

Biosorption of Pb^{2+} and Cr^{2+} Using *Moringa Oleifera* and Their Adsorption Isotherms

Ongulu Roselyn Adhiambo^{1,2}, Kituyi John Lusweti², Getenga Zachary Morang'a³

¹Department of Pure and Applied Chemistry, Masinde Muliro University of Science and Technology, Kakamega, Kenya

²Department of Chemistry and Biochemistry, University of Eldoret, Eldoret, Kenya

³Department of Physical Sciences, Chuka University, Chuka, Kenya

Email address:

roongulu2012@gmail.com (A. R. Ongulu), rongulu@mmust.ac.ke (A. R. Ongulu), joluki@yahoo.com (K. J. Lusweti),

zgetenga@yahoo.com (G. Z. Morang'a)

To cite this article:

Ongulu Roselyn Adhiambo, Kituyi John Lusweti, Getenga Zachary Morang'a. Biosorption of Pb^{2+} and Cr^{2+} Using *Moringa Oleifera* and Their Adsorption Isotherms. *Science Journal of Analytical Chemistry*. Vol. 3, No. 6, 2015, pp. 100-108. doi: 10.11648/j.sjac.20150306.14

Abstract: In the last three decades attention has been paid on environmental management caused by toxic materials such as heavy metals whose levels have risen due to increased anthropogenic activities. Conventional methods for waste treatment are numerous, some of which are expensive and sometimes inefficient. A search for cheaper and environmentally friendly method of treatment using natural products has taken a central stage in the recent past. *Moringa oleifera* seed powder was investigated with a view of using it as a low cost biosorbent for the removal of toxic heavy metals from wastewater. Fourier transform Infrared (FT-IR) analysis was done for characterization of *Moringa oleifera* seeds powder. Batch biosorption experiments of Pb^{2+} and Cr^{2+} with respect to contact time, pH, particle size, adsorbent dosage, effect of pretreatment and adsorption isotherms were studied. FT-IR showed the presence of $-NH$, $-OH$, $-COOH$ functional groups in the biomass. The maximum biosorption capacity was observed at pH 5 for both metals, with the particle size of adsorbent of 0.250 mm and high adsorbent dosage of 0.6 g. The order of modification for Pb^{2+} was $CaCl_2 > NaOH > KMnO_4 > HCl$, while that of Cr^{2+} was $KMnO_4 > CaCl_2 > HCl > NaOH$. Although the data fitted into both the Langmuir and Freundlich adsorption isotherms high correlation coefficients of about 1.00, the Langmuir gave better results than the Freundlich. The results suggest that *Moringa oleifera* seeds have potential application in Pb^{2+} and Cr^{2+} decontamination from aqueous effluents and that pretreatment further enhances biosorption.

Keywords: Biosorption, Pollution, Langmuir, Freundlich, Moringa, Batch

1. Introduction

Human activities such as agricultural, industrial and domestic wastes discharge their wastewaters containing pollutants including toxic heavy metals into the environment. Heavy metals are a threat to human life and the environment because of their non-biodegradable nature and thus persistence; hence they are toxic and bioaccumulative. The removal of such metals from the environment is necessary. The commonly used procedures for removing metal ions from aqueous streams are expensive and have disadvantages like incomplete metal removal, high cost of treatment and energy requirements, and generation of toxic sludge or waste products that require careful disposal. Therefore, a cost effective treatment method that is capable of removing heavy metals from aqueous solutions (Congeevaram *et al.*, 2007) is needed. Biosorption is one such a technique and has provided

an alternative treatment of industrial effluents from convectional physico-chemical methods (Selatnia *et al.*, 2004). The biological materials that have been investigated for heavy metal uptake include bacteria, fungi, yeast and algae (Ozturk, 2007).

Moringa oleifera (drumstick), is a drought tolerant, cosmopolitan tropical, tree, available throughout the year, it has various pharmacological uses, viz. analgesic, antihypertensive and anti-inflammatory effects. The powdered seed of the plant *Moringa oleifera* has coagulating properties that have been used for various aspects of water treatment such as turbidity, alkalinity, total dissolved solids and hardness. However, its biosorption behaviour for the removal of toxic metals from water bodies has not been given adequate attention (Kumari *et al.*, 2005). The biosorption efficiency of *Moringa oleifera* seeds for Pb^{2+} and Cr^{2+} from wastewaters was investigated by measuring the efficiency of the metal removal from artificial wastewater by varying

contact time, pH, particle size, adsorbent dosage, effect of pretreatment in a batch-process series of experiments. The concentration of metal ions adsorbed in each case was determined by atomic absorption spectroscopy (AAS).

2. Materials and Methods

2.1. *Moringa Oleifera* Seed Biomass

Moringa Oleifera seeds were purchased from farms in Otonglo-Kisumu County. The seeds were deshelled by hand to remove the outer coat. The kernel was washed in de-ionised water to remove dust, and then soaked in 1 M HCl for 3 days, to remove the original content of heavy metals. The seeds were again washed in distilled water, dried in air then ground using a pestle and mortar. Deffating was done using ethanol/acetone mixture followed by shaking in a centrifuge severally until no more fat was left in the biomass. After centrifugation the wet *Moringa oleifera* seeds powder was then dried in an oven at 30°C for 24 hrs after which it was crushed again and sieved through 0.75 mm and 0.25 mm sieves.

2.2. Preparation of Pb^{2+} and Cr^{2+} Solution

Stock solutions of Pb^{2+} and Cr^{2+} were prepared by dissolving 1.599 g of $Pb(NO_3)_2$ and 7.695 g of $Cr(NO_3)_3 \cdot 9H_2O$, in 12% nitric acid and making the solution to one litre mark in a volumetric flask. The solutions contained 1.000 $\mu g/cm^3$ (1000 ppm) of Pb^{2+} and Cr^{2+} . A stock solution of 100 ppm was prepared by pipetting 10.0 cm^3 from the 1000 ppm stock solution into a volumetric flask and making it up to 100.0 cm^3 mark with de-ionized distilled water (DDW). Solutions of different concentrations were prepared by adequate dilution of the stock solution with DDW. Dilute solutions of 0.1 M NaOH and 0.1 M HCl were used to adjust pH to give the required whole number values between 3 and 8.

2.3. Biosorption Studies

A batch method was employed for studying the biosorption of Pb^{2+} and Cr^{2+} by *Moringa oleifera* seed biomass. A set of 250 mL Erlenmeyer flask containing 50 mL of metal solution (5 ppm) was used and 0.4 g of biosorbent (*Moringa oleifera* seeds powder) was added followed with shaking after which the contents of the flask were filtered and filtrates analyzed for residual metal concentration at intervals of 10 minutes. Three sets of experiments were carried out simultaneously; one set involved metal ions in water without biomass, another with biomass alone in water and the other had metal ions in water with biomass. The study of the effect of different experimental parameters such as pH (3-8), biosorbent dose (0.4 and 0.6 g), biosorbent size (0.75 mm and 0.250 mm) and contact time (0–70 minutes).

Further experiments were conducted using *Moringa oleifera* modified with $KMnO_4$, $CaCl_2$, NaOH and HCl at pH 5. About 100 mL of 0.5 M NaOH, HCl and $CaCl_2$ were used for pretreatment. In each pretreatment, the biomass was

slowly stirred in the chemical solution for 1 hr. After each pretreatment the biomass was washed in double distilled water till the pH of the washing solution reached a neutral range (6.8 - 7.2). Finally the pretreated biomass was dried in an oven at 60°C for 25 hours and homogenised in a blender to break the aggregates into small fragments. The biomass was then passed through 75 and 25 μm mesh sieves. $KMnO_4$ oxidized modification was done using a modified procedure of Jeon *et al.* (2002) in which powdered biomass (10 g) was oxidized in 300 mL of 10 mM $KMnO_4$ solution at 30°C for 30 min. The reacted mixture was separated by centrifugation and washed thoroughly with distilled water and dried in an oven at 60°C.

2.4. Analytical Procedures

The concentrations of metal ions were determined by AAS at time intervals of 10 min over a period of 70 minutes. The amount of heavy metal ions adsorbed at equilibrium, q ($mmol\ g^{-1}$) which represents the metal uptake was calculated from the difference in metal concentration in the aqueous phase before and after biosorption, according to the following equation:

$$q = \frac{(C_0 - C_f)V}{M}$$

Where V is the volume of metal solution (mL), C_0 and C_f are the initial and equilibrium concentrations of heavy metal ions in solution ($mmol\ L^{-1}$), respectively, and M is the mass of dry biosorbent (mg).

The Langmuir equation may be written as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

And can be expressed in its linear form as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), q_m (mg/g) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, K_L (L/mg) or b is the constant related to the free energy of adsorption (mg/L).

The Freundlich isotherm is represented by the equation:

$$Q = K_f C_{eq}^{1/n}$$

where C_{eq} is the equilibrium concentration (mg/L), q is the amount adsorbed (mg/g) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity, respectively. The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\log q_e = \log K_f + 1/n \log C_e$$

The plot of $\log q_e$ versus $\log C_e$ has a slope with the value

of $1/n$ and an intercept magnitude of $\log K_f$.

3. Results and Discussion

3.1. Effect of pH

Biosorption of the two metal ions by *Moringa oleifera* seed powder was strongly affected by pH (Figure 1). A sharp

increase in metal uptake was observed with increasing pH. Increase of the initial pH, and the removal efficiency of the metal ions increased at first but generally decreased after attaining the pH of 5. A trend of increasing metal ion binding with increasing pH was observed for both metals between pH 3 to 5. At pH values of 6 to 8 for both metals the metal uptake decreased.

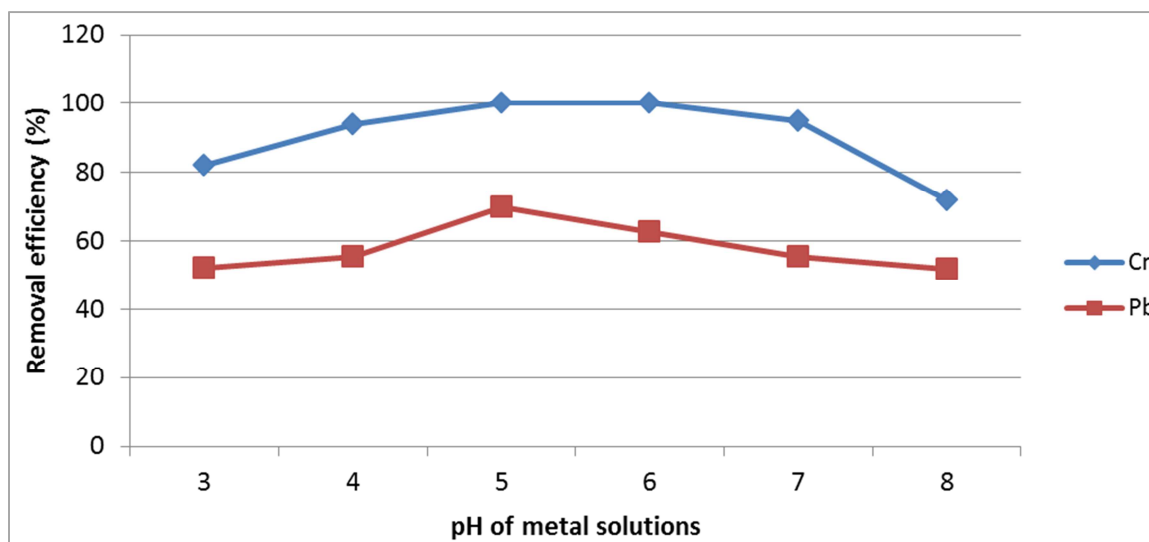


Figure 1. Effect of pH on metal biosorption using *Moringa oleifera* seed powder.

The pH dependence of metal uptake can be attributed to the nature of *Moringa oleifera*. Absorption increased with increasing solution pH since more metal binding sites could be exposed with negative charges, hence subsequent attraction of metal ions with positive charges and absorption occurring onto the cell surface (Taffarel & Rubio, 2009). This phenomenon is also attributed to the fact that substantial H^+ competes for vacant adsorption sites of adsorbents at lower pH values. A decrease in removal of metal ions by the adsorbent was noticed at pH values above 5 where the metal ions were surrounded by anions. It is difficult to combine with the adsorption sites on adsorbent's surface of negative charge. Experiments were carried out up to pH 8 because metal precipitation occurred at higher pH values and interfered with the accumulation or biomass deterioration. A smaller degree of removal at pH levels of 6 and 7 can be explained by the fact that the mobility of some elements may be reduced, which can lead to precipitation of insoluble forms at pH values close to neutral.

Another reason for increasing biosorption of metal ions with increasing pH is the zero point charge (PZC) of the biomass (Abu Al-Ru *et al.*, 2006). The PZC of the *Moringa oleifera* seeds has been found to be between 6.0 and 7.0 (Alves *et al.*, 2010) indicating that the surface of the biosorbent presents acid characteristics. The surface charge of the seeds is positive at $pH < PZC$, is neutral at $pH = PZC$ and is negative at $pH > PZC$ (Cleide *et al.*, 2013). The variation in pH caused by protonation and deprotonation of the adsorbent reflects the presence of functional groups. All these reasons explain the significant increase of the binding

efficiency by increasing the pH from 3 to 5. At pH below 3, biosorption capacity is negligible, probably due to the cation competition effects with hydroxonium H_3O^+ ion. Furthermore, at pH 6 biosorption of metals decreased probably because of chemical precipitation (Aksu & Tezer, 2005).

Other similar results reported by Adelaja *et al.* (2011) who studied the biosorption of Pb^{2+} from aqueous solution using *M. oleifera* pods. Paula *et al.* (2013) found that the highest level of metal removal was achieved at pH 5. In solutions of low pH values, H^+ and metal ions compete for the active sites of adsorption (Adelaja *et al.*, 2011). Different pH values were obtained in another study by Sajidu *et al.* (2013), using *Moringa oleifera* seeds at initial metal concentration of about 4 ppm. The extracts showed complete sorption for Cd^{2+} , Zn^{2+} and Cr^{3+} ions at pH above 7.8, 4.0 and 4.0, respectively, at a dose of 1.0 ml of sorbent in 9.50 ml of metal solution.

3.2. Effect of Contact Time

From figure 2, the biosorption of metal ions increased considerably until contact time reached 60 minutes at $25^\circ C$. Further increase in contact time did not enhance the biosorption process; so, the optimum contact time was taken to be 60 minutes for further experiments (Figure 2). The concentration of both the metal ions studied decreased significantly in solution. The percentage removal was rather fast in the first 20 minutes, after which the removal significantly decreased and eventually reached a plateau after 30 minutes. The rate of removal, however, increased gradually and reached equilibrium at 60 minutes of contact between the adsorbent and the aqueous solution.

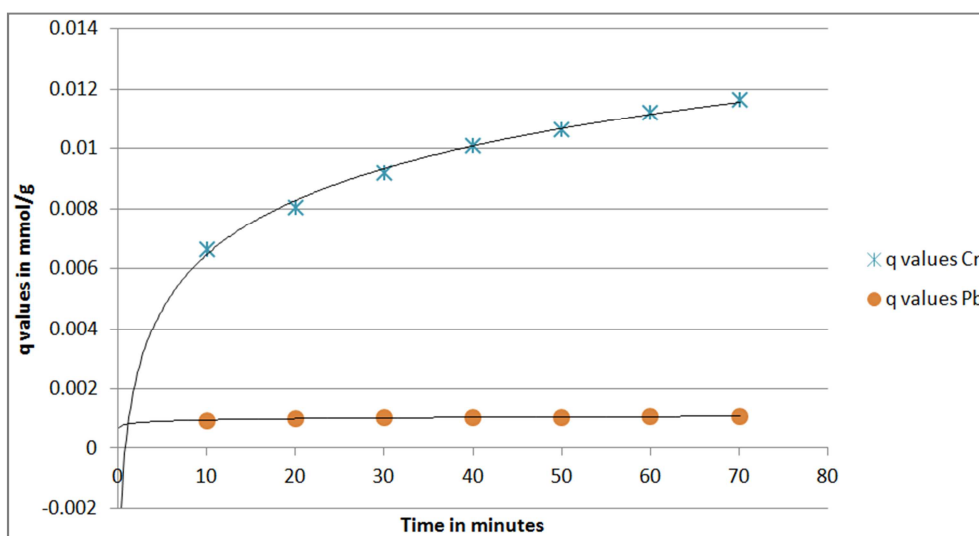


Figure 2. Effect of contact time.

The initial fast phase occurred due to surface adsorption on the biomass. The subsequent slow phase occurred due to diffusion of the metal ions into the inner part of the biomass. Contact time required for a system to reach equilibrium depends on the nature of biosorbent and amount of available adsorption sites. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system (Bhatti *et al.*, 2007).

According to Affonso *et al.* (2012) biosorption of Cd, Cr and Pb using *Moringa oleifera* seeds, the metal removal efficiency increased with the mass increase, a fact that could be attributed to the increased surface area for adsorption and to the availability of active adsorption sites. However, an excessive increase in the adsorbent amount could cause a reduction in the removal, possibly due to the formation of aggregates during sorption, as described by Ekmekyapar *et al.* (2006). Thus, the mass chosen for the procedure was 0.400 g. Cr^{2+} was better biosorbed than Pb^{2+} , which could be attributed to their electronic configurations. As reported by Liu *et al.* (2009), the weak bonding of Pb compared to Cr is attributed to the electron configuration of Pb^{2+} [$6s^2 4f^{14} 5d^{10} 6p^0$] compared to Cr^{2+} [$3d^4 4s^0$]. According to the electron configuration, the outer orbital of Pb^{2+} is full [$3d^{10}$] and there are no suitable empty orbitals to form a strong bond with surface functional groups. However, in Cr^{2+} [$3d^4$] there are outer empty orbitals which have empty spaces (which can be filled up to [$3d^{10}$]). Transient metals such as Zn, Cr and Cu with small ionic radii and empty orbitals easily complex with surface functional groups (Gunawardana *et al.*, 2012). Therefore, Pb forms weak bonds with charge sites compared to Cr which is a transition metal.

Cr^{2+} is a divalent cation which is a hard acid compared to Pb^{2+} which is a borderline acid. Therefore, Cr can compete with Pb for complexation sites and primarily forms strong bonds of chemisorption with solids particles (Gunawardana *et al.*, 2012).

3.3. Effect of Particle Size

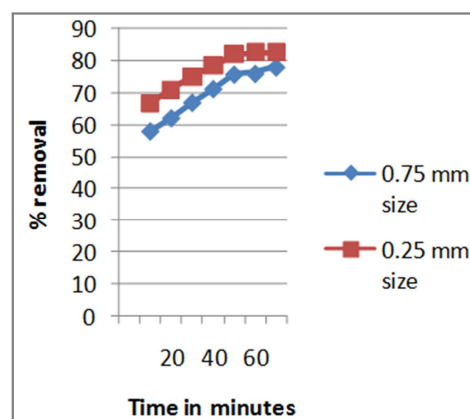


Figure 3. Effect of particle size on Cr^{2+} .

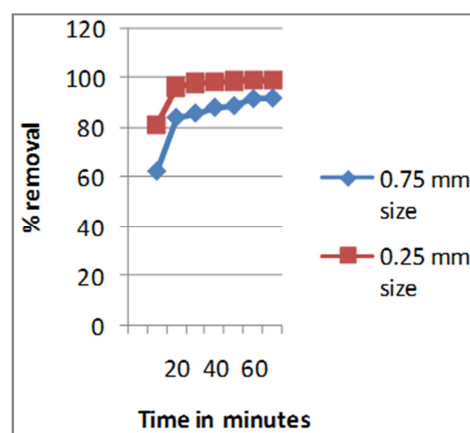


Figure 4. Effect of particle size on Pb^{2+} .

Figures 3 and 4 show that the biosorption capacity of *Moringa oleifera* biomass increased when the size of the particles was decreased from 0.75 mm to 0.25 mm. The range

of percentage increase was 78-82 for Cr^{2+} and 92-98 for Pb^{2+} . It is evident from the figures that biosorption capacity of both the metal ions studied increased with a decrease in particle size of *Moringa oleifera* biomass. The effect of altering particle size on the Cr^{2+} and Pb^{2+} ions uptake by *Moringa oleifera* biomass showed that removal of metal ions was more dominated by smaller particle size. Thus maximum adsorption occurred with 0.250 mm biosorbent size. This was most probably due to increase in the total surface area which provided more sorption sites for metal (Hanif *et al.*, 2007). Similar results were reported by Eman *et al.* (2015), who used *Moringa oleifera* leaves of different particle sizes for the removal of Cd^{2+} from waste waters. The particle size of < 250 μm had the highest removal efficiency (81%) which was due to the large surface area for the smallest particle sizes. Hossein *et al.* (2013) who used *Moringa oleifera* seeds of different particle sizes reported different results. They noted that the greater particle size, gave higher metal removal efficiency, which was due to very small sizes of sorbent used which could have passed through the filter and released the sorbed metal to the filtered solution.

3.4. Effect of Adsorbent Dosage

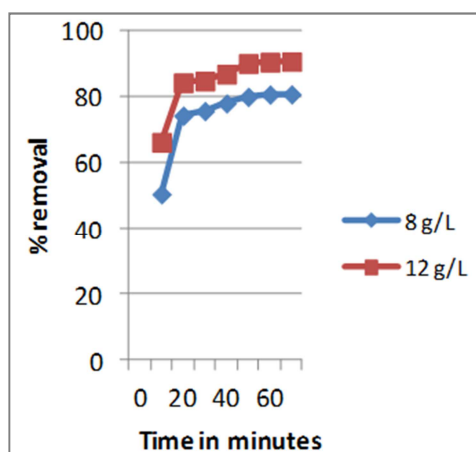


Figure 5. Effect of adsorbent dosage on Cr.

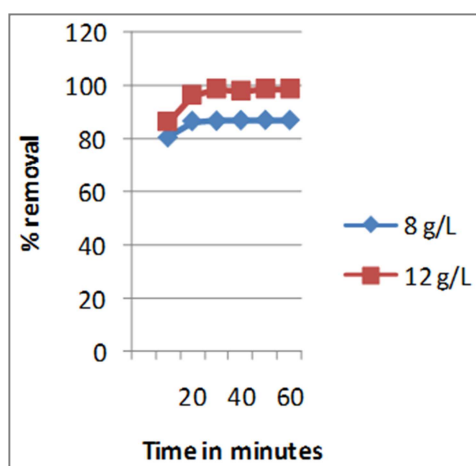


Figure 6. Effect of adsorbent dosage on Pb.

The results of the adsorbent dosage of 0.4 and 0.6 g in 50

mL on the removal of Cr^{2+} and Pb^{2+} from aqueous solution is shown in Figures 5 and 6. It was observed that biosorption was higher when the dosage of biomass was high and vice versa. Increase in metal removal with increasing biomass concentration of both pretreated and raw biomass could be explained by a higher biomass/metal ratio that is, higher number of binding sites available.

Mataka *et al.* (2010) obtained similar results using *Moringa stenopetala* and *Moringa oleifera* seed powders. By increasing *Moringa stenopetala* powder dosage from 0.5-2.5 g/100 ml, increased the Cd^{2+} removal percentage from about 20% to about 58%, and by increasing *Moringa oleifera* dosage from 1.0 g/100 ml resulted in removal percentage of about 20% which increased to about 58% as the dosage increased to 2.5 g/100 ml. Similarly, in this study increasing the dosage of *Moringa oleifera* from 0.4 - 0.6 g/50 mL increased the metal ion removal from 80% - 92% and 85% - 98% for Cr and Pb, respectively. This phenomenon is expected since the metal uptake capacity of the adsorbent increases with the increase in dosage as the number of active sites available for metal increases with increase in the amount of adsorbent.

3.5. Effect of Pretreatment

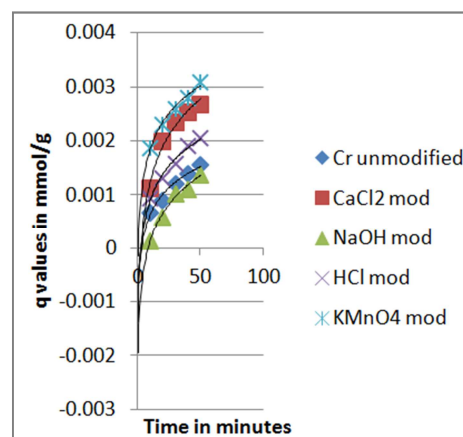


Figure 7. Biosorption of Cr^{2+} using treated *M. oleifera*.

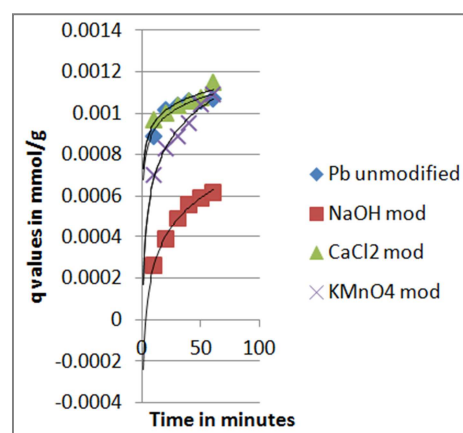


Figure 8. Biosorption of Pb^{2+} using treated *M. oleifera*.

Figures 7 and 8 show that treatment of biomass with HCl,

NaOH, CaCl₂, and KMnO₄ enhanced the removal of Cr²⁺ and Pb²⁺ by *Moringa oleifera* seeds. For Pb²⁺ the order was CaCl₂ > NaOH > KMnO₄ > HCl while for Cr²⁺ it was KMnO₄ > CaCl₂ > HCl > NaOH. However, only CaCl₂ pretreated biomass improved the biosorption of Pb²⁺ ions. Surprisingly, all the chemical pretreatments used improved the biosorption of Cr²⁺ except NaOH. The order of biosorption for each metal was different with different pretreatments; this could be because the mechanism of biosorption varies from metal to metal. Specific pretreatment shows a specific behaviour that may be due to the specific interaction between the biomass and the chemical used for that treatment (Bhatti *et al.*, 2008).

Acids can enhance uptake capacity of biomass by increasing surface area and porosity of original sample (Kapoor & Viraraghavan, 1997). The increase in uptake capacity depends on the nature of reagents used. Surfactants and acids can enhance uptake capacity of biomass by increasing the surface area and porosity of original sample (Bhatti *et al.*, 2007).

Enhancement in metal removal potential of biomass after the pretreatment with dilute HCl was probably due to the removal of previously adsorbed cations (ions present in the nutrient medium), thus freeing the binding sites for metal binding. Acid treatment might have also caused hydrolysis of functional groups and may have generated more anionic sites for metal removal (Fourrest & Roux, 1992). Acid treatment also reduces the positive charge on cell surface and this may also be the reason for increase in metal removal (Ting *et al.*, 1995). Generally, acid treatment has been used for cleaning the cell wall and replacing the natural mixture of ionic species bound on the cell wall with protons and sulphates (Davis *et al.*, 2003; Yun, 2004).

Alkali pretreatment can increase the biosorption of heavy metals because it may destroy autolytic enzymes causing putrefaction of biomass, remove lipids and proteins that mask binding sites and could release certain biopolymers from the cell wall that have a high affinity towards heavy metal ions (Yan & Viraraghavan, 2003; Rao *et al.*, 2010).

3.6. Adsorption Isotherms

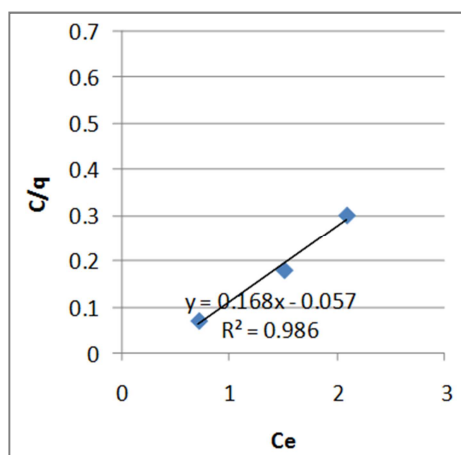


Figure 9. Langmuir isotherm for Cr²⁺.

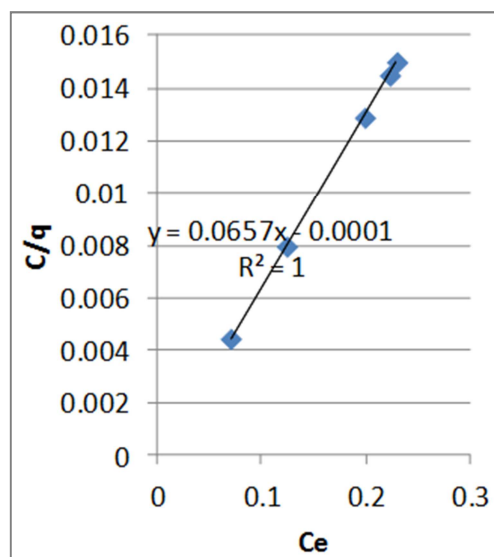


Figure 10. Langmuir isotherm for Pb²⁺.

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the *Moringa oleifera* seed powder. The specific plots of sorption (C_e/q_e) against the equilibrium concentration (C_e) for Cr²⁺ and Pb²⁺ are shown in Figures 9 and 10, linear isotherm parameters, q_m , K_L (b) and the coefficient of determinations (R^2) are presented in Table 1. The saturated monolayer sorption capacity, q_m , is a function of many parameters such as pH and temperature, it provides a good measure for comparing the efficiency of different sorbents in removing a given metal (Chang *et al.*, 1997).

Table 1. Sorption isotherm constants and coefficients.

Langmuir equation				Freundlich equation		
Metal ion	q_{max}	b	R^2	K_F	n	R^2
Pb(II)	15.38	0	1	14.791	-47.61	0.981
Cr(II)	5.952	-2.947	0.986	9.268	-2.597	0.972

The Langmuir equation was used to describe the data derived from the solution by *Moringa oleifera* seeds. The plot of C_e/q_e versus C_e fitted reasonably with the linearised Langmuir equation and the correlation coefficients, R^2 values were close to 1 confirming the data for both metals fitted the Langmuir isotherm. The sorption capacity, q_m , which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the *Moringa oleifera* seeds had a mass capacity for Pb²⁺ (15.38 mg/g) which was higher than for Cr²⁺. The order of sorption for these metals for *Moringa oleifera* seeds was therefore: Pb²⁺ > Cr²⁺, which is the same as the theoretically order of biosorption that is attributed to the size of the ions according to Pauling, Pb²⁺ = 1.20 Å and Cr²⁺ = 0.83 Å. Binding strength to the biomass depends on metal chemistry (including parameters such as charge, ionic radius, and Pauling electronegativity), affinity for binding sites, and the type of metal binding (electrostatic or covalent) (Fourrest & Roux, 1992; Veglio & Beolchini, 1997). Deviation from the theoretical expectation of biosorption that depends on ionic

sizes could be attributed to other factors coming into play such as varying initial concentration.

Freundlich isotherms were basically obtained by agitating the adsorbate solution of a fixed concentration and 0.4 g of the adsorbent for a contact time greater than the equilibrium time. The plot of $\log q_e$ versus $\log C_e$ gives a slope with the value of $1/n$ and an intercept magnitude of $\log K_f$. K_f and n were calculated from the slope and intercept of the Freundlich plots, where the gradient of the straight line was $1/n$ and the antilog of the intercept equal K_f .

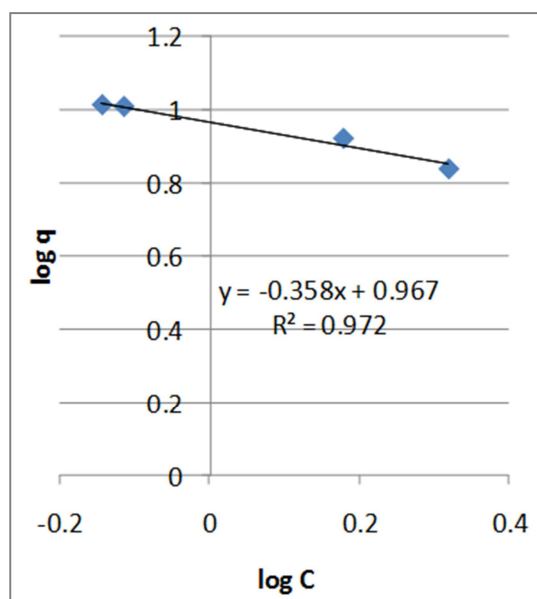


Figure 11. Freundlich isotherm for Cr^{2+} .

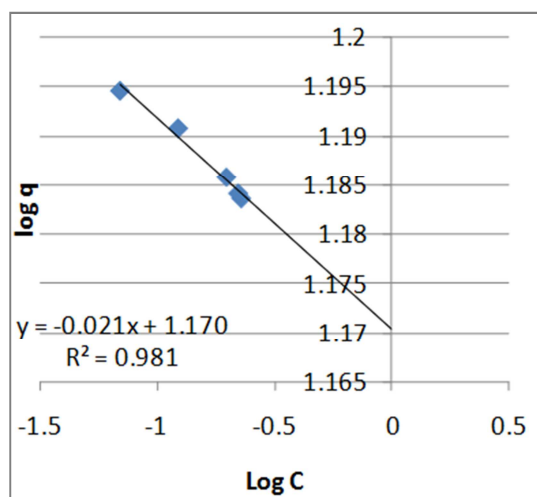


Figure 12. Freundlich isotherm for Pb^{2+} .

The Freundlich isotherm basically indicates whether the adsorption proceeds with ease or difficulty. Freundlich isotherm model was obeyed by both the adsorbates (Pb^{2+} and Cr^{2+}) under the studied conditions with R^2 values of between 0.972 and 0.998 (Figures 11 and 12, and Table 1).

These results may be explained if adsorbent surface sites have a spectrum of different binding energies as suggested by Anwar and Rashid (2007). Since $n < 1$ (Table 1), this

indicates that the biosorption of the metal ions under this study is a chemical process. Affonso *et al.* (2012) reported n values of 1.46, 0.57 and 0.54 for Cd^{2+} , Pb^{2+} and Cr^{2+} , they concluded that the biosorption of Pb and Cr was practically favourable while the biosorption of Cd on *Moringa oleifera* was unfavourable to heterogeneous surfaces.

Anwar (2013) reported n values of 0.748, 2.582, 2.393 and 1.989 for biosorption of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} , respectively on Garden grass and concluded that only the biosorption of Cu^{2+} was practically favourable since it had a value $n < 1$. Waghmare and Chaudhari (2014) reported a value of $n = 0.048$ for the biosorption of Mn^{2+} on *Moringa oleifera* bark and concluded that the bark was favourable for the adsorption of Mn^{2+} since $n < 1$. The Langmuir and Freundlich constants calculated from the isotherm equations are given in Tables 1 for the adsorption of metal ions. From this Table the values of R^2 (approximately 0.99) indicated that the Langmuir model fitted better and can be used to describe the biosorption of Pb and Cr on this biomass. The Freundlich R^2 values were 0.981 and 0.972 for Pb and Cr, respectively. Thus, biosorption of the two metal ions followed monolayer surface mechanism.

The preferential sorption behaviour of adsorbents for metal ions acquired in present investigations could also be explained in terms of ionic radii of the metal ions. Thus, the element with larger ionic radius will compete faster for exchange sites than those of smaller ionic radius because the ones with smaller ionic radius are more hydrated. Adsorption may be related to the loss of the entire hydration sphere that precedes hydrolysis. According to Horsefall and Spiff (2005), the smaller the ionic radius, the greater its tendency to hydrolyze leading to reduction of sorption. The observed order indicates that Pb^{2+} may have greater accessibility to the surface of certain pores than Cr^{2+} due to its larger ionic radius.

4. Conclusions

Moringa Oleifera seed powder biosorbent has a great potential for the removal of Pb and Cr from contaminated water. The biosorption of all metals on the adsorbent was rapid as over 80 % of the metals were removed within the first 20 minutes of interaction. It was observed that the biosorption which fitted better to the Langmuir isotherm model strongly depends on parameters such as pH of the solution, contact time, biosorbent dose and particle size. Pretreatment of *Moringa oleifera* further enhanced biosorption process.

Acknowledgement

We are grateful to National commission for science Technology and innovation (NACOSTI), Kenya for partially funding this research. We are also indebted to Mr. Ekeyya (Chief Technician, University of Eldoret) for assisting throughout the lab work.

References

- [1] Abu Al-Rub, F. A., El-Naas, M. H., Ashour, I., and Al-Marzouqi, M. (2006). Biosorption of Cu(II) from Aqueous Solutions by Pre-treated Biomass of Marine Algae *Padina* sp. *Biochem.* 41: 457–464.
- [2] Adelaja, O. A., Amoo, I. A., Aderibigbe, A. D. (2011). Biosorption of Lead (II) ions from aqueous solution using *Moringa oleifera* pod. Scholar's research library Archives of Applied Science Research 3(6): 50-60.
- [3] Affonso, C. G. J., Ana, P. M., Fernanda, R., Leonardo, S., Douglas, C. D. and Gustavo, C. F. (2012). Applicability of *Moringa oleifera* Lam. pie as an adsorbent for removal of heavy metals from waters. *Revista Brasileira de Engenharia Agrícola e Ambiental* 17(1): 94–99 UAEA/UFCG – <http://www.agriambi.com.br>.
- [4] Aksu, Z., and Tezer, S. (2005). Biosorption of Cadmium (II) from Aqueous Solutions by Pre treated Biomass of Marine Algae *Durvillaea potarotum*. *Process Biochem* 40: 1347–1361.
- [5] Alves, V. N., Mosquetta, R., Coelho, N. M. M., Bianchin, J. N., Roux, K. C. P., Martendal, E., and Carasek, E. (2010). Determination of cadmium in alcohol fuel using *Moringa oleifera* seeds as a biosorbent in an on-line system coupled to FAAS. *Talanta* 80(3): 1133-38.
- [6] Anwar, F., and Rashid, U. (2007). Physico-chemical characteristics of *Moringa oleifera* seeds and seeds oil from a wild provenance of Pakistan. *Pakistan Journal of Botany* 39(5): 1443-53.
- [7] Anwar, H. (2013). Development of novel biosorbents in removing heavy metals from aqueous solution. D.Phil thesis in environmental engineering. University of technology, Sydney 4: 17-24.
- [8] Bhatti, H. N., Mumtaz, B., Hanif, M. A., and Nadeem, R. (2007). Removal of Zn (II) ions fro aqueous solution using *Moringa oleifera* Lam. (Horseradish tree) biomass,” *Process Biochem.* 42: 547-553.
- [9] Bhatti, H. N., Khalid, R., and Hanif, M. A. (2008). Dynamic biosorption of Zn(II), Cu(II) using pretreated *Rosa* grass an teplitz (red rose) distillation sludge. *Chem. Eng. J.* 148: 434–443.
- [10] Chang, J., Law, R., and Chang, C. (1997). Biosorption of Lead, Copper and Cadmium by Biomass of *Pseudomonas aeruginosa*, *Water Research* 31(7): 1651-1658. doi: 10.1016/S0043-1354(97)00008-0.
- [11] Cleide, S. T., Araújo, D. C., Carvalho, H. C., Rezende, I. L. S., Almeida, S., Luciana, M., Coelho, N. M. M., Coelho, T. L., and Vanessa, N. A. (2013). Bioremediation of Waters Contaminated with Heavy Metals Using *Moringa oleifera* Seeds as Biosorbent. <http://dx.doi.org/10.5772/56157>.
- [12] Congeevaram, S., Dhanarani, J., Park, M., Dexilin, K., Thamaraiselvi, B. (2007). Biosorption of Cr and Ni by heavy metal resistant fungal and bacterial isotopes, *J. Hazard. Mater* 146: 270-277.
- [13] Davis, T. A., Volesky, B., and Mucci, A. (2003). A review of the biochemistry of heavy metal biosorption by brown algae. *Wat. Res.* 37(18): 4311-4330.
- [14] Ekmekyapar, F., Aslan, A., Kemal, B. Y., and Cakici, A. (2006). Biosorption of copper(II) by non-living lichen biomass of *Cladonia rangiformis* hoffm. *Journal of Hazardous Materials* 137: 293-298.
- [15] Eman, N., Ali, S. R., Alfarra, M. M. Y., and Lutfor, R. M. (2015). Environmentally friendly biosorbent from *Moringa oleifera* leaves for water treatment. *International Journal of Environmental Science and dev.* 6: 3.
- [16] Fourest, E., and Roux, J. C. (1992). Heavy metal biosorption by fungal mycelial by-product; mechanisms and influence of pH. *Applied Microbiology and Biotechnology* 37(3): 399-403.
- [17] Gunawardana, C., Goonetilleke, A., Egodawatta, P., Dawes, L., and Kokot, S. (2012). Role of solids in heavy metal pollution of receiving waters. *Journal of Environmental Engineering* 138(4): 490-498.
- [18] Hanif, M.A., Nadeem, R., Bhatti, H. N., Ahmed, N. R., Ansari, T. M. (2007). “Ni(II) biosorption by *Cassia fistula* (Golden Shower) biomass,” *J. Hazard. Mater* 139: 345-355.
- [19] Horsefall, M. J., and Spiff, I. F. (2005). Effect of Metal ion concentration on Biosorption of Pb²⁺ and Cd²⁺ by *Caladium Bicolor* (Wild Cocoyam), *African J. Biotechnol.* 4: 191-196.
- [20] Hossein, F., Tahari, E., Afshin, E., Ali, F., Marzieh, V. D and Bina, B. (2013). Effectiveness of *Moringa oleifera* powder in removal of heavy metals from aqueous solution. *Fresenius Environmental Bulletin.* 22: 5a.
- [21] Jeon, C. J. Y., Park, Y. J., and Yoo, S. (2002). Characteristics of metal removal using carboxylated alginic acid, *Water Res.* 36, 1814-1824.
- [22] Kapoor, A., and Viraraghavan, T. (1997). Heavy metal biosorption sites in *Aspergillus niger*. *Bioresource Technology* 61(3): 221-227.
- [23] Kumari, P., Sharma, P., Shalini, S., and Srivastava, M. M. (2005). Arsenic removal from the aqueous system using plant biomass: a bioremedial approach, *J. Ind Microbiol Biotechnol.* 32: 521–526.
- [24] Liu, C. C., Wang, M., Chiou, C., Li, Y., Yang, C., and Lin, Y. (2009). Biosorption of chromium, copper and zinc by wine-processing waste sludge: Single and multi-component system study. *Journal of Hazardous Materials* 171: 386-392.
- [25] Mataka, L. M., Henry, E. M. T., Masamba, W. R. L., and Sajidu, S. M. (2010). Cadmium sorption by *Moringa stenopetala* and *Moringa oleifera* seed powders: *Int. J. Environ. Sci. Tech* 3: 131-139.
- [26] Ozturk, A. (2007). Removal of nickel from aqueous solution by bacterium *Bacillus thuringiensis*, *J. Hazard. Mater* 147: 518–523.
- [27] Paula, M. A., Gonçalves, J. R., Affonso, C., Teixeira, T., César, R., Stangarlin, J. R., Rubio, F., Nacke, H. (2013). Studies of Pb²⁺ adsorption by *Moringa oleifera* Lam. seeds from an aqueous medium in a batch system. *Water Science & Technology Academic Journal* 69(1): 163.
- [28] Rao, H. J., Kalyani, G., Rao, K. V., Kumar, T. A., Mariadas, K., Kumar, Y. P., Vijetha, Pallavi, P., Sumalatha, B., and Kumaraswamy, K. (2010). Kinetic studies on biosorption of lead from aqueous solutions using eggshell powder. *International Journal of Biotechnology and Biochemistry* 6(6): 957 – 968.

- [29] Sajidu, S. M. I., Henry, E. T., Persson, I., Masamba, W. R. L., and Kayambazinthu, D. (2013). 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 chemistry* 1(2): 063-066.
- [30] Selatnia, A., Bakhti, M. Z., Madani, A., Kertous, L., Mansouri, Y. (2004). Biosorption of Cd²⁺ from aqueous solution by a NaOH treated bacterial dead streptomyces rimosus biomass, *hydrometallurgy* 75: 11–24.
- [31] Taffarel, S. R., and Rubio, J. (2009). “On the removal of Mn²⁺ ions by adsorption onto natural and activated Chilean zeolites,” *Minerals Engineering* 22(4): 336–343.
- [32] Ting, V. P., Lawson, F., and Prince, I. G. (1995). *Biotechnol. Bioeng.* 3: 990–999.
- [33] Veglio, F., and Beolchini, F. (1997). Removal of metals by biosorption: a review. *Hydrometallurgy* 44(3): 301-316.
- [34] Waghmare, V. H., and Chaudhari, U. E. (2014). *Equilibrium uptake and sorption dynamics for the retrieval of divalent manganese from aqueous solution using Moringa oleifera bark. Rasayan J. Chem* 7(3), 214 – 218.
- [35] Yan, G. Y., and Viraraghavan, T. (2003). Heavy-metal removal from aqueous solution by fungus *Mucor rouxii*. *Water Res.* 37: 4486-4496.
- [36] Yun, Y. S. (2004). Characterization of functional groups of protonated *Sargassum polycystum* biomass capable of binding protons and metal ions. *J. Microbiol. Biotechnol.* 14: 29.