Equilibrium and Kinetic Studies for The Biosorption System of Cu(Ii) Ions From Aqueous Solution Using Eucalyptus Bark Powder

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ABSTRACT
Eucalyptus bark, an agricultural solid waste by-product has been developed into an effective and efficient biosorbent the removal of Cu(II) from aqueous solutions. Batch biosorption experiments were carried out as a function of pH, biosorbent dosage, contact time and initial metal ion concentration. The biosorbent Eucalyptus bark powder was characterized by FTIR analysis. The experimental isotherm data were analyzed using Langmuir and Freundlich equations. The equilibrium data fit well the Langmuir isotherm. The maximum biosorption capacity was 47.15 mg/g of Cu(II) ions onto Eucalyptus bark powder. Kinetic studies showed the pseudo-second-order described the biosorption experimental data better than the pseudo-first-order kinetics. The Desorption studies were carried out using dilute HCl, and the effect of HCl concentration on desorption was studied. The finding of the present study indicates that Eucalyptus bark can be successfully used for separation of Cu(II) from aqueous solutions.

Key words: Biosorption; Eucalyptus bark; Cu(II); Kinetics; Isotherms

1. INTRODUCTION
Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. The production of copper has lifted over the last decades and due to this copper quantities in the environment have expanded. Copper is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives and it is highly toxic [1]. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. World Health Organization (WHO) recommended a maximum acceptable concentration of Cu(II) in drinking water of 1.5 mg/L [2]. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants have a chance of survival. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [3]. Since heavy metal ions are not biodegradable agents, they are usually removed from the contaminated water by physical or chemical treatment processes. The conventional methods for removing the heavy metals include coagulation, chemical precipitation, ion-exchange, adsorption, membrane separation, reverse osmosis, oxidation, evaporation, electro-flotation, solvent extraction, etc. However, most of these methods have some disadvantages such as complicated treatment process, high cost and huge amount of energy consumption. Among these methods, adsorption is the most widely used method because it is an economically feasible, simple, effective, versatile and environmentally friendly method in practice [4-6].

In recent years, there has been considerable interest in the used of biological materials, including algae, bacteria, fungi, agricultural by-products and residues as biosorbents to remove toxic metals from aqueous solution by biosorption [7-12]. Among these materials, agricultural by-products and biomass are relatively cheap and exhibit very high biosorption capacities. The present work focused on the potential use of Eucalyptus bark powder for removal of Cu(II) ions from aqueous solution. Experimental parameters affecting the biosorption process such as pH, contact time, biomass dosage and initial metal ion concentration. The experimental equilibrium biosorption data are analyzed by both Langmuir and Freundlich isotherm models. The biosorption
kinetics was examined using the Lagergren’s pseudo-first-order and pseudo-second-order models. The desorption of Cu(II) from Eucalyptus bark powder was also studied using HCl (0.05 to 0.25 M) solution.

2. MATERIALS AND METHODS

2.1 Materials
All of the chemical reagents used in the experiments were of analytical grade. A stock solution of copper of 1000 mg/L was prepared by exact quantities of 2.682 g using CuCl₂·2H₂O in double distilled water. Purified water was prepared a Millipore Milli-Q water purification system. Cu(II) solutions of different concentrations were obtained by diluting the stock solution. The pH value of each test metal solution was adjusted to desirable value with 0.1M HCl and 0.1M NaOH.

2.2 Preparation of biosorbent
Eucalyptus bark was collected from a local Eucalyptus tree near Udayagiri, Nellore District, Andhra Pradesh, India. Eucalyptus bark was thoroughly washed with distilled water to remove mud and dirt. Then Eucalyptus bark powder as soaked in 0.1 N NaOH to remove lignin based colour materials followed by 0.1N H₂SO₄. Finally it was washed with distilled water several times and dried in an oven at 70 °C for 8 h and cooled at room temperature in desiccators. The dried bark was ground to fine powder and used as biosorbent.

2.3 Characterization of biosorbent
The characterization of biosorbent was conducted using Fourier transform infrared spectroscopy (FTIR; Nicolet 6700 Thermo Scientific, USA) to determine the functional groups on the biosorbent. In the biosorbent, the sites responsible for the biosorption process are due the chemical functional groups such as the carboxyl, amide and hydroxyl groups.

2.4 Analysis
The concentration of nickel in the solutions before and after equilibrium was determined by Atomic Absorption Spectrophotometer (AA-6300, Shimadzu, Japan). A pH meter (Sartorius pp-15, Germany) was used for pH measurements. The pH meter was calibrated using buffer standard solutions of pH 7.0, 4.0 and 10.0.

2.5 Biosorption experiments
Batch biosorption experiments were conducted at room temperature to study the effect of solution pH, biosorbent dosage, contact time and initial metal ion concentration. Each experiment was carried out in a 50 mL of falcon bottle containing 30 mL of Cu(II) solution, with constant agitation at 160 rpm. The pH edge experiment was conducted at variable pH by controlling HCl and NaOH. After 24 h, which was sufficient to attain equilibrium, the final pH values were measured and the biomasses were separated by centrifugation. The Cu(II) concentrations remaining in the supernatant were analyzed using an Atomic Absorption Spectrophotometer after appropriate dilution. In kinetic studies, samples were taken out at different time. Samples were taken at given time intervals and centrifuged at 1000 rpm for 10 min, then the supernatant fractions were separated and analyzed for the remaining metal concentration. In order to evaluate the Cu(II) sorption capacity of the biomasses, isotherm experiments were also conducted over an initial metal ion concentration range of 50-300 mg/L. The pH of the solution was maintained at the desired value during the experiments. All other experimental conditions were the same as those used in the pH edge experiments.

The amount of metal adsorbed by the biomass was calculated using the following equation.

\[ q = \frac{(C_i - C_f)V}{M} \]  

where \( q \) is the amount of metal adsorbed by biomass (mg/g), \( C_i \) is the initial concentration of metal ion (mg/L), \( C_f \) is the final concentration of metal ion (mg/L), \( M \) is the mass of the biomass in the adsorption medium (g) and \( V \) is the initial volume of the biosorption medium (L).

3. RESULTS AND DISCUSSION

3.1 FTIR analysis
The FTIR results are presented in Fig. 1. The broad and strong bands at 3300-3580 cm⁻¹ represent the bounded hydroxyl (-OH) groups of the Eucalyptus bark powder. The peaks at 2335 and 2362 cm⁻¹ signify the stretching vibrations of -NH₂, -NH⁺ and -NH groups of the biosorbent. The bands peaks at 1643, 1517 and 1423 cm⁻¹ may be attributed to asymmetric and symmetric stretching vibration of carboxyl (-C=O) groups. The bands observed at 1049 and 1105 cm⁻¹ were assigned to C-O stretching of a alcohols and carboxylic acids. Some bands in the fingerprint region could be attributed to the phosphates groups. After Cu(II) biosorption, the stretching vibration bands of hydroxyl were shifted to 3290-3588 cm⁻¹ for Cu(II) –loaded Eucalyptus bark powder. The stretching vibration bands of amide groups were shifted to 2329 and 2358 cm⁻¹. The asymmetric and symmetric stretching vibration bands of carboxyl groups were shifted to 1648, 1512 and 1419 cm⁻¹. The bands assigned to C-O stretching were also shifted to 1108 and 1045 cm⁻¹. These results indicate that the chemical interactions as ion exchange between the metal ions and the hydrogen atoms of carboxyl, hydroxyl, and amide groups of the biomass were mainly involved in the biosorption.
3.2 Effect of pH
The pH of solution has been identified as one of the most important parameters affecting metal ion sorption. This is partly because hydrogen ions themselves are strongly competing with sorbate. The biosorption of Cu(II) as a function of hydrogen ion concentration was examined over a pH range of 1-7 and the results were presented in Fig. 2. At high pH values (pH>5), the biosorption yield was dramatically decreased. The effect of pH can be explained considering the surface charge on the biosorbent. At low pH value (pH 1), due to high positive charge (protons) density on the surface sites, electrostatic repulsion will be high during the biosorption of metal ions resulting in lower biosorption yield. Electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal biosorption. When the pH values increased, biosorbent surfaces were more negatively charged and the biosorption of the metal ion with positive charge (Cu$^{2+}$) process was reached maximum around pH 5.0. Decrease in biosorption at higher pH (pH>5) is due to the formation of soluble complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease again. The maximum biosorption efficiency for Cu(II) ions on Eucalyptus bark powder was observed at pH 5.0. Previous studies also reported that the maximum biosorption efficiency for Cu(II) metal ion on biomass was observed at pH 5.0 [13-15]. Therefore, further experiments were carried out with an initial pH value of 5.0.

3.3 Effect of biomass dosage
The effect of biomass dosage on the biosorption of Cu(II) ions was studied using different biomass dosage in the range 100-700 mg (Fig. 3). Results showed that the biosorption efficiency was highly dependent on the increase in biomass dosage of solutions up to 500 mg where the maximum biosorption (91%) of the metal ions was attained. This can be expected because the higher dose of biosorbent in the solution, the greater availability of exchangeable sites for the ions. However, the biosorption efficiency was almost the same at biomass dosage higher than 500 mg. This could be attributed to a partial aggregation of biomass which reduces effective surface area for the biosorption. Therefore, the optimum biomass dosage was selected as 500 mg for further experiments.

3.4 Kinetic experiment
For any practical applications, the process design, operation control and sorption kinetics are very important [16]. The sorption kinetics in a wastewater treatment is significant, as it provides valuable insights into the reaction pathways and the mechanism of a sorption reaction. In addition, the kinetics describes the solute uptake, which in turn controls the residence time of a sorbate at the solid-solution interface. To examine the contact time required to reach the equilibrium state, the kinetic experiments of Cu(II) sorption were carried out at constant pH 5.0. The sorption kinetics curves for Cu(II) are shown in Fig. 4. The experimental biosorption kinetic data were modeled using pseudo-first-order [17] and pseudo-second-order kinetics [18], which can be represented in their non-linear regressions by the following equations.

**Pseudo-first order model**

\[
q_t = q_e (1 - \exp(-k_1 t))
\]

**Pseudo-second order model**

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}
\]

where \(q_e\) is the amount of metal sorbed at equilibrium (mg/g), \(q_t\) the amount of metal sorbed at time \(t\) (mg/g), \(k_1\) the pseudo-first order rate constant (1/min) and \(k_2\) the pseudo-second order rate constant (g/mg min). The pseudo-second-order model correlation coefficient was higher (\(R^2=0.9850\)) than the first-order model.
A comparison between the pseudo-first-order and pseudo-second-order kinetic rate constants suggest that biosorption of Cu(II) by Eucalyptus bark followed closely the pseudo-second-order kinetics rather than the pseudo-first-order kinetics. This is clear from Table 1, since the values of \( q_e \) obtained

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

(4)

where \( q \) is the amount of adsorbed metal (mg/g), \( q_m \) the maximum Cu(II) uptake (mg/g), \( b \) the Langmuir equilibrium constant (L/mg), \( C_e \) the equilibrium concentration of the Cu(II) in the solution (mg/L). As seen from the Fig. 5, the coefficient of determination \( (R^2) \) was found to be 0.9974. This result indicates that the biosorption of the Cu(II) onto Eucalyptus bark fitted well the Langmuir isotherm model. In other words, the sorption of Cu(II) using Eucalyptus bark was taken place at the functional groups/binding sites on the surface of the biosorbent, which is regarded as monolayer biosorption. The maximum biosorption capacity \( (q_m) \) of Eucalyptus bark was found to be 47.15 mg/g. The constants and correlation coefficients obtained from the isotherm models are listed in Table 2.

Figure 3: Effect of biosorbent dosage on the biosorption of Cu(II) on Eucalyptus bark powder.

Figure 4: Kinetic plots for the biosorption of Cu(II) on Eucalyptus bark powder.

from pseudo-second-order kinetic equation was close to the experimental \( q_e \) value, whereas that of pseudo-first-order \( q_e \) value did not agree with the experimental value.

3.5 Biosorption isotherms

For optimization of the biosorption process design, it is necessary to obtain the appropriate correlation for the equilibrium curve. In this study, the equilibrium data were evaluated by two isotherms models, which are namely the Langmuir and Freundlich isotherm models were analyzed. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. The Langmuir equation can be written in non-linear form [19].

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

(5)

where \( b \) is the Langmuir constant and \( C_0 \) the initial Cu(II) concentration (mg/L). The value of \( R_L \) indicates the shape of the isotherm as being either unfavourable (>1), linear (=1), favourable (0<<1) or irreversible (=0). As all the positive \( R_L \) values calculated using Eq. (3) were less than unity, the favourability of the sorption was confirmed. The Freundlich equation is often used as an empirical relationship between the concentration of a sorbate on the surface of an adsorbent and the concentration of the sorbate in the solution. The Freundlich equation based on the hypothesis of multi-layer biosorption has been widely used to

Figure 5: Langmuir and Freundlich isotherm plots for the biosorption of Cu(II) on Eucalyptus bark powder.
examine the biosorption isotherm. The Freundlich model [20] is

\[ q_e = K_f C_e^{1/n} \]  

(6)

where \( K_f \) is a constant relating the biosorption capacity and \( 1/n \) is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material. Fig. 6 shows the Freundlich equation obtained for the biosorption of Cu(II) onto the Eucalyptus bark using Eq. (6). From the plot \( K_f \) and \( 1/n \) values were found to 15.37 and 0.201 respectively. The \( 1/n \) value were between 0 and 1 indicating that the biosorption of Cu(II) using Eucalyptus bark powder was favourable at studied conditions. The \( R^2 \) value was found to be 0.9911. This result means that the Freundlich model was not able to adequately to describe the relationship between the amount of sorbed Cu(II) and its equilibrium concentration in the solution.

3.6 \( \chi^2 \) analysis

The Chi-square (\( \chi^2 \)) test was also carried out to find the best fit among the biosorption isotherm models that are used. The equation for evaluating the best fit model is to be evolved as

\[ \chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \]  

(7)

where \( q_{e,m} \) is the equilibrium capacity obtained by calculating from the model (mg/g) and \( q_e \) is the experimental data on the equilibrium capacity (mg/g). The \( \chi^2 \) values are presented in Table 2. If the data from the model are similar to the experimental data, \( \chi^2 \) will be a small number, while if they differ; \( \chi^2 \) will be a bigger number. Therefore, it is necessary also to analyze the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the biosorption system. The \( \chi^2 \) values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and better fits to Langmuir as its \( \chi^2 \) value is less than that of Freundlich model.

3.7 Comparison of the biosorption capacity with that of different biosorbents

Table 3 presents the comparison of biosorption capacity of Eucalyptus bark for Cu(II) ions with that of different biosorbents in the literature [21-29]. As clearly seen in Table 3, the biosorption capacity of Eucalyptus bark for Cu(II) is higher than that of the majority of the presented biomass. Therefore, it can be noteworthy that the Eucalyptus bark has important potential for the removal of Cu(II) from aqueous solution.

3.8 Desorption studies

Desorption is of utmost importance when the biomass preparation/generation is expensive. A successful desorption process requires the proper selection of the eluents, which strongly depends on the type of biosorbent and the mechanism of biosorption. Dilute solution of mineral acids could be employed for desorption studies. In this study,
HCl solution was selected as an eluent to desorb Cu(II) ions from the metal-loaded Eucalyptus bark powder. Desorption studies were performed with different hydrochloric acid concentrations and the results are shown in Fig. 6. From the results of this study, with the increasing of hydrochloric acid concentrations, the desorption rate also increased initially, and then become almost stable. The maximum percentage recovery of Cu(II) was 94% with 0.2 M HCl solution.

4. CONCLUSIONS
The present study focuses on biosorption of Cu(II) from aqueous solution using the Eucalyptus bark powder as a low cost biosorbent. The biosorption characteristic has been examined with the variations in the parameters of pH, contact time, biosorbent dosage and initial Cu(II) ion concentration. The maximum biosorption capacity of Eucalyptus bark powder for Cu(II) was determined to be 47.15 mg/g. The interactions between metal ions and the functional groups on the biosorbent surface were estimated by FTIR spectroscopy analysis. The experimental data were analyzed using Langmuir and Freundlich isotherm models. The equilibrium data fitted well with the Langmuir isotherm. Kinetic evaluation of the equilibrium data showed that the biosorption of Cu(II) on Eucalyptus bark powder followed well the pseudo-second-order kinetic model. The highest desorption efficiency (94%) was achieved using 0.2 M HCl. Based on all results, it can be also concluded that the Eucalyptus bark powder can be evaluated as an alternative biosorbent for the treatment of wastewater containing Cu(II) ions, due to its being low-cost biosorbent and having a considerable high sorption capacity.

5. REFERENCES
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Bibliographical Sketch

Dr. Vijaya Yarramuthi, published 15 research articles in refereed journals. She research work focuses on removal of fluorides from aqueous solutions using chitosan based sorbents. Presently, She is working as Assistant Professor in Department of Chemistry, Vikrama Simhapuri University, Nellore, Andhra Pradesh, India.