Evaluation of Immobilized Brachystegia Eurycoma Seeds For the removal of $\text{Fe}^{3+}$, $\text{Pb}^{2+}$, $\text{Cr}^{2+}$, $\text{Cd}^{2+}$, $\text{Cu}^{2+}$ and $\text{Mn}^{2+}$ in Aqueous Solution

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Abstract- This research studied the sorption capacity of Brachystegia eurycoma seeds (BES) for the removal of heavy metal ions from waste water. The plant seeds was immobilized by entraping or caging the bio-sorbent within a polymeric matrix of calcium-alginate to produce immobilized Brachystegia eurycoma seeds (IBES) .The sorption efficiencies of heavy metals ($\text{Fe}^{2+}$, $\text{Pb}^{2+}$, $\text{Cr}^{2+}$, $\text{Cd}^{2+}$, $\text{Cu}^{2+}$ and $\text{Mn}^{2+}$) were investigated in aqueous solution using the IBES and the residual metal ions in solution was determined using atomic absorption spectrophotometer (AAS). The effect of various parameters such as contact time, pH, ionic strength, initial metal ion concentration and temperature variation on the sorption of the above metal ions were investigated using batch experiments. The result obtained showed that the sorption efficiencies of $\text{Pb}^{2+}$, $\text{Cr}^{2+}$, $\text{Cu}^{2+}$, $\text{Cd}^{2+}$, $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ by IBES were 97.50%, 67.44%, 81.48%, 98.09%, 79.50% and 94.00% respectively. Result also shows that metal ion sorption increases with increase in contact time; initial metal ion concentration and increase in pH, and decreases with increase in ionic strength. In view of the above result, the abundant but presently wasted Brachystegia eurycoma seeds can be used as a low-cost sorbent for the removal of heavy metal ions in waste water.

Index Terms- Immobilization, Brachystegia eurycoma, Seeds, Metal ions, Sorption capacity, Aqueous solution

I. INTRODUCTION

Water is our lifeline that bathes us and feeds us. In ancient cultures water represented the very essence of life. The Romans were the first to pipe water into their growing cities, especially with their aqueducts (Onwu and Ogah, 2014). Water provides the Earth with the capacity of supporting life. An organism doesn’t have to be told how important water is to their existence. The only organism that doesn’t understand the importance of water is humans, especially in industrialized countries (Onudi et al, 2010). With two thirds of the earth's surface covered by water and the human body consisting of 75 percent of it, it is evidently clear that water is one of the prime elements responsible for life on earth. Water circulates through the land just as it does through the human body, transporting, dissolving and replenishing nutrients and organic matter, while carrying away waste material (Onwu and Ogah, 2014).

Nowadays water pollution by heavy metals is fast growing due to natural processes and increasing human activities which include mining, agriculture, and manufacturing industries. These heavy metal ions are non degradable and cannot be detoxified biologically (korrpati and Parca, 2009). Lead (Pb) is among those contaminants that must be removed from water, due to its high toxicity and tendency to accumulate in tissues of living organisms. Heavy metals are among the contaminants in the environment. Beside the natural activities, almost all these contaminants goes into the non contaminated areas as dust, leachates through the soil. These are few examples of events contributing towards contamination of the ecosystems (korrpati and Parca, 2009).

Several methods are already being used to clean up the environment from these kinds of contaminants, but most of them are costly and far away from their optimum performance. Increased knowledge about eco-toxicological effects of heavy metals as well as increased legal requirements for reduction in industrial emissions necessitates research and development in the area of wastewater treatment. Since heavy metals accumulate in the food chain and because of their persistent nature, it is necessary to remove them from waste water (Onwu and Ogah, 2014).

Recent concerns regarding the environmental contamination have initiated the development of appropriate technologies to assess the presence and mobility of metals in soil, air water, and wastewater (Sanchez et al 2008). Brachystegia eurycoma whose seeds are employed as biosorbent in this present study is a plant that grows mainly along the river banks or swamps in Western and Eastern Nigeria. It is a large tree with irregular and twisted spreading branches. The seed has a roundish flat shape with brown colour and hard hull. In Nigeria, the main culinary use of the gum from Brachystegia eurycoma seed is in the thickening soups. Thickeners are usually added as condiments in the preparation of most soups. They are known to cause increased viscosity in soups, giving it more palatability and good mouth feel (Onwu and Ngele, 2015). This property of Brachystegia Eurycoma seeds present it as a potential biosorbent (Osemeahon et al, 2007).

The objectives of this study is to evaluate the application of immobilized Brachystegia eurycoma seeds with sodium alginate as a biosorbent for the removal of Iron, Lead, Chromium, Cadmium, Copper and Manganese from wastewater and for possible industrial application.
II. MATERIALS AND METHODS

2.1 Materials

The materials used were Sodium alginate, Sodium chloride, Sodium hydroxide, Calcium chloride, and Hydrochloric acid. The chemicals were obtained from British Drug House (BDH). Brachystegia eurycoma seeds were obtained at Afikpo North Eke Market, Ebonyi State, Nigeria. The materials were used as obtained.

2.2 Methods

2.2.1 Sample Preparation

The Brachystegia eurycoma seeds were dried, roasted, soaked in warm water and the shells removed manually and further dried in an oven at 60°C for 48 hrs (Igwenyi and Akubugwo, 2010). They were milled with blender into powdery form and sifted with 100µm mesh to obtain a fine powder and then store in a clean polyethylene bag ready for immobilization process (Wuyep et al., 2007).

2.2.2 Dispersion of Brachystegia eurycoma seeds

4.00g Brachystegia eurycoma powder were weighed and dissolved in a 100cm³ distilled water and the mixture was poured into a separating funnel and live to stand for 12 hours for separation into various fractions.

2.2.3 Preparation of Sodium alginate and Calcium chloride 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 over night for complete dissolution to give 4 % w/v solution. Calcium chloride (0.12 M) was prepared by weighing 26.28 g into 1 litre volumetric flask and making it up to the mark with distilled water (Wuyep et al., 2007).

2.2.4 Immobilization Procedure of Brachystegia eurycoma(IBE) Solution.

50 cm³ of viscous layer of dissolved IBE seed was thoroughly mixed with 50 cm³ of 4% stock solution sodium alginate and stir vigorously for even mixing in a 250 cm³ beaker. The mixture was transferred into another beaker containing 60 cm³ of 0.12 M calcium chloride solution and the reaction allowed standing for 2 hrs for complete precipitation. The solid form was allowed to dry at room temperature for 7 hrs. The dry solid was washed in distilled water and store in a clean polyethylene bag for further usage (Wuyep et al., 2007).

The above process was repeated at different ratio of sodium alginate and IBE (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).

2.2.5 Preparation of Synthetic Wastewater (Metal Ion Stock Solution)

Pb²⁺, Fe³⁺, Cr³⁺, Cd²⁺, Cu²⁺ and Mn²⁺ were the heavy metal ions chosen for this study. These metal ions solution were prepared from their salt by dissolving 1.60, 3.55, 3.04, 1.63, 2.68 and 2.29 g of Lead nitrate, Iron (III) chloride, Chromium (II) chloride, Cadmium(II) chloride, Copper(II) chloride, and Manganese(II) chloride respectively in distilled water and make it up to 1 liter of solution to obtain 1000 ppm of each metal ion, then from the solution and using serial dilution, 200 ppm of each metal ion solution were prepared with distilled water. The synthetic waste water was kept for further use (Ogali et al., 2007).

2.2.6 Sorption experiment using Immobilized Brachystegia eurycoma seed

Experiments were carried out in the batch mode for the measurement of sorption capacities. From 200 ppm of each metal ion solution, 50 ml was taken into a 250 ml conical flask and 0.2 g of the immobilized Brachystegia eurycoma seed was added, corked with a rubber bung and shaken with a flask shaker for 2 hours at room temperature (30°C) at 150 rpm. The separation of the sorbents and solutions was carried out by filtration with whatman filter paper No 42 and the filtrates were stored in Sample cans for use. The residual metal ion Concentrations was determined using Atomic Absorption Spectrophotometer (AAS) Buck Scientific Model 210. (Air /Acetylene Flame, Integrated Model) Normal Parameters for Fe, Pb, Cd Cr, Cu and Mn The percentage sorption was calculated using the following equation: % Adsorption = [( Cx – Ce / Cx )] x 100/1

Where Cx = Initial metal ion Concentration and Ce = Equilibrium metal ion Concentration (mg/l) (Osemeahon et al., 2015)

2.2.7 Determination of the Effect of pH on Sorption Capacity.

At different pH values (i.e. 1.0 to 6.0), the sorption characteristics of the IBES were investigated at 30°C. The pH of the solutions was adjusted using 1.0 M hydrochloric acid and 1.0 M sodium hydroxide. Concentrations of residual metal ions were measure as earlier reported by Charmarthy et al., 2001.

2.2.8 Determination of Effect of Ionic Strength on Sorption Capacity.

The stock solutions containing known quantity of NaCl, were prepared and diluted to various desired concentrations (0.2-1.0 % W/W). 0.2 g of the sample was added to 50 cm³ of each of the solution and the equilibrium concentration of the residual metal ions were determined as reported by Wuyep et al., 2007.

2.2.9 Determination of the Effect of Contact Time on Sorption Capacity.

To determine the kinetics of the sorption for the metal ions, different set of sample consisting of 0.2 g of the dried sorbent (IBES) and 50 cm³ of the metal ion solution for each of the ions were prepared. Then the samples were shaken using flask shaker. Each set, was removed at a time intervals ranging from 30 minutes to 24 hours and thereafter, the solution were filtered and analyzed for residual metal ion. This was done for all the metal ions at 30°C as earlier reported by wuyep et al., ( 2007).

2.2.10 Determination of the Effect of Initial Metal ion Concentration on Sorption Capacity.

The effect of initial metal ion concentration on the sorption capacity of different samples were carried out 50 cm³ (each) of different metal ion concentration ranging from 5 ppm-100 ppm and, 0.2 g of the dried IBES were mixed together and shaken until equilibrium has obtain 2 hrs. The artificial wastewater was filtered and analyzed for metal ion concentration as reported by Osemeahon et al. ( 2015).

III. RESULTS AND DISCUSSIONS

3.1 Immobilization of Brachystegia Eurycoma seeds

The immobilization of Brachystegia Eurycoma seeds (IBES) was achieved by entrapping or caging it within the polymeric matrix of calcium alginate. It has been established that
sodium alginate consists of L. guluronic acid (G) and D mannuronic acid (M) units. The contacting of Ca$^{2+}$ ions with guluronic acid blocks forms an ionically cross-linked structure in aqueous environment. The cross-linking of the polymer is due to binding of divalent cations (Ca$^{2+}$) to the – COO– group of L – guluronic acid block (Mary et al., 2009).

Divalent cations Ca$^{2+}$ act as a cross-linker and cause an ionic binding between G – blocks in polymer chains and forms three dimensional network (Negin, 2011). This network mobilizes Brachystegia Eurycoma seeds to produce a biosorbent.

### 3.2 Sorption Capacity of IBES

Moisture diffusivity is an important transport property, necessary for the design and optimization of all the processes that involve internal moisture movement, including drying (Simpson, 1993). This result could be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction, also shows the difference in the metal ion affinity, sorption capacity and availability of binding sites on the biomass account for the differences in sorption capacity of different metal ion. The maximum sorption percentage reached was 99.92% for lead and least at 90.13% for manganese. From Fig 1; The sorption capacity was 99.92%, 99.22%, 98.43%, 96.21%, 95.51%, 93.67% and 90.13% for Pb$^{2+}$, Cr$^{3+}$, Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Fe$^{2+}$ and Mn$^{2+}$ respectively. The rapid sorption of metal ions can be attributed to the highly porous structure of the biosorbent which provides a less and large surface area for sorption of the metal ions to the binding sites (Ogbonna et al., 2014).

#### 2.3 Effect of pH on Sorption of IBES

The amount of metal ions adsorbed onto the sorbent at the various pH values are shown in Figure 1. The sorption capacity of the biosorbent increased with increase in pH of the solution and maximum pH value for sorption of Cd$^{2+}$ and Mn$^{2+}$ by IBES was observed at pH 5 with sorption capacities of 98% for Cd$^{2+}$ and 95% for Mn$^{2+}$. Generally the pH at which the metal ions recorded high sorption capacity are pH 4 for Cr$^{3+}$ and Cd$^{2+}$; pH 5 for Mn$^{2+}$ and pH 6 for Pb$^{2+}$-Fe$^{2+}$ and Cu$^{2+}$ respectively. The difference in pH may have resulted from the protonation of the ligands at the surface of the IBES and precipitation due to formation of hydroxides. Also the generation of hydroxonium ions [H$_3$O$^+$] in the bulk solution at different pH could result in competition between the hydroxonium ions and the metal ions for active sites and such a competition may have caused a difference in the amount of metal ions sobbed (Demirbas, 2008, Ogali et al., 2008).

![Fig 1; Sorption Capacity on metal ions of IBES](image-url)

The interaction between the metal ions and the functional groups of the biomass depends on the nature of the biosorbent as well as the solution chemistry of the biosorbate, which in turn depends on the pH of the solution that considerably influences the metal speciation, sequestration, and/or mobility (Anayurt et al., 2009).

The main factors influencing the pH on biosorption process were metal ions species and surface functional groups on the sorbents. It is generally known that at low pH values, concentration of H$^+$ ions far exceeds that of the metal ions and hence H$^+$ ions compete with metal ions for the surface of the sorbent which would hinder the metal ions from reaching the binding sites of the sorbent resulting in low sorption amount of metal. As the pH increases, there are fewer protons in the solution and consequently there is lesser competition with metal ions for binding sites. This results in an increase of the sorption amount of metal ions (Anayurt et al., 2009).
3.4 Effect of Ionic Strength on Sorption of IBES

Another important parameter in biosorption is the ionic strength. The value of percentage sorption capacity decreased with increase in the ionic strength as shown in Fig 3; these may be as a result of less availability of active sites, surface area and capacity of biosorbent to concentrate on specific amount of metal ion sorbate in the aqueous solution (Adeyinka et al., 2007). Also that high sodium concentrations lead to high ionic strength at which the amount of heavy metals bound is reduced (Greene et al., 1987).

The difference in osmotic pressure between the sorbent and the external solution increases as the ionic strength of the external solution increases. Therefore, the sorption of metal ions decreases when the ionic strength of external solution increases as shown in Fig 3 (Adeyinka et al., 2007; Reza and Amin, 2010), also active sites for sorption remain buried inside and do not take part in biosorption, resulting in poor biosorption capacity (Reza and Amin, 2010).
3.5 Effect of Contact Time on Sorption Capacity of IBES

Fig 4 shows that the sorption capacity of IBES increased sharply with contact time in the first 30 min and equilibrium sorption was established within 4 hours. The plot revealed that the rates of percent lead, iron and chromium sorbed are higher at the beginning. This was probably due to larger surface area of the plants being available at beginning for the sorption of Pb^{2+}, Fe^{3+} and Cr^{3+} ions. As the surface sorption sites become exhausted, the sorption rate was controlled by the rate at which the sorbate is transported from the exterior to the interior sites of the sorbent particles. Most of the maximum percent lead, iron and chromium sorbed were attained after about 4 hours of time (Sham and Gad, 2010).

The rate of moisture diffusivity is an important transport property, necessary for the design and optimization of all the processes that involve internal moisture movement, including drying (Simpson, 1993). The reason for higher metal ions sorption rate at the beginning can be explained by the diffusion phenomenon. The rate of metal ions sorption depends on the difference between the saturation moisture content and the metal ions content at a given time, which is called the driving force. As hydration proceeds, the metal ions content increases, decreasing the driving force and consequently the sorption velocity decreases. The metal ions sorption process ceases when the sample attains the equilibrium in aqueous solution (Khazaei, 2008).

3.6 Effect of Initial Concentration on Sorption Capacity of IBES

The result of metal ions sorption by IBES at different initial concentration is shown in Figure 6, indicating that the sorption capacity increases with an increase in the initial concentration of the metal ion. The phenomenon may be due to the feasibility and efficiency of a biosorption process not depending only on the properties of the biosorbent, but also on concentration of the metal ion. This behaviour can also be explained in terms of increase in flux of the metal ion. The flux of the metal ion varies directly with the metal ion concentration and hence there should be an increase in flux with increase in initial concentration (Meunier et al., 2004; El-Ashtoukhy et al., 2008). The initial concentration provides an important driving force to overcome all mass transfer resistant of the metal ion between aqueous and solid phase (Addagalla et al., 2009).

This result could also be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction, whereas by increasing the metal ion concentration, a number of sites available for biosorption site has increased (Demirbas, 2008).
IV. CONCLUSION

In this research work, the immobilization of Brachystegia Eurycoma seeds (BES) was achieved by caging it within a polymeric matrix with sodium alginate and calcium chloride. The result of sorption capacity recorded was satisfactory. The sorption capacity of BES obtained for Pb\(^{2+}\), Cr\(^{3+}\), Cu\(^{2+}\), Cd\(^{2+}\), Fe\(^{2+}\) and Mn\(^{2+}\) was found to be 97.50, 67.44, 81.48, 98.09, 79.50 and 94.00\% respectively. In the same value, the sorption capacity decreases with an increasing ionic strength, but increases with increase in pH values, initial metal ion concentration and contact time. Based on the result obtained, it can be concluded that BES can be evaluated as an alternative bio sorbent for removal of metal ions from waste water.

REFERENCES


AUTHORS

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