Adsorption of 4-Chlorophenol onto Optimum Activated Carbon from An Agricultural Waste

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Abstract: Potentials of Prosopis africana seed hulls (PASH) were explored by preparing optimal activated carbon (PASH-AC) using sodium acetate as chemical activating agent in order to remove 4-chlorophenol (4CP) from aqueous solution. The isotherm parameters of the process were determined by using Langmuir, Freundlich and Temkin isotherm equations. The kinetic parameters were predicted with Lagergren’s pseudo-first order and pseudo-second order equations. The PASH-AC was mesoporous with surface area of 1085.92 m². Langmuir isotherm model was the best fit for the equilibrium data with monolayer adsorption capacity of 347.47 mg/g while pseudo-second-order was the best kinetic model that described the adsorption process. PASH-AC was established to be a good precursor for producing activated carbon that is capable of removing high percentage of 4CP from aqueous solution.

Keywords: Prosopis africana seed hulls; optimal activated carbon; Linearized Langmuir equations; 4-chlorophenol; Adsorption

1. Introduction

Chlorophenols (CPs) are a group of organochlorides of phenol comprising one or more covalently bonded chlorine atoms [1] with their toxicity depending on the degree of chlorination and the position of chlorine atoms relative to the hydroxyl group [2]. They are usually characterized by strong odour, not readily biodegradable and persistent in the environment thus are environmental contaminants that are very fatal and causes cancer posing a serious ecological problem and public health risk [3], therefore, removing them from the recycled water is very crucial.

Adsorption process has been proven globally as one of the best and most effective water treatment technologies [4, 5] for the removal of contaminants such as chlorophenols. Activated carbon has been the most widely used adsorbent due to its simplicity in design, high adsorption capacity and fast adsorption kinetics [6, 7].

Activated carbon is a versatile porous carbon material with popular demand as adsorbent in liquid and gas treatments as well as in catalytic applications [8]. As environmental pollution is becoming a more serious problem especially in developing countries, the need for activated carbons continues to grow with varieties of agricultural wastes employed as precursors for activated carbon production. Borassus aethiopum [9], sugarcane bagasse [10], waste biomass [11], apricot stone [12], and citrus peel [13] are some of the precursors that were successfully transformed into activated carbons on a laboratory scale.

Nigeria being an agrarian country is battling with issues related to environmental contamination due to improper way of dealing with varieties of agricultural wastes in the country. The necessity to research on these wastes and possibly convert them into agents of environmental control is very imperative [14]. Preliminary studies revealed PASH to contain high carbon and low ash content which makes it a good precursor material for preparing activated carbon. This research work was therefore targeted at investigating the effect of pH, initial adsorbate concentrations and contact time in the adsorption of 4CP from aqueous solution using PASH-AC. The equilibrium, kinetic data modeling and mechanism of the adsorption process were also investigated.

2. Materials and Methods

2.1. Adsorbate (4-chlorophenol)

4CP supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate. Deionized water was used to prepare its solution. 4CP as shown in Fig. 1 has a chemical formula of C₆H₅ClO with molecular weight of 128.56 g/mol.

![Figure 1: Chemical structure of 4-chlorophenol](image)

2.2. Preparation of Activated Carbon

Prosopis africana seed hulls (PASH) used as the precursor in this study was obtained locally. The activated carbon preparation procedure was referred to our previous work [14] where the pre-treated PASH was impregnated with CH₃COONa, and loaded in a stainless steel vertical tubular reactor placed in a tube furnace. The optimum preparation conditions of 795 °C activation temperature, 62 minutes activation time and 2.45 IR were applied [15] to prepare the activated carbon which gave high activated carbon yield as well as high 4CP removal.
2.3. Batch Adsorption for the Removal Efficiency of 4CP in Aqueous Solution.

In a conventional batch adsorption experiment, 0.1g of the prepared activated carbon was added into 250 mL reagent bottles with each bottle containing 100 mL of 100 mg/L initial 4CP concentration. The samples were placed on an isothermal water bath shaker at 140 rpm at 30 °C until equilibrium was reached. The concentration of the 4CP in the supernatant solutions was determined before and after adsorption using Ultraviolet–Visible (UV-Vis) spectrophotometer (SHIMADZU, UV-2600) at its maximum wavelength of 281 nm. The percentage removal of 4CP at equilibrium (% R) was calculated using equation 1.

\[ \text{4CP removal} \% \left( \frac{C_o - C_e}{C_o} \right) \times 100 \]  \hspace{1cm} (1)

where \( C_o \) and \( C_e \) are the liquid-phase concentrations at initial and equilibrium states (mg/L), respectively.

The equilibrium amount of 4CP adsorbed per unit mass of adsorbent (PASH-AC), \( q_e \) (mg/g), was calculated by equation 2:

\[ q_e = \frac{(C_o - C_e)V}{W} \]  \hspace{1cm} (2)

where \( V \) (L) is the volume of the solution and \( W \) (g) is the mass of the PASH-AC used. In order to study the kinetics of the adsorption process, concentration of the 4CP solution was determined at intervals of time, and the amount of the 4CP adsorbed at time \( t \), \( q(t) \) (mg/g) was calculated using equation 3:

\[ q_e = \frac{(C_o - C_t)V}{W} \]  \hspace{1cm} (3)

where \( C_o \) and \( C_t \) (mg/L) are the liquid-phase concentration of 4CP at the initial and any time \( t \), respectively.

The effect of initial pH (2–12) on the adsorption of the 4CP by PASH-AC was conducted by adjusting the solution pH with 0.1 M HCl and 0.1 M KOH solutions and measured using a pH metre (Martini instrument, Mi 150). The 4CP initial concentration was 100 mg/L with PASH-AC dosage of 0.1g at a temperature of 30 °C for 12 h. The %R was calculated using equation (1).

3. Results and Discussion

3.1 Effect of Contact Time and Initial 4CP Concentrations

Fig. 1 shows the effect of contact time on the removal of 4CP by PASH-AC for six different initial concentrations at 30 °C, characterized by a very rapid increase at the beginning for all concentrations, followed by a long period of much slower uptake till equilibrium.

![Figure 2: Effect of contact time on 4CP adsorption onto PASH-AC at various initial concentrations (30–350 mg/L) at 30 °C.](image)

The adsorption continued to be slow until a time when insignificant adsorption was observed that is the dynamic equilibrium stage where the rate of adsorption onto the adsorbent surface was equal to the amount of desorbed by same surface. The dynamic equilibrium stage acts as the determinant time to evaluate the adsorption capacity of an adsorbent for the 4CP [16].

Equilibrium position was attained at shorter time for lower initial concentrations than at higher initial concentrations as can be observed. The difference in equilibrium time attainment was attributed to the faster extinction or disappearance of adsorbates molecules at different initial concentrations [17]. The influence of sodium acetate activating agent for the development of mesoporous and high surface area of PASH-AC with numerous functional groups as seen in our previous work [15] enhanced the faster adsorption process observed.

3.2. Effect of solution pH

As can be seen from Fig. 3, 4CP percentage removal shows significant decrease with an increase in the solution pH from 2 to 12.

![Figure 3: Effect of initial solution pH on 4CP adsorption onto PASH-AC.](image)

The significant decrease of percentage removal with an increase in the solution pH from 2 to 12 for 4CP was attributed to it being proton donor. At definite pH, 4CP become anion; when the solution pH is greater than its pKa (9.1-9.4), the negativity charge of phenoxide ion increases and the adsorption decreases due to a repulsive force between the negative groups on the surface and the phenoxide ions [18].

3.3 Adsorption Isotherms Modeling

Adsorption isotherms are applied to obtain the relationship between amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution
3.3.1. Langmuir Isotherm

The monolayer adsorption on a surface with a finite number of identical sites is validated by Langmuir isotherm [20]. The linear equation for Langmuir isotherm is given as:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

(4)

where \(C_e\) (mg/L) is the equilibrium concentration of 4CP, \(q_e\) (mg/g) is the amount of 4CP adsorbed per unit mass adsorbent. \(q_{\text{max}}\) (mg/g) and \(K_L\) are Langmuir constants which are related to the adsorption capacity and rate of adsorption, respectively. When \(C_e/q_e\) was plotted against \(C_e\), a straight line with slope of \(1/q_{\text{max}}\) was obtained (Fig. 4).

![Figure 4: Langmuir isotherm for the adsorption of 4CP onto PASH-AC at 30 °C](image)

Dimensionless factor (\(R_L\)) can be used to express the essential characteristics of Langmuir equation which is given as [18]:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

(5)

where \(K_L\) is the Langmuir constant and \(C_0\) is the highest initial MB concentration. The value of \(R_L\) indicates whether it is unfavourable (\(R_L > 1\)), linear (\(R_L = 1\)), favourable (0 < \(R_L < 1\)) or irreversible (\(R_L = 0\)).

3.3.2. Freundlich Isotherm

Freundlich isotherm is based on the adsorption on a heterogeneous surface of varied affinities [20]. The linear form of Freundlich isotherm is given as:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

(6)

where \(q_e\) (mg/g) is the amount of MB adsorbed per unit mass adsorbent, \(C_e\) (mg/L) is the equilibrium concentration of MB. The \(K_F\) and \(n\) are Freundlich constants which are related to the adsorption capacity and adsorption intensity, respectively. When \(\log q_e\) was plotted against \(\log C_e\), a straight line with the slope of \(1/n\) was obtained (Fig. 5). For \(n>1\), it indicates physical adsorption and that the adsorbate is favourably adsorbed on the adsorbent while for \(n<1\), it shows that the adsorption process is chemical in nature [18].

![Figure 5: Freundlich isotherm for the adsorption of 4CP onto PASH-AC at 30 °C](image)

3.3.3. Temkin Isotherm

Linear decrease in the heat of adsorption of all the molecules in the layer with coverage due to adsorbent-adsorbate interaction is the assumption made in Temkin isotherm [19]. The linear form of the isotherm is given as follows:

\[
q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e
\]

(7)

where \(RT/b = B\) (J/mol) and \(A\) (L/g) are Temkin constants which are related to the heat of sorption and maximum binding energy, respectively, \(R\) is the gas constant (8.314 J/molK) and \(T\) (K) is the absolute temperature. When \(q_e\) was plotted against \(\ln C_e\), a straight line with \(B\) as the slope was obtained (Fig. 6).

![Figure 6: Temkin isotherm for the adsorption of 4CP onto PASH-AC at 30 °C](image)

Table 1 summarizes the isotherm parameters for all three isotherm models at 30 °C. From the \(R^2\) values, it can be concluded that the adsorption data followed Langmuir isotherm better than Temkin and Freundlich isotherms.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>4CP adsorption parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>(q_{\text{max}}) (mg/g)</td>
</tr>
<tr>
<td></td>
<td>(K_L) (L/mg)</td>
</tr>
<tr>
<td></td>
<td>(R_L)</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>(K_F) (mg/g)</td>
</tr>
<tr>
<td></td>
<td>(n)</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
</tr>
</tbody>
</table>

Table 1: Isotherm parameters for removal of 4CP by PASH-AC

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The $R^2$ values for Langmuir, Freundlich and Temkin isotherm were 0.9962, 0.9806 and 0.9711 respectively. This indicated that the 4CP adsorption onto PASH-AC was a monolayer adsorption on a homogenous surface. It can also be seen from Table 2, that the $R_i$ value obtained was 0.094 which lies between 0 and 1 connoting that the adsorption of 4CP onto PASH-AC was favourable under the studied experimental conditions.

The $K_F$ and $n$ values obtained from Freundlich isotherm were 15.81 and 1.565 respectively with the $n$ value greater than 1 indicating that the adsorption was physical and favourable. The values of $A$ and $B$ were 0.384 and 66.467 respectively from Temkin isotherm.

The value of monolayer adsorption capacity ($q_{\text{max}}$) obtained in this work at 30°C was equal to 347.47 mg/g which compares well with some other adsorbents reported from literature as shown in Table 2.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASH-AC</td>
<td>347.47</td>
<td>This study</td>
</tr>
<tr>
<td>Refused derived waste activated carbon</td>
<td>16.00</td>
<td>21</td>
</tr>
<tr>
<td>Rattan sawdust based activated carbon</td>
<td>188.68</td>
<td>22</td>
</tr>
<tr>
<td>Date stone activated carbon</td>
<td>28.57</td>
<td>23</td>
</tr>
<tr>
<td>Chemically modified chitosan</td>
<td>66.43</td>
<td>24</td>
</tr>
</tbody>
</table>

### 3.4. Kinetic modelling

The kinetics of 4CP adsorption onto PASH-AC was studied by applying pseudo-first order and pseudo-second order models. The pseudo-first order is written as [25]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

where $k_1$ (h⁻¹) is the rate constant of the pseudo-first order sorption, $q_e$ (mg/g) is the amount of sorption at time $t$ (h), and $q_t$ (mg/g) is the amount of sorption at equilibrium. When log ($q_e - q_t$) was plotted against time, $t$, the rate constant, $k_1$, can be determined from the slope (Fig. 7).

For pseudo-second order kinetics, the equation is expressed as [26]:

$$\frac{1}{q_e} = \frac{1}{k_2 q_{\text{max}}^2} + \frac{1}{q_{\text{max}}} t \quad (9)$$

where $k_2$ (g/mg h) is the rate constant of a second order adsorption. The $k_2$ and calculated $q_{\text{max}}$ can be obtained from the slope and the intercept when a straight line of $t/q_e$ was plotted against time (Fig. 8).

### 3.5. Intraparticle Diffusion Study

Diffusion mechanism was further applied to analyze the kinetic results. Intraparticle diffusion model was used to identify the diffusion mechanisms and rate controlling steps in the MB adsorption process. The intraparticle diffusion equation according to [27] is expressed as:

$$q_t = k_{ip} t^{0.5} + C$$

![Figure 7: Linearized plot of pseudo-first-order kinetic model for the adsorption of 4CP on to PASH-AC at 30°C.](image)

![Figure 8: Linearized plot of pseudo-second-order kinetic model for the adsorption of 4CP on to PASH-AC at 30°C.](image)
where \( k_\text{ip} \) is rate constant of the intra-particle diffusion equation and \( C \) gives information about the boundary layer thickness: larger value of \( C \) is associated with the boundary layer diffusion effect. If the adsorption process follows the intraparticle diffusion model, then \( q_t \) versus \( t^{1/2} \) will be linear and if the plot passes through the origin, then intraparticle diffusion is the sole rate limiting step. Otherwise, some other mechanisms along with intraparticle diffusion are also involved [28].

The intraparticle diffusion plots for the adsorption of 4CP on PASH-AC at 30 °C for various initial concentrations are shown in Fig. 9. The values of \( k_\text{ip} \), \( C \) as well as the correlation coefficients, \( R^2 \) obtained from the plots are given in Table 5.

Table 5: Intraparticle diffusion model parameters for adsorption of 4CP onto PASH-AC

<table>
<thead>
<tr>
<th>( C ) (mg/L)</th>
<th>( k_\text{ip} ) (mg/g h(^{1/2}))</th>
<th>( C )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>10.849</td>
<td>4.309</td>
<td>0.9091</td>
</tr>
<tr>
<td>60</td>
<td>16.816</td>
<td>13.447</td>
<td>0.9035</td>
</tr>
<tr>
<td>100</td>
<td>30.316</td>
<td>19.860</td>
<td>0.8822</td>
</tr>
<tr>
<td>150</td>
<td>42.826</td>
<td>30.791</td>
<td>0.9372</td>
</tr>
<tr>
<td>250</td>
<td>75.048</td>
<td>31.755</td>
<td>0.9269</td>
</tr>
<tr>
<td>350</td>
<td>98.022</td>
<td>33.705</td>
<td>0.9622</td>
</tr>
</tbody>
</table>

The values of \( k_\text{ip} \) as can be seen from Table 4 increased with increase in the initial 4CP concentration, which was attributed to the greater mass transfer driving force at higher concentration [29] and hence this resulted into higher diffusion rates of 4CP within the adsorbent’s pores [27]. The values of \( C \) also increased with increase in initial 4CP concentration from 30 to 350 mg/L signifying an increase in the thickness of the boundary layer [30].

Figure 9: Intraparticle diffusion model plot for 4CP adsorption on PASH-AC at 30 °C.

4. Conclusion

The adsorption of 4CP onto optimal activated carbon from Prosopis africana seed hulls was investigated using CH\(_3\)COONa and CO\(_2\) as chemical and physical activating agents respectively. The results showed that the 4CP removal increased as the initial concentration and contact time increases but decrease with increase in solution pH. For the equilibrium data, the adsorption was best described by the Langmuir isotherm with maximum adsorption capacity of 347.47mg/g at 30 °C. The adsorption kinetics process followed pseudo-second-order model with the adsorption mechanism suggesting the presence of intraparticle diffusion along with some other rate controlling steps. Based on the obtained results, PASHAC can be recommended as an effective adsorbent for 4CP removal aqueous solution over a wide range of initial concentrations.

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References


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