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SORPTION STUDIES OF *Thaumatococcus daniellii leaves FOR REMOVAL OF CADMIUM AND LEAD FROM AQUEOUS SOLUTION*

[2]H.Ataitiya, [1]O.N Maitera & [1]A.Akinterinwa
[1.] Department of Chemistry Modibbo Adama University Yola Adamawa State Nigeria.
[2.] Department of Chemical Sciences Federal University Wukari Taraba State Nigeria.

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Abstract: The efficiency of Thaumatococcus daniellii leaves as an alternative low-cost sorbent for removal of cadmium and lead, preliminary test was carried out at pH 6, with 0.5g of biomass reacted with 10ppm of cadmium and lead then stirred for one hour, filtered and metal concentration was studied using AAS to obtain optimum condition for the sorption studies. Batch adsorption studies were carried out to evaluate effect of pH, Dosage, Time and Initial metal concentration on adsorption capacity. The adsorption data were used to plots graphs showed in figures 2 - 5. Characterization studies were carried out using SEM-EDS, and FTIR respectively. The surface morphology and elemental composition of the biomass showed loose aggregates with cracks and uniformly distributed pores with carbon and Oxygen present in the sample, the presence of hydroxyl, amide and carboxylic groups as the main functional groups that may be involve in complexation of metal ions for sorption processes

Keywords: Characterization; Metal ion; Sorption; Thaumatococcus daniellii.

Introduction

Environmental contamination by heavy metals has become an issue due to the potential hazard it poses to living organisms, a lot of efforts have been devoted to minimize the harmful effects of these pollutants to plants, animals and humans (Moradi *et al.*, 2015). The presence of heavy metals in the environment has become a major source of concern to environmentalists because it is considered a toxic, hazardous and priority pollutant (Afaj*et al.*, 2015). Heavy metals discharged from pesticide, soap, paint, solvent, pharmaceuticals, paper and pulp industries, and also water disinfecting process constitute a major source of heavy metals (Girish and Murty, 2013).

Heavy metals have been reported to cause health problems due to its high toxicity, non-biodegradable and bio-accumulation in living organisms (Dawodu*et al.*, 2012). Naturally, they are introduced into the soil system as a result of weathering rocks, from volcanic eruptions and from a variety of human activities involvingherbicides, pesticides, organic chemicals, rubber and use of other substances containing metal contaminants (Ahmed *et al.*, 2015). Heavy metals have been reported to be highly toxic because it is an enzyme inhibitor and is responsible for kidney tubular, affects calcium metabolism, skeletal calcification and ion regulation (Srivastava*et al*., 2006). It has also been reported to cause diarrhoea, vomiting, a choking sensation, severe abdominal pain and liver damages (Dawodu*et al.*, 2012). Because of the danger posed on human health it is therefore necessary to treat this pollutant to an environmentally acceptable limit (Okafor and Aneke, 2006). The development of low cost but highly efficient materials especially for sorption of heavy metals is essential because of high cost of available conventional methods of adsorbents and absorption, the technologies involved in producing them. Sorption is one of the physicochemical treatment processes used for pollutant removal. This is due to their low cost and high efficiency. Agricultural and industrial waste as well as natural minerals are widely used as alternative biosorbents for many years, some examples of materials reported as adsorbents for heavy metals are: Tea waste (Mahyi et al., 2005), palm pressed fibers and coconut husk (Tan *et al*., 1993), and leaves of indigenous biomaterials (Singanan *et al.*, 2006), Neem Leaves (Vijay *et al*., 2013 ; Innocent et al., 2009). Apart from plant base material, wood waste such as sawdust (Kumar and Dara, 1982), agricultural byproducts such as Maize cab, and rice husk, sun flower stalk, sago waste (Igwe and Abia 2003) etc.

Thaumatococcus daniellii is a plant species from Africa, known for being the natural source of thaumatin, an intensely sweet protein which is of interest in the development of sweeteners. When the fleshy part of the fruit is eaten, this molecule binds to the tongue taste buds, causing a sweet sensation that slowly builds and leaves a lingering aftertaste (Csurhes *et al.*, 1998). *Thaumatococcus daniellii* grows three to four meters in height, and has large papery leaves up to 46 centimeters long. It bears pale purple flowers and a soft fruit containing a few shiny black seeds. The fruits are covered in a fleshy red aril, which is the part that contains thaumatin. In its native range, the plant has a number of uses besides flavoring. The study of leaf petioles is used as tools and materials, the leaves are used to wrap food, and the leaves and seeds have a number of traditional medicinal uses (Bentham *et al*., 2013 and African Flowering Plants Database 2008). The plant has antimicrobial properties, effective against bacteriocin producing microorganism (Ajayi*et al*., 2016). In traditional medicinal use the leaf sap is used as antidote against venoms, stings and bites. There is not a lot known about the physiological and agronomic aspects of this plant, phytochemical observation shows that Alkaloids, Flavonoids, Tannins, Saponins, Anthraquinones, Anthocyanosides, Cardic glycosides, cardenolides and Steroidal nuclueus are present (Bickels & kloter 2001). The objective of this research is to develop low-cost sorbent for removal of Cadmium and Lead from aqueous solution, the effects of solution pH, initial metal concentration and dosage were studied , the equilibrium data were fitted into Freundlich and Langmuir isotherm models, the effects of time was study to know the rate of the reaction. SEM-EDX, XRD and FTIR analysis were performed to elucidate the sorption mechanisms.

Materials and Methods

Thaumatococcusdaniellii was bought from Abon in Kurmi Local Government Area of Taraba State the leaves of these plants were authenticated in Plant Science Department of ModibboAdama University Yola, it was washed with water under a running water then rinsed with distilled water to remove adhering particles, it was dried at room temperature for 14days then it was ground and sieved and keep in air tight containers and was used for these Research to determined residual Cadmium and Lead.

Figure 1: *Thaumatococcus daniellii*

Characterizations of Plant Material.

Fourier Transforms Infrared Analysis

The functional groups as well as the binding sites were examined using Shimadzu FTIR spectrometer 8400S,SOP the spectrum was obtained at the range of 600 - 4000cm[3.]

Scanning Electron Microscopy- Electron differential Xray (SEM-EDX)

The surface morphology and elemental composition was probe using SEM-EDX machine, 500- 2000 magnifications were used

Heavy metals stock solution

Method of stock preparation of Heavy Metals was adopted from Dawodu*et al.*, (2012). A stock solution of 1000 mg/L of Heavy metals was prepared by dissolving appropriate amount of Lead and Cadmium in 1000 cm^3Lvolumetric flask and made up to the mark with distilled water. Several working solutions were prepared from the stock solution.

Batch Sorption Studies.

The experiments were carried out in the batch mode for measurement of adsorption capacities. From 100ppm of Cadmium and Lead solutions, 50ml was measured into 250ml conical flask and 0.5g of *Thaumatocccocus daniellii* biomass was added and shaken for two hours at the range of pH1-9 for both Cadmium and Lead under room temperature on a magnetic stirrer. The optimum pH was determined in the range of 3-6 effects of time and temperature were also studied. The solution pH was adjusted using 0.5mol/L of HCl and NaOH respectively. The effect of initial metal concentration was studied from 10ppm- 50ppm, the effects of time and temperature were also studied. The residual metal ions concentrations were determined using atomic absorption spectrophotometer (AAS). Percentage removal was calculated using

$$\% \text{ Removal}=\frac{CO-Ce}{CO}\times 100$$

Results and Discussions

Batch Sorption Studies

The experiments were carried out in the batch mode for the measurement of Sorption capacities, metal concentrations were determined using AAS then the percentage adsorption was calculated the values were used for plotting of graphs.

Effect of initial solution pH on Adsorption of Cadmium and Lead

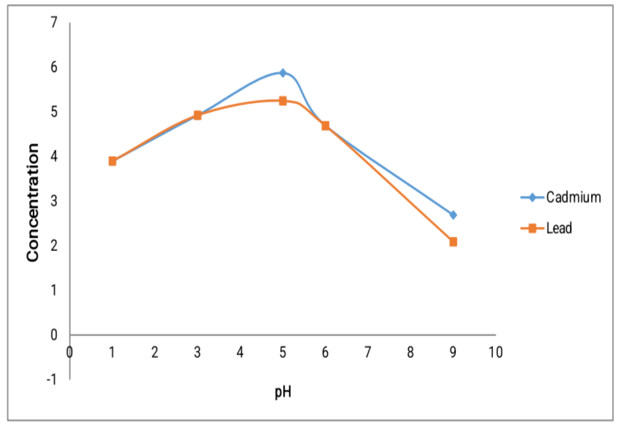

Figure2: Effects of pH on Sorption of Cadmium and Lead on *Thaumatococusdaniellii*

The results showed that the percentage removal increases from 92.56% for Cadmium and 93.06% for Lead both at pH5, with the highest percentage removal for Cadmium was 99.82% at pH 5 and that of Lead was 99.78% at pH 5 also, the sorption capacity increases with increase in pH until it reached maximum values at 5 for both lead and cadmium The results obtained from all the adsorbents showed that optimum removal was achieved at pH 5 which may be due to electrostatic attraction between the sorbate and sorbent (Bolat*et al*., 2010). From the results obtained the increase in adsorption at low pH could be explained that acidic pH Favors' cation exchange that occurs between the sorbates and sorbents (Dawodu*et al*., 2012

Effects of Initial Metal Concentration.

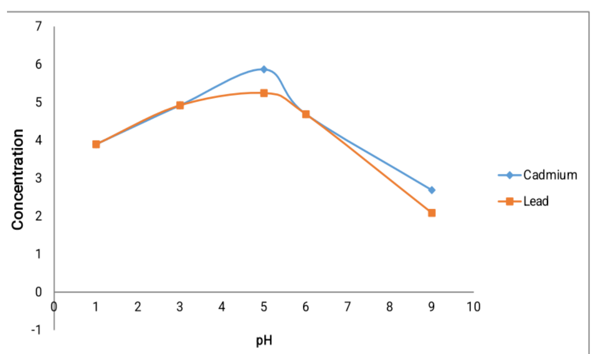

Figure 3: Effects of Initial Metal Concentration on Thaumatococus daniellii

The effects of initial metal concentration on adsorption of Cadmium and Lead for *Thaumatococcus daniellii* leaves is shown in figure 3. The percentage removal increase when initial concentration increases from 83.52% to92.00% for Cadmium and 80.56% to 91.54% for Lead from 10ppm to 40ppm then with further increase in the metal concentration the percentage removal decreases to 80.68% for Cadmium and 81.98% for Lead. The increase in sorption can be attributed to increase in the interaction between the metal ions and the active sites of the adsorbent similar results was reported by Kumar 2012 were increase in concentration may leads to strong competition for sorption site.. Under these circumstances, the unit mass of the adsorbent could take up many more Cadmium and Lead ions compared to that at lower concentration, so from the results obtained it is evident that*thaumatococcusdaniellii* is a good sorbent for removal of Cadmium and Lead which may be attributed to their porosity and high surface area Mohanty *et al.,* 2005.

Effects of Adsorbents Dosage on Cadmium and Lead.

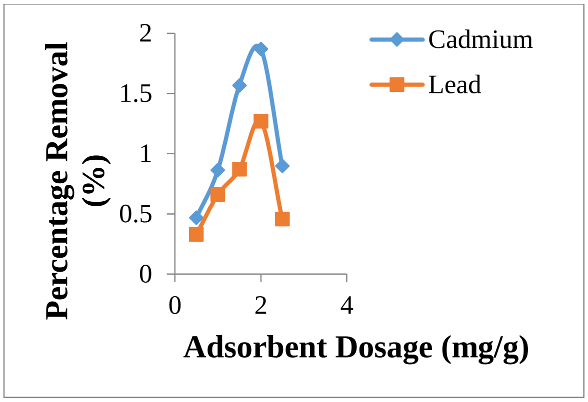

Figure 4; Effects of Sorbent Dose on Thaumatococcus daniellii

The effects of sorbents dosage on percentage removal of Cadmium and lead for *Thaumatococcusdaniellii* can be seen in figure 4 above, which showed that as the dose increases from 0.5- 2.5g percentage removal also increases with increase in sorbents dose the percentage removal increase from 85.00% -98.30 % for Cadmium and from 81.06% - 93.61% for Lead. The increase in sorbent dose with increase in sorption is generally due to availability of wider surface area and availability of binding sites. The result obtained is similar to results reported by Torab-Mostaedi *et al*., 2013 which looked at biomass dosage effects on biosorption of Cd(ll) and Ni(ll) by grape fruits peel. At higher dose when it has reached maximum saturation, the sorption does not increase due to lower availability sites for metal ions in solution and overloading of the sorbent on the sorbate resulting to low active surface sites the results obtained showed increase in sorption trends as dosages increases these may be attributed to increase in surface area and presence of available sorption sites which leads to higher sorption capacity (Nanganoa et al., 2014).

Effect of Contact Time on Adsorption of Cadmium and Lead.

The effects of contact time was studied on the sorption capacity of *Thaumatococcus daniellii* for Cadmium and Lead is shown in figure 5 below.

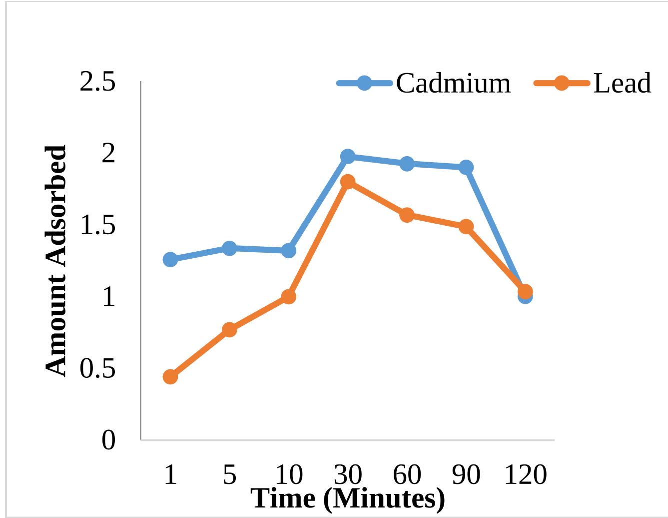

Figure 5. Effects of Time on *Thaumatococcus danielli*

Figure 5 above showed increase in percentage removal of Cadmium and lead for*Thaumatococcusdaniellii* for 120mins agitation time, there was massive increase in sorption from the first min to 30 mins from 73.30% to 99.70% for Cadmium and 76.54% to 94.47% for Lead, then there was decrease in the percentage removal to 95.90% for Cadmium and 91.67% for Lead after 60min agitation time, further increase in the agitation time leads to decrease in percentage removal to 76.57% Cadmium and 72.45% for Lead, these showed that the reaction has reached equilibrium at 30mins contact time so further increase in agitation time would eventually lead low percentage removal. For these result it showed that once the agitation time reached 30min it was saturated and further increase in the contact time brings about decrease in percentage removal of metal ions. The increase in contact time increases the removal efficiency until equilibrium concentration is reached, The ions occupied the active sites on the sorbent which as the contact time increased, the active sites on the sorbent becomes saturated similar studies was carried out by Ahmed et al., (2015) on characterization and application of Kaolinite for removal of copper ions from environmental waste water samples.

The equilibrium state occurs when the biomass is saturated with metal ions. Moreno- Pirajan *et al*., (2011) found out that the removal of heavy metals (Mn, Fe, Ni) from waste water by activated carbon from coconut shell was increased with increase contact time and reached equilibrium at just 8miniutes of solution agitation.

Instrumental characterazations of adsorbents

FTIR Analysis

The FTIR spectrum gives information about the functional group in the sample which can be use to identify chemical composition in the sample. The spectrum was recorded in the spectral range of 4000-600 cm^{-1}. A broad peak at 3396 cm^{-1} and 3328cm^{-1} corresponds to O-H intra and interbonds stretching (3500cm^{-1}-3000cm^{-1}). The sharp peaks at 2926cm^{-1} and2928cm^{-1} is due to C-H asymmetrical stretching and bending vibrations due to methyl linkage. The double bond region has peaks at 1688cm^{-1} and 1655cm^{-1} which corresponds to C=O stretching due to anhydride compounds formed by (carboxyl group) –COOH. It possessed some peaks at 3100cm^{-1}- 3400cm^{-1} and at 1600cm^{-1} the peaks corresponds to O-H, -COOH which might have overlapped N-H peaks .The peaks at 1458cm^{-1} and 1423cm^{-1} are complementary peaks for C-C, O-H and C-H bending and wagging respectively there was also absorbance peaks in the finger print region 1200cm^{-1}-600cm^{-1} the peaks and their intensities at the finger print the wave number1092cm^{-1},1013 cm^{-1}belongs to the vibrations by C-N,C-O, and N-H by amino groups, the peaks at 728cm^{-1}and 725cm^{-1} corresponds to the C-C and –CH stretching. There was addition of some peaks corresponding to N-H at 1602cm^{-1}, C-N at 1028cm^{-1}, N-O at 1520cm^{-1}and C-O at 1013cm^{-1} which appeared in the modified biomass that were not present in the unmodified biomass, the FTIR is in line with the characteristics spectra reported by Sharma *et al*., 2020.

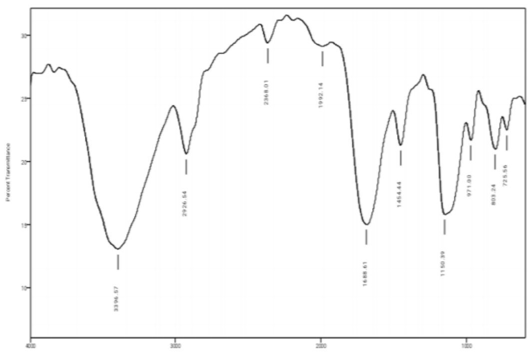

Figure 6.a. Spectrum for Unmodified *Thaumatococcus* danielli

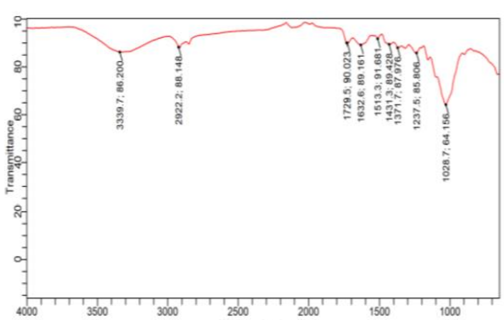

Figure 6.b. Spectrum for Modified *Thaumatococcus danielli*

Scanning Electron Microscopy –Energy Dispersive Spectroscopy of Adsorbents (SEM-EDS).

Figures 7a- 7d showed the surface morphology and elemental composition of *Thaumatococcus daniellii*biom

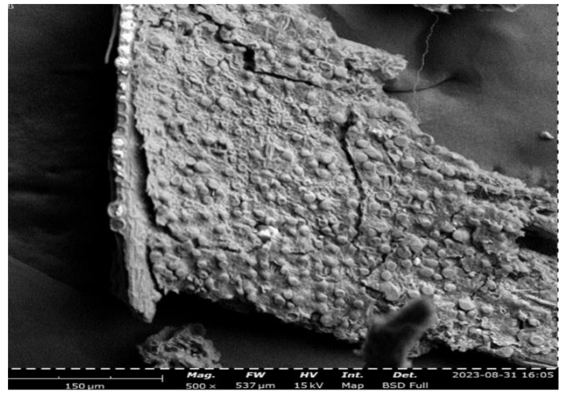

Figure 7a. SEM-EDS of *Thamatococcus daniellii* Leaf 500 X Magnifications

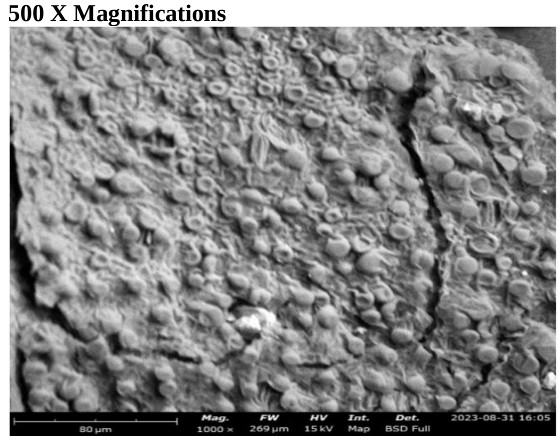

Figure 7b. SM-EDS of *Thamatococcus daniellii* Leaf 1000 X Magnifications

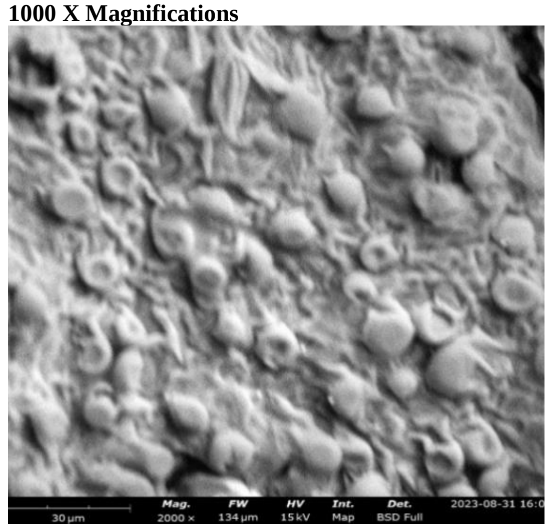

Figure 7c. SEM-EDS of *Thamatococcus daniellii* Leaf 2000 X Magnifications

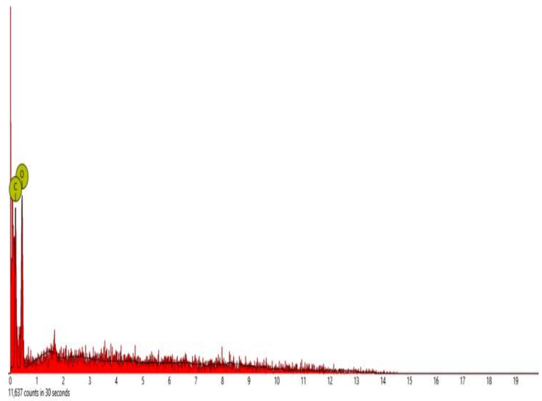

Figure 7d.SEM-EDES of *Thaumatococcus damielli* Leaf

Figures 7a - 7d showed micro graph of *Thaumatococcus daniellii* biomass, from the result obtained it was observed that the biomass showed loose aggregates with cracks and uniformly distributed pores all over the sample surface. These large pores are requirements for any potential sorbent. Porous structures could act as active sites for metal ion adsorption. Physical sorption plays important role in this regards. These biomass are suggested to be amorphous in nature, an amorphous material shows the presence of pores and void spaces on the material and these aid in sorption and subsequent removal of ions. *Thaumatococcus daniellii* has particle average pore diameter distribution values ranging from 2.140nm, 2.108nm and micro pore volume 0.188cc/g and pore area of 348.44m2/g, 269. Similar observation was reported by Ahmed *et al*., 2015, the EDS analysis result for *Thaumatococcus daniellii* showed that it contains Carbon 83.35% and Oxygen 16.65%. From the result obtained *Thaumatococcus daniellii* showed porous and irregular surface with amorphous structures which indicates more micro-pores which are good for sorption. Similar result was obtained by Ahmed *et al.*, (2015)

Conclusion.

From the results obtained from this study, *Thaumatococcuss daniellii* leaves can be used as an alternative low-cost biosorbent for the removal of cadmium and lead from aqueous solution. The presence of functional groups in the sorbents favors metal ion binding. The sorption and characterization studies showed the feasibility of *thaumatococcuss daniellii* leaves for water treatment. It is recommended that the effectiveness of the biomass to treat industrial effluents be evaluated.

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