Accessing the potential of *Lonchocarpus laxiflorus* roots (LLR) plant biomass to remove Cadmium (II) ions from aqueous solutions: Equilibrium and kinetic studies

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The potential of *Lonchocarpus laxiflorus* roots (LLR) for the removal of Cd (II) ions from aqueous solutions has been investigated. The adsorption of Cd (II) ions was found to be affected by solution pH, contact time, adsorbent dosage, initial metal ion concentration, and temperature. The equilibrium was analysed using Langmuir and Freundlich isotherm models. The data was found to have a closer correlation with the Langmuir isotherm as evidenced by a higher correlation coefficient ($R^2$). The adsorption capacity for *L. laxiflorus* was found to be 19.35 mg g$^{-1}$ and the removal efficiency of the LLR was found to be 98% under optimized conditions. The kinetics data was also subjected to pseudo-first-order and the pseudo-second-order kinetic models. The data could be explained better using the pseudo-second-order kinetic model. The selected biosorbent has been analyzed by FT-IR for identification of contributing functional groups, x-ray powder diffraction (XRD) for its structural properties and scanning electron microscope (SEM) for the structural morphology analysis.

**Key words:** Biosorption, cadmium, isotherms, kinetics, *Lonchocarpus laxiflorus*.

**INTRODUCTION**

Despite the requirement for healthy environment, the environment has been found to be contaminated with various pollutants. This has now posed a great challenge to human wellbeing. Such pollutants may be found in air, water soil, coastal erosion, overfishing and deforestation as well as disposal of waste, which constitute several heavy metals. Contamination of water by heavy metals is one of the most challenging environmental issues currently. Cadmium is one of the most toxic metals apart from lead and mercury. It has been reported to cause renal dysfunction, hypertension, lung insufficiency, bone lesions and cancer (Feng et al., 2010) which is a leading cause of death. The cadmium drinking water guidelines value recommended by WHO is 0.003 mg L$^{-1}$ (WHO, 2008). Cadmium accumulates both in the environment and the body causing long term damage to life (Nida et al., 2012). Cadmium is one of the heavy metals with a greatest potential hazard to humans and environment.

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(Fouad et al., 2012).

The principal sources of Cd into the environment are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes (Gupta and Nyaka, 2012). Once released into the environment, cadmium is toxic to plants, animals and microorganisms (Bailey et al., 1999). The metal is non-biodegradable, persistent and bioaccumulate mainly in the kidneys and liver of vertebrates, invertebrates and also in algae (Ajay et al., 2005). A number of methods have been employed to remove Cd (II) ions from the environment including ion exchange, reverse osmosis (Gupta and Nyaka, 2012), membrane filtration, electrochemical treatment, and adsorption. etc where each of them have limitations such as high cost and production of hazardous by-products are found expensive and sometimes ineffective, especially when metals are present in solution at very low concentration within the range 1 to 100 mg/cm³ (Santhi and Manonmani, 2012).

Consequently, it is essential to find new methods for effective removal of cadmium from water and wastewater. Compared with other traditional methods, adsorption is quite popular due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents (Orhan and Buyukgungor, 1993; Babel and Kurniawan, 2003). Activated carbon is the best useful adsorbent of heavy metals from waste water. However, the cost of activated carbon is high; its regeneration also requires additional expense. Therefore there is need to come up with other alternative that provide an easy, feasible, reliable, low cost adsorbents especially those of biological origin commonly referred to as biosorbents to improve the water quality. Biosorption has gained a lot of credibility currently because of its eco-friendly nature, excellent performance and cost-effectiveness (Davis et al., 2003). Equilibrium isotherm models and kinetic models were applied to the data obtained for a better understanding of the adsorption process. Thus the objective of the present study is to investigate the binding of metal ion cadmium (II) by Lonchorcarpus laxiflorus roots (LLR) in its immobilized form from aqueous solutions and to study the effect of various factors affecting the efficiency of the process.

MATERIALS AND METHODS

Biomass preparation

Plant collection and treatment

The roots of L. laxiflorus plant were collected from a tree behind Modibbo Adama Federal University of Technology Yola, Nigeria. The plant was wash thoroughly under running water to remove dust and any adhering particle and then rise with distilled water. The sample was air dry for 2 weeks and the dry roots was grinded in analytical mill and sieve to obtain adsorbent of known particle size range. The biomass powder was kept in an air tight bottle for further study (Igwe and Abia, 2006). Our studies indicated that though there was no big difference in the adsorption rates of the various parts of plant, the roots were better. Therefore roots were used in this adsorption experiments.

Chemicals

All chemicals used in the present work were of analytical grade. The stock solution of Cd²⁺ ions was prepared in 1.0 g L⁻¹ concentration. Cadmium solution of 1000 mg/cm³ concentration was prepared by dissolving 2.103 g of Cd(NO₃)₂ in 250 cm³ of distilled water and make up to 1000 cm³ in a volumetric flask. The pH of the solutions was adjusted using 0.1 mol L⁻¹ HCl and NaOH solutions.

Analysis of metal ions

Atomic absorption spectrophotometer equipped with an air acetylene flame, controlled with computer was used to investigate the concentration of cadmium metal ion. The hollow cathode lamp of Cd, was used at 283.3 nm wavelength, while slit is 0.2 nm, operated at 8 mA (Suleimain et al., 2007).

Preparation of sodium alginate and calcium chloride stock solution

Sodium alginate was prepared by weighing 4.00 g and making it up to 100 cm³ mark with distilled water in a volumetric flask and left overnight for complete dissolution. 0.12 M of calcium chloride was prepared by weighing 26.28 g in to 1000 cm³ volumetric flask and making up to mark with distilled water according to a standard procedure described by Osemeahon and Esenowo, (2012).

Immobilization of the roots of L. laxiflorus plant

Sodium alginate was used for immobilization of the roots of L. laxiflorus plant. 50 cm³ of sample solution prepared by dissolving 4 g of each test sample in 100 cm³ of distilled water and mix with 50 cm³ of 4% stock solution of sodium alginate and stir vigorously in 250 cm³ beaker, to obtain a homogenous mixture. After mixing, the solution the solution was drawn through hyperdermic needles and was added drop wise to a stirred solution of 1 M CaCl₂. A retention time of 1 h was allowed for the reaction to obtain complete precipitation of the immobilized leave powder of L. laxiflorus plant. The beads thus formed that is, sodium alginate were kept in fresh CaCl₂ solution. Before sorption studies, the beads were removed and allowed to dry at room temperature. The dried solid mass was stored in a polyethylene bag for further use (Mishra, 2013).

Biosorption experiments

The experiments were carried out in the batch mode for the measurement of adsorption capacities. From 100 ppm of cadmium metal ion solution, 50 ml was taken into a 250 ml conical flask and 0.2 g of the LLR was added corked with a rubber bung and shaken with a flask shaker for 2 h at room temperature (30°C) at 180 rpm. The separation of the adsorbents and solutions were carried out by filtration with whatman filter paper No 42 and the filtrates were stored in sample cans for use. The residual metal ions concentrations were determined using atomic absorption spectrophotometer (AAS), Pyeunicam Model SP. For studies on effect of temperature the adsorption studies were carried out at 25, 30, 40, 50, 60 and 70°C. The percentage adsorption was calculated using the following equation:

\[
\%\text{Adsorption} = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]  

(1)
Where $C_0$ = Initial metal ion concentration and $C_f$ = Equilibrium metal ion concentration (mg/L).

The amount of metal absorbed by the biosorbent was also calculated as

$$q = \frac{V(C_0 - C_f)}{M}$$  \hspace{1cm} (2)

Where, $q$ is the amount of metal adsorbed in mg/g; $C_0$ is the initial metal ion concentration in mg/cm$^3$; $C_f$ is the final concentration in mg/cm$^3$, $V$ is the volume of metal ion solution in liters; $M$ is the mass of the root of *L. laxiflorus* powder used in gram.

**RESULTS AND DISCUSSION**

The FTIR is measured in the range of 400 to 4000 cm$^{-1}$ wave number. The FTIR of the adsorbent displays a number of adsorption peaks, indicating the complex nature of the studied adsorbent. The IR bands consisted of four regions, the broad OH band (3200-3600 cm$^{-1}$), C-H stretching region (2800-3000 cm$^{-1}$), carbonyl group stretching region (1550 -1750 cm$^{-1}$), and finger print bands (below 1550 cm$^{-1}$) (Shin et al., 2007).

From Figure 1, the absorption of peak at approximately 3400 were due to stretching vibrations of hydroxyl groups which are one of the main components of cell wall polysaccharides of the plants (Suantak et al., 2011). The adsorption peak at 2930 cm$^{-1}$ is likely due to the presence of C-H asymmetric stretching vibration in –COOH group (Kumar et al., 2012) of methylene groups on the surface. The absorption band at 1630 cm$^{-1}$ may be assigned to Amide I and II (protein) respectively (Pradhan et al., 2007). While the peaks in the range of 1427 to 1328 cm$^{-1}$ could be attributed to carboxylate group (Pradhan et al., 2007). The broad peak at 1240 could be due to (C- C) or (C-H) or (C-O) stretching of the carboxyl groups (Singh et al., 2010). The peak in the region 1051 cm$^{-1}$ is due to the presence of C- C Stretching of the polysaccharides (Singh et al., 2010). In conclusion, the FTIR spectroscopic analysis of the plant biomasses indicated the presence of hydroxyl, amide and carboxylate groups as the main functional groups involved in the complexation of metal ions for biosorption processes.

The adsorption capacity of the adsorbent depends upon porosity as well as chemical reactivity of the functional groups at the adsorbent surfaces. It seems that these functional groups participate in metal binding process.

Scanning electron microscope (SEM) analysis is another important tool used in the determination of the surface morphology of an adsorbent. The SEM image and micro- analysis of LLR plant is shown in Figure 2. The external surface of LLR is full of cavities with well developed porous structure. The external surfaces show a rough area having different pore diameters distributed over the surface of the biomass which may be responsible for metal removal. This analysis reveals a highly porous structure for LLR biomass. It could also be seen that more uneven and rough surface morphology exist in all the adsorbent.

X-ray diffraction (XRD) analysis was carried out by using XRD system with Cu-Kα radiation. The XRD patterns for LLR in raw powdered form is shown in Figure 3. These gives information about the changes in the crystalline and amorphous nature of the adsorbents. Sharp intensity XRD peaks have been observed at typical scanning angles of 2θ = 20. The sharp peaks present in the figures indicated the crystalline nature of the material. In addition, the presence of other weak intensity peaks in the spectra indicates the amorphous nature of the three adsorbents. The amorphous nature of the adsorbents suggests that metal ions can easily penetrate the surface which is desirable for an effective removal. These results are in good agreement with those reported Kugbe et al. (2009).

**Effect of pH on metal biosorption**

Hydrogen ion concentration is one of the important factors that influence the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of metal ions in solution, replaces some of the positive ions found in active sites and affects the degree of ionization of the adsorbate during the process of biosorption. This is because it affects solution chemistry and also the
speciation of the metal ions. The effect of initial pH on biosorption of Cd (II) ions onto *L. laxiflorus* was evaluated in the pH range of 3.0 to 7.0. Studies in pH range above 7.0 were not attempted as there is precipitation of cadmium (II) hydroxides.

From Figure 4 it could be seen that Cd (II) ions adsorption increased as the pH increased. At low pH values, protons occupy the biosorption sites on the biosorbent surface and therefore less Cd (II) ions can be adsorbed because of electrostatic repulsion between the metal cations and the protons occupying the binding sites. When the pH was increased, the biosorbent surface became more negatively charged and the biosorption of the metal cations increased drastically until equilibrium was reached at pH 6.0 to 7.0. At pH of >7.0 there is formation of hydroxylated complexes of the metal ions and these complexes compete with the metal cations for the adsorption sites hence a reduction in the effective metal cations removal. Therefore adsorption experiments at pH above this were not considered.

**Effect of biosorbent dosage**

The effect of biomass dosage on adsorption of Cd (II) ions is indicated in Figure 5. The number of available binding sites and exchanging ions for the biosorption depends upon the amount of biosorbent in the biosorption system. This is attributed to the fact that it determines the number of binding sites available to remove the metal ions at a given concentration. The dosage also determines the adsorption capacity of the biosorbent with an increase in mass reducing the biosorption capacity as the mass increase from 0.1 to 2.5 g per 20 ml of adsorbate. An increase in the % adsorption is attributable to an increase in the number of binding sites for the metal cations. Similar results were recorded in the literature for other adsorbents. However, the mass could not be increased infinitely as at some point all the solution is sequestered leaving no residual solution for concentration determination. Similar trend have been found by Mahajan and Sud (2011).

**Effect of initial metal concentration**

The initial concentration remarkably affected the uptake of Cd (II) ions in solution. The efficiency of Cd (II) ions adsorption by LLR at different initial concentrations (10 to 80 mg L⁻¹) was investigated as shown in Figure 6. At a lower concentration, the adsorption sites take up the available metal ions much quickly due to less competition among the metal ions for the available binding sites which are fixed in this case. However, as the concentration increases the competition for the limited
Figure 6. Effect of initial cadmium concentration on adsorption of LLR biomass.

Figure 7. Effect of contact time on adsorption of Cd (II) ions by LLR.

Effect of initial cadmium concentration on adsorption of LLR biomass.

Effect of contact time

Contact time is an important parameter for any successful use of the biosorbents for practical purposes. Effect of contact time on adsorption of Cd (II) ions was investigated keeping the biomass in contact with the metal ion solution for different time periods between 0 to 60 min. It was noted that as adsorption proceeds, the sorbent reaches saturation state, at this point the soaked solute tends to desorbs back into solution (Figure 7). Eventually, the rate of adsorption and desorption are equal at equilibrium. When the system attains equilibrium, no further net adsorption occurs. The time taken to attain equilibrium is very important for process optimization. The rate of adsorption is very fast at first and over 95% of total biosorption of Cd (II) ions occurs in the first 5 min and thereafter it proceeds at a slower rate and finally no further significant adsorption is noted beyond 20 min of contact time. The very fast adsorption makes the material suitable for continuous flow water treatment systems (Sarin and Paint, 2006).

Effect of temperature

Temperature of the medium affects the removal efficiency of pollutants in aqueous solutions. This is because a change in temperature in turn affects the solubility of pollutants and also the kinetic energy of the adsorbing ions. Therefore the effect of temperature on adsorption of Cd (II) ions was investigated and the data is shown in Figure 8. The results indicate that the percentage adsorption increases with increase in temperature up to 40°C, after that any increase in temperature is accompanied by a reduction in % adsorption. This can be attributed to the fact that with increase in temperature of the solution, the attractive forces between the biomass surface and Cd (II) ions are weakened thus decreasing the sorption efficiency. This could be due to increase in the tendency for the Cd (II) ions to escape from the solid phase of the biosorbent to the liquid phase with increase in temperature. Finally increased temperature beyond 40°C could have destroyed some of the binding sites on the biosorbent surface due to bond rupture (Meena et al., 2005).

Biosorption kinetics

Kinetic study provides useful information about the mechanism of adsorption and subsequently investigation of the controlling mechanism of biosorption as either mass transfer or chemisorption. This helps in obtaining the optimum operating conditions for industrial-scale batch processes. A good correlation of the kinetic data explains the biosorption mechanism of the metal ion on the solid phase (Garima and Dhiraj, 2013). In order to
evaluate the kinetic mechanism that controls the biosorption process, the pseudo-first-order models (Lagergren, 1898) were applied for biosorption of Cd (II) ions on the biosorbent. The Lagergren pseudo-first-order rate model is represented by the equation:

\[ \log q_e - q_t = \log q_e - \frac{K_1}{2.303} t \]  

Where \( q_e \) and \( q_t \) are the amounts of metal adsorbed (mg g\(^{-1}\)) at equilibrium and at time \( t \) respectively, and \( K_1 \) is the rate constant of pseudo-first-order biosorption (min\(^{-1}\)). The \( q_e \) and rate constant were calculated from the slope and intercept of plot of \( \log (q_e - q_t) \) against time \( t \).

The pseudo-second-order equation (Ho and Mckay, 1999) assumes that the rate limiting step might be due to chemical adsorption. According to this model metal cations can bind to two binding sites on the adsorbent surface. The equation can be expressed as shown below:

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e b} \]  

Where \( K_2 \) is the rate constant of the pseudo-second-order adsorption (g/mg/min). If the adsorption kinetics obeys the pseudo-second-order model, a linear plot of \( t/q_t \) versus \( t \) can be observed as shown in Figure 9.

**Biosorption isotherms**

For optimization of the biosorption process design, it is imperative to obtain the appropriate correlation for the equilibrium data. Biosorption isotherms describe how adsorbate interacts with the biosorbent and the residual metal ions in solution during the surface biosorption. The isotherms also help in determination of adsorption capacity of the biosorbent for the metal ions. The data on Cd (II) ions biosorption was fitted with the Langmuir (1918) and Freundlich (1906) isotherms (Figures 10 and 11).

The Langmuir isotherm assumes monolayer coverage of the adsorbate onto a homogeneous adsorbent surface and the biosorption of each cation onto the surface has equal activation energy. The Langmuir isotherm can be expressed as:

\[ \frac{c_e}{q_e} = \frac{1}{q_{max} b} + \frac{c_e}{q_{max}} \]  

Where \( q_{max} \) is the monolayer capacity of the biosorbent (mg g\(^{-1}\)), and \( b \) is the biosorption constant (L mg\(^{-1}\)). The plot of \( c_e/q_e \) versus \( c_e \) should be a straight line with a slope of \( 1/q_{max} \) and intercept of \( 1/q_{max} b \) when the biosorption follows Langmuir equation. The Freundlich equation can be expressed as:

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

Where \( K_f \) and \( 1/n \) are the Freundlich isotherm constants related to biosorption capacity and biosorption intensity respectively. If the equation applies then a plot of \( \log q_e \) versus \( \log C_e \) will give a straight line of slope \( 1/n \) and intercept as \( K_f \).

LLR has a higher value for \( n \) suggesting multilayer sorption on the surface of the plant biomass, which is due to its various chemical functional groups. The values of \( b \) and \( K \) obtained for LLR also confirms a higher sorption capacity and superior performance of LLR adsorbents for Cd (II) ions adsorption from aqueous solution. Similar results are reported by Mahajan et al. (2013), Iqwe et al. (2005) and Kurniawan and Thiam (2010).
Conclusion

Adsorption of cadmium ions from aqueous solution using the *Lonchocarpus laxiflorus* plant roots material was investigated. Various contributing parameters such as contact time, initial metal ion concentration, solution pH, and adsorbent dose was optimized for maximum removal efficiency. The sorption data fitted well with Langmuir isotherm with high $R^2$ values. The kinetic studies indicated that the pseudo second order model was the best one in describing the kinetics of cadmium (II) adsorbed onto roots powder. A large number of carbonyl and hydroxyl groups were observed in the FTIR analysis, XRD studies reveal the crystalline structure of the biosorbent and SEM studies showed the presence of various moieties that enhances the adsorption phenomenon. Excellent removal efficiency in its encapsulated form explores the utilization of the biomass at the commercial scale for small scale industries, making it of potential commercial use.

Conflict of Interest

The authors have not declared any conflict of interest.

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