Column Removal of Phenol and Chlorophenol Using a Commercial Activated Carbon

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ABSTRACT

The adsorption of phenol and 2-chlorophenol from aqueous solution on a commercial activated carbon was studied using a fixed bed column. A glass column (20 x 1.4 cm) was packed with the activated carbon on a glass wool support. The fixed bed column of activated carbon was prepared by a dry packing technique. In order to yield different bed heights 1.90, 3.40 and 4.50g of activated carbon was added to the glass column to produce bed heights of 3, 6 and 9 cm. the effect of bed height, various concentrations (100,150 and 200mg/l) and flow rate (2, 3 and 4ml/min) were determined. The absorbance was measured with a UV –Visible spectrophotometer. The value for bed capacity of the column was compared to the equilibrium capacity for the batch adsorption. The experimental data were correlated using the bed depth service time (BDST) model. The critical bed depth increased with increasing phenol and chlorophenol concentrations. These results correlate well with the observed performance in the breakthrough curves. An increase in chlorophenol concentration increased the rate constant (Kc) of phenol 0.019, 0.031, 0.666 and chlorophenol, 0.022, 0.034 and 0.089 Lmg^-1hr^-1 respectively. The column adsorption capacity (Nc) using the BDST model also increased with an increase in initial phenol concentrations as follows, 76.6, 99.9, 126.4mg/g and chlorophenol 78.6, 109.8 and 153.2mg/g respectively. The critical bed depth (Dc) increased with an increase in initial phenol concentration. In all parameters determined chlorophenol had better adsorption than phenol.

Key words: Activated carbon, Phenol, Chlorophenol, Column removal.

Introduction

There has been an intense interest in using activated carbon for the adsorption of many potential pollutants from aqueous solutions. Removal of phenolic pollutants from wastewater is necessary because of its toxicity and slightly pungent odour. In the seventies of the last century, the combined global production of phenol and chlorophenols approached 200 million Kg [4], which has been manufactured in paper, textiles, pharmaceuticals and fertilizer industries. These compounds usually cannot be totally utilised and eventually will be discharged out from industrial processes. Hence a proper waste water treatment method or strategy is needed to tackle industrial effluents. Adsorption has gained increasing popularity in recent years as a unit operation for removing pollutants from effluents [22,29], because the process produces a high quality treated effluent which can meet stringent environmental emission standards. In the search for potential low-cost sorbents for pollutant attenuation in aqueous medium, a number of materials have been investigated for their ability for pollutant attenuation. Some of these sorbets are; (cassava waste biomass, tea factory waste, fluted pumpkin stem waste and water spinach [ 17,9,27].

Although batch systems produce interesting information in the form of isotherms, adsorption columns, simulate commercial and industrial adsorbers and real world environmental solutions. The

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Advantages of a fixed bed system include little operator attention, easy inspection and cleaning for regeneration of adsorbent, and fewer instances of adsorbent particles in the effluent. Disadvantages include the large physical area needed to operate the fixed bed and higher capital investment.

The objective of the current investigation was to examine the sorption of phenol on to a commercial activated carbon (AR) (Sifico Ltd., Surrey, England) bought from a scientific store in Port Harcourt, Nigeria in a downward flow packed bed column arrangement. The effects of design parameters, such as bed height, initial phenol and chlorophenol concentration and flow rate have been investigated. The breakthrough profiles for the sorption of phenol and chlorophenol were analyzed using bed depth service time (BDST) model.

Materials and methods

The commercial activated carbon (AR) (Sifico Ltd., Surrey, England) was bought from a scientific store in Port Harcourt, Nigeria.

Column Sorption Studies:

A glass column (20 x 1.4 cm) was packed with the activated carbon on a glass wool support. The fixed bed column of activated carbon was prepared by a dry packing technique [24]. In order to yield different bed heights 1.90, 3.40 and 4.50 g of activated carbon was added to the glass column to produce bed heights of 3, 6 and 9 cm respectively. The bed was flushed several times with distilled water to ensure a close packing of the activated carbon particles to avoid cracks, channels or void during the transit of the waste water through the column. The bed was allowed to drain completely before the loading of the activated carbon bed with the sorbate. The phenol solution was fed through the bed in a downward flow under gravity. The effluent from the activated carbon bed was collected at fixed volume (10 ml) and the time of each collection noted. The loading of the carbon bed continued until the phenol and chlorophenol concentration in the effluent was 90% of the influent concentration which was regarded as the exhaustion point. Experiments were carried out at varying concentration (100, 150 and 200 mg/l) and flow rate (2, 3 and 4 ml/min) respectively.

Analysis of Column Data:

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of an adsorption column. The breakthrough behaviour shows the loading behaviour of phenol to be removed from solution at a fixed bed usually expressed in terms of adsorbed phenol and chlorophenol concentration (C_{ad}) = inlet phenol and chlorophenol concentration (C_{0}) – outlet phenol and chlorophenol concentration (C_{t}) or normalized concentration defined as the ratio of effluent phenol and chlorophenol concentration to inlet phenol and chlorophenol concentration (C_{t}/C_{0}) as a function of time or volume of effluent for a given bed height [3]. Effluent volume (V_{eff}) can be calculated from Eq (1):

\[ V_{eff} = Q t_{total} \]  

Where t_{total} and Q are the total flow time (min) and volumetric flow rates (ml/min). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad}; mg/l) versus time (t; min) plot can be used to find the total adsorbed phenol and chlorophenol quantity (maximum column capacity). Total adsorbed phenol and chlorophenol quantity (q_{total}; mg) in the column for a given feed concentration and flow rate (Q) is calculated from Eq. (2):

\[ q_{total} = \frac{Q A}{1000} = \frac{Q}{1000} \int_{t=0}^{t_{total}} C_{ad} dt \]  

Total amount of phenol and chlorophenol sent to column (m_{total}) is calculated from Eq (3).

\[ M_{total} = \frac{C_{0} Q t_{total}}{1000} \]  

Total removal is calculated from Eq (4).

\[ Total removal (\%) = \frac{q_{total}}{M_{total}} \times 100 \]  

Equilibrium phenol and chlorophenol uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by Eq. (5) as the total amount of phenol and chlorophenol sorbed (q_{total}) per g of sorbent (X) at the end of total flow time [21].

\[ q_{eq} = \frac{q_{total}}{X} \]  

Successful design of a column sorption process required prediction of the concentration–time profile or breakthrough curve for the effluent [7, 27]. Various mathematical models can be used to describe the fixed bed adsorption.

Among these, The BDST model [5] is simple to use in the design of a fixed bed adsorption column and the BDST model is one of the most general and widely used method in column performance theory. Therefore, the breakthrough data obtained from the column studies was examined using the BDST model developed by Bohart and Adams [5].
Bohart and Adams [5] put the original basis for BDST and proposed that there is a relationship between the bed depth, \( D \) and service time \( t \).

This relationship was related to the process concentrations and adsorption parameters in a linearised form [19], according to the following equation.

\[
\ln\left(\frac{C_o}{C_t} - 1\right) = (e^k - N_o D / Q - 1) - K_a C_o t \tag{6}
\]

Where \( C_t \) is the breakthrough phenol and chlorophenol concentration (mg/L), \( N_o \) the sorption capacity of bed height (mg/L), \( Q \) the solution flow rate (mL/min), and \( K_a \) is the rate constant (L/mg/min). \( D \) is bed height (m); \( t \) is the service time of a column (hr). \( C_o \) is initial concentration of sorbate at breakthrough value (mg/dm^3). Since the exponential term \( e^k = N_o D / Q_o \) is usually much larger than unity, the unity term within the brackets in the right hand side of equation \( 1 \) is often neglected and therefore approximation is being made which leads to equation \( 7 \) [8]

\[
t = \frac{N_o}{C_o} - \frac{1}{K_a} \ln\left(\frac{C_o}{C_t} - 1\right) \tag{7}
\]

Equation \( 7 \) enables the service time \( t \) of an adsorption bed to be determined for a specified bed depth, \( D \), of the adsorbent. The second term on the right hand side of the equation \( 7 \) represents the time required for the pollutants to establish its breakthrough curve; that is, it represents that part of the bed which is not saturated when the pollutant concentration in the solution leaving the bed is above the breakthrough value of \( C_t \). The BDST model can predict service time versus bed depth according to the desired percentage breakthrough value and can measure the capacity of the bed at various percentage breakthrough values [20]. The critical bed depth (\( D_o \)) is the theoretical depth of adsorbent sufficient to prevent the sorbate concentration from exceeding breakthrough concentration \( (C_t) \) at \( t \approx 0 \). By letting \( t=0 \), \( D_o \) is obtained from equation 6 by solving for \( D \).

\[
D_o = \frac{Q}{K_a N_o} \ln\left(\frac{C_o}{C_t} - 1\right) \tag{8}
\]

It is important to mention that the BDST model ignores the intra-particle mass transfer resistance and the external film resistance such that the adsorbate is adsorbed onto the adsorbent surface directly.

This model also considered the adsorption capacity \( N_o \) to be constant throughout the bed when the adsorption zone was moving at constant speed along the column.

It was stated that this model applied well for activated carbon processes and other adsorbents [30,20 and 10].

**Results:**

Effect of Initial Concentration.

![Fig. 1: Effect of concentration on packed column for phenol and chlorophenol on CAC: bed height 6cm; Flow rate =2ml/min; pH = 6.0.](image-url)
Discussion:

Figures 1 shows the characteristic “S” shape exhibited by breakthrough curves. It was a plot of the dimensionless liquid phase concentration, C/C₀ versus volume of liquid phenol and chlorophenol treated. It was evident from the curve that, by increasing the initial phenol and chlorophenol concentration, the slope of the breakthrough curve increased and became steeper, thus reducing the volume of phenol and chlorophenol solution treated before the breakthrough. Increasing the initial phenol concentration from 100 to 200mg/l results in a decrease in the volume of phenol and chlorophenol solutions treated from 1000 to 300ml and 1200 to 500ml at the breakthrough point. Since a constant mass of adsorbent can only absorb a certain amount of phenol and chlorophenol, increasing the initial phenol and chlorophenol concentrations led to a decrease in the breakthrough time. Similar trends were observed by Walker and Weatherly, [30]; Kim et al., (2002); Kumar et al., [1] Al-Degs et al., [23] Tarawou et al., [27]. This may be due to the fact that, by increasing the initial phenol and chlorophenol concentration, the driving forces increases which enhance the rate of phenol and chlorophenol diffusion within the adsorbent particles and saturates the binding sites more quickly.

The sorption capacity of the commercial activated carbon obtained from the batch sorption studies was compared with the bed sorption capacity (Nₑ) of the column studies. It was found that the carbon bed sorption capacity for phenol and chlorophenol (76.6 and 78.6 mg/g) were higher than the equilibrium sorption studies (Similar results have also been reported earlier [14,27]. This is due to the inherent difference in the nature of continuous and batch operations. A higher capacity of column operation is established by continuously increasing concentration gradient at the interface of the adsorption zone as it passes through the column while the concentration gradient decreases with time in batch adsorption. As seen from the experimental data, 2-chlorophenol is more adsorbed than phenol in all concentrations studied. This shows that solubility seems to play a very significant role in adsorption. A decrease in solubility and pKₐ is associated to an increase in adsorption capacity. The adsorption capacity for phenol and chlorophenol are a function of molecular weight and cross sectional area. Additionally, it seems that the adsorption capacity is directly proportional to the adsorbate hydrophobicity [16]. An increase of the initial phenol and chlorophenol concentrations from 100 to 200mg/l, when other experimental conditions are kept constant, significantly affected the BDST model as illustrated in Fig 2 and Table 2.

The critical bed depth (Dₑ) shows an increase with increasing phenol and chlorophenol concentrations. These results correlate well with the observed performance in the breakthrough curves. An increase in chlorophenol concentration increased the rate constant (Kₑ) of phenol 0.019, 0.031, 0.666 and chlorophenol, 0.022, 0.035 and 0.089 Lmg⁻¹hr⁻¹ respectively. This is in line with the findings of [30,22] The Kₑ values were higher for phenol than chlorophenol. If Kₑ is large even a short bed will avoid breakthrough, but as Kₑ decreases a progressively longer bed is required to avoid breakthrough Walker and Weatherley, [30]. The column adsorption capacity (Nₑ) using the BDST model also increased with an increase in initial phenol concentrations as follows, 76.6, 99.9, 126.4mg/g and chlorophenol 78.6, 109.8 and 153.2mg/g respectively. The data shows higher bed sorption capacity for chlorophenol compared to phenol Figure 2 show linearity with very high correlation coefficient (R²) ranging from 0.956 to 0.994 for phenol and chlorophenol indicating the validity of BDST model for the present system.

The effect of flow rate on phenol and chlorophenol sorption by the commercial activated carbon was studied by varying the flow rate from 2 to 4ml/min, while the bed height and initial nickel concentration were held constant at 6cm and 100mg/l, respectively. The plots of C/C₀ versus time at different flow rates are shown in Fig 3, as the flow rate increased, the breakthrough curve becomes steeper. The breakthrough time, exhaustion time, uptake capacity decreased as the flow rate increased. The reason for this behaviour can be explained in the following ways: (1) when the flow rate increased, the residence time of the solute in the column decreased, this makes the chlorophenol and phenol solution in the column to decrease, which causes the chlorophenol and phenol solution to leave the column before equilibration occurs; (2) when the process is intraparticle mass transfer controlled, a slower flow rate favours the sorption and when the process is subjected to external mass transfer control; a higher flow rate decreases the film resistance [20].

Both bed capacity and exhaustion time increased with increasing bed height, as more binding sites available for sorption, also resulted in a broadened mass transfer zone as illustrated in figure 4.
increase in adsorption with that in bed depth was due to the increase in adsorbent doses in larger beds which provide greater service area and adsorption sites. The maximum bed capacities for different bed heights of 3, 6 and 9cm for phenol were 24.63, 27.94, 32.40mg/g for chlorophenol 25.26, 29.29, 32.80mg/g respectively. In addition, the chlorophenol uptake capacity of commercial activated carbon (CAC) increased with the increase in bed height due to availability of more binding sites for sorption as observed by Vijayaraghavan et al., [10] and Tarawou et al., [27].

The chlorophenol and phenol removal percentage was significantly affected by bed height. When the bed height increased from 3 to 9cm, the percentage chlorophenol removal increased as follows 85.11, 87.37, 90.44 % and phenol removal percentage was 79.59, 84.53 and 85.56% respectively.

![BDST plots at breakthrough concentration of 10% for the sorption of phenol and chlorophenol solution by CAC at different concentrations](image1)

**Fig. 2:** BDST plots at breakthrough concentration of 10% for the sorption of phenol and chlorophenol solution by CAC at different concentrations

![Effect of flow rate on packed bed column for phenol and chlorophenol on CAC: Co 100mg/l bed height 6cm.](image2)

**Fig. 3:** Effect of flow rate on packed bed column for phenol and chlorophenol on CAC: Co 100mg/l bed height 6cm.

![Effect of bed height on packed bed column for phenol and chlorophenol on CAC: Co 100mg/l flow rate 2ml/min.](image3)

**Fig. 4:** Effect of bed height on packed bed column for phenol and chlorophenol on CAC: Co 100mg/l flow rate 2ml/min.
Table 2: Effect of concentration on BDST parameters and correlation coefficients for the sorption of phenol and chlorophenol on commercial activated carbon

<table>
<thead>
<tr>
<th>Concentration (mg/l)</th>
<th>Bed sorption capacity (N0) (mg/g)</th>
<th>Rate constant (Ka) (L/mg/hr)</th>
<th>Critical bed depth, (D0) (cm)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenol 76.6</td>
<td>0.019</td>
<td>3.018</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>Chlorophenol 78.6</td>
<td>0.022</td>
<td>2.510</td>
<td>0.990</td>
</tr>
<tr>
<td>100mg/l</td>
<td></td>
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<tr>
<td>150mg/l</td>
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<td></td>
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<tr>
<td>200mg/l</td>
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</tbody>
</table>

Conclusion:

The study demonstrated that commercial activated carbon could be used for the removal of phenol and chlorophenol from aqueous solution. The increase in flow rate decreased the breakthrough time, exhaustion time and uptake capacity of chlorophenol and phenol, probably due to insufficient residence time of the chlorophenol and phenol in the column. The BDST model was suitable for describing the experimental data generated in the present study with very high correlation coefficients values. The critical bed depth (D0) and the column sorption capacity (N0) were found to increase with an increase in initial phenol concentration. In all parameters determined chlorophenol had better adsorption than phenol.

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