Effect of pH on Cu (II) removal from water using Adenanthera pavonina seeds as adsorbent

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ABSTRACT

The sorption of Cu(II) on the powdered seeds of Adenanthera pavonina is investigated as a function of pH over a range of initial Cu(II) concentrations. Maximum adsorption of Cu(II) from aqueous solution is obtained at pH 5. The data obtained is fitted to Langmuir and Freundlich isotherm models and Langmuir isotherm model is found to represent the adsorption data better. The FT-IR study show the role of hydroxyl, carboxyl, organosulfur and amino groups in the adsorption of Cu(II) on the surface of the biosorbent. The results are also supported by the data obtained from scanning electron micrographs and energy dispersive x-ray analysis.

Keywords: Copper (II), FT-IR, SEM, pH, biosorption, Adenanthera pavonina.

1. Introduction

Heavy metals released from different industrial activities have lead to the contamination of water resources. Conventional methods of treatment of water include coagulation, ion-exchange, reverse osmosis, chemical precipitation, membrane separation, engineered nanoparticles. (Bilal et al. 2013). However, these methods are efficient in treatment of high concentrations of heavy metals and involve high operational costs. In recent times, a lot of emphasis has been laid on the use of agricultural by-products as sorbents for removal of heavy metals from contaminated water sources (Ho and Mckay, 1999). Different polar functional groups like alcohols, aldehydes, ketones, acids, phenolic hydroxides along with other chemical bonding agents present in the biosorbents, help in the adsorption of heavy metals from aqueous solutions (Adler and Lundquist, 1963). Thus the use of biosorbents is an economically viable and chemically efficient alternative for treatment of water contaminated with heavy metal ions.

The pH values of the waste water discharged from different industrial operations vary widely (Ho, 2005). Extensive literature review has shown that the initial pH of a solution plays an important role in the percentage adsorption of heavy metal ions on biosorbents. The potentiality of powdered seeds of Adenanthera pavonina in removal of Cu(II) ions from aqueous solutions has been recently investigated (Sen et al. 2015). The present study aims at examining the effect of pH on Cu(II) removal from water using powdered Adenanthera pavonina seeds.

2. Material and methods

2.1 Preparation of biosorbents
The seeds of *Adenanthera pavonina* are collected, washed and dried thoroughly. The dried seeds are then powdered, sieved to 250 μm and stored in air tight containers for future use. The powdered seeds of *Adenanthera pavonina* are used as biosorbents without any chemical pretreatment throughout the experiment.

### 2.2 Effect of initial pH of the solution

A range of initial pH from pH 1-7 is used for the current study. 1000mg/L stock solution of Cu(II) is prepared and from this stock solution working solutions of different initial concentrations (10-70 mg/L) are prepared with adequate dilutions using distilled water. The initial pH of the working solutions is adjusted from 1-7 using 0.1 N HNO₃ or 0.1N NaOH for all initial concentrations of Cu(II). 0.5g of powdered *Adenanthera pavonina* seeds is added to 100 ml of Cu(II) solution and an agitation speed of 120 rpm is used for all experiments. The mixture is then filtered after a fixed duration of 40 minutes determined experimentally (Sen et al. 2015) and the filtrate is then analyzed using Atomic Absorption Spectrophotometer (AAS) for the concentration of Cu(II) after adsorption. The percentage removal of Cu(II) can be calculated using the following expression:

\[
\% \text{ Removal of Cu}(II) = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]

Where, \(C_i\) and \(C_f\) denotes the initial and final concentrations of Cu(II) in mg/L. The metal uptake, \(q_e\) at equilibrium is calculated from the equation

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

Where \(q_e\) is the adsorption capacity in mg/g, \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of Cu(II) in mg/L, \(V\) represents the volume of Cu(II) solution, in L, and \(W\) is the total amount of powdered *Adenanthera pavonina* seeds in grams.

### 2.3 Characterization of the adsorbent

For the proper understanding of the mechanism of adsorption of metal ions on the surface of the biosorbents, the characterization of the biosorbent is an important analysis. The different functional groups present on the surface of powdered *Adenanthera pavonina* seeds are analyzed using Fourier Transform Infrared (FTIR) spectroscopy using KBr pellets. FTIR spectra are recorded using a Parkin Elmer FTIR spectrometer Spectrum 2 within a range from 400 to 4000 cm\(^{-1}\).

Scanning electron microscopy (SEM) coupled with energy dispersive x-ray analysis (EDX) are also carried out in order to understand the morphological characteristics of the biosorbent before and after the sorption of heavy metals.

### 2.4 Sorption isotherms

In order to understand the equilibrium relationship like, the ratio between the quantity of metal ions already sorbed and the quantity remaining in the solution under constant temperature at equilibrium, sorption isotherms must be analyzed (Ho et al. 2002). In the current study, both Langmuir and Freundlich isotherm models are studied. The Langmuir isotherm model (Langmuir, 1916) suggests monolayer adsorption on homogenous surface of the adsorbent. However, the interactions between the adsorbed molecules are not taken into
consideration by this model. The Langmuir equation can be represented linearly by the equation:

$$
\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m}
$$

(3)

Where, $b$ is $K_a/K_d$ ($K_a$ and $K_d$ are rate constants for adsorption and desorption respectively) (L/mg), $q_e$ (mg/g) is the amount adsorbed on unit mass of the adsorbent, $Q_m$ (mg/g) is the saturated monolayer sorption capacity and $C_e$ (mg/L) is the equilibrium concentration.

A dimensionless equilibrium parameter, $R_L$ also known as separation factor has been developed on the basis of the Langmuir equation (Hall et al. 1966).

$$
R_L = \frac{1}{1+bC_e}
$$

(4)

The value of $R_L$ should be $0<R_L<1$ for favorable adsorption, while $R_L>1$ represents the unfavorable adsorption, $R_L=1$ represents linear adsorption and $R_L=0$ represents irreversible adsorption process.

The Freundlich equation can be linearly expressed as

$$
\log q_e = n \log C_e + \log K_f
$$

(5)

Where $K_f$ represents the binding energy and $n$ indicates the intensity of adsorption (Montanher et al. 2005)

3. Results and discussion

3.1 Effect of pH on adsorption of Cu(II)

Biosorption depends on a range of variables of which pH of the metal ion solution is the most significant (Wan Ngah et al. 2002). The chemical speciation of copper ions and the surface binding sites of the biosorbent are influenced by the pH of the sorbate. According to the chemical speciation diagram of copper, Cu(II) is the dominant species at pH<5 (Wang and Qin, 2005). A smaller amount of CuOH$^+$ is also present. With increase in pH beyond 5, the situation is reversed and as the concentration of CuOH$^+$ increases, the Cu(II) concentration decreases sharply (Oliveira et al. 2008). In the present study, as the pH increases from 5 to 7, the concentration of insoluble Cu(OH)$_2$ increases whereas the concentration of positively charged Cu(II) ions declines resulting in the decrease of percentage removal of Cu(II) from the metal ion solution in the range of pH 5 to 7 with a maximum removal of 94% at pH 5 for all concentrations of Cu(II) (Figure 1).

At lower pH, the functional groups on the surface of the biosorbent are closely associated with the protons, as the concentration of protons is higher in acidic conditions (Tunali et al. 2006). This association of protons and the functional groups induces increased density of positive charge on the binding sites thereby repelling the approach of metal ions (Iqbal and Edyvean, 2004). Thus the percentage removal of metal ions at lower pH is very low. However, as the pH increases, the functional groups like amino, carboxyl and hydroxyl groups carry more negative charges resulting in attraction of Cu(II) towards the adsorption sites (Aksu, 2001). According to the results obtained, it can be concluded that the biosorption capacity is increased from pH 1 to 5 with no significant change in the amount of Cu(II) adsorbed beyond pH 5 for all concentrations of Cu(II) (Figure 2).
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3.2 Sorption isotherm study

Both Langmuir and Freundlich models are examined to study the metal sorption isotherms at pH 5 where maximum removal of 94% is obtained (Table 1). The sorption of Cu(II) from the aqueous solution is better described by the Langmuir isotherm model than the Freundlich isotherm model. The separation factor $R_L$ lies within the range of 0.0 to 0.323 which fulfills $0 < R_L < 1$ and thus adsorption is favorable (Namane et al. 2005). The maximum adsorption capacity, $Q_m$, obtained from the plot of $C_e/q_e$ versus $C_e$ (Figure 3) is calculated to be 10.706 mg/g and the adsorption energy, $b$, is found to be 0.2092 L/mg. The Freundlich isotherm model derived from the plot of $\log q_e$ versus $\log C_e$ (Figure 4) gives the values of $K_f$ and $n$. Table 1 shows the calculated values of $K_f$ and $n$, which are found to be 2.428 mg/g and 2.307 respectively.

3.3 FT-IR spectral analysis

The FT-IR spectrum of powdered Adenanthera pavonina seeds (Figure- 5a) displays a number of adsorption peaks, which is indicative of the presence of different functional groups in the biosorbent. The broad and strong band ranging from 3047-3680 cm$^{-1}$ indicates the presence of $-\text{OH}$ and $-\text{NH}$ groups. The peak at 3011 cm$^{-1}$ can be attributed to $-\text{OH}$ stretch from carboxylic acids and $-\text{NH}_2$ or $-\text{NH}$ groups. The peaks at 2925 and 2854 cm$^{-1}$ can be assigned to asymmetric and symmetric $\text{CH}_2$ groups. The peak characteristic of the carbonyl group stretching from carboxylic acid or ester groups is located at 1747 cm$^{-1}$ where as the peak at 1650 cm$^{-1}$ corresponds to carboxylate (COO$^-$), C=C or $-\text{NH}_2$ groups. The peak at
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1239 cm\(^{-1}\) can be assigned to the C-N stretching of aliphatic amines. The stretching at 1107 cm\(^{-1}\) indicates the presence of C=S group.

The FT-IR spectrum of copper loaded powdered

![Figure 3: Langmuir isotherm of Cu(II) adsorbed on powdered A. pavonina seeds at pH 5](image)

![Figure 4: Freundlich isotherm of Cu(II) adsorbed on powdered A. pavonina seeds at pH 5](image)

**Table 1:** Langmuir and Freundlich constants for sorption of Cu(II) on powdered *Adenanthera pavonina* seeds

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q_m) (mg/g)</td>
<td>b (L/g)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>10.706</td>
<td>0.209</td>
</tr>
</tbody>
</table>

*Adenanthera pavonina* seeds (Figure-5b) shows that the polar groups on the surface of the biosorbent are mainly responsible for Cu(II) uptake from aqueous solution. It is found that some peaks are shifted or are considerably lower than that observed before biosorption. This suggests that groups like –OH, COO\(^-\), NH\(^2\), NH and C=S are mainly responsible or Cu(II) biosorption. The wavenumbers shifted from 1747, 1650 and 1239 cm\(^{-1}\) to 1705, 1618 and 1195 cm\(^{-1}\) respectively after uptake of Cu(II). The peak at 3011 cm\(^{-1}\) and the stretching at
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1107 cm\(^{-1}\) attributed to C=S disappeared after Cu(II) biosorption. Thus the removal of Cu(II) is mainly due to binding of the metal ions to functional groups through surface complexation (Wan Ngah and Hanafiah, 2008). The functional groups mainly responsible for the binding of Cu(II) ions are the hydroxyl, carboxyl, amino and the organosulfur groups.

![Figure 5: FT-IR spectra of powdered Adenanthera pavonina seeds (a) before Cu(II) biosorption (b) after Cu(II) biosorption](image)

3.4 SEM and EDX analysis

The SEM micrographs and the EDX spectra of the biosorbent investigated both before and after the sorption of Cu(II) are presented in Figures 6 and 7 respectively. The SEM micrograph of Cu(II) loaded adsorbent appears to be brighter than the fresh adsorbent. The EDX analysis enables us to acquire the elemental information of the biosorbent. The appearance of a new signal of copper in the EDX spectrum of the metal loaded adsorbent confirms the biosorption process by binding of metal ions on the surface of the biosorbent.

4. Conclusion

The powdered seeds of Adenanthera pavonina can be considered as a potential adsorbent for removal of Cu(II) from water. The initial pH value of the metal ion solution is found to influence the biosorption of the metal ion and the optimum pH for Cu(II) removal is found to be 5 in the current study.
The equilibrium study shows that the biosorption data obtained in the concentration range is fitted well to the Langmuir isotherm model. The FT-IR spectra confirmed that the binding of copper on the surface of the adsorbent takes place through the hydroxyl, carboxyl, amino and the organosulfur groups. SEM micrographs and elemental analysis through EDX of the fresh and metal loaded biosorbents show a clear difference which further confirms biosorption of Cu(II) on the surface of powdered *Adenanthera pavonina* seeds.
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5. References


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