The Use of *Adansonia digitata* L. Seed Cake Residue as a Biosorbent in the Bioremediation of Lead (Pb^{2+}) from Aqueous Solution

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Abstract

In this study, the use of *Adansonia digitata* L. seed cake residue as a biosorbent for the removal of Pb^{2+} from aqueous solution was evaluated. Dried fruits of *Adansonia digitata* L. were collected from the Department of Biological Sciences, Ahmadu Bello University, Zaria. The seeds were mechanically removed, washed with sterile distilled water, sun dried, powdered, defatted using n-hexane and stored in the refrigerator for further studies. Standard stock solution (30 mg/l) of Lead Nitrate $Pb(NO_3)_2$ was prepared by weighing 30mg of the salt and dissolving in 1L of deionized water this was further diluted for further study and serve as model polluted water. Batch experiments were carried out to study the effect of pH, initial concentration of metal salts, dosage of biosorbent, and contact time. The experimental design was Cross Randomized Design (CRD) and one way Analysis of Variance (ANOVA) was used to determine significant difference among means of the various parameters measured. Duncan Multiple Range Test (DMRT) was used in separating means where significant. The level of significance was taken at $p < 0.05$. The result revealed that the removal efficiency of Pb^{2+} from aqueous solution increased as pH increased from 2 – 10, initial concentration of metal salt increased from 0 - 30 mg/L, dosage of biosorbent increased from 0 - 200mg/l, and as contact time increased from 0 - 60 min. From this study *Adansonia digitata* L. seed could be considered as a potential, eco-friendly, low cost, biosorbent for the removal of Pb^{2+} from aqueous solution.

Key words: *Adansonia digitata* L., Bioremediation, Biosorbent, Lead, Seed, Water

I. INTRODUCTION

Water is one of the most essential commodities in life; humans, plants and animals all need it for survival. Apart from just survival man in particular explore this resource for a number of other things which include domestic, agricultural, industrial, transportation, commercial, economic and social purposes. These anthropogenic activities have resulted in pollution which in turn has led to the decrease in the availability and accessibility of water to man. Water pollution has become a global phenomenon and a lot of efforts are put from different quarters to tackle the menace [1].

As at 2015, it was estimated that 663 million people worldwide still make use of unimproved drinking water sources, including unprotected wells and springs and surface water [2]. A higher proportion of them live in two regions. Nearly half of all the people using unimproved drinking water sources live in Sub-Saharan Africa, while one fifth live in Southern Asia [2]. It is estimated that 79% of people using unimproved sources and 93% of people using surface water live in rural areas [2].

Heavy metal pollution in water is very common and this has adverse effects on man and his environment. Heavy metals find their way into surrounding water bodies by some adverse practices such as: discharge of untreated industrial wastes into water bodies; improper use of agro-allied chemicals such as pesticides, herbicides and fertilizers; mining activities [3,4,5].

Lead (Pb) is the commonest of the heavy elements, accounting for 13 mg/kg of Earth's crust. Lead is used in the production of lead acid batteries, solder, alloys, cable sheathing pigments, rust inhibitors etc. and it can easy find its way into water bodies through run offs from the soil [6]. Lead is also universally used in the manufacture of plumbing materials and as a result of this lead can easily leach into tap water [6]. Mining is also another source of Lead contamination [7]. Illegal mining of gold in Zamfara, northern Nigeria was reported to have killed hundreds of people especially children in 2010, and this was related to lead poisoning which resulted from lead containing gold ore [7, 8]. Health complications that arises from lead include: Carcinogenic effects, neurological effects in infants and children, mutagenic effects, reproductive dysfunction, kidney damage to mention but a few [6].

There are a number of conventional methods for the removal of lead from water, these include: ion exchange [9], coagulation [10], floatation [11], co-precipitation [12], solvent extraction [13], membrane technology [14, 15] and adsorption [16]. These methods are relatively expensive and there is therefore a need for alternative, sustainable, less expensive methods for the removal of heavy metals such as biosorption [5].

Biosorption is a method of removal of heavy metals that involves the use of natural materials especially of plant origin (agricultural waste are good sources of biosorbents). Several researches have been carried out on the use of biosorbents in the removal of heavy metals from water, and they have been reported to have promising potentials such as low cost, high uptake rates, metal selectivity, reusability, no sludge formation, possibility of metal recovery from solution and competitive performance with other conventional adsorbents; but there are also some limitations in their use such as early saturation, inability to carry out biological process improvement (such as genetic engineering of cells) since cells are not metabolizing, and the inability to biologically improve metal valency; there is therefore a need for further research in this area [5].

This study was carried out to evaluate the efficiency of *Adansonia digitata* L. seed cake residue as a potential biosorbents in the removal of Pb^{2+} from model polluted water. *Adansonia digitata* L. is a large deciduous tree indigenous to arid central Africa belonging to the Malvaceae family. It possess large pendulous shaped fruits containing numerous bean shaped seeds. It has been reported that all parts of the tree are useful [18].

II. METHODOLOGY

A. *Collection, verification, and preparation of plant material*

Dried fruits of *Adansonia digitata* L. were collected from a single tree in the Botanical Garden of the Department of Biological Sciences, Ahmadu Bello University, Zaria, and were taken to the herbarium of the Department for verification and confirmation. It was assigned a herbarium voucher number of 2512. The fruits were cracked open, seeds were mechanically removed, properly washed with distilled water, sun dried, pulverized into powder using mortar and pestle, sieved through a pore size of about 1mm, and stored in airtight containers for further usage.

B. *Preparation of Adansonia digitata cake residue (ADCR)*

The powdered seed sample (*Adansonia digitata* seeds) was de-fatted using n-hexane in electro-thermal Soxhlet extractor (Gallenkamp, England). 30g of powdered seed was weighed and put into the thimble of the Soxhlet extractor, the apparatus was mounted and allowed to run for 1 hour, after which the powder was removed and dried over a hot plate at low heat (to evaporate the excess n-hexane) to give *Adansonia digitata* cake residue (ADCR). This was then used as the biosorbent for further study.

C. *Preparation of stock solution of heavy metal*

All chemicals that were used was of analytical grade. Standard stock solution of $Pb(NO_3)_2$ salt was prepared by weighing 30mg of the salt and dissolving in 1L of deionized water [16]. Further dilutions were made from the stock solutions for the study.

D. *Batch adsorption experiments*

The effect of pH (pH was varied from 2 - 10 using HCl and NaOH), initial concentration of metal salt (5, 10, 20, 30 mg/L), dosage of biosorbent (50mg/l, 100mg/l, 150mg/l and 200mg/l), and contact time (5, 15, 30, 60 min) on adsorption was studied by varying the parameter of concern and making all others constant. In all the experiments 100ml of metal solution of known concentration was taken in polyethylene bottles along with the required amount of biosorbent (de-fatted powdered *Adansonia digitata*). The bottles were covered properly and agitated with a laboratory shaker (Gallenkamp England) for a particular period of time corresponding to the desired contact time to achieve equilibrium. After agitation the mixture was passed through filter papers (Whattman No. 1) and stored in polyethylene sample bottles. The residue concentration of Pb^{2+} in solution was determined using Atomic Absorption Spectrophotometer (AA 240 FS Varian).The experiments were carried out in triplicates with their respective controls [16, 19, 20].

The removal efficiency R_e (%) of heavy metal ions was calculated using:

$$R_e = \frac{(C_o - C_e)}{C_o} \times 100$$

Where C_o and C_e (mgL^{-1}) are the liquid-phase concentration of metal ions at initial and equilibrium, respectively

E. *Statistical Analysis*

The experimental design used was Complete Randomized Design (CRD). ANOVA (Analysis of Variance) was used to compare the mean removal efficiency of Pb^{2+} for the different groups of treatment, and DMRT (New Duncan Multiple Range Test) was used to separate means where there was significance. In the kinetic studies of adsorption, regression analysis was used to examine the relationship between the amount of heavy metal ions adsorbed per unit mass of the biosorbent and the contact time. The confidence level of was taken at 95% ($p < 0.05$). SPSS software (version 20.0) was used to run the analysis.

III. RESULTS AND DISCUSSION

It was observed that ADCR was able to absorb Pb^{2+} significantly ($p < 0.05$) from aqueous solution and this is consistent with an earlier work carried out by Edogbanya et al. [21] which reported that *Adansonia digitata* seed cake residue had the ability to remove Pb^{2+} ions from surface water. The biosorption of metal ions by agricultural by products have been attributed to two mechanisms: coulombic interaction and intrinsic adsorption [22]. The coulombic mechanism results from the electrostatic energy of interactions between the adsorbents (biosorbent) and adsorbates (metal ion solution). The strength of charges on biosorbent and biosorbate are mostly responsible for the intensity of the interaction. Coulombic interaction is observed from the adsorption of cationic species versus anionic species on adsorbents [22]. The intrinsic mechanism of adsorption is due to the nature of the surface area of biosorbent, different kinds of surfaces of biosorbents tend to have different affinities for metal ions [23, 24]. Variation of different parameters had a significant effect ($p < 0.05$) on the biosorption efficiency of ADCR.

A. *Effect of pH on biosorption efficiency*

It was observed that as the pH was adjusted from 2 – 10, while other parameters remained constant (initial concentration of metal ion at 30mg/L; dosage of ADCR at 200mg/L; contact time of 30min and rotation speed of 120rpm), the biosorption efficiency of the biosorbent increased significantly ($p < 0.05$). Maximum biosorption efficiency of 94.57% was obtained at pH 10 (Fig 1). This is due to the fact that at a lower pH (acidic) the hydrogen ions (H^+) from the acid make the overall surface of the biosorbent to be positively charge and this leads to the repelling of the metal ions and hence a reduction in the biosorption efficiency of the biosorbent. At higher pH (basic) the hydroxide ions (OH^-) introduced by the base causes the overall surface of the biosorbent to be negatively charge leading to the attraction of more metal and hence an increase in the biosorption efficiency of the biosorbent. This is similar to the findings of Kumari et al. [25].

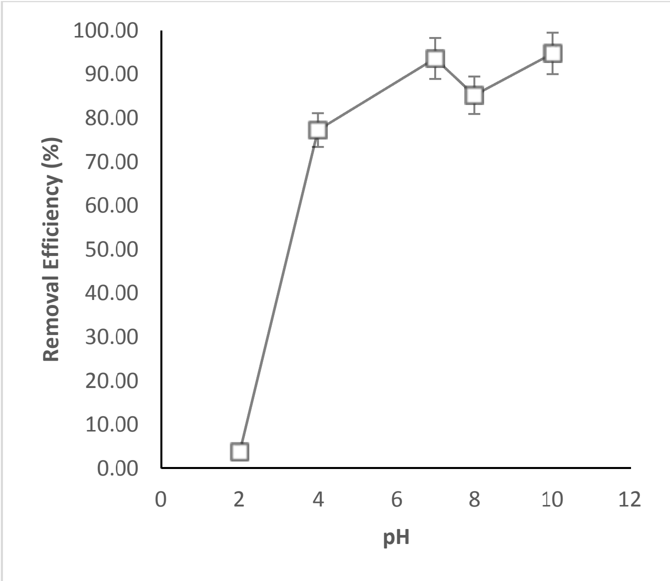

Fig 1 Effect of pH on the biosorption efficiency of ADCR for Pb^{2+}
initial concentration of metal ion = 30mg/L;
dosage of ADCR = 200mg/L;
contact time = 30min;
rotation speed = 120rpm

B. *Effect of initial concentration of Pb^{2+} on biosorption efficiency of ADCR*

As the initial concentration of Pb^{2+} ion was increased from 0 – 30mg/L, while other parameters were kept constant (Dosage of ADCR at 200mg/L; contact time of 60min; pH 7 and rotation speed of 120rpm) the biosorption efficiency also increased significantly ($p < 0.05$). A biosorption efficiency of 97.49% was observed at an initial concentration of 30mg/L (Fig 2). This may be due to the fact that an increase in the initial concentration of ions caused an increase in the concentration gradient that serves as a driving force [26]. This was similar to the findings of Njoku et al.[18] that worked on the adsorption of heavy metals using cocoa pod husk.

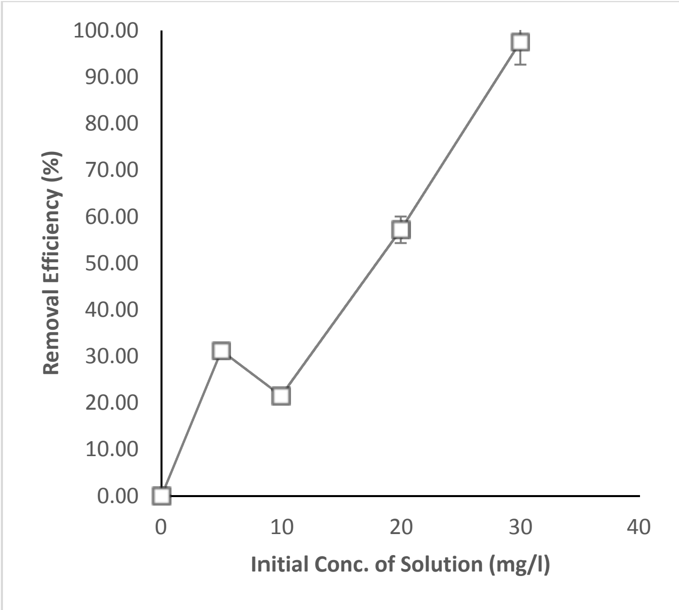

Fig 2 Effect of initial concentration of Pb^{2+} on the biosorption efficiency of ADCR
dosage of ADCR= 200mg/L
contact time =30min
pH 7
rotation speed = 120rpm)

C. *Effect of contact time on the biosorption efficiency of ADCR*

It was observed that as the contact time of ADCR with metal solution was increased from 0 – 60 min, while the other parameters were kept constant (dose of ADCR at 200mg/L; initial concentration of metal ion at 30mg/L; pH of 7; and rotation speed of 120rpm) the biosorption efficiency increased significantly ($p < 0.05$). A maximum biosorption efficiency of 99.97% was observed at a contact time of 60min (Fig 3). It was observed that the biosorption of Pb^{2+} took place in two distinct phases: a rapid phase which took place within 5 minutes and a slow phase that took until 60 minutes. The rapid biosorption was probably due to the initial availability of many binding sites and as the binding sites became exhausted biosorption took place at a slower rate. This is similar with the findings of Aravind et al. [27] that worked on the adsorption of Nickel ions (Ni^{2+}) onto *Cajanus cajan* pods.

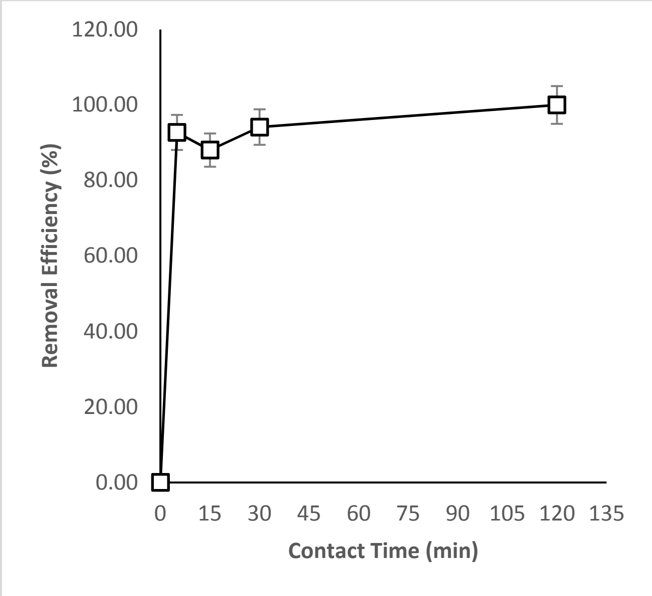

Fig 3 Effect of contact time on the biosorption efficiency of ADCR for Pb^{2+}
dosage of ADCR = 200mg/L
initial concentration of metal ion =30mg/L
pH = 7
rotation speed = 120rpm

D. *Effect of dosage on the biosorption efficiency of ADCR*

As the dosage of biosorbent increased while other parameters were kept constant (initial concentration of metal ion at 30mg/L; pH of 7; contact time of 30min and rotation speed of 120rpm), there was a significantly increase ($p < 0.05$) in biosorption from 0 - 50mg/L but beyond this dose no significant increase ($p > 0.05$) was observed. A maximum efficiency of 95.47% was observed at the optimum dose of 50mg/L (Fig 4). This is probably due to the fact that an increase in dosage from 0 – 50mg/l provided sufficiently available binding sites for the removal of most of the metal ions from the solution, hence the sharp increase in the biosorption efficiency, and beyond this point biosorption continued at a negligible rate with further increase of dosage from 50mg/l – 200mg/l [27].

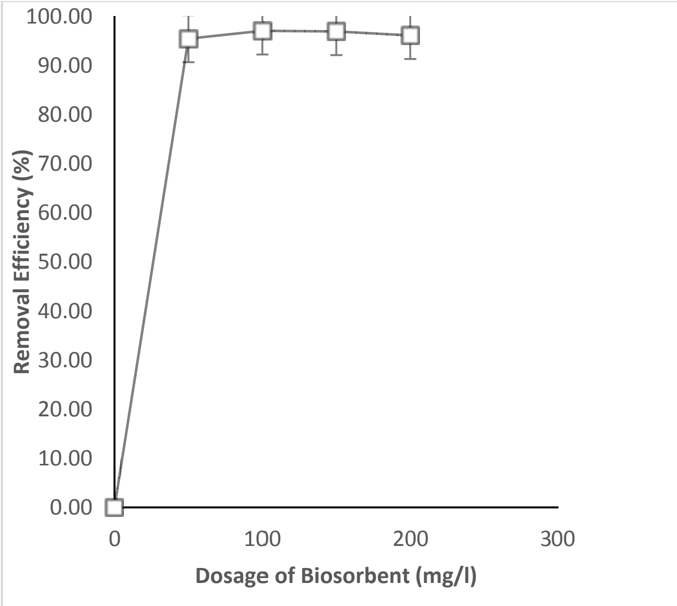

Fig 4 Effect of dosage on biosorption efficiency of ADCR for Pb^{2+}
initial concentration of metal = 30mg/L
contact time = 30min
pH = 7
rotation speed of 120 rpm)

IV. CONCLUSION

From the research carried out it may be concluded that ADCR had the ability to remove Pb^{2+} ions from aqueous solution. Various factors such as pH, initial concentration of ions, contact time and dosage played significant roles on its biosorption efficiency. ADCR appears to be a promising biosorbent which is eco-friendly and low in cost. With further research on optimization of conditions, and modification for enhanced performance, it may be adapted for large scale use.

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