

Removal of heavy metals using treated- waste material (Moringa oleifera seed pods)

Irene Wangari Maina

Department of Chemical and Forensic Sciences,
Botswana International University of Science and
Technology..
Palapye, Botswana
irene.maina@studentmail.biust.ac.bw

Veronica Obuseng, Florence Nareetsile

Chemistry Department, University of Botswana
Gaborone, Botswana
obusengv@mopipi.ub.bw, nareetsile@mopipi.ub.bw

Abstract— The use of waste materials as low-cost adsorbents is attractive due to their contribution in the reduction of costs for waste disposal, therefore contributing to environmental protection and most importantly, offers an attractive potential alternative to conventional methods of removal of toxic ions from the environment. A study to investigate the possible use of powdered *Moringa oleifera* seed pods (MOSP) was conducted. Removal of selected metal ions were studied including Pb, Cd, Cu, Fe and Zn. Quantification of the extracted metal ions was done using flame atomic absorption spectroscopy (FAAS). One variable at a time optimization method was employed. Using 50 mL of aqueous sample prepared from the metal standard, the optimized parameters were 60 minutes contact time, 1 g of powdered MOSP, pH 8, 100 µm particle size and at 35°C. To determine the functional groups in the sorbents, Fourier Transform Infrared spectroscopy (FTIR) was used. SEM-EDX was used to determine the morphology and the elemental analysis of the sorbents. The optimized parameters were applied on aqueous water samples and the efficiency was in the range of 65.9 ± 3.5 to 99.6 ± 6.69%. *Moringa oleifera* seed pods were proposed as a cheap, simple and an effective alternative for purification of water contaminated with metals.

Keywords: waste-material, heavy metals, *Moringa oleifera*, seed pods, efficiency

I. INTRODUCTION

Pollution of aqueous environments by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain [1]. The rate at which these pollutants enter the environment has been an upward trend due to rapid development of industrial activities [2]. Due to bioaccumulation of these metals, scientists have been motivated to develop treatment methods using various techniques that have been successful but are challenged in some ways. Such methods include chemical and surface chemistry processes such as precipitation, membrane processes, ionic exchange and reverse osmosis [3]. However, these methods have limitations such as poor efficiency, sensitive operating conditions, they incur high installation and operating cost; and have detrimental effects on the environment due to production of secondary sludge. These challenges together with the need for economical and effective methods for recovering the metals have resulted in the development of

alternative treatment technologies. This justifies the need to investigate alternative methods such as biosorption, in which certain types of biomass are able to bind and concentrate metals from even dilute aqueous solutions. Biosorption has gained important credibility during recent years as a low-cost, readily available and efficient treatment technology for effective removal of heavy metals [4]-[6] due to their several advantages such as (i) readily available, (ii) require little processing, (iii) can be regenerated (iv) Metals can be recovered from biomass [7].

For this reason, use of low cost materials for metal removal from water has been investigated. Using agricultural waste has advantages since it uses what is considered waste product. Several waste material have been used to remove toxic metals such as apple waste [8]; corn cobs [9]; cereal crops [10] woody materials such as bark, leaves and sawdust [11] and banana peels [12]. These materials were successful in removing heavy metals to varying degrees. *Moringa oleifera* has also been used for such purposes.

Moringa oleifera (MO) is multipurpose plant of the developing world, as it can easily be cultivated and adaptable in semi-arid climates. Biomass from *Moringa Oleifera* tree has been used for water purification as a coagulating agent and to remove heavy metals. However, limited work has been done on application of *Moringa oleifera* seed pods (MOSP). Therefore, this study focused on use of treated MOSP for removal of selected heavy metals.

II. MATERIALS AND METHODS

A. Materials

All reagents were of analytical grade. Acids were used for digesting and adjusting pH. HNO₃ (69%, Skylabs), HCl (32%), Minema Chemicals, Double deionized water (Millipore-Q Millipore 18.2 MΩ/cm resistivity) was also used for dilutions of samples to be analysed with FAAS. Elemental standards solutions used for calibration were prepared from 1000 ppm of stock solutions supplied by Minema Chemicals (Pb and Fe), Merck Pty Ltd (Cu, Cd and Zn) NaOH (≥97.0%, Rochelle chemicals) was used to adjust pH, Hanna Instruments HI 991001 pH, orbital shaker (scigenics), agate pestle and mortar was also used for reducing the particles further. A 100

µm, 200 µm, 500 µm stainless steel sieves were used for sieving the sorbents. The filter papers used were ash less Whatmann filter paper no.1 from England. The filter papers were used to filter the mixtures of sorbents and solution.

B. Instrumental analysis

A Varian 220FS atomic absorption spectrometer operated with air/acetylene was used for determination of seven selected metal ions which included lead (Pb), iron (Fe), zinc (Zn), copper (Cu), and cadmium (Cd). Varian hollow cathode lamps for each of the analysed metals were used as radiation source. 1000 mgL⁻¹ ppm stock solutions of metals were used to prepare working standards (in the range 0.0 to 5.0 mgL⁻¹) in deionized water. The instrument was calibrated manually by aspirating the prepared working standards of the cations of interest one by one into the flame. The samples were also aspirated manually into the flame for atomization. The instrumental conditions applied were according to AAS manual.

FTIR spectroscopy was used to characterize the sorbents to determine the functional groups responsible for metal removal. The FTIR spectra were recorded in the wavenumber range 400-6 4000 cm⁻¹ on a Perkin Elmer system 2000 FTIR. The sorbents were kept at ambient temperature. 1 mg seed powder per 200 mg of KBr was weighed. The powder was pressed into pellets by using a 15 ton hydraulic press. The data were collected at 2.0 cm⁻¹ resolution, and each spectrum was a result of 256 scans. In order to observe the surface morphology of the sorbents, a Philips XL 30 ESEM model environmental scanning electron microscope (ESEM) was used.

C. Preparation and characterization of *Moringa Oleifera* seed pods (MOSP)

The seed pods (deseeded) were obtained from various sampling points in Artesia, Botswana. Dried MOSP were washed with double deionized water, further dried in an oven at 65 °C for 24 hrs. The dried samples were ground then sieved to different mesh sizes (100, 200, and 500 µm) and stored in glass bottles until further analysis. The MOSP were also characterized by Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope (SEM) as described in section B.

D. Acid treatment of MOSP

15 g of powdered MOSP was weighed and put in a conical flask, 200 mL of 0.1M HNO₃ was added and the mixture was soaked for 24 hrs. The mixture was then filtered and the sorbent washed several times with deionized water until the pH of the sorbent was neutral (around pH 7). The sorbent was then dried in an oven at 50 °C overnight and then put in glass bottle until further use.

Using the optimized sorption parameters (section E), the ability to remove heavy metals from water samples by the acid treated was conducted.

E. Biosorption of heavy metal ions

Batch experiments were used for the biosorption of Cd, Cu, Fe, Zn, and Pb. Stock solutions at various concentrations were prepared from 1000 mgL⁻¹ of each metal standard. Solution of

known metal ion concentration was prepared and known amount of sorbent (MOSP) was added. The mixture were shaken with a controlled orbital shaker and the concentrations of the unadsorbed metal ions in solutions were determined after separation of the sorbent by filtration using whatman paper No.1 filter papers. The effects of contact time (0-240 min), initial metal concentration (1-20 mgL⁻¹), pH (2.0-10.0), sorbent dose (0.5-2.5 g, in 50 mL⁻¹), particle size (100-500 µm) and temperature (298-333 K) were studied. Analysis and instrumentation were done using FAAS with air/acetylene. The amount of the metal adsorbed (% removal) by the sorbent was calculated using equation 1 below

$$\% \text{ Removal} = (C_i - C_f) / C_i \times 100 \quad (1)$$

Where C_i is the initial concentration before adsorption and,

C_f is the concentration after adsorption of metal ions. All experiments were done in replicates and reported as the average of the experiments.

III. RESULTS AND DISCUSSION

A. Scanning Electron Microscopy

Scanning electron Microscope (SEM) is used to determine the morphology of a sample. It produces images of a sample by scanning it with focused beam of electrons and produces information about the sample surface topography and composition. Fig. 1 image reveals the surface texture and morphology of MOSP.

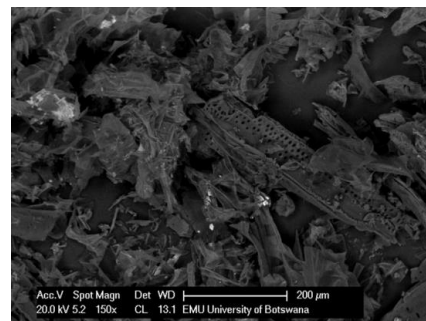


Fig. 1: SEM image of *Moringa Oleifera* seed pods (MOSP)

The results show that the materials have relatively porous surface. The micrographs of MOSP reveal cylindrical structures with different diameters. These surface (physical) characteristics would result in high metal removal due to available binding cavities for the metal ions. The efficiency of a sorbent depends on available number of pores, pore size and the surface area. The particles with higher surface area and have many pores is expected to be more efficient for metal removal.

B. Fourier Transform Infrared (FTIR) spectroscopy

The IR spectra of MOSP as shown on Fig. 2a show broad bands around 3333 cm^{-1} attributed to the surface hydroxyl group. The bands at 2917 and 2849 cm^{-1} are due to C-H group of the alkenes, at 1741 cm^{-1} are the C=O from esters, at 1593 cm^{-1} are the C=C aromatics and C-O from carboxylic acids at 1104 to 1027 cm^{-1} . Decrease in intensity and shift of the above mentioned peaks as shown in Fig. 2b could be due to interaction of the metal with the specific functional groups. The metal adsorption capacity is influenced strongly by the surface structures of carbon [13]. Studies done with other biomass sorbents have shown similar functional groups responsible for metal removal [14]–[17]. The functional groups responsible for metal removal in MOSP are therefore hydroxyl (OH), C-H of the alkenes, C=C alkenes and C-O from the carboxylic acids. The success of heavy metal uptake by agricultural products is believed to be dependent on a number of factors, one of which is chemical composition. One compositional characteristic of successful heavy-metal adsorption products is the presence of lignocellulosic biomass. Lignocellulosic biomass refers to plant biomass that contains cellulose, hemicellulose, and lignin [18], [19]. Another characteristic of successful agricultural products is the presence of acidic groups such as carboxylic and phenolic groups. Carboxylic acids are the most common type of organic acids and are characterized by the presence of at least one carboxyl group

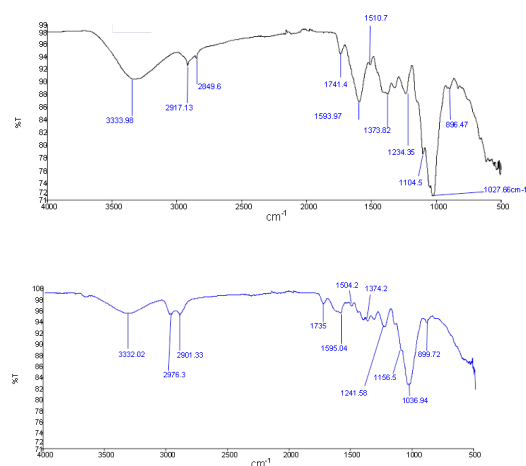


Fig. 2: Spectra of MOSP (a) before metal ion removal (b) after metal ion removal.

It can be speculated that combination of the following could be the principal mechanism for metal removal [44]. i) electrostatic interactions between the conjugate base of either carboxyl group or amine group (at pH 8) reacting with metal ions, (ii) Coordination or complex formation (using empty d-orbitals of metal ions) to interact with the electron pairs from the oxygen in the carboxyl, hydroxyl and nitrogen of the amine groups, (iii) Ion exchange processes in which the ionisable

hydrogen on the carboxyl and amine groups exchange with metal cations, (iv) Microprecipitation (especially at higher pH) where the OH⁻ ions forms insoluble hydroxides with the metal ions and the sorbent here then acts as a filter, (v) Acid-base interactions. Most of these metal ions are hard acids and the interact with atoms on the functional groups such as oxygen on the carboxyl and hydroxyl group and nitrogen on the amine groups (vi) Adsorption for example with the presence of alkenes, the concentration of electron density on them actually creates dipole moments with negative dipole moment concentrated on the center of the double bond and the positively charged metal ions will sit on these areas with high electron density [20].

C. Parameters

Effect of contact time

Contact time is an important parameter for determining the equilibrium time required for the sorption of metal ions on a sorbent as it is directly proportional to amount of metal ions removed from aqueous solution. It was observed that the percentage efficiency of the MOSP increased with time and subsequently reached a constant value at the optimal time where no more ions were adsorbed from the solution. At then constant value, the amount of ions being adsorbed by the MOSP was concluded to be in a state of dynamic equilibrium. The time required to attain this state of equilibrium is referred to as the equilibrium (optimal) time [21]. The amount of ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under optimal conditions. The result showed that the adsorption of ion increases with time up to the optimal time of 60 minutes as reflected on Fig. 3.

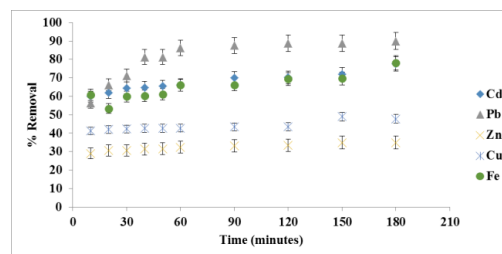


Fig. 3: Effect of contact time on metal removal using MOSP (all other variables kept constant)

Effect of biomass dosage

It is expected that as the sorbent amount increases, the number of sorbent particles surrounding the metal ion or ratio of sorbent particle to metal ion increases. Increases the surface area on which the metal ions binds to the surface of the sorbents and hence increasing the removal efficiency. The adsorption of ions increased with the MOSP dosage as shown in Fig. 4. At MOSP dosage above the optimal dosage, adsorption equilibrium was reached. The percentage of ions removal increased with the increasing amount of MOSP upto 1g of the sorbent. This may be attributed to the availability of

more binding sites for complexation of ions [22]. Further increment in MOSP dose did not cause significant improvement in adsorption for Cd, Pb and Fe. This seems to be due to the binding of almost all ions to the MOSP leading to equilibrium between the ions bound to the adsorbent and those remaining unadsorbed in the solution. However, removal of Zn and Cu decreased when more than 1g of the sorbent was used. This is attributed to possibility of metal bleeding from the material and also the fact that there is possibility of the particle overlapping and overcrowding resulting in a reduction of the total adsorbent surface area and hence decreases the percentage removal [20]. ANOVA showed no significant difference when 1g was used as the optimal dosage for all the selected metal ions.

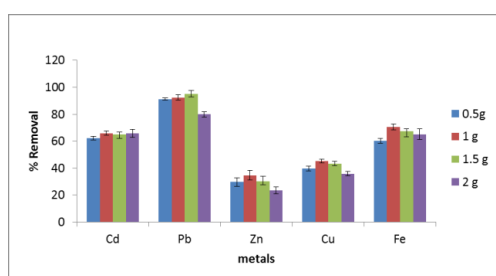


Fig. 4: Effect of biomass dosage on metal removal using MOSP (all other variables kept constant)

Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [21]. An increase in pH of solution while keeping all other factors (time, temperature, metal concentration, sorbent dose and particle size) constant increased the percentage removal (rise of curves) of the selected metal ions using the MOSP as shown in Fig. 5. This could be due to the surface charge on the sorbent. The functional group such as amines, carboxylic and hydroxyl, form anionic sites as pH is raised from acidic to basic conditions. The anionic sites could be responsible for binding with the metal cations. At low pH, the cations compete with the hydrogen ion in the solution for the active sites and therefore lower adsorption. But at higher pH, the surface of the adsorbent has a higher negative charge which attracts more cations. At pH>8, precipitation occurred. Therefore pH 8 was taken as the optimum pH.

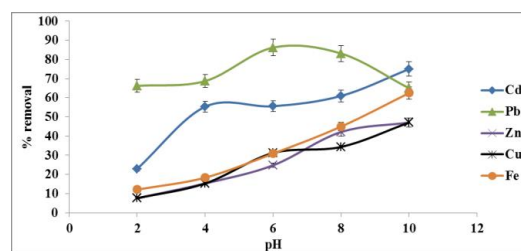


Fig. 5: Effect of pH on metal removal using MOSP (all other variables kept constant)

Effect of Metal Ion concentration

The rate of adsorption is a function of initial concentration of ions. The initial concentration provides essential driving force to overcome all mass transfer resistance of metal ions between the aqueous and the solid sorbent [23]. It was observed that at higher adsorption was found to take place at lower concentrations as shown in Fig. 6. This is due to the interaction of all the ions present in the solution with binding sites on the MOSP surface. At higher concentrations, more ions are left unadsorbed in the solution due to saturation of adsorption sites. The number of ions adsorbed from a solution of higher concentrations is more than that removed from less concentrated solutions. At lower ions concentration, the percentage removal was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of ions increases, the percentage removal decreased due to decrease in available sites for adsorption which is as the result of saturation of adsorption sites. At a higher concentration of ions, the ratio of initial number of moles of ions to the adsorption sites available was higher, resulting in lower adsorption percentage [24]–[26].

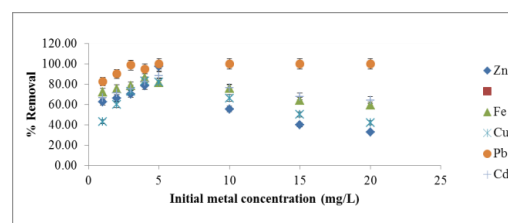


Fig. 6: Effect of metal ion concentration on metal removal using MOSP (all other variables kept constant)

Effect of particle size

The particle size varies with surface area, and with the number of micropores. Since sorption is particle diffusion controlled, the increase in micropore increases the number of accessible sites, hence increases the amount adsorbed. Smaller particle sizes gave higher adsorption capacities [18], [27]. This

may be attributed to the higher external surface available with smaller particles at a constant total mass. This was observed when the particle size were varied from 100 to 500 μm . Higher efficiencies were recorded with 100 μm particles as shown in Fig. 7. Besides adsorption at the outer surface of the adsorbent, there is also the possibility of intraparticle diffusion from the outer surface into mass transfer, which is greater for large particles [28], [29]. As a result of various factors, such as diffusion part length or mass transfer resistance, contact time and blocked sections of the particle may not be utilized for adsorption, therefore, the adsorption capacity of large particles may be low [11]. Therefore 100 μm was taken as optimal particle size.

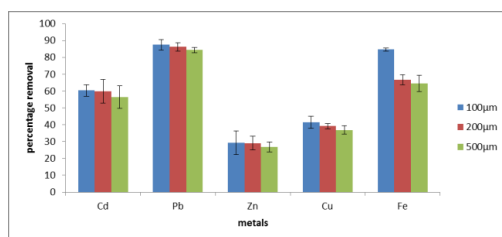


Fig. 7: Effect of particle size on metal removal using MOSP (all other variables kept constant)

Effect of Temperature

Increase of removal efficiency with increase in temperature has been attributed to two factors. An increasing number of molecules could also acquire sufficient energy to undergo an interaction with active sites at the surface and increasing temperature may produce a swelling effect within the internal structure of sorbent enabling large metal ions to penetrate further [30]. Temperature effect on metal removal by the sorbents was investigated using batch experiments conducted in water bath with temperature range from 25°C to 60°C. There was no significant change in percentage removal for other metals except for lead where there was increase as shown in Fig. 8. . It was also observed that there was no significant change when higher temperatures up to 60°C were used; hence 35°C was used as optimum temperature. Similar results have been reported [31], [32].

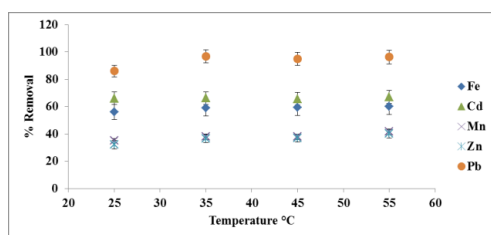


Fig. 8: Effect of temperature on metal removal using MOSP (all other variables kept constant)

D. Removal of metal ions from aqueous solution using optimized conditions

After determining the optimum parameters as shown in Table 1, the parameters were applied in a 50 mL aqueous solution in similar procedure as section II (E). The percentage removal of metal ions was as shown in the Fig. 9

Table 1: Optimized extraction parameters using 20 ppm standard mixture solution.

Material	Contact time (min)	pH	Temp (°C)	Biomass dose (g)	Particle size (μm)
MOSP	60	8	35	1.0	100

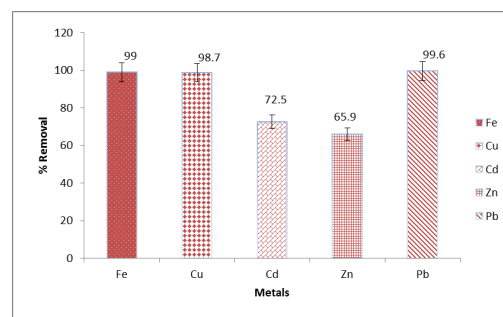


Fig. 9: Percentage removal of the selected ions from aqueous water using the optimized conditions

The removal efficiency trend was $\text{Pb} > \text{Fe} > \text{Cu} > \text{Cd} > \text{Zn}$. Higher percentage removal using MOSP could be attributed to a number of factors like (i) possibility of more binding sites on the surface of MOSP ; (ii) there was interaction of the metal to the functional groups in represented in FTIR spectra. The ionic sizes trend of the metals is $\text{Pb} > \text{Cd} > \text{Zn} > \text{Cu} > \text{Fe}$ for divalent cations. The larger ions are expected to be removed first and the order of removal should decrease from Pb to Cu, but in some cases it will be different depending on the environment of the interacting sites. This trend was not observed completely and this could be attributed to the fact that the metals were interacting differently MOSP adsorbing sites.

E. Conclusion

In this study, an attempt to add value to waste material by developing an ecofriendly method for removing Pb, Cu, Cd, Zn, and Fe ions from aqueous water was conducted. These studies demonstrated that pH, particle size, sorbent dose, contact time, temperature and concentration are significant factors in adsorption. The percentage removal efficiency of Fe, Cu, Cd, Zn and Pb ions using treated MOSP was found to be 99.0 ± 4.27 , 98.7 ± 3.89 , 72.5 ± 2.14 , 65.9 ± 1.64 and 99.6 ± 6.69 respectively. The developed method was found to be a cheap

and effective method therefore can be implemented on decontaminating polluted water samples.

F. REFERENCES

- [1] M. Tüzen, "Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry," *Food Chem.*, vol. 80, no. 1, pp. 119–123, Jan. 2003.
- [2] A. M. Mathew, "Phytoremediation of heavy metal contaminated soils," vol. VI, pp. 95–97, 2005.
- [3] G. Abbasse, B. Ouddane, and J. C. Fischer, "Determination of total and labile fraction of metals in seawater using solid phase extraction and inductively coupled plasma atomic emission spectrometry (ICP-AES)," *J. Anal. At. Spectrom.*, vol. 17, no. 10, pp. 1354–1358, Sep. 2002.
- [4] M. V Balarama Krishna, K. Chandrasekaran, S. V Rao, D. Karunasagar, and J. Arunachalam, "Speciation of Cr(III) and Cr(VI) in waters using immobilized moss and determination by ICP-MS and FAAS," *Talanta*, vol. 65, no. 1, pp. 135–43, Jan. 2005.
- [5] R. J. . Fourest E Serre, "Contribution of carboxy group to heavy metal binding sites in fungal wall," *Toxicol. Environ. Chem.*, vol. 54, pp. 1–10, 1992.
- [6] P. Sharma, P. Kumari, M. M. Srivastava, and S. Srivastava, "Ternary biosorption studies of Cd(II), Cr(III) and Ni(II) on shelled Moringa oleifera seeds," *Bioresour. Technol.*, vol. 98, pp. 474–477, 2007.
- [7] S. Barua, I. M. M. Rahman, M. Nazimuddin, and H. Hasegawa, "Evaluation of Moringa oleifera Carbon for the As (III) Removal from Contaminated Groundwater," vol. 8, no. 3, pp. 1390–1399, 2014.
- [8] Jimoh, T. O., "Utilization of Blighia sapida (Akee apple) pod in the removal of lead, cadmium and cobalt ions from aqueous solution," *J. Environ. Chem. Ecotoxicol.*, vol. 4, no. July, pp. 178–187, 2012.
- [9] M. Nasiruddin Khan and M. Farooq Wahab, "Characterization of chemically modified corncobs and its application in the removal of metal ions from aqueous solution," *J. Hazard. Mater.*, vol. 141, no. 1, pp. 237–244, 2007.
- [10] N. Foidl, H. P. S. Makkar, K. Becker, N. Foidl, and S. Km, "the Potential of Moringa Oleifera for Agricultural and Industrial Uses," *What Dev. potential Moringa Prod.*, pp. 1–20, 2001.
- [11] A. Shukla, Y. H. Zhang, P. Dubey, J. L. Margrave, and S. S. Shukla, "The role of sawdust in the removal of unwanted materials from water," *J. Hazard. Mater.*, vol. 95, no. 1–2, pp. 137–152, 2002.
- [12] G. Annadural, R. S. Juang, and D. J. Lee, "Adsorption of heavy metals from water using banana and orange peels," *Water Sci. Technol.*, vol. 47, no. 1, pp. 185–190, 2003.
- [13] M. Taha, M. Hassan, S. Essa, and Y. Tartor, "Use of Fourier transform infrared spectroscopy (FTIR) spectroscopy for rapid and accurate identification of yeasts isolated from human and animals," *Int. J. Vet. Sci. Med.*, vol. 1, no. 1, pp. 15–20, 2013.
- [14] P. Sikiti, T. A. Msagati, B. B. Mamba, and A. K. Mishra, "Synthesis and characterization of molecularly imprinted polymers for the remediation of PCBs and dioxins in aqueous environments," *J. Environ. Heal. Sci. Eng.*, vol. 12, no. 1, p. 82, 2014.
- [15] M. A. Abdullah, A. U. Rahmah, and Z. Man, "Physicochemical and sorption characteristics of Malaysian Ceiba pentandra (L.) Gaertn. as a natural oil sorbent," *J. Hazard. Mater.*, vol. 177, no. 1–3, pp. 683–91, May 2010.
- [16] M. Rajiv Gandhi, G. N. Kousalya, N. Viswanathan, and S. Meenakshi, "Sorption behaviour of copper on chemically modified chitosan beads from aqueous solution," *Carbohydr. Polym.*, vol. 83, no. 3, pp. 1082–1087, 2011.
- [17] S. Hashemian and J. Shayegan, "A comparative study of cellulose agricultural wastes (almond shell, pistachio shell, walnut shell, tea waste and orange peel) for adsorption of violet B dye from aqueous solutions," *Orient. J. Chem.*, vol. 30, no. 4, pp. 2091–2098, 2014.
- [18] M. Helen Kalavathy and L. R. Miranda, "Moringa oleifera-A solid phase extractant for the removal of copper, nickel and zinc from aqueous solutions," *Chem. Eng. J.*, vol. 158, no. 2, pp. 188–199, 2010.
- [19] E. Pehlivan, T. Altun, S. Cetin, and M. Iqbal Bhangar, "Lead sorption by waste biomass of hazelnut and almond shell," *J. Hazard. Mater.*, vol. 167, no. 1–3, pp. 1203–1208, Aug. 2009.
- [20] I. W. Maina, V. Obuseng, and F. Nareetsile, "Use of Moringa oleifera (moringa) seed pods and Sclerocarya birrea (morula) nut shells for removal of heavy metals from wastewater and borehole water," pp. 1–33, 2016.
- [21] W. S. Wan Ngah and M. a K. M. Hanafiah, "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review," *Bioresour. Technol.*, vol. 99, no. 10, pp. 3935–3948, 2008.
- [22] B. H. Hameed, "Grass waste: a novel sorbent for the removal of basic dye from aqueous solution," *J. Hazard. Mater.*, vol. 166, no. 1, pp. 233–8, Jul. 2009.
- [23] S. V. Dimitrova, "Metal sorption on blast-furnace slag," *Water Res.*, vol. 30, no. 1, pp. 228–232, 1996.
- [24] L. V. A. Gurgel and L. F. Gil, "Adsorption of Cu(II), Cd(II) and Pb(II) from aqueous single metal solutions by succinylated twice-mercerized sugarcane bagasse functionalized with triethylenetetramine," *Water Res.*, vol. 43, pp. 4479–4488, 2009.
- [25] O. S. Amuda, a. a. Giwa, and I. a. Bello, "Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon," *Biochem. Eng. J.*, vol. 36, pp. 174–181, 2007.
- [26] N. Unlü and M. Ersoz, "Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions," *J. Hazard. Mater.*, vol. 136, no. 2, pp. 272–80, Aug. 2006.
- [27] E. Demirbas, M. Kobya, E. Senturk, and T. Ozkan, "Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes," *Water SA*, vol. 30, no. 4, pp. 533–539, 2004.
- [28] S. Communication, "Sorption kinetics and intraparticle diffusivities of Cd , Pb and Zn ions on maize cob," vol. 4, no. June, pp. 509–512, 2005.
- [29] D. H. K. Reddy, K. Seshaiah, a. V. R. Reddy, M. M. Rao, and M. C. Wang, "Biosorption of Pb2+ from aqueous solutions by Moringa oleifera bark: Equilibrium and kinetic studies," *J. Hazard. Mater.*, vol. 174, pp. 831–838, 2010.
- [30] E. I. El-Shafey, "Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk," *J. Hazard. Mater.*, vol. 175, no. 1–3, pp. 319–327, Mar. 2010.
- [31] S. Qaiser, A. R. Salcemi, and M. Umar, "Biosorption of lead(II) and chromium(VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study," *Electron. J. Biotechnol.*, vol. 12, no. 4, 2009.
- [32] C. M. Zvinowanda, J. O. Okonkwo, M. M. Sekhula, N. M. Agyei, and R. Sadiku, "Application of maize tassel for the removal of Pb, Se, Sr, U and V from borehole water contaminated with mine wastewater in the presence of alkaline metals," *J. Hazard. Mater.*, vol. 164, pp. 884–891, 2009.