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INVESTIGATION OF SOME PHYSICAL PROPERTIES ON SORPTION CAPACITY OF AFZELIA AFRICANA SEEDS MEMBRANE

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ABSTRACT

The membrane of Afzelia Africana Seeds (AAS) was developed. The bio-sorbent was used for the removal of Pb^{2+}, Cd^{2+}, Fe^{3+}, Cu^{2+}, Cr^{3+} *and* Mn^{2+} *in aqueous solution. Membrane sorption capacities were found to be: 99.59%, 98.50%, 97.38%, 97.20%, 94.77% and 93.61% for* Fe^{3+}, Cr^{3+}, Cd^{2+}, Mn^{2+} *and* Cu^{2+} *respectively. The sorption behavior with respect to pH, contact time, ionic strength and initial metal ion concentration were investigated so as to determine the optimum sorption conditions. The result revealed that metal ion sorption by the membrane increased with increasing initial metal ion concentration, pH values and contact time while metal ion sorption decreased with increasing ionic strength. Maximum sorption was found to occur at pH 5 for all the six metal ions studied. The ability of the membrane to remove some heavy metal ions from aqueous solution was satisfactory and may be used in the treatment of wastewater.*

Keywords*: Afzeliaafricana seeds, membrane, sorption, metal ions,wastewater.*

Introduction

A healthy environment is an integral part of a vast human requirement for healthy life and productivity. Environmental pollution is currently one of the most important issues facing humanity. It has increased tremendously in the past few years and reached alarming levels in terms of its effect on living creatures (Ashiraji, 2005). Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Such pollutants may be found in the air, water and soil. Industrial wastewater containing lead, copper, cadmium, chromium, iron and manganese, etc for example can contaminate ground water resources and thus lead to a serious groundwater pollution problem. (Nilanjana*et al.,* 2008). The increase in industrial activities has resulted to the increase in environmental pollution by heavy metals which is now a serious problem to both man and animal.

Contamination of water with substances which have adverse effect on human beings, animals and plants is called water pollution. Water pollution is a global problem and it's control has become increasingly important in recent years. The conventional methods for the removal of these heavy metals from wastewater include chemical precipitation, membrane separation, ion exchange, dialysis etc. [Sao *et al*., 2014]. These conventional methods have the following problems: incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost effective treatment method that is capable of removing heavy metals from aqueous effluents.

Bio-sorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto it's cellular structure [Sao *et al*., 2014]. Though using biomass in environmental clean-up has been in practice for a while, scientists and engineers are hoping that, this phenomenon will provide an economical alternative for removing toxic heavy metal ions from industrial wastewater and aid in environmental remediation. The major advantages of bio-sorption over conventional methods are high

efficiency, minimization of chemical and or biological sludge, zero additional nutrient requirement, regeneration of bio-sorbent and possibility of metal recovery. Therefore, the short comings of the conventional methods and the merits of the bio-sorption methods over the conventional methods, had necessitated the search for low cost and environmental friendly bio-sorbents.

Afzeliaafricana seeds is used as a thickener in soup and other traditional products in Nigeria because of their binding properties, viscosity and swelling tendency(Igwenyi*et al.,* 2014). The results of the phytochemical analysis of *Afzeliaafricana* Seeds showed that the seeds contained: Alkaloid (59.62%), flavonoid (9.75%), Tannins (62.22%), Beta Carotene (2.64%), Glycosides (5.64%), Soluble Carbohydrates (24.81%), Saponins (0.88%). Flavoniods are a group of polyphenolic compounds that are found in fruits and vegetables, these metabolites possess some functional groups and their presence in the seeds indicates that they could have potential to bind metal ions from aqueous solution. The objective of this study is to develop a low cost and effective bio-sorbent that is easily available in large quantities from *Afzeliaafricana* Seeds for the purpose of wastewater treatment.

MATERIALS AND METHODS

Materials

Sodium alginate, methanol, glutaraldehyde, hydrochloric acid, sodium hydroxide and sodium chloride were obtained from British Drug House (BDH). *Afzeliaafricana* seeds were bought at Jimeta market, Yola south Local Government Area, Adamawa State, Nigeria. All chemicals used in this work were of analytical grades and were used as supplied.

Preparation of Biomass

The seeds were sorted to remove debris and were stored in Polyethylene bags to avoid contamination. The traditional methods of processing were used in treating the seeds. The seeds after storing were dried, roasted, soaked in warm water and the shells were removed manually. The dehulled seeds were dried in an oven at 60^0C for 48 hours. They were then milled with blender and the pulverized samples were stored in paper bags for further analysis [Baminas*et al.,* 2005]. The powdered seeds were filtered through 100 µm sieve screen to obtain fine powder, which was packaged in a polyethylene bag and stored at room temperature. Sodium alginate solution (4% w/w) was prepared and left overnight for complete dissolution.

Membranes Preparation

Sodium alginate (80 ml) and 20 ml of *Afzeliaafricana* seeds solution (4%) were mixed with 0.5 ml of glutaraldehyde solution. This mixture was stirred for 2hrs at room temperature and then poured uniformly on a plastic tray. The membrane was allowed to dry at room temperature (250C) for 72 hours. The cast membrane was cross-linked by immersing in a 1% HCl solution taken in an equimolar mixture of methanol and water for 24 hrs. It was washed thoroughly in water and allowed to dry [Baminas*et al.*, 2005].

Determination of metal ion in solutions

The metal ions chosen for this study were Cd^{2+}, Fe^{2+}, Cr^{3+}, Mn^{2+}, Pb^{2+} and Cu^{2+}. The standard of the metal ions solutions of Pb, Fe, Cr, Cd, Mn and Cu were prepared from their salts by dissolving 1.60g, 3.55g, 3.04g, 1.63g, 2.29g and 2.68g in distilled water respectively and were made up to 1 litre mark in a volumetric flask to give the stock solutions of 1000 ppm of the metal ions. Serial dilutions of 200 ppm of each metal ion solution were prepared with de-ionized. From the above concentration, 50ml of solution of metal ion was taken into a conical flask; 0.2g of dried membrane was added and it was shaken vigorously for 2 hrs with the flask shaker (Stuart Scientific, SF1). The residual metal concentrations was analysed by Atomic Absorption spectrophotometer (AAS) (210 VGP Buck Scientific) [Osemeahon*et al.*, 2007]. This process was repeated for all the metal ions studied.

Membrane sorption capacity

To determine the sorption capacity, the method reported by [Chamarthy*et al.*, 2001] was adopted. The membrane (0.2 g) was shaken in 50 ml of 200 ppm of metal ion solution at room temperature for 2 hrs. The heavy metal ion concentration in the synthetic wastewater was analysed by Atomic Absorption Spectrophotometer (AAS).

Effect of pH on sorption capacity

In order to investigate the influence of pH on bio-sorption, the membrane of AAS was subjected to different pH values (1 – 6). The dried membrane (0.2 g) was shaken in 50ml of 200 ppm of various metal ion solutions at varying pH values of (1-6) with the flask shaker (Stuart Scientific, SFI) for 2 hours. The required pH value was adjusted using a 2.0 M hydrocholoric acid and 2.0 M sodium hydroxide. The residual metal ion concentration was analysed by AAS. The experiment was repeated for all the metal ions studied with appropriate controls.

Effect of ionic strength on sorption capacity

To examine the effect of ionic strength on the sorption capacity of AAS, 0.2g of the membrane was subjected to varying concentrations of NaCl in 50ml of 200 ppm of metal ion solutions using the flask shaker. Varying concentrations (0.2 – 1.0 M) of NaCl were added to adjust the ionic strength of metal ion solutions. The residual metal ions were analysed using AAS.

Effect of contact time on Sorption Capacity

Experiments to determine the equilibrium time required for bio-sorption was performed using 0.2g of the membrane in 50ml of 200 ppm of metal ions solution. The samples in a 250ml conical flask underwent agitation with flask shaker. They were removed one after the other at a specified time interval ranging from 30min – 24hrs at room temperature. The solutions were filtered and their residual metal ions were analysed using AAS.

Effect of initial metal ion concentration on sorption capacity

To evaluate the effect of initial metal ion concentration, the experiments were performed at different initial concentrations ranging from 5 – 100 ppm. The membrane (0.2 g) was mixed with 50 ml of 5 ppm of each metal ion solutions and were shaken with the flask shaker for 2 hrs. The solutions were filtered and the residual metal ions were analysed using AAS. This processes were repeated at different concentrations ranging from (5 – 100 ppm) for all metal ions studied.

RESULTS AND DISCUSSIONS

Sorption capacity of different metal ions by AAS.

Figure 1 shows the equilibrium sorption for $Pb2^{+}$, Fe^{3+}, Cr^{3+}, Cd^{2+}, Mn^{2+} and Cu^{2+} by *Afzeliaafricana* seeds membrane. It was observed that the membrane can take up significant quantities of $Pb2^{+}$, Fe^{3+}, Cr^{3+}, Cd^{2+}, Mn^{2+} and Cu^{2+} at 99.59%, 98.50%, 97.38%, 97.20%, 94.77% and 93.61% respectively.

The sorption capacity of the biomass can be attributed to the amount of cellulose content, the porosity of the fibres, (Chakravarty, 2011). The surface chemistry of the fibre could also be an influential factor to the biomass sorption capacity (Baltazar*et al.*, 2007).

The differences observed in the sorption capacity for the different metal ions can be explained in terms of differences in hydration free energy, the ability of the metal ions to form covalent bond with ligands, the metal polymeric cations within the membrane structure and the nature of the surface sites available [Cooper *et al.*, 2002] the hydrated sizes of the different ions could also affect the sorption.

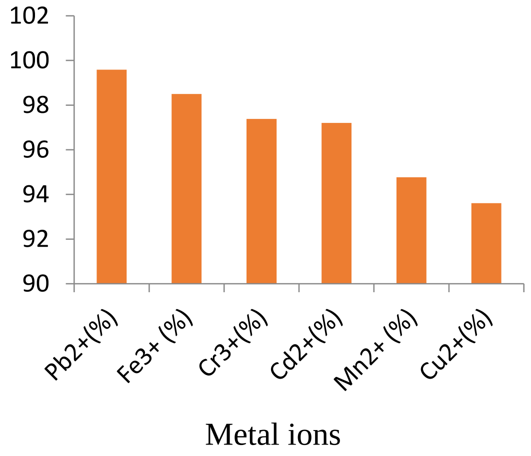

Figure 1: *Sorption capacity of various metal ions by AAS (Time:2hours, temperature: 30^0C, initial metal concentration: 200ppm)*

Effect of PH on the sorption capacity of AAS

Figure 2 shows the effect of pH on sorption of metal ions on *Afzelia africana* seeds membrane in the range of pH 1.0 – 6.0. More metal ions were absorbed as the pH was increasing. The uptake of free ionic metals depends on pH. The optimal metal removal efficiency occurs at pH 5 and then declined at pH 6, for all the metal ions studied. From the result, Cd^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Pb^{2+} and Cu^{2+} optimal pH sorption values were found to be 99.14%, 98.40%, 98.60%, 98.95%, 99.00% and 98.00% respectively. It can be suggested that the differences in sorption capacities at the optimum pH for different metal ions could be probably due to the solution chemistry of the metal ions [Adesola*et al.*, 2008]. Decreasing the pH leads to the precipitation of insoluble hydroxides or hydrated oxides, thereby lowering the metal ions availability for sorption. On the other hand, an increase in pH results in the increase in the hydrogen ion concentration and hence possible competition for bonding sites by cations [Liping*et al.*, 2007]. On the whole, the percentage of sorption capacities increases with increasing pH values which showed that alkaline pH favors higher sorption by DMS and AAS membranes. This is due to the presence of the –OH group in solution with increasing pH value (Yen-Peng and Sung, 2000).

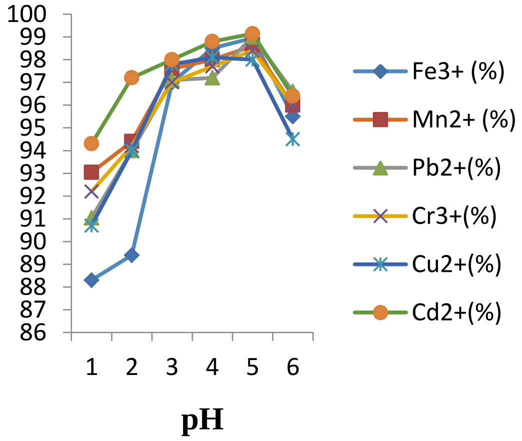

Figure 2: *Effect of p^H on AAS Sorption capacity (Time: 2hours, temperature: 30^0C, initial metal concentration: 200ppm)*

Effect of time on sorption capacity of AAS

Figure 3 shows the effect of contact time on sorption capacities for Cd^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Pb^{2+} and Cu^{2+}. Sorption equilibrium was reached after 4 hrs for Cd^{2+}, Cr^{3+} and Cu^{2+} while 12 hrs was recorded for Fe^{2+}, Mn^{2+} and Pb^{2+}. The rapid sorption of metal ions can be attributed to the highly porous structure of the bio-sorbent which provides a less and large surface area for sorption of the metal ions to the binding sites [Charkravaty, 2011]. The contact time is a key parameter for waste water treatment. A short contact time to attain the saturation point and maximum amount of the metal ions absorbed at equilibrium, indicates the rapid transport of metal ions from the bulk to the outer and inner surface of bio-sorbent. Thus, the period of equilibrium is an important factor by which to judge the feasibility of a bio-sorbent for its use in water quality control [Charkravaty, 2011].

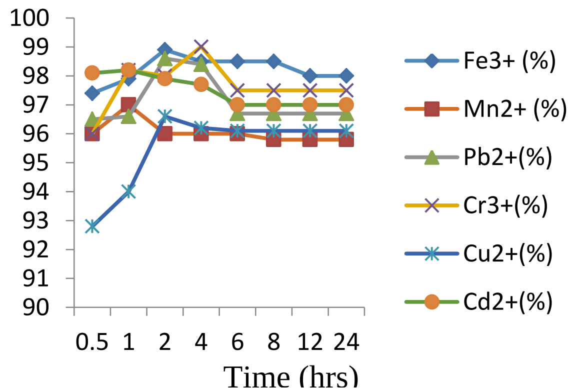

Figure 3: *Effect of contact time on AAS on water uptake(Temperature: 30^{0}C, initial metal concentration: 200ppm)*

Effect of Initial Metal Ions Concentration on Sorption Capacity of AAS.

Figure 4 presents the effect of initial metal ions concentration on the sorption capability of AAS.It can be observed that the removal of the metal ions by the sorbent increases with the increase in initial metal ion concentration and this is similar to the report by [Mahmood*et al.*, 2011]. This behaviour can be explained in terms of increase in flux of the metal ions. The flux of the metal ions varies directly with the metal ions concentration and hence there should be an increase in flux with increase in initial concentration [Meunier*et al.*, 2004 and El-Ashtouky*et al.*, 2008]. It can also be attributed to the basis that; at lower initial metal ion concentration, the ratio of the initial mole of the metal ions to the available surface area will be low. Therefore, sorption becomes independent of the initial concentration. However, at higher concentration, the sites available for sorption becomes less in comparison to the moles of the metal ion present in solution and hence the removal of metal ion is strongly dependent upon the initial solute concentration [Preeti and Syed 2011]. The feasibility and efficiency of a bio-sorption process depends not only on the properties of the bio-sorbent, but also on concentration of the metal ions. The initial concentration provides an important driving force to overcome all mass transfer resistant of the metal between aqueous and solid phase (Mustafa *et al.*, 2012).

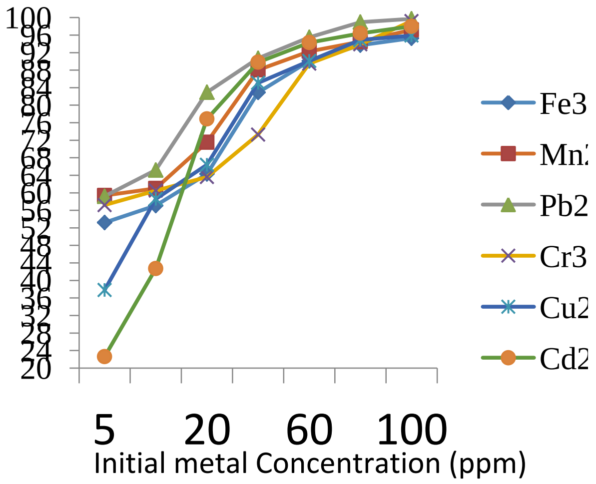

Figure 4: *Effect of initial concentration on AAS Sorption Capacity (Time: 2 hours, temperature: 30^0C)*

Effect of ionic strength on the sorption capacities of AAS

Figure 5 shows the effect of ionic strength on sorption capacities of heavy metal ions. It is observed that the sorption capacities decrease as the ionic strength increases. This is attributed to the difference in the ionic osmotic pressure between the sorbent and the external solution [Reza *et al.*, 2010]. This may also be due to the decrease in the expansion of the polymer network, which can be as a result of the repulsive forces of the counter ions in the polymeric chain shielded by the ionic charge. Therefore, the difference of the osmotic pressure between the external solution and the polymer network decreases with increase in the ionic strength of the saline concentration [Murali*et al.*, 2006].

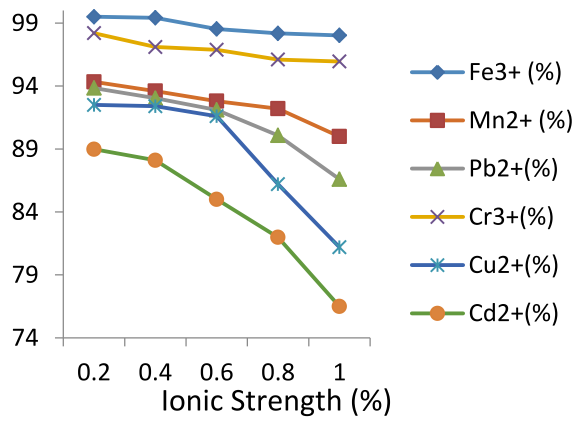

Figure 5: *Effect of ionic Strength on AAS Sorption Capacity (Time: 2 hours, temperature: 30^0C, initial metal concentration: 200ppm)*

CONCLUSION

This study investigated the sorption capacities of the membrane from plant seed (AAS) for the removal of Cd^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Pb^{2+} and Cu^{2+} from aqueous solution. The result obtained from this investigation shows that membrane of AAS can absorb all these metal ions from their aqueous solution. The maximum sorption capacities of the membrane were 99.59%, 98.50%, 97.38%, 97.20%, 94.77% and 93.61% for Pb^{2+}, Fe^{3+}, Cr^{3+}, Cd^{2+}, Mn^{2+} and Cu^{2+} respectively.

The sorption equilibrium studied showed that metal ions sorption by the membrane increased with increased in initial metal ions concentration as well as pH and contact time while decreasing with increase in ionic strength of the aqueous solution. Therefore, the sorption capacities of this membrane (AAS) has demonstrated that it has the potential for the removal of Cd^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Pb^{2+} and Cu^{2+} metal ions from wastewater, hence can be recommended for the treatment of wastewater.

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