Research Article

Biosorption of Lead (II) and Copper (II) Metal Ions on *Calotropis procera* (Ait.)

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Abstract

Heavy metals are present in some industrial effluents, being responsible for environmental pollution. Biosorption of heavy metals can be an effective method for the removal of heavy metal ions from wastewaters. In this study Pb(II) and Cu(II) biosorption by Calotropis procera (Ait.) was investigated in batch system from a binary mixture. The effects of some important parameters such as pH, initial concentration of heavy metals and modification of biomass surface by heat/acid treatment on biosorption capacity were studied. The maximum biosorption capacity of Calotropis procera (Ait.) was 14.5mg/g at pH 5.0 for Cu(II) and 22.8 mg/g at pH 4.0 for Pb(II) metal ions. The biosorption capacity of Pb(II) and Cu(II) ions on the acid/heat-treated biomass was increased as 1.37 and 1.46 times than untreated form, respectively. The biosorption of Pb (II) and Cu (II) heavy metal ions on Calotropis procera (Ait.) appears to be an efficient and low cost alternative to be considered in industrial wastewater treatment.

Keywords*:* Biosorption, *Calotropis procera* (*Ait.*), heavy metals, modification, pollution.

Introduction

Many industrial processes produce large amounts of wastewater, which are leading to detrimental effects on human life and environment. Scientists have therefore taken on the challenge to examine myriad issues arising from industrial processes, environmental management and plausible choices that need to be made in our quest for cleaner, friendlier and safer environment.

The major pollutants in wastewater are heavy metals such as lead, zinc, copper, cadmium, mercury, chromium and arsenic. These metals accumulate in living tissues/organs and can cause accumulative poisoning and serious health problems such as cancer and brain damage. There are numerous methods currently employed to remove these metals from aqueous environment. Some of these methods are chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation. Biosorption as a wastewater bioremediation process has been found to be an economically feasible alternative for metal removal. This method offers the advantages of low operating cost, minimizing secondary pollution and high efficiency in wastes (Volesky & Holan, 1995; Tien, 2002). The use of non-living biomass in biosorption is more practical and advantageous because living biomass cells often require the addition of fermentation media which increases the biological oxygen demand or chemical oxygen demand in the effluent. In addition, non-living biomass is not affected by the toxicity of the metal ions, and they can be subjected to different chemical and physical treatment techniques to enhance their performance.

Physical treatment methods such as heat, acid and base treatments have usually shown an increase in biosorption capacity of plant biomass due to re-organization of cell wall structure (Gong *et al*., 2005).

Calotropis procera (Ait.), also called rooster tree, giant milkweed or Sodom apple, is a member of flowering plant species in the dogbane family, *Asclepiadaceae.* This plant is a soft wooded, evergreen, perennial shrub. Giant milkweed is native to West Africa as far south as Angola, North and East Africa. The leaves are widely used in Nigeria for coagulation of milk in preparing cheese (Ogugua & Muller, 1987).

In this study, the biosorption of Pb(II) and Cu(II) by *Calotropis procera* (Ait.) powdered from single and binary mixtures are investigated. Also the effect of the system parameters such as pH, initial metal concentration and acid/heat-treatment on the biosorption capacity of the biomass were investigated.

Materials and Methods
Biomass
Calotropis procera (Ait.) leaves were collected locally from Oyo West local government area of Oyo State, Nigeria. The leaves were authenticated at the Forestry Research Institute of Nigeria (FRIN), Ibadan, Oyo State. Samples were washed twice with distilled water. The washed biomass was oven-dried at $50^{o}C$ for 24 h, crushed with an analytical mill, sieved (size fraction of 0.5–1 mm) and stored in polyethylene bottles until use.

Biosorption Studies
The biosorption experiments were conducted in Erlenmeyer flasks containing 50 ml of heavy metal solutions and 0.1 g of *Calotropis procera* (Ait.) biomass. The flasks were agitated on a shaker at 150 rpm constant shaking for 6 hours to ensure equilibrium was reached. Studies were performed at a constant temperature of 25°C to represent the environmental conditions. At the end of experimental period, metal solutions were separated from the biomass by centrifugation at 4000 rpm and analyzed using Atomic Absorption Spectrometer (GBC 933 AAA). The amount of metal adsorbed on biomass, Qm (mg/g), was calculated according to the following equation:

$$Qm = (Ci – Ceq) V / m, \text{------------------}(1)$$

where V is the volume of metal solution (ml), m is the mass of dry *Calotropis procera* (Ait.) (g), Ci and Ceq are the initial and equilibrium concentration of metal in solution (mg/l), respectively.
Also the effect of solution pH on biosorption of metal ions was studied. For this purpose aqueous solutions adjusted to the predetermined pH values in the range of 2.0 to 6.0 were used.
To determine the effect of initial metal concentration on biosorption capacity of *Calotropis procera* (Ait.), five different Pb(II) and Cu(II) concentrations(25–200 mg/l) of metal solutions were prepared.

Competitive Biosorption
The competitive biosorption of divalent cations Pb (II) and Cu (II) was tested through batch experiments. For this purpose, the binary mixtures composed of 100 mg/l Pb (II) and Cu (II) were prepared. Biosorption of metal ions with binary aqueous solutions containing fungal biomass were carried out similarly as in a single-component metal systems, as explained under "Biosorption Studies" section, but only at pH 5.0 and 4.0.

Modication of Biomass
Here, the biomass modification with acid and heat treatments were performed together. The biomass was treated with 2% hydrochloric acid for 2 hours with continuous stirring at 150 rpm in the water bath at $80^{o}C$. Treated biomass were filtered, washed with deionized water and dried in oven at $50^{o}C$. Biosorption

experiments were repeated with acid/heat treated biomass as mentioned above.

Results and Discussion
Effect of pH

pH has a very significant effect on biosorption of metal ions from solutions. It is known that the solution of pH affects the surface charge of the biomass, the specification of the functional groups such as carboxylate, phosphate, hydroxyl and amino groups of the cell wall (Vilar, Botelho & Boaventura, 2005).

Figure 1 shows the biosorption of Pb(II) and Cu(II) on *Calotropis procera* (Ait.) as a function of pH. The % error calculated for each data point is less than 0.01 and therefore not visible in the figure. The maximum Pb(II) biosorption was reached at pH 4.0 and the maximum recorded Pb(II) adsorptions was 22.8 mg/g. In the case of Cu (II) biosorption, maximum biosorption capacity was 14.5 mg/g at pH 5.0.
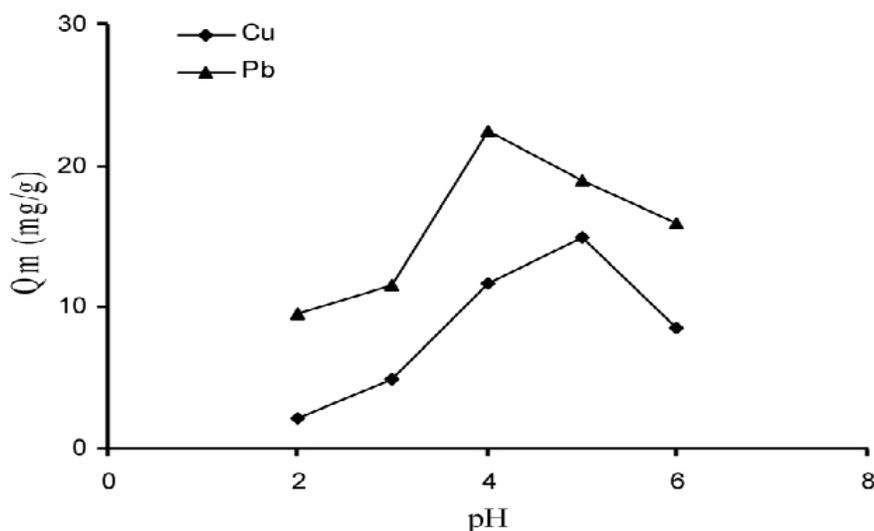

Figure 1: Effect of pH on biosorption of Pb (II) and Cu (II) metal ions

As it can be depicted from Figure 1, the biosorption of Pb(II) and Cu(II) metal ions by *Calotropis procera* (Ait.) was strongly affected by pH. A sharp increase in metal uptake was observed with increasing pH. These results can be explained using the fact that with increasing pH, functional groups available on biomass surface would be exposed will increase, and thus negative charges will result. So the attraction between the negatively charged cell wall and the metals would increase. Another reason for increasing biosorption of metal ions with increasing pH is the the zero-point charge of the biomass (pH 2.9–3.0) (Abu Al-Rub, El-Nass, Ashour, & Al-Marzou, 2006). At pH values above the zero-point charge, the leaf cells would have negative net charge and the electrostatic attractions between positively charged cations such as Pb(II) and Cu(II) and negatively charged binding sites on the biomass surface is enhanced. All these reasons explain the significant increase of the binding efficiency by increasing the pH from 3.0 to 5.0. At pH below 3, biosorption capacity of Pb(II) and Cu(II) were negligible, probably due to the cation competition effects with hydroxonium ion H_3O^+. Furthermore, at pH 6.0 biosorption of metals decreased probably because of chemical precipitation (Aksu, 2005).

Initial Metal Concentration

The metal distribution between the biomass and the aqueous solution at equilibrium is of importance in determining the maximum biosorption capacity of the biomass for Pb (II) and Cu(II) metals. The effect of initial metal concentration on the biosorption capacity was investigated at pH 4.0 for Pb (II) and pH 5.0 for Cu(II) metal ions. In Figure 2, biosorption of Pb(II) and Cu(II) increased much quickly with increasing initial metal concentration from 25 to 100 mg/l.

A higher initial concentration provides an important driving force to overcome all mass transfer resistances between the metal solution and *Calotropis procera* (Ait.) cell wall, and therefore the the biosorption capacity increases. In addition, the number of collisions between metal ions and the biosorbent increases with increasing initial metal concentration so the biosorption process is enhanced (Aksu, 2005). Biosorption rate was decreased with increasing initial concentration from 100 to 200 mg/l and this can be explained by the saturation of the biosorption sites on the biomass surface.
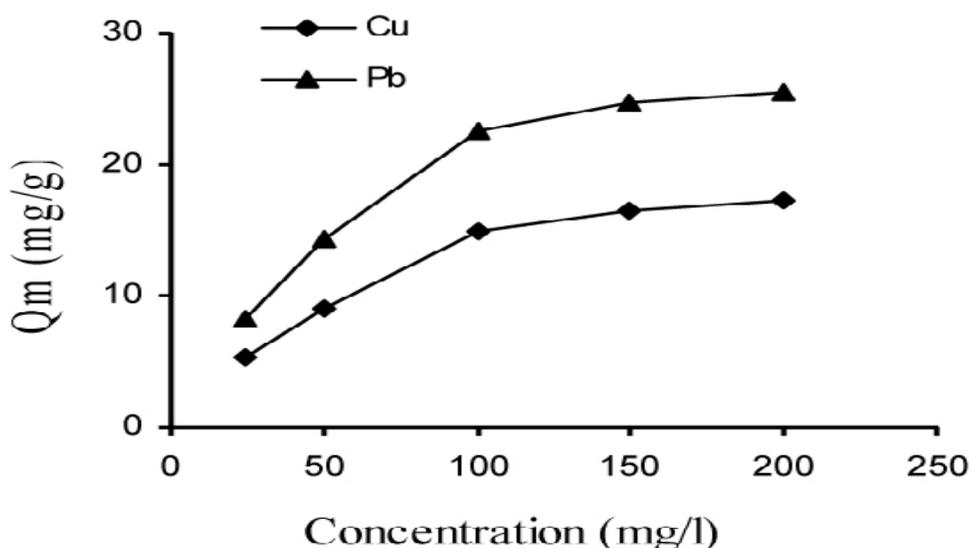

Figure 2: *Effect of initial metal concentration on biosorption capacity*

Competitive Biosorption

In wastewaters, synergistic or antagonistic interactions can be caused by the presence of other cationic and anionic metal ions. Therefore the competitive effect becomes important in the wastewater treatment applications. The results of the competitive biosorption of the Pb(II) and Cu(II) metal ions on the biomass cells are shown in Figure 3. The % error calculated for each data point is less than 0.01 and therefore not visible in the figure.

The presence of another cationic metal resulted in a suppression of metal uptake. The biosorption capacity was decreased 20% and 41.2% in the competitive biosorption at pH 4.0 for Pb(II) and Cu(II) metal ions, respectively. At pH 5.0 biosorption capacity was decreased 37% and and 28% for Pb(II) and Cu(II) metal ions, respectively. The suppression in Cu (II) uptake in the presence of Pb(II) was much more significant than the suppressions in Pb(II) uptake in the presence of Cu(II) ions. These

suppressions in competitive biosorption indicate an overlap in the biosorption site of the leaf cell wall. In the presence of another metal, chemical interactions between metal ions and a competition for the binding sites occurred and the biosorption capacity decreased (Abu Al-Rub *et al.*, 2006).
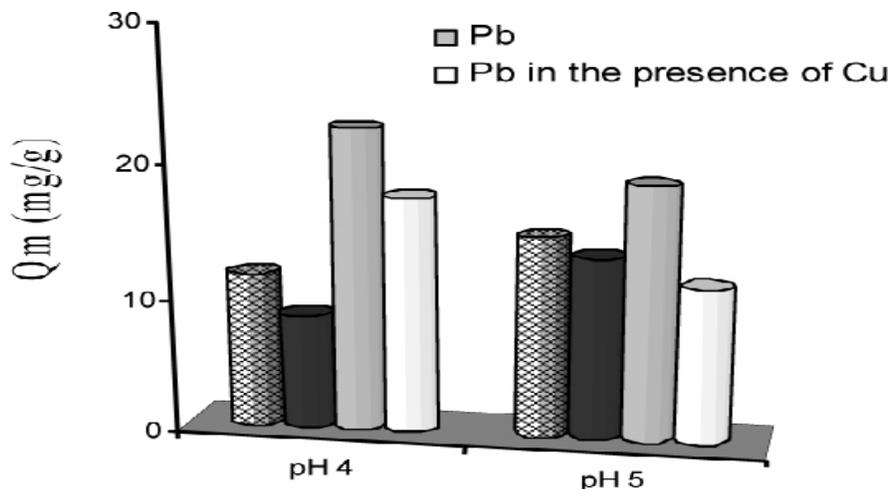

Figure 3: Competitive biosorption of Pb(II) and Cu (II) Metal ions

Since most of the functional groups present on the plant cell wall are non-specific for a metal so the different metals interact with the binding sites and the competition occur. It has been reported that the biosorption process is enhanced with the increasing ionic radii of metals, which follows the order Pb(II) > Cu(II) (Aksu, 2005).

The differences in biosorption capacities may be explained by differences in the electronegativity of the metal ions, which also follows the order Pb(II) > Cu(II). The greater the electronegativity, the greater is the affinity, which also explains the significant suppression of copper uptake in the presence of lead (Chong & Volesky, 1995).

Modification of Biomass

Biosorption capacities of un-treated and acid/heat-treated biomass are shown in Figure 4. The % error calculated for each data point is less than 0.01 and therefore not visible in the figure. An increase in biosorption capacity was observed after acid/heat-treatment. The biosorption capacity of Pb(II) and Cu(II) ions on the acid/heat-treated biomass was 1.37 and 1.46 times higher than untreated form, respectively.
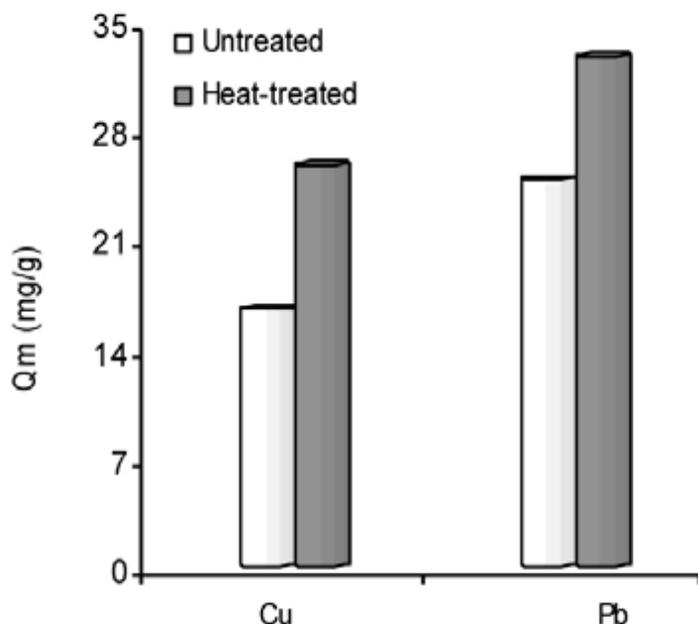
Fiureg 4: *Effect of acid/heat treatment on biosorption capacity of Pb(II) and Cu (II) metal ions*

Modification of biomass by heat and acid treatment results a re-organization of cell wall so the additional binding sites occurred. Acid and heat treatment degrade some components of the plant cell wall. The hydrochloric acid breaks the pectose down to pectin or pectic acid. By heating some compounds in cell wall dissolved and new binding sites formed (Yu *et al.*, 1999). In addition, proteins located in cell wall are denaturated by the acid treatment and structural changes occurred. All these cumulative effects of modification explain the increased biosorption capacity. The increase in biosorption capacity with modification may be a result of these changes in cell wall structure.

Conclusions

Biosorption technology, utilizing natural materials for effectively removing metals from aqueous media, offers an efficient alternative compared to traditional chemical and physical treatments. The goal of this work was to explore the potential use of *Calotropis procera* (Ait.) biomass as a low-cost sorbent for the removal of Cu(II) and Pb(II) heavy metal ions from aqueous solutions. Batch experiments showed that *Calotropis procera* (Ait.) have a remarkable ability to take up Cu(II) and Pb(II) heavy metal ions. The maximum biosorption capacity of heavy metal ions on *Calotropis procera* (Ait.) were 15.8 mg/g for Cu(II) and 25.8 mg/g for Pb(II) and the affinity Pb(II) > Cu(II). The results obtained showed that the pH and initial metal concentration affected the uptake capacity of the biosorbent. And also acid/heat modification affected the biosorption yield and metal uptake positively. In competitive biosorption the presence of other cationic metal ions significantly decreased efficiency of metal biosorption. Many workers have also investigated the performance of algae for the removal various heavy metal ions (Ni, Cu Pb, Zn, Cd, and Al) from wastewater. Yu *et al.* reported that capacities of macro marine algae for lead, copper, and cadmium were in the ranges of 1.0 to 1.6, 1.0 to 1.2 and 0.8 to 1.2 mmol/g, respectively. Munoz *et al.* reported a 8.5 ± 0.4 mg/g maximum Cu(II) adsorption capacities of algal-

bacterial biomass at an initial Cu(II) concentration of 20 mg/l. Mihova and Godjevargova studied the biosorption of Cu heavy metal on different microorganisms and reported the higher adsorption capacity for S.cerevisiae (3.5 mg/g) than Ph.chrysosporium (2.5 mg/g). When compared the adsorption capacity values obtained by similar metals in literature, *Calotropis procera* (Ait.) shows great promise for the removal of heavy metal ions.

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