J. Chem. Soc. Nigeria, Vol. 46, No.3, pp 0574 – 0582 [2021]

BIOSORPTION OF Pb(II) AND Cu(II) IONS FROM AQUEOUS SOLUTION USING COFFEE SENNA (*Senna occidentalis*) LEAVES AS BIOMASS

*R. A. Lawal , Y. N. Lohdip, J. J. Gongden and J. R. Gungshik

Department of Chemistry, University of Jos, Jos, Nigeria.
Email: lawalrac@gmail.com

ABSTRACT

Conventional reagents for the remediation of heavy metals from wastewaters are expensive. Plant materials are being investigated to serve as alternative. The potential of *Senna occidentalis* leaves in removing Pb (II) and Cu (II) ions from aqueous solution was investigated using Batch adsorption method. The process was subjected to different experimental conditions such as initial metal concentration, solution pH, contact time, biosorbent dose, temperature and shaking speed. Atomic absorption spectroscopy (AAS) was employed in the determination of metal ion concentrations in solution after agitation, and characterization of plant biomass was done using infrared (IR) and scanning electron microscopy (SEM) analytical techniques. The adsorption process vary with the pH of the reaction medium. The optimum adsorption of Pb (II) and Cu (II) ions was achieved at pH 6 and 4 with percent uptake recorded at 97.70% and 82.32% respectively. At optimum temperatures of 40°C & 60°C for Pb (II) and Cu (II) ions, reaction equilibrium was attained after 120 min and 90 min of contact with 20 mg and 40 mg doses of the biomass respectively. The adsorption data for Pb (II) ion fitted well to Langmuir, Freundlich, Temkin and Dubbinin-Radushkevich isotherms. However, Cu (II) ion adsorption mechanism showed exception to Langmuir adsorption isotherm. The plant material was found to be effective in removing Pb (II) and Cu (II) ions and thus, can serve as a substitute for costly adsorbents in the remediation of Pb (II) and Cu (II) ions from wastewaters.

Keywords: Biosorption, *Senna occidentalis* leaves, Lead, Copper, Isotherms

INTRODUCTION

Biosorption is a process which involves the use of materials that are of plant and animal origin, to remove metal ions from aqueous solution such as wastewater and effluents. The solid material used is known as the adsorbent while the solution is called the adsorbate. In this process, the mechanism of metal uptake can be either physical (physisorption) or chemical (chemisorption). Physisorption occurs when the metal ions adhered to the surface of the adsorbent are bonded by a weak Van der Waaal's forces and is reversible [1] while in chemisorption, metal ions from the solution are strongly bonded to the functional groups present on the surface of the adsorbent and the process is irreversible [2]. Based on this principle, biomaterials which are known to possess binding sites (functional groups) of different types are used in the remediation of toxic metals from aqueous solution or effluent. Among the functional groups in plants that are responsible for the removal of metal ions are the carbonyl (acids and esters), hydroxyl and amino groups [3]. Phosphate, cyanide and sulphate groups are sometimes found useful depending on the type of plant [4]. In addition to the presence of functional groups, other factors can influence the efficiency of the plant material as a metal adsorbent. Some of these factors include: pH. charge of the metal ion, temperature of the reaction medium, status of adsorbent-whether dead of living and presence of competing ions [1, 3, 5, 6]

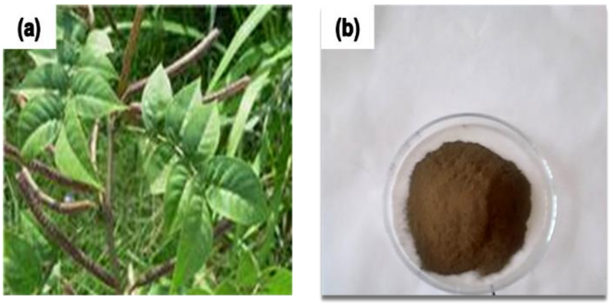
Since plant materials are abundant, readily available and cheap, they can be used as substitute to the expensive conventional ones like resins used for the removal of heavy metals from wastewater. These heavy metals have been known to have serious health implications even in traces [7, 8, 9]. They have the potential to affect brain, kidney, liver, ovaries and lungs causing organ damage [10, 11, 12, 13]. The existence of heavy metals naturally in the lithosphere makes them to be indestructible [14], and hence the need to device a means of remediating them from the water source, wastewater or effluent. Methods that are affordable and environmentally friend when employed can reduce these toxic metals to a bearable level.

Many plant materials have been tested for their capacities to adsorb heavy metals from aqueous solution, which include peanut shell [15], rice husk [16], bear yeast [17], *Sesame indicum* [3] and *Equisetum horsetail* [18]. However, *Senna occidentalis* leave has not been adequately explored for this function. In this study, we have investigated the potential of *Senna occidentalis* leave biomass for heavy metal remediation in aqueous solution.

MATERIALS AND METHODS

Materials

Senna occidentalis leaves were collected in October 2014 at the time of bloom, washed with tap water and finally with distilled water. It was then air-dried at room temperature under the shade for 14 days. The biomass was ground to powder using grinding mill and sieved to a particle size of 1mm. It was stored in polyethylene bottles prior to analysis.



Plates 1: Pictures of (a) *Senna occidentalis* plant (b) *Senna occidentalis* leave powder

Methods

Preparation of copper and lead solutions

Metal salts used are BDH chemicals obtained from Department of Chemistry of the University of Jos. Standard solutions of lead (II) and copper (II) were prepared from the stock solutions of their salts using serial dilution. Exactly 1.598 g of lead nitrate [$Pb(NO_3)_2$] and 3.9296 g $CuSO_4.5H_2O$ BDH were used in the preparation of the stock solutions of 1000 mg/L [19, 20]. The HCl and NaOH used for pH control were all of analytical grade and were used without further purification.

Sorption experiment

Batch adsorption method adopted by Gongden [21] was employed in the biosorption study and the elemental analysis was done using AAS model varian spectr. A.A 200.

Determination of effect of initial metal ion concentration

Exactly 0.05 g of plant leave powder was weighed and added to 50 cm^3 of metal ion solution prepared at different concentrations (2.0 mg/l – 10.0 mg/l) in a 250 cm^3 conical flasks. The mixtures were shaken using for 120 minutes at 250 rpm. The mixtures were filtered using Whatman No.1 filter paper and the concentrations of Pb (II) and Cu(II) ions in the filtrates were determined using AAS.

Determination of effect of pH

The sorption experiment was carried out at different pH values ranging from 2 – 10 in order to investigate its effect on the percent metal adsorption. Exactly 0.05 g of plant leave powder was weighed and transferred into 250 cm^3 conical flask containing 50 cm^3 of optimum metal ion concentration (i.e. the concentration with the highest adsorption). Solution of 1.0 M HNO_3 or 1.0 M NaOH was added in dropwise until the desired pH was obtained. The mixtures were agitated at 250 rpm for 120 minutes and filtered. The concentrations of Pb (II) and Cu(II) ions in the filtrates were determined using AAS.

Determination of effect of biosorbent dose

Various masses (0.01 g – 0.2 g) of the leave sample were weighed and added to the respective metal ion solutions of optimum concentration. The pH of the mixtures were adjusted to the optimum pH and the resulting mixtures were shaken vigorously for 120 minutes at 250 rpm and filtered. The concentrations of Pb (II) and Cu(II) ions in the filtrates were determined using AAS.

Determination of effect of contact time

Optimum biosorbent dose of leaves sample was added to 50 cm^3 of different metal ion solutions of optimum concentrations at optimum pH and room temperature. The resulting mixtures were shaken vigorously at 250 rpm and at different time intervals of 30, 60, 90,120 and 180 minutes respectively. The mixtures were filtered and the filtrates obtained were used to analyse the concentrations of Pb (II) and Cu(II) ions using AAS.

.

Determination of effect of temperature

Metal ion solution of optimum concentration and pH were prepared. The optimum biosorbent dose of the leaves sample was weighed and added to each of the metal solutions at different temperatures of 30°C, 40°C, 60°C, 80°C and 100°C. The mixtures were shaken vigorously at optimum contact time and filtered. The concentrations of Pb (II) and Cu(II) ions in the filtrates were determined using AAS.

Determination of effect of agitation speed

All optimal conditions were observed with agitation speed ranging from 100 rpm – 300 rpm on leave sample. The separation of the adsorbent from solutions was carried out by filtration with Whatman No.1 filter paper and the filtrates were analyzed for residual metal ions using AAS.

Sorption capacity

The mass balance equation was used for the evaluation of metal uptake capacity by the plant leave sample as given below:

$$\%\, adsorption = \frac{100 * (Co - Ce)}{Co}$$

Where Co and Ce are the initial and equilibrium concentration of metal ions (mg L^{-1}) in solution.

Adsorption capacity, q_t at specific time, t, was calculated by the following equation

$$qt = \frac{(Co - Ce)V}{M}$$

Where qt is the adsorption capacity (mg/g), Co is the initial concentration of metal in solution (mgL^{-1}), Ce is the equilibrium concentration of metal in solution (g L^{-1}), V is the volume of metal ion solution (L) and M is the mass of the adsorbent (g).

The results obtained were subjected to various adsorption models such as Langmuir, Feundlich, Temkin and Duvunin-Radushkevich isotherms models, adopting the methods by [3, 22, 23]

Biomass Characterization

Characterization of the native biomass was done using Infrared (IR) and Scanning Electron Microscopy (SEM) analytical techniques.

RESULTS AND DISCUSSION

IR and SEM characterization

The IR spectrum of the *Senna occidentalis* leaves biomass indicates the presence of binding sites such as hydroxyl, carbonyl and ester as shown in the Table 1.

Table 1: IR Characteristic Bands and their Functional Group Assignment for Raw and Modified Blends of *Senna occidentalis* (cm^{-1})

SOL	Functional group	Similar functional group assignment
3264.54	O-H str.	[24, 25]
2917.78	C-H str. , alkanes	[23, 26]
1604.67	C=O	[27]
1403.32	C-H bending, alkanes	[24]
1024.35	C-O-C	[28]

SOL=*Senna occidentalis* leaves

The presence of these functional groups is an indication of the absorptive potential of this adsorbent for heavy metals.

The SEM micrograph as shown in Plate 2 revealed the porous nature of the adsorbent, necessary for metal uptake.

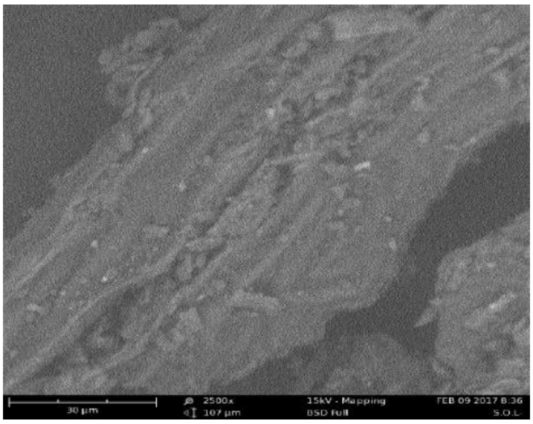


Plate 2: Scanning Electron Micrograph of Native *Senna occidentalis* Leaf (SOL) Biomass

The presence of pores on the surface of the adsorbent and the irregular nature of the surface suggest the possibility that the metal ions can be trapped and adsorbed onto the surface [26].

Effect of initial metal concentration

The results of the effect of initial metal concentration for Pb(II) and Cu(II) adsorption by *Senna occidentalis* leaves adsorbents are shown in figure 1. Variation in the extent of adsorption of the metal ions by the adsorbents was observed.

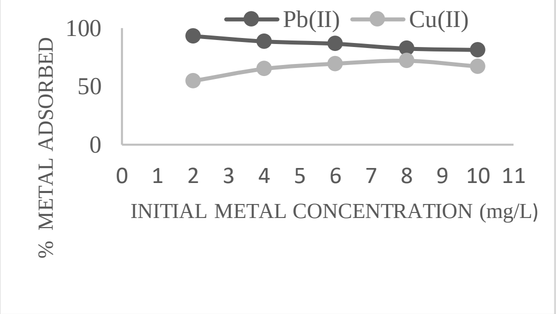


Figure 1: Effect of initial metal concentration (mg/L) on the adsorption of Pb (II) and Cu (II) ions onto *Senna occidentalis* leaves at constant temp of 298K, biomas dosage of 0.05 g, contact time of 2 hrs and shaking speed of 250 rpm.

Maximum adsorption of Pb (II) was achieved at 93.15% with 2.0 mg/l initial metal concentration. The percent adsorption decreased with the increase in concentration of the metal solution. The maximum adsorption of Pb(II) at the lowest concentration is similar to the earlier report by Amer et al., [29] and Jimoh et al., [30]. The presence of abundant adsorption sites at the initial stage may be the cause of initial fast rate of Pb (II) uptake by the biomass [31]. The progressive increase in electrostatic interaction between the Pb(II) ions and the adsorbent active sites may be an added advantage. On the other hand, Cu (II) witnessed a gradual increase in adsorption with a corresponding increase in initial metal concentration to the optimum of 8 mg/l. This gradual increase in adsorption may be linked to the availability of adsorption sites which become occupied as the concentration increases up to the point of saturation (8 mg/l) where the sites are assumed to be completely bonded to the available metal ions in solution [4, 32]

Effect of pH

The results of the effect of pH is presented in Figure 2. The optimum uptake of Pb (II) was observed at pH 6 while that of Cu (II) ions was observed at pH 4.

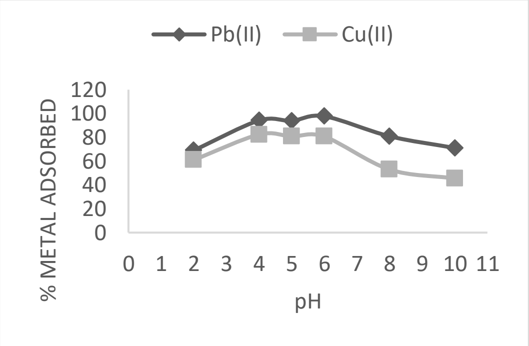


Figure 2: Effect of pH on the adsorption of Pb (II) and Cu (II) ions onto *Senna occidentalis* leaves at constant metal concentration of 2 mg/L (Pb) & 8 mg/L (Cu), Temp of 298K, biomas dosage of 0.05 g, contact time of 2 hrs and shaking speed of 250 rpm.

pH is one of the factors which influences the speciation and biosorption affinity of metal ions [1, 4, 5]. From the results in Figure 2, low uptake of Pb (II) and Cu (II) was observed at low pH of 2. This can be attributed to the competition between the proton on the adsorbent surface and the metal ions in solution for adsorption sites. The presence of protons on the adsorbent surface has been reported to affect metal adsorption [16, 17]. As the pH of the metal solutions increases, an increase in the Pb (II) and Cu (II) uptake was observed. This may probably be due to the decrease in the amount of proton on the adsorbent surface, providing an avenue for metal- adsorbent interaction and resulting in high metal uptake. This continues until an equilibrium was established.

At the point of equilibrium, the metal reached its optimum level of extraction. Exactly 82.32 % of Cu(II) and 97.70 % of Pb(II) was optimally extracted from solution at pH 4 & 6 by *Senna* leaves respectively. Cu(II) adsorption at pH 4 was reported earlier by other researchers [17, 28]. Many plant materials have been reported to absorb metals at pH 6 [16, 18]; which is in conformity with this finding with respect to Pb(II).The binding of the metals to the adsorbents at this pH range can be linked to the presence of carbonyl group [4].

Effect of dosage

The results of the effect of biomass dosage on Pb(II) and Cu(II) ions adsorption by *Senna occidentalis* leaves are presented in Figure 3. Cu(II) was observed to have higher dosage requirement than Pb(II). The percent adsorption of the metals was affected by the biomass dosage.

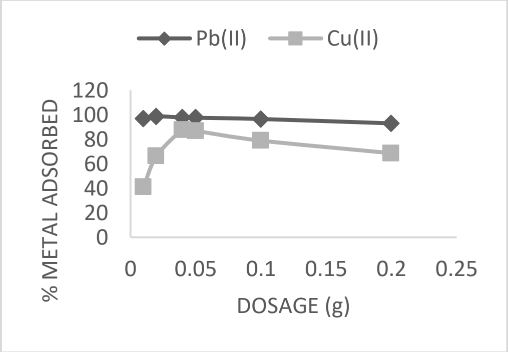


Figure 3: Effect of biomass dosage (g) on the adsorption of Pb (II) and Cu (II) ions onto *Senna occidentalis* leaves at constant metal concentration of 2 mg/L (Pb) & 8 mg/L (Cu), Temp of 298K, contact time of 2 hrs, pH of 6 (Pb) & 4 (Cu) and shaking speed of 250 rpm.

The capacity of biomass to adsorb cations depends on the biomass dosage. Metal uptake is expected to increase with the increase in biomass concentration. The metal studied experienced early fast metal uptake due to the availability of sufficient metal ions to limited active sites. Low adsorbent dose can also lead to early saturation of the adsorbent surface.

From Figure 3, it can be observed that the optimum adsorbent dose for all the metals ranged from 0.01 – 0.05 g, beyond which decrease in metal uptake occurred. The break through points for Pb (II) was observed at 0.02 g and that of Cu (II) was 0.04 g. The initial increase in metal uptake with the corresponding increase in dosage may be connected to the increase in surface area and active sites up to the point of equilibrium. A decrease in the percent metal uptake was observed after the equilibrium has been attained. The decrease may be due to the presence of limited amount of metal ions in solution to the increasing adsorbent dosage. Another factor which might contribute to the decrease in adsorption of the metals is the reduction in surface area as a results of agglomeration of adsorbent particles [27, 33]

Effect of contact time

The results of the effect of contact time on Pb (II) and Cu (II) ions adsorption by *Senna occidentalis* leaf adsorbent are shown in Figure 4. The adsorbent showed different adsorption potential for the metals at various contact time.

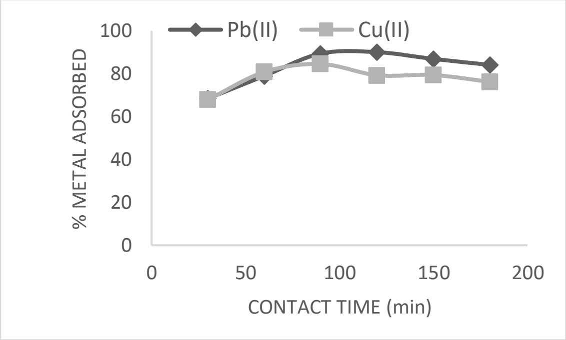


Figure 4: Effect of contact time on the adsorption of Pb (II) and Cu (II) ions onto *Senna occidentalis* leaves at constant metal concentration of 2 mg/L (Pb) & 8 mg/L (Cu), Temp of 298K, dosage of 0.02 g (Pb) & 0.04 g (Cu), pH of 6 (Pb) & 4 (Cu) and shaking speed of 250 rpm

Contact time is an equilibrium factor which determines how fast an adsorbent can remove heavy metals from solution. The optimum percent adsorption of Pb (II) ions (90.05%) onto the biomass took place at a higher contact time of 120 min despite the low dosage requirement of 0.02g. This is probably due to the high molecular weight of Pb (II). Similarly, maximum uptake of Cu (II) at 79.28% at the same time of contact might be due to the high dosage requirement of 0.04g. The adsorption of

Pb (II) ions after 120 min and that of Cu (II) ions after 90 min of contact is similar to the earlier reports [29, 34]. The rate of metal uptake is a function of not only the time but the nature of substrate and the metal ions [31]. Desorption might likely be the cause of decrease in the percent Pb(II) and Cu(II) adsorbed after the optimum time. Optimum time of contact of 180 min has also been reported for Pb(II) [4].

Effect of Temperature

The results of the effect of temperature on Pb (II) and Cu (II) ions adsorption by *Senna occidentalis* leaves are presented in Figure 5. The adsorption of all the metals was affected by the change in temperature.

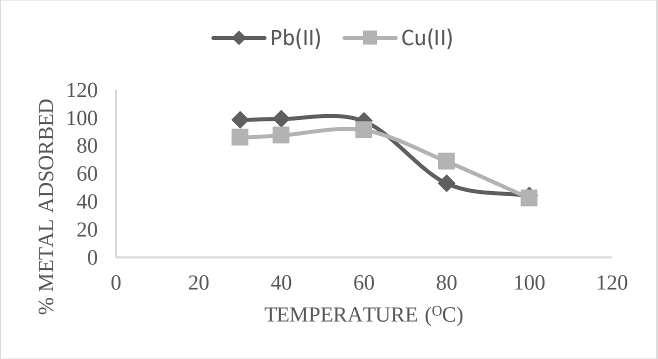


Figure 5: Effect of temperature on the adsorption of Pb (II) and Cu (II) ions onto *Senna occidentalis* leaves at constant metal concentration of 2 mg/L (Pb) & 8 mg/L (Cu), Temp of 298K, dosage of 0.02 g (Pb) & 0.04 g (Cu), pH of 6 (Pb) & 4 (Cu), contact time of 120 min (Pb) & 90 min (Cu) and shaking speed of 250 rpm

The adsorption of Pb (II) and Cu (II) onto *Senna* leaves was found to be temperature dependent. The results revealed that Cu(II) adsorbed at a higher temperature of 60ºC than Pb (II) at 40ºC. This is not far from the fact that metal adsorption is favoured by endothermic process. Beyond these optimum temperatures, adsorption of these metals were observed to have reduced drastically. This decrease in adsorption may be attributed to the desorption of the metals from the adsorbent surface since adsorption is not favoured at higher temperature [5].

Effect of shaking speed

The results of the effect of shaking speed on Pb (II) and Cu (II) uptake by *Senna occidentalis* leaf adsorbent are presented in Figure 6. The figure indicates that the uptake of the metal ions assumed a similar scenario of increasing and decreasing fashion. All the metals attained optimum removal between 150 – 200 rpm by the biomass.

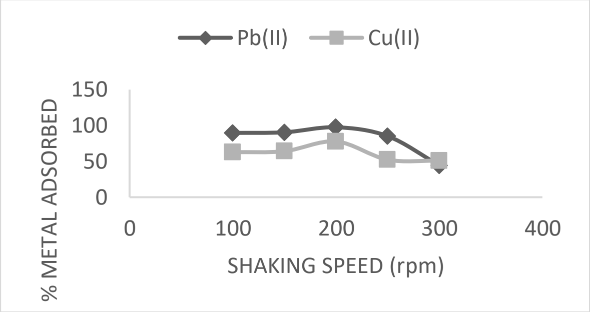


Figure 6: Effect of shaking speed on the adsorption of Pb (II) and Cu (II) ions onto *Senna occidentalis* leaves (rpm) at constant metal concentration of 2 mg/L (Pb) & 8 mg/L (Cu), Temp of 298K, dosage of 0.02 g (Pb) & 0.04 g (Cu), pH of 6 (Pb) & 4 (Cu) and contact time of 120 min (Pb) & 90 min (Cu)

Shaking induces collision between the metal ions and the biosorbent particles. These collisions are necessary for a successful biosorption process [28]. As the shaking speed increases, frequency of collision also increases, resulting in the increase in percent metal uptake. However, excessive increase in the agitation speed increases the mobility of the two phases, denying the adsorbent the adequate time for metal uptake, and consequently resulting in the detachment of already adsorbed metal ions. Therefore, removal capacity drops at extremely high shaking speed [28]. From the results of the adsorption of Pb(II) and Cu(II) onto *Senna occidentalis* leaves, it can be observed that both the metals were adsorbed maximally at 200 rpm. The initial low uptake of the metals at 100 rpm may be linked to the low frequency of collision between the metals and the adsorbents surfaces.

The leaves have proven to be good adsorbents for Pb(II) and moderate for Cu(II). The results show that approximately 90-100% Pb(II) and 78-80% Cu(II) ions were removed from the aqueous solutions at various optimum experimental conditions.

ISOTHERMS

The correlations of the adsorption mechanism of Pb (II) and Cu (II) extraction from aqueous solution to the Langmuir, Freundlich, Temkin and Davinin – Radushkevick (D-R) isotherm models are presented in Table 2. Good correlations were observed for both the metals with all the isotherms. However, Cu does not fit to Langmuir isotherm.

Table 2: Isotherms constants for the adsorption of Pb (II) and Cu (II) ions onto *Senna occidentalis* leaves biomass

Isotherm	Langmuir				Freundlich			Temkin			D-R		
Element	R^2	q_e (mg/L)	B (L/mg)	R_L	R^2	kf	n	R^2	BT_e	aT_e	R^2	q_{max} (mg/L)	E (kJ/mol)
Pb (II)	0.96	11.3	1.14	0.31	1.00	0.05	0.56	0.95	5.54	-6.05	0.91	6.09	0.17
Cu (II)	0.41	-8.24	-0.16	-3.89	0.94	1.49	0.69	0.97	0.49	0.31	0.97	8.24	2.11

CONCLUSION

This study revealed that *Senna occidentalis* leaves are capable of removing 90 - 99% Pb (II) and 71-91% Cu (II) ions from aqueous solution at optimum conditions so established. The adsorption processes of both metals followed heterolayer mechanism. In addition, Pb (II) adsorption also occur at monolayer surface. The energy of adsorption indicates that the binding of the metals onto the surface of the adsorbent is due to weak van der Waals forces - indicating physisorption. This shows that *Senna occidentalis* leaves can be used as an alternative adsorbent to the expensive conventional ones for the removal of lead and copper from waste water.

ACKNOWLEDGEMENT

The authors appreciate the University of Jos in collaboration with TETFund for the financial assistance.

REFERENCES

[1] Z. Michalak, K. Chojnacka and A. Witek- Krowiak (2013). State of art for the biosorption process- a review. *Applied Biochemistry and Biotechnology, 170* (60), 1389 -1416.

[2] P. Atkins and J. De Paula (2006). *Atkins Physical Chemistry*. Oxford University YMCA library building, Jai singh, New Delhi 110001, 916-923.

[3] T. B. Venkatesan, N. Bommannan, K. Kulanthai and S. Krishnamoorthy (2014). A comparative study of removal of Cu(II) from aqueous solution by thermally and sulphuric acid activated sesanum indicum carbons. *International Journal of Scientific and Technological research, 3(*3), 42 – 49.

[4] O. A. Adelaja, I. A. Amoo and A. D. Aderigbigbe (2011).Biosorption of lead (II) ions using Moringa oleifera pods. Scholars Research Library. *Archives of Applied Science Research, 3* (6), 50 – 60.

[5] D. Nilanjana, R. Vimala and P. Karthika (2008). Biosorption of heavy metals-an overview. *Indian Journal of biotechnology, 7*, 159-169.

[6] F. Fomina and F. M. Gadd (2014). Biosorption, current perspectives on concept, definition and application. *Bioresource Technology, 160*, 3-14.

[7] C. R. Ekeanyanwu, C. A. Ogbuinyi and O. F. Etienjirhevwe (2010). Trace metals distribution in Fish tissues, bottom sediments and water from Okumeshi River in Delta State, Nig. *Ethiopian Journal of Environmental Studies and Management, 3*(3), 12- 17.

[8] R. A, Olowu, O. O. Ayejuyo, G. O, Adewuyi, I. A, Adejoro, A. A. B. Denloye, A. O. Babatunde and A. L. Ogundajo (2010). Determination of heavy metals in fish tissues, water and sediment from Epe and Badagry Lagoons, Lagos, Nigeria. *E- Journal of Chemistry, 7* (1), 215-216.

[9] S. Dobaradaran, K. Naddafi, S. Nazmara and H. Ghaedi (2010). Heavy metals (Cd, Cu, Ni and Pb) content in two fish species of Persian Gulf in Bushehr Port, Iran. *African Journal of Biotechnology, 9* (37), 6191 – 6193.

[10] E. J. Itumoh, T. Izuagie, N. O. Omaka, A Uba, M. Shuaibu, I. A, Dogonyaro, A. Isa, A. Dange U. and S. I. Isah (2011). Trace Metals Analysis of Soil and Water Samples from Limestone-Mining site in Sokoto State, Nigeria. *Journal of Physical Sciences and Innovation, 3,* 62 – 71.

[11] Y. Chervona, A. Arita and M. Costa (2012). Carcinogenic metals and the epigenome: Understanding the effect of nickel, arsenic and chromium. *Metallomics, 4* (7), 619 – 27.

[12] C. C. Elekes (2014). Assessment of historical metal pollution of land in the proximity of industrial area of Targoviste, Romania. *Textbook of Environmental Risk Assessment of Soil Contamination (*257-284). Retrieved December 24, 2017 *from* http://www.intechopen.com/books/environmental-risk-assessment-of-soil-contamination.

[13] Lenntech (2017). Manganes- Mn. Chemical properties of manganese-health effects of manganes-environmental effect of manganese. Retrieved December 25, 2017 from https:www.lenntech.com/periodic/elements/mn.htm.

[14] U. U. Egereonu, L. N. Ukiwe, S. Oti and J.C. Egereonu (2012). Investigation of pollution index of surface and ground water of Ndibe River Catchment, Afikpo, Nig. *Journal of Chemical Society of Nigeria, 37(*2), 27 – 31.

[15] M. Jaishankar, B. B. Mathews, M. S. Shah, K. T. P. Murthy and S. K. R. Gowda (2014). Biosorption of few heavy metals ions using agricultural wastes. *Journal of Environmental Pollution and human health. 2* (1), 1 – 6.

[16] A. G. El-Said (2010). Biosorption of Pb (ii) ions from aqueous solutions onto rice husk and its ash. *Journal of American Science 6*(10), 143-140.

[17] A. Krishnaiah, M. V. Subbaiah, G. Yuvavaja and Y. A. Vijaya (2011). Equillibrium kinetics and thermodynamic studies on biosorption of Cu(II), Cd(II), Pb(II), and Ni(II) from aqueous solution by chitosan-abrus precatorius blended beads. *Journal of chemical and Pharmaceutical Research,3*(2), 365-378.

[18] A. H. Sulayman and H. L. Swacli (2014). Biosorption of organic and inorganic pollutants from simulated wastewater by using equisetum horsetail. IMPACT. *International Journal of Research in Engineering and Technology (IMPACT: IJRET): 2347-4599, 2(*6), 151-164.

[19] D. G. Mlelemba (2008). *Levels of Cadmium, Chromium and Lead in* (*Glarias gariepinas*-Cat fish) *inhabiting some streams of Blantyre city-Malawii*. Manuscript at Department of Chemistry, Chancellor College, Zomba, Malawi, 32pp, Retrieved December 24, 2017 from www.tiguri.org/images/resources/tool/docs/2323.doc

[20] E. G. Ibrahim (2013). *Speciation of selected trace metals in soil samples from dumpsite in Lafia, Nasarawa state*. Unpublished MSc thesis, Department of Chemistry of the University of Jos, Jos, 84pp.

[21] J. J. Gongden (2015). *Water quality assessment of four surface dams in Langtang South Local Government Area of Plateau State central Nigeria and Green Chemistry approach to improving the potability of the water*. Unpublished PhD theses, Department of Chemistry, Faculty of Natural Sciences, University of Jos, Jos, September, 2015, pp 254.

[22] M. A. Hubbe, S. H. Hassan and J. J. Ducoste (2011). Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals. *Journal of Bioresources 6* (2), 2161-2287.

[23] O. O. S. Ogunleye, M. A. Ajala and S. E. Agarry (2014). Evaluation of biosorptive capacity of banana (*Musa praradisiaca*) stalk for lead (II) removal from squeary solution. *Journal of Environmental Protection, 4,* 1451-1456.

[24] B. Shrestha, J. Kour, P. L. Homagai, M. R. Pokhrel and K. N. Ghimire (2013). Surface Modification of the Biowaste for Purification of Wastewater contaminated with Toxic Heavy Metals- Lead and Cadmium. Advances in Chemical Engineering and Sciences, 3,178-184.

[25] A. S. M. Naspu, M. L. Kamal, Z. Hamzah and S. Hassan (2014). A study on adsorption of cadmium by using chemically modified *salvinia. The malaysian journal of analytical sciences, 18 (1), 78 – 84.*

[26] R. Saravanan and I. Ravikumar (2015). The use of new chemically modified cellulose for heavy metal ion adsorption and antimicrobial activities. *Journal of Water Resources and Protection, 7,* 530-545.

[27] K. Z. Elwakeel and A. M. Yusuf (2010). *Adsorption of malathion on thermally treated egg shell material.* Fourteenth international water technology conference TWTC 14, Cairo Egypt, 53 – 64.

[28] P. K. D. Chathuranga, D. M. R. E. A. Dissanayake, N. Priyantha, S. S. Izbal and M. C. Mohammed Iqbal (2014). Biosorption and desorption of lead (II) by *Hydrilla verticillata, bioremediation Journal, 18*(3), 192-203.

[29] M. W. Amer, R. A. Ahmed and A. M. Awwad (2015). Biosorption of Cu (II), Ni (II), Zn (II), and Pb (II) ions from aqueous solution by saphard japonica pods powder. *International Journal of Industrial Chemistry, 6,* 67-75. doi: 10.1007/s40090014-0030-8.

[30] T. O. Jimoh, Y. A. Iyaka and M. M. Nubaye (2012). Sorption study of Co(II), Cu(II) and Pb(II) ions removal from aqueous solution by adfsorption on flamboyant flower (Delonix regia). *American journal of Chemistry, 2*(3), 165-170. Doi:10.5923/j.Chemistry.20120203.12.

[31] J. N. Egila, B. E. N. Dauda and T. Jimoh (2010). Biosorptive removal of cobalt (II) ions from aqueous solution by Annaranthus hydrides L. stalk wastes. *African Journal of biotechnology, 9* (48), 8192-8198.

[32] A. U. Augustine and J. N. Egila (2013). Removal of chromium (VI) and Nickel (II) Ions from aqueous solutions using sunflower (Helianthus annus) leaves as adsorbent. *International Journal of Modern Chemistry,* 4 (3), 167-179.

[33] M. O. Omorogie, J. O.Babalola, E. I. Unuabonah, W. Song and J. R. Gong (2016). Efficient chromium abstraction from aqueos solutionusing a low-cost biosorbent:*Nauclea diderrichii* seed biomass waste. *Journal of Saudi Chemical Society, 20,* 49-57.

[34] A. C. John, O. L. Ibironke, V. Adedeji and O. Olafisoye (2011). Equillibrium and Kinetic studies of the biosorption of heavy metal (Cadmium) on cassia siamea bark. *American-Eurasian journal of Scientific Research, 6* (3), 123-130.