Removal of phenol from wastewater using sawdust, polymerized sawdust and sawdust carbon

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The adsorption of phenol on sawdust, polymerized sawdust and sawdust carbon was investigated to assess the possible use of these adsorbents for the processing of phenolic wastewater. The influence of various factors such as initial concentration, agitation speed, and amount of adsorbent, temperature and pH on the adsorption capacity has been studied. The percentage removal of phenol is observed to increase, with the increase in initial concentration of phenol. With increase in temperature the adsorption of phenol decreases, indicating exothermic nature of the reaction. Adsorption isothermal data could be interpreted by the Langmuir and Freundlich equations. Kinetic data has been studied, using pseudo-second order equation for understanding the reaction mechanism. Thermodynamic parameters such as $\Delta G$, $\Delta H$ and $\Delta S$ for the adsorption process were calculated.

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Discharge of organic pollutants into water contaminates the environment. Phenol and its compounds are the ones that are present in the wastewater as discharge from oil refineries, coke plants and phenolic resin plants. Because of their high volatility and water solubility, phenol and its compounds impart taste and odour problems to drinking water supplies even at the part per billion levels. Phenol is protoplasmic poison, so they damage all kinds of cells. Hence there is a need to remove the phenolic waste effluent from oil refineries, coke plants and phenolic resin plants before discharging it into the natural water streams.

At very low concentration (less than 0.1 mol/L), phenol can be digested by biological treatment, whereas at higher concentrations (more than 20 mol/L), solvent extraction is being used. Adsorption can be effective for the treatment of phenols at the intermediate concentrations. The adsorption process can be pictured as one in which molecules of adsorbate are held on the solid surface of adsorbent by chemical and physical bonding. Activated carbon (granular and powdered form) is the most widely used adsorbent for this process. It has a good capacity for the adsorption of many organic molecules. In spite of this it suffers from few disadvantages. Activated carbon is quite expensive and its regeneration produces additional effluent and results in considerable loss (10-15%) of the adsorbent. This has let many workers to search for cheaper substitutes. Bottom ash, flyash, flyash-wallastonite, lignite, peat, soil, wallastonite, wallastonite-china clay 1:1 and sawdust carbon are some new adsorbents, which have been tried with varying success.

The study of adsorption kinetics in wastewater treatment is significant, as it provides valuable insights into the reaction pathways and mechanisms of sorption reaction. The pseudo-first order rate equation of Lagergreen has been widely applied since 1898. Numerous studies report pseudo-first order Lagergreen kinetics for the sorption of organic pollutants on 1:1 ratio of flyash to coal and water hyacinth roots. Adsorption of phenol on a flyash and impregnated flyash has also been studied. Adsorption kinetics data can be explained satisfactorily by using pseudo-first order Lagergreen equation. Ho Y S developed a pseudo-second order kinetic expression for the sorption system of divalent metal ions with sphagnum moss peat. It has also been applied to the sorption system of lead ions. The pseudo-second order rate equation of Ho Y S has also been successfully applied to sorption systems, such as, organic dyes with peat, wood and pith.

In the present investigations, it has been shown, that, out of various non-conventional adsorbents, sawdust, polymerized sawdust and sawdust carbon have good adsorption capacity for the phenolic waste...
from aqueous solution. This work reports some results of batch and kinetic studies on the removal of phenol from aqueous solution by adsorption technique, using sawdust and modified sawdust as adsorbents. The effect of various parameters like initial concentration, amount of adsorbent, agitation speed, pH and temperature has been studied. Pseudo-second order rate equation is also applied to the present study to understand adsorption mechanism.

**Experimental Procedure**

**Material**
The saguan sawdust used for the preparation of adsorbents was collected from a local timber industry (Thane timber mark, Thane, Maharashtra, India). To prevent colour leaching and to remove the water-soluble impurities, it was boiled with distilled water and supernatant solution was poured off. This process was repeated several times, until the clear supernatant solution is obtained. Finally, the washed adsorbent was dried in an oven at 80°C. The sawdust [SD] prepared in this way is used as one of the adsorbents, after sieving through 100-mesh sieve and for preparation of other two adsorbents.

To improve the physical characteristics of the adsorbent, polymerization of sawdust is carried out\(^\text{23}\). Two parts of this sawdust powder are treated with 20 parts of 0.2 N sulphuric acid and 5 parts of 39% formaldehyde. It was kept in an oven at 50°C for 6 h with occasional stirring. The product—polymerized sawdust [PSD] was washed several times with distilled water and dried at 60°C and then powdered and sieved through 100-mesh size.

Sawdust carbon [SDC] was prepared by incinerating the SD at 700°C for one hour in oxygen deficient atmosphere. The condition is achieved by filling the SD in a steel container with a tight lid, allowing only limited presence of air, trapped in the material being activated. The carbon obtained, is washed several times with distilled water to remove the water-soluble impurities. The physical and chemical characterization of SD, PSD and SDC is carried out using standard methods\(^\text{24}\) and results are given in Table 1. Finally the adsorbents were stored in a desiccator for further use.

The phenol used for adsorption study was procured from LOBA Chemie Private Ltd., India and was 99.5% pure. The reagents used for detection of phenol \textit{i.e.} 4-aminoantipyrine and potassium ferrocynide are supplied by S.D. Fine-Chem. Ltd., India and were 98% pure. The pH of the solution is adjusted by using phosphate buffer. All other chemicals used are of AR grade. Double distilled water is used for the dilution of solution.

**Batch adsorption studies**
The adsorption isotherm study was performed by batch adsorption technique. A series of 250 mL Erlemeyer stoppered flasks were employed, each having 50 mL of aqueous solution of phenol of various concentration (25-800mg/L) at natural pH and temperature. 100mg of adsorbent was then added into each flask and agitated for 24 h. Preliminary investigations showed, that, equilibrium is attained in 6-8 h, beyond which the uptake of phenol remained constant. When equilibrium is attained the contents of the flasks were centrifuged at 1000 rpm. The supernatant solution obtained on centrifugation was analyzed for phenol concentration. The phenol estimation was done spectrophotometrically by the 4-aminoantipyrine method\(^\text{25}\), using a GBC cintra 5 spectrophotometer. The pH of the adsorbate was determined using a pH meter Equivitronics model Eq-610 with combined glass electrode.

The adsorption equilibrium data obtained from the various systems investigated, were applied to the Langmuir and Freundlich equations. The general forms of Langmuir and Freundlich equations are as follows\(^\text{26}\).

\[
\ln q_e = \ln K_f + 1/n \ln C_e \quad \text{... (1)}
\]

\[
C_e/q_e = 1/Q^o + C_e/Q^o \quad \text{... (2)}
\]

where \(q_e\) is the amount of solute adsorbed per unit weight of adsorbent (SD, PSD and SDC), \(C_e\) is the solute phase concentration, and \(Q^o\) is the solid phase concentration corresponding to complete coverage of available adsorption sites. The value of \(K_f\) can be used as an alternative measure of adsorption capacity, while \(1/n\) determines the adsorption intensity, and \(b\)
signifies the equilibrium constant of the adsorption process.

**Kinetic studies**

Kinetic study of adsorption of phenol on SD, PSD and SDC was carried out in a glass jacketed baffled vessel. In each experiment, 500 mL aqueous solution of adsorbate of known concentration was taken in a vessel and stirred by using an eight-blade glass stirrer. The speed of the stirrer was monitored by a digital inbuilt speed indicator. Temperature of the system was controlled (±2°C) by means of thermostatic water bath in which the reactor vessel is immersed. A weighed amount of adsorbent was then added and the kinetic measurements were started. The kinetics of adsorption was carried out at various predetermined time durations by withdrawing the required aliquot from the reactor vessel.

To investigate the mechanism of adsorption, the adsorption kinetic data is tested by using pseudo-second order model18:

\[ \frac{t}{q_e} = \frac{1}{Kq_e^2} + \frac{1}{q_e} \] \hspace{1cm} \ldots (3)

\[ h = Kq_e^2 \] \hspace{1cm} \ldots (4)

where \( q_e \) = amount adsorbed at equilibrium, \( t \) = time of kinetic study, \( K \) = pseudo-second order rate constant and \( h \) = initial adsorption capacity.

The straight-line plot of \( t/q_e \) against \( t \) gives the applicability of the equation. The value of pseudo-second order rate constants like initial adsorption capacity \( (h) \), equilibrium concentration \( (q_e) \) and correlation coefficients \( (r) \) for phenol, under variable conditions were calculated from the data represented in these plots. The kinetics of solute transport from solution phase to the surface of adsorbent particles is also controlled by film or external diffusion. The film or surface mass transfer is one of rate-controlling parameters and is a function of surface physical properties. The contact time data can be effectively used to test whether the intra-particle diffusion is a rate-controlling step.

Linearisation of the data is obtained by plotting the amount adsorbed per unit weight of adsorbent \( (q) \) versus \( t^{1/2} \), as described by the equation,

\[ q = K_p t^{1/2} \] \hspace{1cm} \ldots (5)

where \( K_p \) is the intraparticle diffusion rate constant. The adsorption rates for intraparticle diffusion at different initial concentrations of the systems were calculated from the slope of the linear portion of the respective plot with unit mg/g min\(^{0.5}\). The reaction rate calculated from this equation is not true, but it is the relative rate which is useful for comparative purposes. The values of free energy change, enthalpy change and entropy change have been calculated, using standard equations.

**Results and Discussion**

**Adsorption isotherm study**

Adsorption isotherms of phenol, on SD, PSD and SDC were obtained by stirring the various concentrations of phenol (25-800 mg/L) with 0.1 g of adsorbent. The adsorption isotherms thus obtained, are shown in Fig.1. From the nature of the curve these isotherms can be classified as L type according to the Gile’s classification system. From Fig.1 it can be seen that amount of phenol adsorbed increases with increase in concentration and after particular concentration it remains more or less constant.

Freundlich and Langmuir adsorption isotherms of phenol on SD, PSD and SDC follow both Freundlich and Langmuir isotherm models with regression constant greater than 0.90. The values of Freundlich and Langmuir constants are listed in Table 2. The adsorption capacity \( K_f \) and the intensity of adsorption \( n \), which is calculated from intercept, and the slope of Freundlich isotherm plot is
higher for PSD-phenol and SDC-phenol system than SD-phenol. The value of $Q^\circ$ (i.e. maximum uptake) is significantly higher for PSD-phenol system than SD-phenol and SDC-phenol systems.

**Effect of pH**

The effect of pH on adsorption of phenol on SD, PSD and SDC was studied by changing the pH of the system from 2 to 10 and the results are shown in Fig. 4. From Fig. 4, it is found that the pH of the solution is an important controlling parameter in this adsorption process. The pH of the phenol solution was adjusted by using 0.05M phosphate buffer solution. With the increase in pH of the solution, the extent of removal was found to range from 14.82 to 23.65 %, 22.75 to 31.35 % and 26.06 to 36.50 % for SD, PSD and SDC respectively. The maximum removal occurs at a pH around 6.0.

As the pH decreases, the surface of the sawdust as well as phenol molecules gets protonated. Due to this, there is formation of positive charge on both the adsorbent/adsorbate systems. This results in the net reduction of phenol adsorption. With the increase of pH from 5 to 7, molecular form of phenol persists in the medium and surface protonation is minimum, leading to the enhancement of phenol adsorption. Similar results were obtained by Achari and Anirudhan, who studied the adsorption of phenol on Jackwood sawdust.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q^\circ$ (mg/g)</td>
<td>$b$</td>
</tr>
<tr>
<td>SD</td>
<td>146.25</td>
<td>$4.0160 \times 10^{-3}$</td>
</tr>
<tr>
<td>PSD</td>
<td>185.18</td>
<td>$6.5831 \times 10^{-3}$</td>
</tr>
<tr>
<td>SDC</td>
<td>138.88</td>
<td>$7.7142 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Kinetic study

Effect of contact time and initial concentration

The contact time experiment of adsorption of phenol on SD, PSD and SDC is carried out by agitating fixed amount of phenol with 0.1 g of adsorbent for various time intervals. From this study, it is found that amount of phenol adsorbed, increases with increase in time and after a time interval of 80 min, it remains more or less constant. From the experimental data, it is also found that more or less 90% of adsorption of phenol on SD, PSD and SDC has occurred within first 30 min. Hence, for further kinetic study an equilibrium time of 80 min was selected.

The effect of initial concentration of phenol on adsorption is studied at three different concentrations (i.e. 50, 100 and 150 mg/L). The effect of initial concentration of phenol on adsorption on SD is shown in Fig. 5. Similar trends were obtained in case of PSD and SDC. From Fig. 5 it is seen, that, adsorption of phenol on SD, PSD and SDC is found to be concentration dependent. The removal of phenol increases with increase in initial concentration where as the percentage removal decreases. This is in agreement with the finding, that, the rate of uptake of adsorbate is found to increase non-linearly with increasing concentration of solute\(^3\). The values of various pseudo-second order rate constants are listed in Table 3. From Table 3, it is observed, that, the experimental data obtained with varying concentrations of the phenol follows pseudo-second order equation with regression constant greater than 0.98. The initial adsorption capacity of phenol on SD, PSD and SDC increases with increase in initial concentration. The values of intra-particle diffusion rate constants calculated using Eq. (5) are listed in Table 4 and also support the results obtained.

Effect of agitation speed and mass of adsorbent

Effect of agitation speed and mass of the adsorbent were studied by changing the agitation speeds of the system from 300 to 800 rpm. The effect of mass of adsorbent is studied by changing the mass of adsorbent from 0.5 to 1.5 g. The results obtained for adsorption of phenol on SD at different agitation speeds and mass of adsorbent is shown in Figs 6 and 7. Similar trends were obtained in case of PSD and SDC. From Fig. 6, it is seen that the amount of phenol adsorbed, increased up to 20% with increase in agitation speed. This is because with increase in agitation speed, boundary layer resistance to mass transfer in the bulk decreases and increases the driving force of phenol towards adsorbent\(^3\). Where as the amount of phenol adsorbed, decreases upto 20% as shown in Fig. 7 with increase in adsorbent dose. This may be due to the aggregation of adsorbent particle at higher concentration. This aggregation leads to decrease in the surface area, available for adsorption.

![Fig. 5—Effect of initial concentration on adsorption of phenol on SD](image)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Conc. (mg/L)</th>
<th>(K) (g/mg min(^0.5))</th>
<th>(q_e) (mg/g)</th>
<th>(h) (mg/g min(^0.5))</th>
<th>(r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD</td>
<td>50</td>
<td>0.00124</td>
<td>14.16</td>
<td>2.5</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.0063</td>
<td>28.11</td>
<td>5.0</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.0073</td>
<td>45.11</td>
<td>15.0</td>
<td>0.982</td>
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<tr>
<td>PSD</td>
<td>50</td>
<td>0.0013</td>
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<td>0.0030</td>
<td>40.59</td>
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<tr>
<td></td>
<td>150</td>
<td>0.0061</td>
<td>56.82</td>
<td>20.0</td>
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<td>SDC</td>
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<td>23.89</td>
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<td>40.01</td>
<td>6.66</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.0166</td>
<td>42.60</td>
<td>30.30</td>
<td>0.999</td>
</tr>
</tbody>
</table>

![Table 3—Pseudo-second order kinetic constants for adsorption of phenol on SD, PSD and SDC at different concentrations](table)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial conc. (mg/L)</th>
<th>(K_p) (mg/g min(^0.5))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD</td>
<td>50</td>
<td>2.398</td>
</tr>
<tr>
<td></td>
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<td>3.448</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>4.199</td>
</tr>
<tr>
<td>PSD</td>
<td>50</td>
<td>2.750</td>
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<tr>
<td></td>
<td>100</td>
<td>3.000</td>
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<tr>
<td></td>
<td>150</td>
<td>4.250</td>
</tr>
<tr>
<td>SDC</td>
<td>50</td>
<td>2.800</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3.600</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>3.830</td>
</tr>
</tbody>
</table>

![Table 4—Intraparticle diffusion rate constants for adsorption of phenol on SD, PSD and SDC at different initial concentration](table)
adsorption, hence, amount of phenol adsorbed decreases with increase in amount of adsorbent. Similar types of results were reported in earlier study on adsorption of various adsorbates on SD surface\textsuperscript{32}.

**Effect of temperature**

Temperature study on adsorption of phenol on sawdust, polymerized sawdust and sawdust carbon is carried out at three different temperatures, \textit{i.e.} 30, 45 and 60\textdegree C. The effect of temperature on SD/phenol system is shown in Fig. 8. Similar trends were obtained with PSD/phenol and SDC/phenol system. From Fig. 8, it is observed that the adsorption of phenol decreases with increase in temperature. The adsorption of phenol on SD, PSD and SDC is found to decrease from 25.48 to 20.94\%, 34.84 to 18.7\% and 35 to 25.85\% respectively, with increase in temperature from 30-60\textdegree C. This suggests that the process is exothermic. Hence, the lower temperature is more favourable for the adsorption of phenol on all the three adsorbents. The decrease in adsorption with increase in temperature, is partly due to the weakening of the attractive force between the phenol and adsorbent, and partly due to the enhancement of thermal energies of the adsorbate, thus, making the attractive force between adsorbent and phenol insufficient to retain the adsorbed molecules at the binding sites\textsuperscript{29}. The kinetic data obtained at different temperatures follow pseudo-second order equation and are listed in Table 5. From these values it is seen that the initial adsorption capacity decreases with increase in temperature. Various thermodynamic constants\textsuperscript{33,34} calculated are listed in Table 6. The free energy of the system increases with increase in

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temp. (\textdegree C)</th>
<th>K (g/mg min)</th>
<th>q&lt;sub&gt;e&lt;/sub&gt; (mg/g)</th>
<th>h (mg/g min)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD</td>
<td>30</td>
<td>0.0063</td>
<td>28.11</td>
<td>5.0</td>
<td>0.999</td>
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<tr>
<td></td>
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<td>0.0039</td>
<td>26.14</td>
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<td>60</td>
<td>0.0033</td>
<td>24.32</td>
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<tr>
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<td>0.997</td>
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<tr>
<td>SDC</td>
<td>30</td>
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<td>40.61</td>
<td>6.6</td>
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<td></td>
<td>45</td>
<td>0.0019</td>
<td>36.22</td>
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<td>60</td>
<td>0.0015</td>
<td>34.27</td>
<td>1.7</td>
<td>0.941</td>
</tr>
</tbody>
</table>

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Effect of agitation speed on adsorption of phenol on SD}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{Effect of mass of adsorbent on adsorption of phenol on SD}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{Effect of temperature on adsorption of phenol on SD}
\end{figure}
temperature decreasing the spontaneity of the process. The value of enthalpy change and entropy change suggests, that the process is exothermic in nature.

Conclusion
It may be inferred from the above observation that: (i) sawdust, polymerized sawdust and sawdust carbon shows good adsorption capacity to remove phenol from wastewater, (ii) the adsorption of phenol on SD, PSD and SDC was found to be dependent on temperature and pH of the solution, (iii) the amount of phenol adsorbed on PSD and SDC is higher than on SD, (iv) adsorption capacity of phenol decreases with increase in temperature, (v) the kinetics of adsorption of phenol on SD, PSD and SDC can be explained satisfactorily using pseudo-second order model with regression coefficient greater than 0.98, and (vi) intra-particle diffusion is also found to be one of the rate-controlling steps.

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