Removal of Cadmium(II) from Aqueous Solutions by Pinecone Biochar

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ABSTRACT
Due to the toxicity of heavy metals, innovative methods for the treatment of heavy metals contaminated waters have been developed. In this study, pinecone was pyrolysed at temperatures between 300°C and 400°C for three hours in an inert environment. This was done to compare the adsorption capacities of the pinecone and its biochar. Batch adsorption studies were conducted to investigate the effects of pH, adsorbent mass, contact time, initial metal ion concentration and temperature on adsorption. To explain the mechanism of adsorption, adsorption isotherms were applied. The monolayer adsorption capacity of Cd²⁺ on raw pinecone was found to be 10.31mg/g and 8.62mg/g for the biochar. Kinetic data was found to show best fit with the pseudo second order kinetic model.

Keywords: Heavy metals, Adsorption, Pinecone, Biochar, Wastewater.

INTRODUCTION
Industrial effluents, which contain heavy metals, find their way into natural water systems and are a cause of serious environmental concern. Beyond certain limits, these heavy metals are toxic to living organisms and cause serious hazards to public health [2]. As a result, the treatment of these effluents becomes important. Heavy metals tend to accumulate in organisms causing diseases and disorders: abdominal pain, convulsions, hypertension, renal dysfunction, loss of appetite, fatigue, sleeplessness, hallucinations, headache e.t.c [6]. They are known to enter the human body through food, water, air or absorption through the skin [9]. Once in the environment, they tend to bioaccumulate and they cannot be degraded or destroyed. Cadmium is one of the heavy metals classified as priority pollutants by the United States Environmental Protection Agency [5].

Many physicochemical methods have been proposed for the removal of heavy metals from industrial effluents. These methods include chemical precipitation, membrane filtration, ion exchange, electrodialysis, liquid extraction [10,12]. However, these methods are often inefficient and or cost prohibitive when used for heavy metals especially at low concentrations [4, 13]. Adsorption is one of the most preferred methods for the removal of heavy metals because of its efficiency and low costs. Activated carbon is an efficient and versatile adsorbent for the purification of water. However, its use is limited by high preparation cost. This has led to the investigation of alternative low-cost materials that may be efficiently applied for the removal of heavy metals. Of these studies, sorption mechanism by pinecones and methods to improve its sorption capacity through pyrolysis of the biomass in a low or no oxygen environment for the removal of heavy metals is not known. This work is aimed at evaluating the possibility of pinecone and its biochar as inexpensive sorbent materials for the removal of Cd²⁺ from aqueous solution.

MATERIALS AND METHOD
Dried pinecones were collected from the University of Ibadan. Some of the pinecones were grinded to dust and sieved to be used in their raw form as adsorbent.

BIOCHAR PREPARATION
The pinecones were put in a crucible and placed in a furnace for three hours at 300°C. Nitrogen gas at a pressure of 6.21 bar was introduced into the furnace to create an inert environment. The biochar...
produced was then treated with 1M HCl for 12 hours to demineralise it and the slurry separated by vacuum filtration. The residue was washed several times with distilled water. Stock solution of 2000mg/L of Cd\(^{2+}\) was prepared and lower concentrations of this stock solution were prepared by progressive dilution of the stock solution using 0.01M NaCl as indifferent electrolyte.

**ADSORPTION STUDIES**

Batch adsorption studies were conducted to investigate the effect of operating variables on the adsorption of Cd\(^{2+}\) using pinecones and its biochar. All experiments were carried out in duplicates and the mean computed.

The sorption capacity of pinecones was obtained using the following equation: 

\[
\% \text{ adsorption capacity} = \frac{(C_0 - C_e)}{C_0} \times 100; \text{ Where } C_0 \text{ (mg/L)} \text{ and } C_e \text{ (mg/L)} \text{ are the initial metal concentration and metal concentration at equilibrium respectively.}
\]

The amount of Cd\(^{2+}\) adsorbed, \(q_e\) was evaluated using the equation:

\[
q_e = \frac{(C_0 - C_e)}{W}V
\]

In this equation, \(q_e\) (mg/g) represents the rate of the adsorbed metal ion per unit mass of the absorbent and \(V\) (L) and \(W\) (g) are the volume of the metal ion solution and the weight of the adsorbent respectively.

**RESULT AND DISCUSSION**

**Effect of pH:** The pH of the solutions were conditioned using 0.1M NaOH and 0.1M HCl to pH of 3, 4, 5, 6, 7, 8, 9 and the suspensions agitated at room temperature. The optimum adsorption within the pH range studied was 9. Increase in adsorption as pH increased may be due to an increase in negative charge of the pinecones as pH increased. At a lower pH, the amount of H\(^+\) ions present is high and these compete with the metal ions for active sites but as the pH increases, the amount of H\(^+\) decreases and this leads to an increase in the number of sites available for the metal ion to adsorb on which increases the adsorption. This is in line with the observation of Aydin et al (2008).

**Effect of sorbent mass:** 1g, 2g, 3g, 4g and 5g of the pinecone and its biochar were agitated with 200mg/L of the metal solution which was kept at a pH of 5±/- 0.3. Increase in adsorbent dose from 1g – 5g resulted in a decrease in the amount adsorbed for both the raw pinecone and its biochar as shown in figure 2. However, the biochar was found to have a higher percentage adsorption than the raw pinecone. An increase in percentage adsorption as the mass increased is due to more surface area is available for adsorption due to increase in active sites on the adsorbent.

**Effect of contact time:** In order to study the effect of contact time, other parameters were held constant and the suspension agitated at different times of 30, 60, 120, 180, 240, 360 minutes. The adsorption of Cd\(^{2+}\) on the pinecone and its biochar increased as the contact time was increased (Fig 3). Further experiment can however be conducted beyond the maximum time studied (6 hours).

**Effect of sorbate concentration:** The effect of sorbate concentration was studied at room temperature by increasing the initial concentration of the metal ion (100mg/L – 500mg/L). Adsorption increased as the initial concentration of the metal ion increased. Consequently, the adsorption by pinecone is dependent on initial metal ion concentration.

**Effect of indifferent electrolyte:** The effect of the indifferent electrolyte, NaCl was studied at three different concentrations, 0.01M, 0.1M and 1M. With increase in concentration of electrolyte, there was a decrease in the adsorption capacity for both adsorbents. This effect may be due to the competition between cations of the electrolyte and the metal ion for active sites. Cay et al, 2004 showed that the cations of these electrolytes compete effectively for permanent negatively charged sites on the adsorbent surfaces. This means that an increase in the concentration of the electrolyte causes screening of the surface negative charges by the electrolyte, which leads to a drop in the adsorption of the metal ion [11].

![Fig 1: Effect of pH](image-url)
**Fig 2: Effect of mass on the adsorption of cadmium**

- **Cadmium**
- **Pineone biochar**

**Fig 3: Effect of contact time**

- **Raw pine cone**
- **Modified pine cone**

**Fig 4: Effect of initial metal concentration**

- **Raw pine cone**
- **Pine cone biochar**
Two different sorption isotherms, the Langmuir and Freundlich models were used to fit the experimental sorption data. Langmuir model is based on monolayer sorption and can be described by the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o C_e}
\]

The Langmuir constant \(Q_o\) is used to compare the performance of adsorbents. Thus, for a good adsorbent, a high \(Q_o\) is desirable. Thus the raw pinecones and the biochar are good adsorbents. (\(Q_o = \) for both the raw pinecone and biochar)

The Freundlich model is based on multilayer sorption and is given by the following equation:

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

where \(q_e\) is the equilibrium sorption amount of \(Cd^{2+}\) adsorbed on pinecones (mg/g), \(C_e\) is the equilibrium concentration of the adsorbate in aqueous solution (mg/L), \(K_f\) is a constant determined by plotting \(C_e/q_e\) versus \(C_e\), \(K_f\) and \(1/n\) are the constants related to the sorption of adsorbent and intensity of the sorption respectively.

The experimental data was more suited to the raw pinecones than the biochar. Overall, the experimental sorption data best fit the Freundlich isotherm which confirms the heterogeneous nature of the adsorbents. The calculated isotherm constants and correlation coefficients of Langmuir and Freundlich models are listed in the table below. The sorption capacities of the pinecones on \(Cd^{2+}\) are 10.31mg/g and 8.62mg/g for the raw pinecone and its biochar respectively.

### ADSORPTION KINETICS

The kinetic data was fitted with pseudo-second-order kinetic model. The relationship between sorption quantity and time can be described with the following equation:

\[
t/\text{qt} = 1/K q_e + t/\text{qt}
\]
where \( q_t \) and \( q_e \) are sorption quantity at time \( t \) and at equilibrium respectively, \( K \) is the rate constant, which can be calculated from the plot of \( t/q_t \) vs. \( t \).

Table 2 lists the kinetic parameters for the removal of \( \text{Cd}^{2+} \) by pinecones using pseudo-second-order model. A linear relationship with high correlation coefficient (\( R^2 = 0.999 \)) for both raw and pinecone biochar was obtained, illustrating that the kinetic data were well fitted with the pseudo-second-order model. This indicates that the rate limiting step is a chemisorption process between the metal ions and the pine cone.

Table 1: Isotherm parameters for the adsorption of \( \text{Cd}^{2+} \) onto pinecones and its biochar

<table>
<thead>
<tr>
<th>Adsorbent material</th>
<th>( 1/n )</th>
<th>( n )</th>
<th>( K_f )</th>
<th>( R^2 )</th>
<th>( Q(mg/g) )</th>
<th>( b(g/L) )</th>
<th>( R^2 )</th>
<th>( R_L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw pinecone</td>
<td>0.46</td>
<td>2.19</td>
<td>1.42</td>
<td>0.985</td>
<td>10.20</td>
<td>0.078</td>
<td>0.988</td>
<td>0.060</td>
</tr>
<tr>
<td>Biochar</td>
<td>0.27</td>
<td>3.69</td>
<td>2.27</td>
<td>0.973</td>
<td>8.62</td>
<td>0.1</td>
<td>0.968</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Table 2: Kinetic parameters for the adsorption of \( \text{Cd}^{2+} \) onto pinecones and its biochar.

<table>
<thead>
<tr>
<th>Adsorbent material</th>
<th>( q_e )</th>
<th>( K_a )</th>
<th>( R^2 )</th>
<th>( h_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw pinecone</td>
<td>3.76</td>
<td>0.067</td>
<td>0.999</td>
<td>0.94</td>
</tr>
<tr>
<td>Biochar</td>
<td>3.68</td>
<td>0.054</td>
<td>0.999</td>
<td>0.73</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The pinecone can be used for the removal of \( \text{Cd}^{2+} \) from aqueous solution with good efficiency. Treating the pinecone by pyrolysis to obtain the biochar increased its efficiency for the removal of the metal ion.

**REFERENCES**


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