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Biosorption Activity of *Moringa oleifera* Seeds Powder

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Abstract:

Conventional methods of heavy metal removal from water such as chemical precipitation and filtration, oxidation and reduction, electrochemical treatment, reverse osmosis, ion exchange or distillation are economically non-viable, because they involve the use of sophisticated equipment and high cost of plant maintenance. This necessitated the search for cheap and promising methods of water treatment. *Moringa oleifera* seeds have been reported to have biosorption properties, however, the efficiency and mechanism of biosorption has not been fully established. In this study, Fourier transform infrared (FT-IR) spectroscopy, batch adsorption and batch kinetics studies were conducted, to determine the functional groups, biosorption performance and probable biosorption mechanism of *M. oleifera* seeds powder. FT-IR analysis revealed the complex nature of the seed with carbonyl group (C=O), amine group (C-NH), hydroxyl group (OH) and stretching of C-H bond of CH₂ groups present. Regression analysis revealed that Pb(II) and Cd(II) adsorption fits better to Freundlich isotherm model than Langmuir model. The theoretical maximum adsorption capacity (q_{max}) and adsorption intensity (b) were higher for Cd(II) when compared to Pb(II). The adsorption of Cd(II) fits the intraparticle diffusion model. The constant depicting boundary layer effect (C), indicated that Cd(II) and Pb(II) adsorption occur via a multilayer adsorption mechanism and mass transfer was not the only rate limiting step in the biosorption process. This finding suggest that *M. oleifera* seeds has higher biosorption activity for Cd(II) than Pb(II), and that the adsorption occurs via physical process rather than chemical process.

1. Introduction

Surface water from sources such as rivers, streams and ponds, although common, may be exposed heavy metals and pollution. In Nigeria, indiscriminate disposal of sewage, industrial and agricultural wastes, coupled with mobilization of unearthed metals from mining sites by runoff, have been the major sources of toxic metals pollution of surface water (Galadima *et al.*, 2011). Also, poverty, ignorance and poor implementation of government policies and regulations, including illegal mining have compounded the problems of metals pollution (Galadima *et al.*, 2011).

Removal of heavy metals from water and wastewater may involve chemical precipitation and filtration, oxidation and reduction, electrochemical treatment, reverse osmosis, ion exchange and/ or distillation. Such methods are economically non-viable especially in developing countries, because they involve the use of sophisticated equipment and require expertise (Basu *et al.*, 2003; Volesky, 2003). High cost of importing chemicals, health safety of such chemicals and cost of plant maintenance are additional challenges in using these conventional methods of water treatment (Glenda and Gregory, 1996). In an effort to develop an alternative, low cost, effective and safe method of improving water quality and heavy metal removal from water and wastewater, researchers have focused on using renewable plants and microbial biomass. *Moringa oleifera* is one of such plant biomass currently receiving enormous attention.

The use of *M. oleifera* for water purification is part of African indigenous knowledge (Sajidu *et al.*, 2006). *Moringa* was first studied and confirmed for its coagulant property by Jahn (1981), after observing women in Sudan use the seeds to clarify the turbid Nile water. The seeds act as a flocculent that attract and aggregate suspended particles in water, these particles then precipitate out of the water as flakes, leaving clearer water. Other works reported the used of the seeds in absorbing and removing a wide range of Gram-

positive and Gram-negative bacteria, algae, organic pollutants and pesticides from water (Suarez *et al.*, 2003; Suarez *et al.*, 2005; Akhtar *et al.*, 2007a, Akhtar *et al.*, 2007b).

The purification and clarification potentials of *M. oleifera* seed is not limited to removal of suspended organic and biological agents only, the seed powder have been reported to have adsorption properties for heavy metals. A study by Veronica *et al.* (2012) reveals that *M. oleifera* seed biomass performed well in biosorption of lead (Pb), copper (Cu), cadmium (Cd), nickel (Ni), manganese (Mn) and zinc (Zn). The study also reveals that the biosorption capacity was neither affected by pH in a range of 3.5-8.0 nor the presence of other metal ions in a multi-metal solution. Mataka *et al.* (2006) reported that *M. oleifera* seed powder at a level of 2.5 g/100 ml reduces lead level in water by over 96%. A laboratory scale experiment reported by Sharma *et al.* (2006) indicated that adsorption data of cadmium uptake by *M. oleifera* seed fits to Freundlich isotherm model with an optimal cadmium uptake of 85.1% at 4.0 g biomass dosage, 25 mg metal concentration, pH of 6.5, contact time of 40 minutes and 200 ml volume of test solution. Earlier report by Sajidu *et al.* (2005) shows that *M. oleifera* seed kernel and press cake has the ability to remove metal ions at a range of 70-89% for lead, 66-92% for iron and 44-47% for cadmium. Though the seeds of *M. oleifera* have been reported to have biosorption potentials, the biosorption process parameters and probable biosorption mechanism has not been fully established.

In this study, Fourier transform infrared (FT-IR) spectroscopy, batch adsorption and batch kinetics studies were carried out, to determine the functional groups, biosorption performance and probable biosorption mechanism of locally available seeds of *M. oleifera*.

2. Materials and Experimental Design/ Methods

2.1. Collection and Preparation of *M. oleifera* Seeds

Dried seeds of *M. oleifera* were collected within Sokoto metropolis; the seeds were stored at room temperature and were shelled manually. The kernels were crushed using pestle and mortar, and then sieved using 200-250 µm apertures Laboratory Test Sieve (Kardam *et al.*, 2010).

2.2. FT-IR Analysis of *M. oleifera* Seeds powder

In order to have an idea of available functional groups in *M. oleifera* seed, FT-IR analysis was conducted. *M. oleifera* seed powder was mixed with a dried spectra grade potassium bromide (KBr), the mixture was then milled with a small agate mortar until the seed powder was completely mixed with the KBr powder. After milling, the mixture was immediately compressed for about 5 minutes, and the thickness of the KBr-sample pellet was controlled to 1 mm (Silverstein *et al.*, 1981). The KBr-sample pellet formed was analysed using MB3000 FT-IR spectrometer (ABB Analytical Measurements, Canada).

2.3. Batch Adsorption and Batch Kinetics Experiment

Batch adsorption experiments were carried out in 250 ml Erlenmeyer flask containing 100 ml of metal solution and 0.4 g of *M. oleifera* seed powder. The pH was adjusted to 6.5 and the mixture was shaken at 120 rpm for 30 minutes. The solution was allowed to equilibrate for 1 hour, filtered using Whatman filter paper (No. 42). The filtrate was analysed for equilibrium metal concentration using AA240FS Atomic Absorption Spectrophotometer (Varian Medical Systems Inc., USA) (Volesky, 2003; Sahabi *et al.*, 2010).

Metal uptake was calculated using equation 2.1.

$$\text{Metal uptake 'q' (mg/g)} = \frac{V(C_i - C_e)}{S} \dots\dots\dots (2.1)$$

Where: C_i and C_e = Initial and Equilibrium Metal Concentration (mg/L); V= Volume of Solution (L); S= Weight of Biosorbent (g).

Adsorption isotherm was obtained from a plot of metal uptake against equilibrium metal concentration.

For batch kinetics studies, duplicate flasks were removed at time intervals of 10, 20, 30, 60, 90 and 120 minutes respectively.

Adsorption kinetics was obtained from a plot of metal uptake against contact time (Volesky, 2003; Sahabi *et al.*, 2010).

2.4. Data Analysis

DATAFIT Software, Version 9.0 (Oakdale, United States) was employed for curves fitting of batch adsorption and batch kinetics data. The evaluation of fitting parameters was done using nonlinear regression analysis.

3. Result and Discussion

3.1. FT-IR Analysis of *M. oleifera* Seeds Powder

The result of FT-IR analysis for *M. oleifera* seed powder is given in Figure 1.

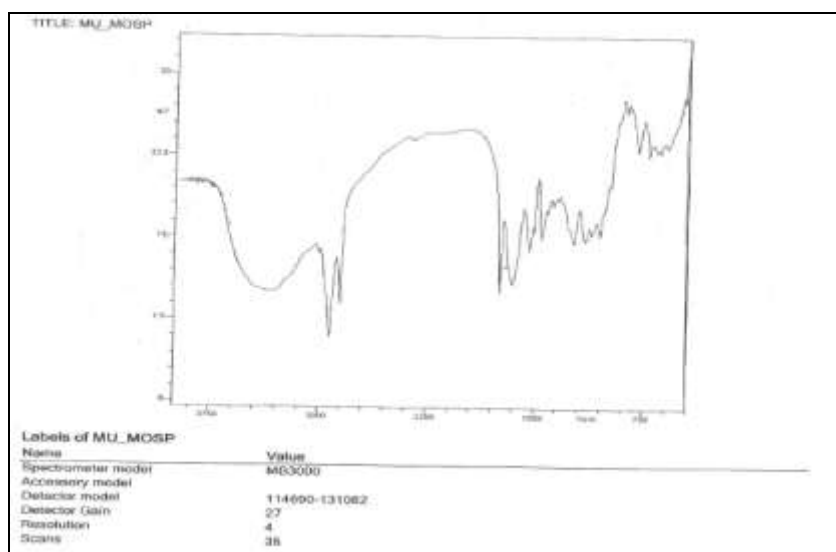


Figure 1: FT-IR Spectrum of *M. oleifera* seeds powder

FT-IR spectra of *M. oleifera* seeds powder revealed a bandwidth around 3400cm^{-1} that is attributed to the stretching of hydroxyl (-OH) functional group present in proteins, fatty acids, carbohydrate molecules and lignin units (Reddy *et al.*, 2012). The peaks at 2850cm^{-1} and 2890cm^{-1} corresponds to asymmetric and symmetric stretching of C-H bond of CH_2 groups, the high intensity of these bands may be as a result of the high lipid content of the seeds. The bands at 1725cm^{-1} and 1650cm^{-1} are as a result of carbonyl (C=O) stretching. The carbonyl functional group may be due to the presence of proteins in the seeds powder. Also, the carbonyl group may be as a result of lipids present in the seed. The stretching at 1575cm^{-1} may be as a result of C-NH group of peptides and amino acid in the seeds (Reddy *et al.*, 2010b).

Hydroxyl, carbonyl and amine functional groups have been proposed to be responsible for metal binding and uptake by plant biomass via adsorption, coordination, chelation, complexation and/ or ion exchange (Volesky, 2003). Thus, these functional groups may be responsible for the biosorption properties of *M. oleifera* seeds powder.

3.2. Equilibrium Isotherms Studies

Figure 2 and Figure 3 shows the curve fittings of Cd (II) and Pb (II) equilibrium adsorption data to Langmuir and Freundlich isotherm models. Table 1 shows the isotherm fitting parameters and corresponding error functions of Pb(II) and Cd(II) to Langmuir and Freundlich isotherm model as obtained by non linear regression analysis using DATAFIT Software (Oakdale, United States).

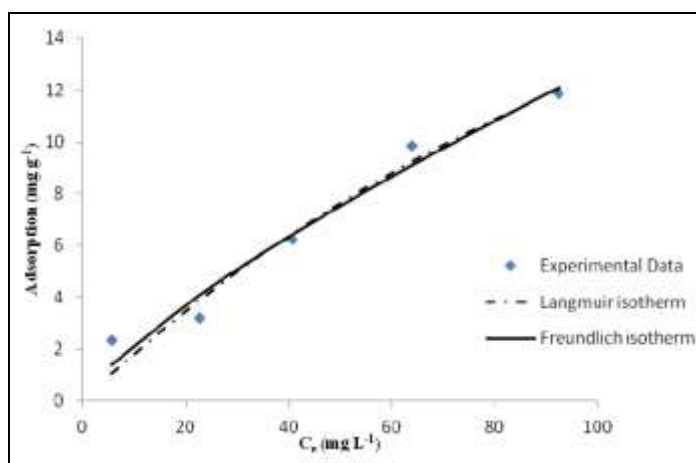


Figure 2: Curve fitting of equilibrium adsorption data with Langmuir and Freundlich isotherm models for Cd (II).

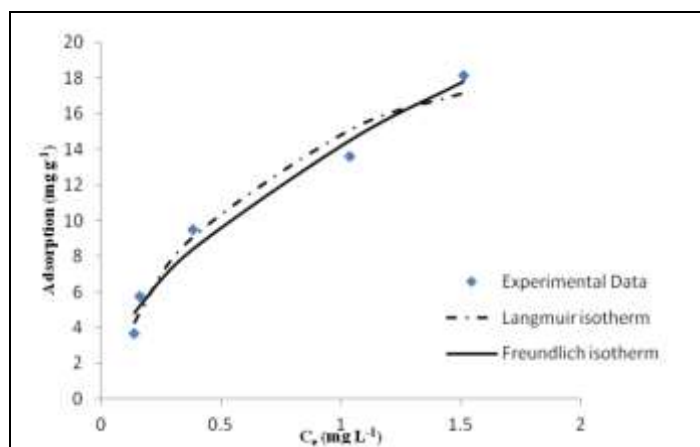


Figure 3: Curve fitting of equilibrium adsorption data with Langmuir and Freundlich isotherm models for Pb(II).

Langmuir isotherm		
Parameters	Pb(II)	Cd(II)
q_{\max} (mg g ⁻¹)	24.504	38.633
b	1.548	4.927
RSS	4.578	2.641
SE	1.235	0.938
R ²	0.967	0.961
Freundlich isotherm		
k_F (L g ⁻¹)	14.219	0.363
n_F	1.838	1.333
RSS	3.654	2.382
SE	1.104	0.891
R ²	0.974	0.965

Table 1: Isotherm Parameters for Adsorption of Pb (II) and Cd (II) onto *M. oleifera* Seeds Powder

Key: q_{\max} = Theoretical maximum adsorption capacity
 b = Langmuir constant related to adsorption-desorption energy
 k_F = Freundlich constant indicating adsorption capacity
 n_F = Freundlich constant adsorption intensity
 RSS = Residual sum of squares
 SE = Standard error
 R² = Coefficient of regression

Based on regression coefficient (R²) values, the experimental data for adsorption of Cd(II) and Pb(II) onto *M. oleifera* seeds powder fit better to Freundlich isotherm model than the Langmuir isotherm model.

The Langmuir isotherm model assumes a monolayer adsorption onto an adsorbent surface containing finite number of identical sites and without interaction between the adsorbed molecules. Theoretical maximum adsorption (q_{\max}) is useful in comparing the adsorption capacity of biosorbent for different toxic metal under experimental conditions (Volesky, 2003). At starting pH 6.5 and biomass dose of 4.0g/L, *M. oleifera* seeds powder gave a higher theoretical maximum adsorption of 38.633 mg g⁻¹ and 24.504 mg g⁻¹ for Cd(II) and Pb(II) respectively. Also, the index of affinity of *M. oleifera* seeds powder for metal ions onto a finite monolayer adsorbent surface, b , revealed a higher value for Cd(II) (4.927) than for Pb(II) (1.548).

Freundlich adsorption isotherm describes absorption as a sorption process that occurs on an energetically heterogeneous surface, which is not limited by monolayer capacity. In other words, it is an indicator of heterogeneity (Volesky, 2003; Sahabi *et al.*, 2010).

Both the multilayer adsorption capacity (n_F) and adsorption intensity (k_F) values of Pb(II) obtained by non linear regression analysis from experimental data were higher than that of Cd(II). This is an indication that Pb(II) adsorption is favoured more by energetically heterogeneous multilayer formation process, while Cd(II) adsorption is less favored by this process. This finding further confirm that the adsorption of Cd(II) may be more of a finite monolayer process while that of Pb(II) is more of heterogeneous multilayer process. The fitting of equilibrium data of Cd(II) to Freundlich isotherm model is in agreement with report of Sharma *et al.* (2006) which earlier revealed that cadmium adsorption onto *M. oleifera* seeds powder fit Freundlich isotherm model. In contrast, the fitting of equilibrium data of Pb(II) to Freundlich and Langmuir isotherm model was not in agreement with the findings of Adelaja *et al.* (2011), that the adsorption of Pb(II) onto *M. oleifera* seeds powder does not conform to Freundlich and Langmuir isotherm model.

3.3. Kinetics Studies

Figure 4 and Figure 5 shows the curve fittings of Cd(II) and Pb(II) kinetics adsorption data to Intraparticle Diffusion model and Elovich model. Table 2 shows the fitting parameters and corresponding error functions for adsorption of Cd(II) and Pb(II) onto *M. oleifera* seeds powder as obtained by non linear regression analysis using DATAFIT Software (Oakdale, United States).

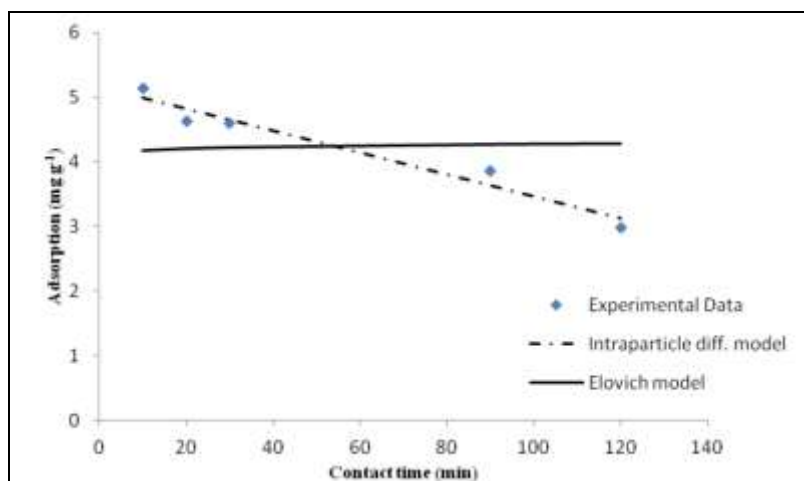


Figure 4: Curve fitting of kinetics data with intraparticle diffusion model and Elovich model for Cd (II)

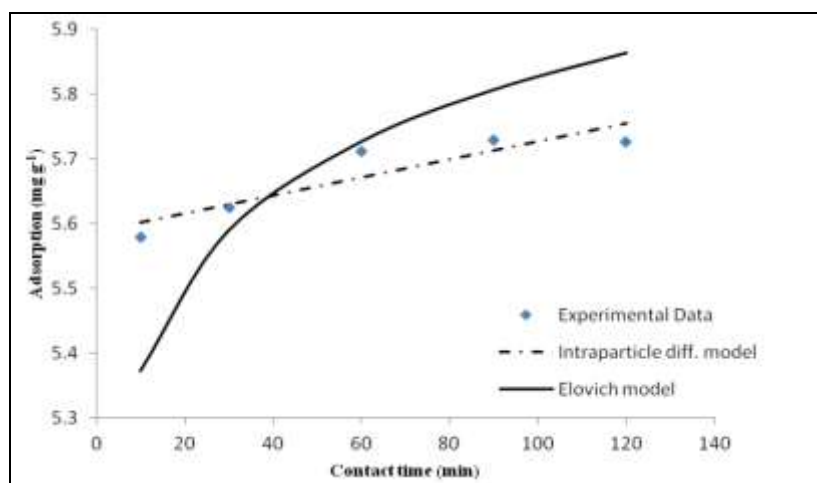


Figure 5: Curve fitting of kinetics data with Intraparticle diffusion model and Elovich model for Pb(II)

Intraparticle diffusion model		
Parameters	Pb(II)	Cd(II)
k_{id} ($\text{mg}^{-1} \text{g}^{-1} \text{min}^{-0.5}$)	2.779	-3.393
C	5.588	5.161
RSS	3.186	0.127
SE	3.259	0.206
R ²	0.827	0.955
Elovich model		
α ($\text{mg}^{-1} \text{g}^{-1} \text{min}^{-1}$)	13011948224.265	1.490
β (g mg^{-1})	5.066	24.026
RSS	6.915	3.094
SE	0.152	1.016
R ²	0.000	0.000

Table 2: Kinetics Parameters for Adsorption of Pb(II) and Cd(II) onto *M. oleifera* Seeds Powder.

Key:

k_{id}	= Intraparticle diffusion rate constant
C	= Constant depicting the boundary layer effect
α	= Constant related to the rate of chemisorption
β	= Constant related to surface coverage involved in chemisorption
RSS	= Residual sum of squares
SE	= Standard error
R ²	= Coefficient of regression

The regression coefficient (R²) obtained indicates that, the adsorption of Cd(II) and Pb(II) onto *M. oleifera* seeds fits Intraparticle diffusion model. However, both Pb(II) and Cd(II) adsorption data did not fit to Elovich model. This suggest that mass transfer may be the rate limiting process in the biosorption of Pb(II) and Cd(II) onto *M. oleifera* seeds powder, while chemisorption process may not play significant role in the biosorption process.

The negative Intraparticle diffusion rate constant (k_{id}) of Cd(II) binding onto *M. oleifera* seeds powder is an indication that equilibrium/ adsorption saturation is attained at low contact time (of 10 minutes), and Cd(II) uptake was reduced as the contact time was increased beyond 10 minutes. Also, because the fitting of Cd(II) and Pb(II) adsorption' to intraparticle diffusion model was not 100% due to the difference in mass transfer rate during the initial and final stages of adsorption, the constant depicting boundary effect (C), show deviation (was above zero). This is an indication that there is some degree of boundary layer control and that intraparticle diffusion is not the only rate limiting step. Thus, several other processes operating simultaneously may be controlling the system (Reddy *et al.*, 2010a). These findings concord with the reports by Santos *et al.* (2012) and Sharma *et al.* (2006), that metal adsorption onto *M. oleifera* seeds powder is a complex process that may involve chemical processes, physical and ionic interaction, as well as sequestration of metal ions by low molecular protein of the seeds.

4. Conclusion

M. oleifera seeds show reasonable biosorption performance for Cd(II) and Pb(II) and the equilibrium adsorption data conform more to Freundlich isotherm than Langmuir isotherm model. Kinetic data suggest that mass transfer may be the rate limiting process for the adsorption of Cd(II) and Pb(II) onto *M. oleifera* seeds powder. Based on these findings, it is logical to say that *M. oleifera* seeds have biosorption activity and can go a long way in the improvement of water quality, as well as reducing the level of Cd(II) and Pb(II) in raw water and wastewater, if properly exploited by communities facing water contamination by these metals.

5. References

1. Adelaja, O.A., Amoo, I.A., Aderibigbe, A.D., 2011. Biosorption of Lead (II) ions from aqueous solution using Moringa oleifera pods. Archives of Applied Science Research 3(6), 50-60.
2. Akhtar, M., Hasany S.M., Bhanger, M.I., Iqbal, S., 2007a. Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions. Chemosphere 66, 1829-1838.
3. Akhtar, M., Hasany S.M., Bhanger, M.I., Iqbal, S., 2007b. Sorption potential of Moringa oleifera pods for the removal of organic pollutants from aqueous solutions. Journal of Hazardous Material 141, 546-556.

4. Basu, A., Kumar, S. Mukherjee, S., 2003. Arsenic Reduction from Environment by Water Lettuce (*Pistia stratiotes* L.). *Indian Journal of Environmental Health* 45(2), 143-150.
5. Galadima, A., Garba, Z.N., Leke, L., Almustapha, M.N., Adam, I.K., 2011. Domestic Water Pollution among Local Communities in Nigeria- Causes and Consequences. *European Journal of Scientific Research* 52(4), 592-603.
6. Glenda, M.H., Gregory, D.J., 1996. Home Drinking Water Treatment Systems. *Water Quality and Waste Management*. North Carolina Cooperative Extension Services. HE- 419.
7. Jahn, S.A., 1981. Tradition water purification in tropical and developing countries: Existing methods and potential application. Publication 117. Deutsche Gesellschaft fur Technische Zusammenarbeit (GTZ) GmbH, Eschborn., pp. 276.
8. Kardam, A., Raj, K.R., Arora, K.J., Srivastava, M.M., Srivastava, S., 2010. Artificial Neural Network Modeling for Sorption of Cadmium from Aqueous System by Shelled Moringa oleifera Seed Powder as an Agricultural Waste. *Journal of Water Resource and Protection* 2, 339-344.
9. Mataka, L.M., Henry, E.M.T., Masamba, W.R.L., Sajidu S.M., 2006. Lead Remediation of Contaminated Water using Moringa stenopetala and Moringa oleifera seed powder. *International Journal of Environmental Science and Technology* 3(2), 131-140.
10. Reddy D.H.K., Harinatha Y., Seshaiaha K., Reddy A.V.R., 2010a. Biosorption of Pb(II) from aqueous solutions using chemically modified Moringa oleifera tree leaves. *Chemical Engineering Journal* 162, 626-634.
11. Reddy D.H.K., Seshaiaha K., Reddyb A.V.R. Leec S.M., 2012. Optimization of Cd(II), Cu(II) and Ni(II) biosorption by chemically modified Moringa oleifera leaves powder. *Carbohydrate Polymers* 88, 1077-1086.
12. Reddy, D.H.K., Seshaiaha, K., Reddy, A.V.R., Rao, M M., Wang, M.C., 2010b. Biosorption of Pb²⁺ from aqueous solutions by Moringa oleifera bark: equilibrium and kinetic studies. *Journal of Hazardous Materials* 174, 831-838.
13. Sahabi, D.M., Minoro, T., Ichiro, S., Jun-ichi, K., 2010. Comparison of Arsenate, Lead, and Cadmium Adsorption onto Aged Biofilter Media. *Journal of Environmental Engineering* 136(5), 493-500.
14. Sajidu, S.M.I., Henry, E.M.T., Persson, I., Masamba, W.R.L., Kayambazinthu, D. (2006). pH dependence of sorption of Cd²⁺, Zn²⁺, Cu²⁺ and Cr³⁺ on crude water and sodium chloride extracts of Moringa stenopetala and Moringa oleifera. *African Journal of Biotechnology* 5(23), 2397-2401.
15. Sajidu, S.M., Henry, E.M.T., Kwamdera G., Mataka, L., 2005. Removal of lead, iron and cadmium ions by means of polyelectrolytes of Moringa oleifera whole seed kernel. *WIT Transactions on Ecology and the Environment* 80, 251-258.
16. Santos, A.F.S., Paiva, P.M.G., Teixeira, J A., Brito, A.G., Coelho, L.C.B.B., Nogueira, R.B. 2012. Coagulant properties of Moringa oleifera protein preparations: application to humic acids removal. *Environmental Technology* 33(1-3), 69-75.
17. Sharma, P., Kumari, P., Srivastava, M.M., Srivastava, S., 2006. Removal of cadmium from aqueous system by shelled Moringa oleifera Lam. seed powder. *Bioresource Technology*. 97(2), 299-305.
18. Silverstein, R.M., Bassler, G.C., Morrill T.C., 1981. *Spectrometric Identification of Organic Compounds* 4th Ed. Wiley, New York, pp. 1-166.
19. Suarez, M., Entenza, J.M., Doerries, C., Meyer, E., Bourquin, L., Sutherland, J., Marison, I., Moreillon, P., Mermod, N., 2003. Expression of a plant-derived peptide harboring water-cleaning and antimicrobial activities. *Biotechnology and Bioengineering* 81, 13-20.
20. Suarez, M., Haenni, M., Canarelli, S., Fisch, F., Chodanowski, P., Servis, C., Michielin, O., Moreillon, P., Mermod, N. 2005. Structure-function characterization and optimization of a plant-derived antibacterial peptide. *Antimicrobial Agents and Chemotherapy* 49, 3847-3857.
21. Veronica, O., Florence, N., Habauka, M.K., 2012. A study of the removal of heavy metals from aqueous solutions by Moringa oleifera seeds and amine-based ligand 1,4-bis[N,N-bis(2-picoyl)amino]butane. *Analytica Chimica Acta* 730, 87-92.
22. Volesky, B., 2003. Sorption and Biosorption. BV Sorbex Inc., Canada, pp. 1-387.