausius-Clapeyron equation.

\[
\frac{d(\ln C_e)}{dT} = \frac{\Delta H_x}{RT^2}.
\]

For this purpose the values of \( C_e \) at constant amount of phenol adsorbed are obtained from the adsorption isotherm data at different temperatures. \( \Delta H_x \) is calculated from the plot of \( \ln C_e \) vs \( 1/T \) for different amount of phenol adsorption (Figure 9). \( \Delta H_x \) values are shown in Figure 10 as a function of the amount of phenol adsorbed. As shown in Figure 10 the isosteric heat of adsorption is varied with the surface loading indicating the activated carbon used as an energetically heterogeneous surface.

Experiments were carried out to investigate whether complete phenol desorption was possible from carbon loaded with phenol. Studies in this direction have been carried out in detail with mineral acids, salts, bases, methanol, distilled water (30°C) and hot water (40-70°C). Hot water at 60°C has been found to be the most effective desorbing agent. Therefore, the process of phenol adsorption on carbon is reversible but slow at 30°C. Due to high adsorbability of phenol at lower temperature onto carbon nearly complete desorption of phenol from used carbon may require high temperature. Only 30.7 per cent desorption took place in distilled water, whereas 99.1 per cent desorption was observed at hot water (Table 3). This is an evidence of physical and exothermic nature of adsorption. After two cycles, the adsorption capacity of carbon decreased from 92.7 to 83.3 per cent, while recovery of phenol decreased from 99.1 in the first cycle to 92.2 per cent in the third cycle. These results show that the spent carbon can be effectively regenerated for further use by hot water.

**Conclusions**

The use of coconut husk based steam-pyrolysed activated carbon as low cost adsorbent for the removal of phenol from aqueous solutions was studied. The carbon seems to be very efficient and
economic for the removal of phenol from wastewaters. About 92–99 per cent phenol removal is possible from synthetic aqueous phenol solutions containing 25-50 mg/L. The maximum removal was observed at pH 5.5. The applicability of external mass transfer diffusion and intraparticular mass transfer diffusion models has been checked and kinetic parameters as a function of initial concentration of sorbate, temperature, agitation speed, and particle size of the adsorbent were calculated. Adsorption equilibrium data follows, both Langmuir and Freundlich isotherm models. Temperature study reveals that adsorption of phenol is exothermic in nature. The desorption data show that spent adsorbent can be regenerated for further use by hot water treatment. The raw material, coconut husk used for preparing activated carbon is available almost free of cost and involving only electrical and chemical (HCl) charges. Coconut husk based activated carbon is likely to be considerably cheaper than conventional activated carbon.

References