Biosorption of Metal Ions from Aqueous Solution by Immobilized *Moringaoleifera* Bark

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ABSTRACT

This study investigated the effectiveness of immobilized *Moringaoleifera* bark (IMOB) for the removal of heavy metal ions from waste water. The concentration of residual metal ion concentration was determined using Atomic Absorption Spectrophotometer (AAS). The immobilization of *Moringaoliefera*(*M. oleifera*) bark was achieved by entrapping it within a polymeric matrix of calcium alginate. The Sorption capacity of 95.43%, 95.51%, 93.67%, was recorded for Zn^{2+}, Cd^{2+} and Fe^{2+} respectively. An increase in sorption capacity was recorded as the pH,contact time, and initial metal ion concentration increases, while there was a decrease in sorption capacity as the ionic strength increases.The result the of study present *M. oliefera* bark as a potential biosorbent for the removal of these heavy metal ions from waste water.

Key Words: Heavy metals, *Moringaoliefera* bark, biosorption, immobilization

INTRODUCTION

Water is considered to bea vital and limited resource.Population growth, industrial development and other pressure faced by developing countries have led to structured measures to ensure sustainable management of this important natural resource (Dobson and Burges, 2007). Water will continue to be a major issue with definite and profound importance on our live and that of the planet earth (Osemeahon and Esenowo, 2012). Water contaminated by heavy metal ions has plagued the human race into a recurring hazard world-wide. The presence of these heavy metal ions in waste water

has pose an important problem for the environment as well as for the treatment process, because the disposal of both treated water and activated sludge contaminated with heavy metal ions give rise to detrimental impacts on the environment. Metals are known primarily and almost exclusively for their potential toxicity in the body, though commercially they have great advantages (Oboh and Aluyor, 2008).

In view of the toxicity and in order to meet regulatory dischargingstandards, it is essential to remove heavy metals from waste water, so as to improve its quality (Adedagalla*et al*., 2009). Conventional methods for the removal of metal ions from wastewater include chemical precipitation, electrolysis, membrane separation, ion exchange and adsorption. Most of thesemethods are hard to come by, because of the high capital and regeneration cost of the material (Huang and Wu., 1975). In the same vein, advanced water treatment techniques are too costly for many developing nations (Monica, 2009).Biosorption utilizes inexpensive dead biomass like algae, bacteria, fungi and yeast. Recent studies have also shown that heavy metals can be removed using plant materials such as palm pressed fibers and coconut husk (Tan *et al.*, 1993), duck weed Wolffiaglobosa (Upatham*et al.*, 2002), Wheat bran (Dupont*et al*., 2003) and Yohimbe bark waste (villaescusa*et al*., 2000).

The *M. oleifera* plant is found and cultivated in most parts of Nigeria, and much concentration is being focused on the use of its seed,which is presently used for many purposes. However, the full potential of *M. oleifera*is yet to be harnessed. Therefore, the aim of this study is to evaluate the potentials of*M. oleifera*bark as bio-sorbent for removal of heavy metal ions from waste water.

MATERIALS AND METHODS

Sodium alginate, calcium chloride, sodium hydroxide and hydrochloric acid wereobtained from British Drug House (BDH). *M. oleifera*bark was sampled from Ngurore in Yola South Local Government Area of Adamawa state, Nigeria. All materials were used as supplied.

Preparation of *M. oleifera*Bark

The *M. oleifera* bark wassun-dried for 21 days. It was then powdered in a mortar and sieved through 100µm mesh to produce a fine powder. The sieved material was packed in polyethylene bag for further use. First, 4.0g of the bark powder was weighed and dissolved in 100 cm^3 of water and left to stand for 12 hours.

Preparation of Sodium Alginate and Calcium Chloride solution.

Sodium alginate was prepared by weighing 4.0g of sodium alginate and making it up to100cm^3mark in a volumetric flask with distilled water. It was left overnight for complete dissolution to give 4% w/v. Calcium chloride, 0.12M, was prepared by weighing 13.32ginto IL flask and made up to mark with distilled water (Wuyep*et al*., 2007).

Immobilization of the *M. oleifera*Bark

50 $cm^3$of dissolved *M. oleifera*bark was thoroughly mixed with 50cm^3 of 4% stock solution of sodium alginate and stirred vigorously for even mixing in a 250 cm^3 beaker. The mixture was subsequently poured into another beaker containing 30cm^3 of 0.12M calcium chloride solution. The reaction was allowed retention time of 1 hour for complete precipitation. The precipitated blend solid was then filtered and allowed to dry at room temperature (30^{0}C). The dried solid mass was stored in a polythene bag for further use.

The above process was repeated by mixing other set of blend with 4% of the stock solution of the sodium alginate and *M. oleifera*bark admixture at a ratio of 100:0 90:10, 80:20, 70:30, 60:40 and 50:50. The precipitates so obtained were dried and kept separately for further use (Wuyep*et al*., 2007).

Preparation of the Metal Ions Stock Solution as Synthetic Waste Water

The metal ions chosen for this study are Zn^{2+}, Cd^{2+} and Fe^{2+}. The stock solution of 1000 ppmwas prepared by dissolving 2.10g and 4.10g and 3.54g of zinc nitrate, cadmium nitrate, and iron nitrate respectively in 1 litre volumetric flask and made up to the mark. From the stock solution,serial dilution of 200ppm of each metal ion was prepared in distilled water.

Sorbent (*M. oleifera*Immobilized Bark) Sorption Capacity

From 200ppm of each metal ion solution, $50cm^3$ was taken into a conical flask (covered with a rubber bung), 0.2g of dried sample added and then shaken with a flask shaker 2 for two hours. The solution was then filtered and the concentration of the residual metal ion in the filtrate was determined using Atomic Absorption Spectrophotometer AAS (Model 210 VGP Buck Scientific) (Charamathy*et al*., 2001). This process was repeated for all metal ions.

Determination of the Effect of pH on Sorption Capacity

The sorption characteristics of the *M. oleifera*immobilized bark at different pH values (1.0 to 6.0) were investigated at 30^0C. 1.0M hydrochloric acid and 1.0M sodium hydroxide were used to adjust the pH of the solution as the case may be. The residual metal ion was measured as stated above (Charamathy, *et al*., 2001).

Determination of the Effect of the Ionic Strength on Sorption Capacity

The ionic strength of the 200ppm solution was adjusted by dissolving about 0.1g, 0.5g, 1.0g, 1.5g,and 2.0g of NaCl to obtain 0.1 – 1.0 w/v. 0.2g of the sample was added to 50 cm^3 of the prepared solution and the equilibrium concentration of the residual metal ion was determined.

Determination of the Effects of the Contact Time on Sorption Capacity

In order to determine the kinetics of the sorption for the various metal ions, several set of samples consisting of 0.2g of the dried sorbent and 50cm^3 of the metal ion solution for each of the ions was prepared. As the samples were undergoing agitation (on the shaker), they were removed one after the other at a predetermined time interval ranging from 0.5 hours to 24 hours for analysis. The solution was filtered and analysed for residual metal ion. This was done for all metal ions at 30^0C.

Determination of the Effect of the Initial Metal Ion concentration on Sorption Capacity

The effect of the initial metal ion concentration on the sorption capacity of different samples consisting of 50cm^3 each of different metal ion concentrations ranging from 5ppm – 100ppm, but each containing 0.2g of the dried *M. oleifera*bark were prepared and shaken until equilibrium was obtained at 30^0C. The synthetic waste water was then filtered and analyzed for residual metal ion concentration

RESULTS AND DISCUSSION

Sorption Capacity

The sorption capacity for Zn^{2+} Cd^{2+} and Fe $^{2+}$is shown in figure 1.The valuesof 98.43%, 95.51% and93. 67% wasrecorded for Zn^{2+} Cd^{2+} and Fe $^{2+}$ respectively. The result from the present study is comparable to the ones reportedby (Osemeahon*et al*., 2007). The sorption capacity for different metal ions is due to the ability of the metal ion to form covalent bond with the functional groups in the biomass, the hydration free energy and the nature of the surface sites which provides large pore structure for sorption of the metal ions in the aqueous solution (Mahvi, 2008)

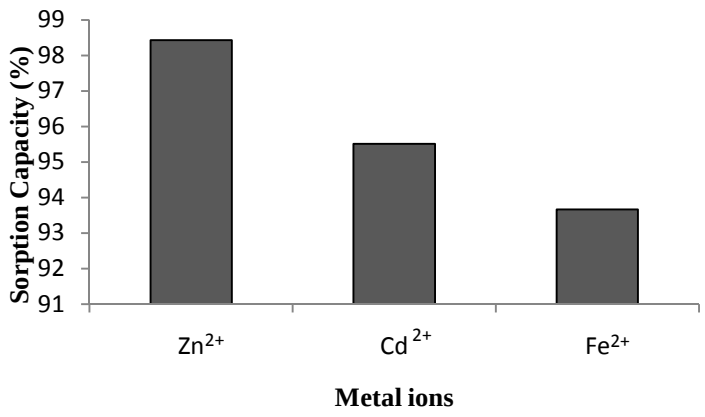

Figure 1: Sorption capacity of metal ions by IMOB

Effect of Contact Time on Sorption Capacity.

The result of sorption studies carried out as a function of contact time for the heavy metal ions is shown in figure 2. It showsthat the removal of the metal ion by Immobilised *MoringaOelifera* bark (IMOB) took place in two distinct steps: a relatively quick phase in which rapid sorption was recorded within 2 hours, followed by a slow increase in sorption capacity, until equilibrium was reached.This sorption is due to existence of functional groups in the biomass, which is capable of forming a complex with the metal ions (Rao*etal*., 2007 and Wu, 2007). The high rate of sorption is due to

the nature of the biosorbent such as surface area, porosity and its available sorption sites(Naiya*et al*., 2009). The high rate of sorption (within 2 hours)is desirable both economically and process operations.

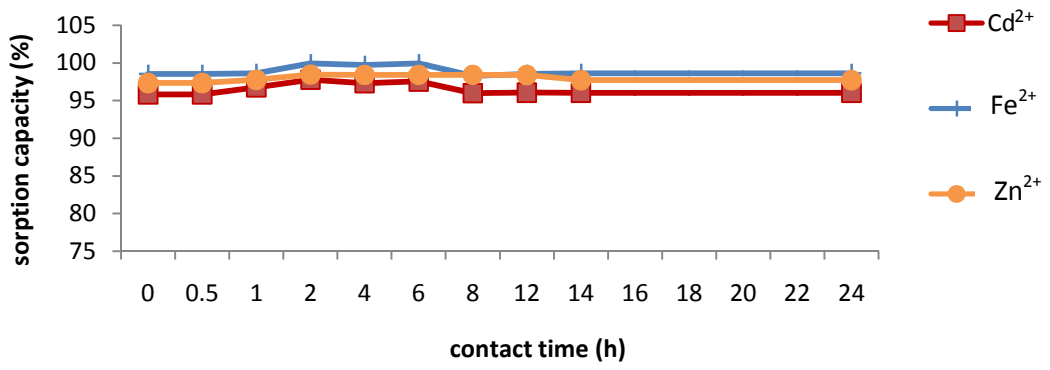

Figure 2: Effect of contact time on sorption capacity of Cd^{2+}, Fe^{2+} and Zn^{2+} by IMOB

Effect of Ionic Strength on Sorption Capacity.

Industrial waste often contains other ions such as Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}, which may interfere with the uptake of heavy metal ions by biomass. The effect of ionic strength on sorption capacity was studied and the result obtained is shown in figure 3. It is evident that the sorption capacity decreases as the ionic strength increases.

The reduction in uptake is probably due to the excess of the Na^{+}ions which inhibit the approach of the metal ions to the active sites of the bio sorbent. (Cieslak–Golanka, 1991). In the same vein there are two possible ways generally by which increasing the ionic strength can influence metal ion uptake on different biosorbent, firstly by decrease in the solution–phase activity of the metal ion and secondly by increase in the concentration of the competing ion (Na^{+}).The competition for active binding sites

between the Na^+ and metal ions could also be implicatedwith respect to the decrease in sorption capacity as the ionic strength increases (Lipinge*t al.,* 2007)

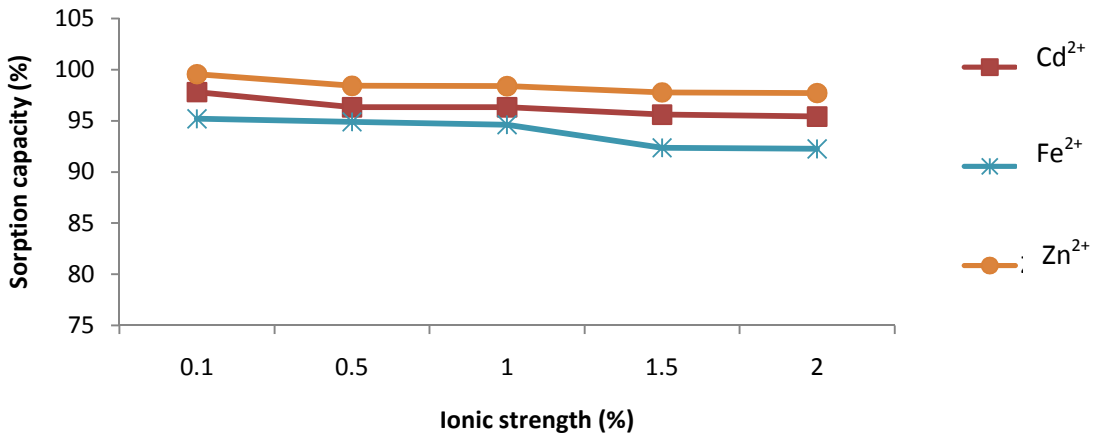

Figure:3 Effect of ionic strength on sorption of Cd^{2+} , Zn^{2+} and Fe^{2+} by IMOB

Effect of pH on Sorption Capacity.

Studies have shown that pH is an important factor affecting biosorption of heavy metals (Sanchez *et al*., 1999; and Huang *et al*., 1990). It is well known that pH affects the protonation of the functional groups on the biomass as well as the solution Chemistry.

The influence of pH on Sorption capacity was studied in the range of 1.0 – 6.0. The relationship between the values and the quantities of heavy metals sorbed on IMOB biosorbent is presented in figure 4. It can be observed that the sorption capacityincreases with increasingpH.This result is due to competition for active sorption sites between the metal ions and protons Hydrogen ions.Speciation and conversion of

metal ions to their oxides are also influential factors in this result.An optimum pH value of 4.0 was recorded for $Zn^{2+}$and Fe^{2+}respectively, 5.0 for Cd^{2+}.

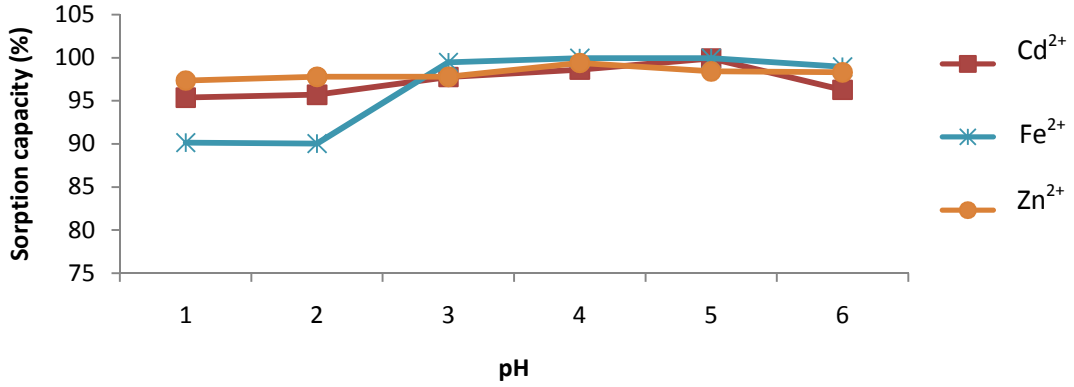

Figure 4:Effect of pH on sorption of Zn^{2+} , Cd^{2+} and Fe^{2+} by IMOB

Effect of Initial Concentration on Sorption Capacity

Figure 5 depicts the effect of initial metal ion concentration on sorption capacity. It is observed that themetal ion uptake increases with increase in initial concentration for all the metal ions studied.The mechanism of metal uptake in particular depends on the initial heavy metal ion concentration, because low concentrations metal ions are absorbed by specific active sites, while with increasing metal ion concentrations the binding sites becomes more quickly saturated as the amount of biomass concentration remained constant (Horsfall and Spiff, 2005).

It is evident from figure 5 that the sorption capacity increases as initial metal ion concentration is increased. This is because at lower concentration, the ratio of the initial number of metal ion to the available surface area is low,subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available site of adsorption becomes fewer and hence the percentage removal of the

metal ion is dependent upon initial concentration (Prabakaran*et al*., 2011).The above result can also be explained on the basis of the pore structure, surface area, and existence of a wide spectrum of surface functional groups of the biosorbent.

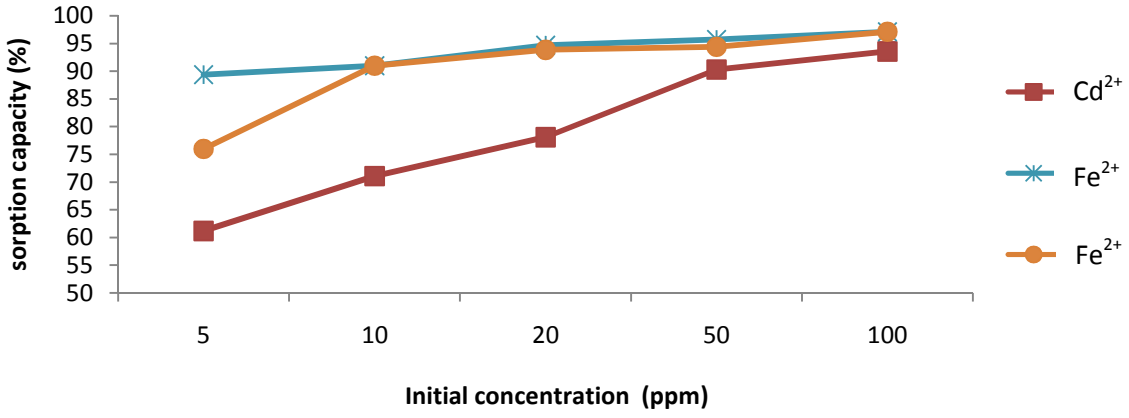

Figure 5: Effect of initial concentration on sorption of Zn^{2+}, Cd^{2+} and Fe^{2+} by IMOB.

CONCLUSION

This study indicates that*M. oliefera* bark which iswidely available in Nigeriaat low cost can be used as an efficient biomaterial for the removal of heavy metal ions from waste water. The biosorption was dependent on sorption capacity, contact time, pH, ionic strength and initial metal ion concentration. The potential portrayed by the biomass shows that it can be used as an environmentally friendly technology for wastewater treatment.

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