

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

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ABSTRACT

Uptake for lead, copper, cadmium, nickel and manganese from aqueous solution using the *Moringa oleifera* seeds biomass (MOSB) and amine-based ligand (ABL) was investigated. Experiments on two synthetic multi-solute systems revealed that MOSB performed well in the biosorption and followed the decreasing orders Pb(II) > Cu(II) > Cd(II) > Ni(II) > Mn(II) and Zn(II) > Cu(II) > Ni(II). The general trend of the heavy metal ions uptake by the amine-based ligand followed decreased in the order Mn > Cd > Cu > Ni > Pb, which is the reverse trend for what was observed for MOSB. Comparing the single- and multi-metal solutions, there was no clear effect in the biosorption capacity of MOSB suggesting the presence of sufficient active binding sites for all metal ions studied. The MOSB performance is also not affected by pH in the range 3.5–8.

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1. Introduction

The most common contaminants in water are heavy metals mainly contributed by anthropogenic sources like electronics assembly and fabrication, battery manufacturing, paper and pulp industries, metal smelters, textiles, usage of fertilizers and pesticides, and mining activities. Natural waters also contain toxic metals depending upon the bed rock. Efforts to minimize the production of hazardous waste and to remediate existing accumulated waste have become one of the most important environmental challenges that the world faces today. Even at low concentrations, heavy metals can be toxic to organisms, including humans [1,2]. The US Environmental Protection Agency (EPA) requires Pb, Cu, Cd, Mn, Zn and Ni in drinking water not to exceed 0.015, 1.3, 0.005, 0.05, 5 and 0.04 mg L⁻¹, respectively [3].

Conventional methods used to remove dissolved heavy metal ions from wastewaters include ultra-filtration, reverse osmosis, ion exchange, solvent extraction and chemical precipitation, to mention but a few [4–8]. Metal extracting ligands have also been reported [9,10]. A recent report, shows that N,N,N-type ligands are selective for Cd(II) ions [11] which suggest that other N-based

ligand systems such as amine based ligands can be used as selective heavy metal removers.

Some of these techniques though effective have serious cost and health implications and others are inefficient especially when the concentration of the heavy metal ion is low, of the order of 1–100 mg L⁻¹.

The cost implications are more serious to the developing countries. Therefore, cost effective and more environmentally friendly materials for removing heavy metals from contaminated water and soils are required. Various chemical and biological materials regarded to be environmentally friendly and cheap have been and continue to be investigated for the remediation of heavy metal-contaminated environmental samples [12,13].

Recently, there has been an increasing trend to evaluate some indigenous cheaper biological materials for wastewater treatment. *Moringa oleifera* (MO) seeds biomass has been found to remove the turbidity and other impurities in water [14–17]. As a tropical multipurpose tree, MO is very interesting from the point of view of the developing world as it can easily be cultivated and adaptable to semi arid climates. Apart from being an environmentally friendly resource, the use of MO has two further advantages in water treatment and, that is, it can be used a primary source of activated carbon and has coagulant/flocculant agent in the seeds.

In this paper, heavy metal removal from synthetic wastewater was investigated using shelled defatted MO seeds biomass (MOSB). An attempt to compare its metal uptake with an amine-based ligand (ABL), 1,4-bis[N,N-bis(2-picoyl)amino]butane, was made. The efficiency of the two materials in heavy metal removal is compared.

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The heavy metal anions selected for the study are of cadmium, cobalt, copper, lead, manganese and nickel.

2. Methods and materials

2.1. Materials

Sodium hydroxide ($\geq 97.0\%$, Rochelle Chemicals), dichloromethane ($\geq 99.9\%$, Sigma–Aldrich), 1-4-diaminobutane ($\geq 98\%$, Sigma–Aldrich), 2-picolylchloride hydrochloride ($\geq 98\%$, Fluka), anhydrous magnesium sulfate ($\geq 97\%$, Merck Chemicals), and distilled water were used in the preparation of the ligand. Petroleum ether (40–60 °C), sieves, ultrasonic bath (Transonic, 820/H, ELMA) and flask shaker (SF1 Stuart Scientific) were used for defatting the MO seeds, separating seed powder according to pore size of the sieves and for agitating the sample solutions, respectively. The universal indicator was also used in the determination of pH. Filtration of the supernatant was done under ultra filtration using a 0.45 μm glass fiber filter paper (Schleicher and Schuell-ME 25/21).

2.2. Preparation and characterization of MOSB

Dry MO seeds were obtained from a local supplier in Gaborone and stored at room temperature prior to use. The seeds were deshelled by hand and the kernels were washed with copious amounts of doubly distilled water to remove any adhering dirt before drying them in the oven at 65 °C for 24 h. The seed kernels were ground to powder using mortar and pestle and the oil extracted by mixing the seeds powder (75–80 g) in 40–60 °C petroleum ether (200 mL) for 30 min on an orbital shaker (Stuart Scientific). The powder was then obtained by suction filtration and dried in at room temperature in open air on a bench. The powder was further dried for 24 h and ground to finer powder using mortar and pestle. Powder was sieved through mesh sieves to obtain a homogeneous biomass. No other chemicals or physical treatments were used prior to biosorption experiments.

The MOSB was also characterized by Fourier Transform Infrared (FTIR) spectroscopy (PerkinElmer System 2000) as described in Section 2.3.

2.3. Instrumental analysis

1000 mg L^{-1} stock solutions of metals were used to prepare working standards (in the range 0–10 mg L^{-1}) in distilled water. The metal ion concentrations determined by flame atomic absorption spectrometry (FAAS) using a Varian Spectra AA spectrometer with air/acetylene flame and different hollow cathode lamps for specific cations. 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 then also aspirated manually into the flame for atomization.

FTIR spectroscopy was used to characterize the MOSB for possible functional groups responsible for metal uptake. The FTIR spectra were recorded in the wavenumber range 400–4000 cm^{-1} on a PerkinElmer System 2000 FTIR. MO seeds powder were kept at an ambient temperature. 1 mg seed powder per 200 mg of KBr was weighed. After homogenizing with an agate mortar and pestle, 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.

2.4. Biosorption of heavy metal ions

Biosorption of Cd (II), Cu (II), Co (II), Ni (II) and Pb (II) from synthetic wastewaters containing single and mixed metal ions were

investigated in batch experiments. Stock metal solutions at various concentrations were prepared by dissolving lead nitrate, copper nitrate trihydrate, cadmium (II) nitrate hexahydrate, cobalt (II) nitrate hexahydrate, nickel nitrate hexahydrate and zinc nitrate tetrahydrate and all were analytical grade reagents. A solution of known metal ion concentration was prepared and a known quantity of adsorbent (MOSB or ligand) was added. The mixtures were shaken with a flask shaker (Stuart Scientific unless otherwise stated) and the concentration of the unadsorbed metal ions in solutions were determined after separation of the sorbent by centrifugation and filtration using Whatman paper No. 1 filter papers. The effects of contact time, initial metal ion concentration and pH were studied. The pH was adjusted using either 0.1 M NaOH or 0.1 M HCl. Analysis and instrumentation for metal uptake tests were done using FAAS with air/acetylene. The amount of metal sorbed by biomass or ligand (expressed as % bound or % removal) was calculated from the difference between the initial metal quantity (C_0) and the metal content of the supernatant (C_f) using the following equation:

$$\% \text{ Removal} = \frac{C_0 - C_f}{C_0} \times 100$$

C_0 and C_f represent the measured metal ion concentration before and after adding the adsorbent, respectively. To eliminate any instrumental errors, (i) solutions were made such that C_0 was less than 20 mg L^{-1} , and (ii) the metal ion concentration before and after adding either MOSB or ligand was analyzed. Each experiment was conducted in duplicate. All data reported represent the mean of the two independent experiments. The difference between the replicate experiments was less than 10% in all cases.

2.4.1. Effect of contact time

Contact time is important in biosorption experiments to determine equilibrium time required for the uptake of metal ions by MOSB and ligand. Aqueous metal ion solutions (25 mg L^{-1} each) were kept in contact while with sorbent for 0.5, 1, 2, 4, 6, 8, 12 and 24 h. The mixtures were centrifuged and filtered prior to analysis of the supernatant with FAAS.

2.4.2. Effect of initial metal ion concentration

To study the effect of the initial metal ion concentration on biosorption capacity of MOSB, solutions of Co(II), Cu(II) and Zn(II) in the concentration range 1–14 mg L^{-1} were prepared and 0.5 g of biomass was added to 60 mL of solution (single, binary and ternary) in 100 mL bottles. The bottles were left shaking on an orbital shaker for 24 h, centrifuged and filtered prior to analysis as described in Section 2.3.

2.4.3. Effect of shaking method and particle size on heavy metal ion removal by MOSB

To test the effect of particle size, the MO seed powder was sieved and the fraction with mesh size 500–1000, 250–500 and 250–106 μm were selected for use in the sorption tests and from here onwards the size ranges are discussed as 500, 250 and 106 μm , respectively. For each of the different particle sizes, 0.5 g of the powder was mixed with 100 mL of a 10 mg L^{-1} synthetic sample mixture of the metals studied. To extract the metal ions from synthetic solutions, two shakers were used, namely, an orbiter shaker and ultrasonic sonicator. The shaking was performed at room temperature (22 ± 1 °C) for 1 h using orbiter shaker at 500 oscillations min^{-1} and sonication for 45 min using an ultrasonic sonicator. Samples from both methods of extraction were then centrifuged at 4000 rpm for 10 min. The supernatant solutions were further filtered under ultra-filtration, with a 0.45 μm glass fiber filter paper. The free metals in the filtrate were then analyzed using FAAS.

Table 1
Analysis of the FTIR spectrum for the MOSB.

Peak wave-number for powder alone (cm ⁻¹)	Peak wave-number for metal-loaded powder (cm ⁻¹)	Peak shift (cm ⁻¹)	Functional group assignment [17]
3321.2	Cu, Pb: 3317.3 Cd: 3313.5	3.9 7.7	—OH aliphatic and aromatic, OH alcohols and phenols, and —NH primary, secondary and tertiary amines
2927.7	Cu, Pb, Cd: 2927.7	0	C—H aliphatic
2862.2 (shoulder) 0	Cu, Pb, Cd: 2862.2 Cu, Cd: 1739.7 Pb: 1743.5	0	COOH stretching vibration, C=O (shoulder)
1658.7	Cu, Pb, Cd: 1658.7	0	CONH ₂ amides, C=O and C—N (Amide I), proteins (peptide bond) N—H (amide II) peptide bond
1539.1	Cu, Pb: 1539.1 Cd: 1535.2	0 3.9	—CN, peptide protein bond
1438.8	Cu, Pb, Cd: 1446.5	−7.7	Symmetric bending of CH ₃ , CO ₃ ²⁻ (1410–1450 cm ⁻¹)
1245.9	Cu, Pb: 1249.8 Cd: 1245.9	−3.9 0	C=O stretching vibration, carboxylate
1060.8	Cu, Cd: 1080.1 Pb: 1091.6	−19.3 −30.8	—OH stretching vibration, polysaccharides
798.5	Cu, Pb, Cd: 0	0	Aromatic amino protons
597.9	Cu, Cd: 601.7 Pb: 605.6	−3.8 −7.7	

2.4.4. Effect of initial pH

It is well documented that pH of the biosorption medium is an important parameter affecting the uptake of heavy metals from aqueous solutions by biosorbent. The effect of initial pH on the sorption was studied by adjusting the pH (using 0.1 M NaOH and 0.1 M HCl) in the range 2–8 of the solutions of 25 mg L⁻¹ ppm Cu(II), Ni(II) and Zn(II) in distilled water. 50 mL of each metal solution was treated with 1 g of MOSB and shaken for 10 h followed by centrifugation and analysis of the supernatant liquid using FAAS.

2.5. Synthesis of the ABL 1,4-bis[N,N-bis(2-picoyl)amino]butane

The ligand was synthesized by a procedure adopted from Marvey et al. [18]. Briefly, 140 mL NaOH (0.1 M_s) was added dropwise to an aqueous solution of 2-picoylchloride HCl (0.0183 moles) in 10 mL of distilled water at 0 °C. An aqueous solution of 1,4-diaminobutane (0.00458 moles) in 10 mL of distilled was added vigorously to the mixture and was maintained at 0 °C. The mixture was then stirred for 20 min after which 60 mL of dichloromethane was added. The pH of the reaction mixture was adjusted to pH 9 by the addition of 0.1 M NaOH solution and the mixture was then stirred for a day at 0 °C and for 7 days at room temperature using a magnetic stirrer. The ligand was then extracted with three 30 mL portions of dichloromethane using a separation funnel. The combined extracts were dried with anhydrous magnesium sulfate. The dried solution was then filtered out using a sintered funnel. Then dichloromethane was removed by means of rotor evaporation. The ligand has been synthesized was characterized by FTIR spectroscopy.

2.6. Metal removal by the ligand

The extraction efficiency for the metal ions Cd(II), Cu(II), Pb(II), Ni(II) and Mn(II) was done with an inorganic ligand (1,4-bis[N,N-bis(2-picoyl)amino]butane). 1 g of the synthesized ligand was homogenized with 100 mL of a 10 mg L⁻¹ synthetic sample mixture of the metals studied. The solution was divided into three parts. The pH of metal solutions were adjusted to pH 2, neutral pH 7 and pH 12, respectively. Metal extraction was performed by sonication method for 45 min using an ultrasonic sonicator (at 22 ± 1 °C room temperature) followed by centrifugation for 10 min at 4000 rpm. The free metal solution was decanted and further filtered using ultra-filtration with a 0.45 μm glass fiber paper. The metals were then analyzed using FAAS. The extraction was only performed using

sonication. Three pH levels were used in the present experiments, i.e. 2, 7 and 12.

3. Results and discussions

3.1. Characterization of the sorbents

The FTIR spectra of the MOSB were observed in the range 400–4000 cm⁻¹. It displayed a number of peaks as shown in Table 1, indicating the complex nature of the adsorbent. It is clear that the carboxylic acid and hydroxyl groups present play a major role in the removal of heavy metal ions as observed from the significant reduction in the intensity or shift in their intensity peaks for metal-loaded MOSB as shown in Table 1. The results reported agree with the findings of Sharma et al. [19] using shelled *M. oleifera* Lam seed powder in the removal of cadmium (Cd) from aqueous system as the FTIR spectrometry highlighted amino acid–Cd interactions responsible for sorption phenomenon. The findings opened up new avenues in the removal of toxic metals by shelled *M. oleifera* seeds from water bodies as low cost, domestic and environmentally friendly safe technology.

The observed characteristic IR frequency peaks of the synthesized ligand are shown in Table 2. Systematic FTIR studies of both adsorbents are required in order to understand the mechanisms of metal removal.

3.1.1. Effect of contact time

Contact time is important in biosorption experiments to determine equilibrium time required for the uptake of metal ions by MOSB and ligand. Fig. 1 shows the effect of time course profiles for the uptake of Cu, Zn and Ni ions by MOSB. For all three metal ions, the biosorption rate was fast and most of the process was completed within 60 min. Therefore, it was assumed that all other metal ions reached sorption equilibrium after an hour and so all experiments were carried out for at least 1 h of contact time with sorbent. The

Table 2
Analysis of the IR spectra for the ligand 1,4-bis[N,N-bis(2-picoyl)amino]butane.

Functional group	Reference IR frequency range (cm ⁻¹) [17]	Observed IR frequency (cm ⁻¹)
Alkenyl stretch (C=C)	1600–1680	1634.21
Benzene ring (C=C) ring	1450–1600, 2–3 bands	1579.72, 1497.18 and 1455.73
Amines (N—H)	3500–3300	3313.48

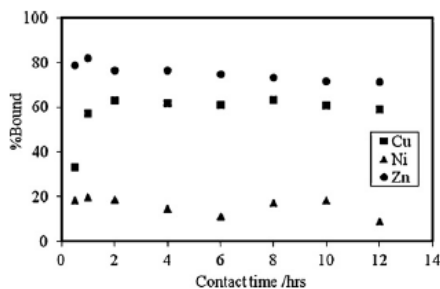


Fig. 1. Effect of contact time for MOSB.

fast sorption kinetics observed with these materials (i.e. MOSB and ligand) represents an advantageous aspect when water treatment systems are designed.

3.1.2. Effect of initial metal ion concentration

Fig. 2 shows the results of single solutions, and binary and ternary mixtures. The general trend is that there is increase in the biosorption of the metal ions as the concentration increases until the biomass saturation point of the available binding sites. There is also a gradual decrease beyond this optimal point as the concentration is increased further. Akar et al. [20] observed a similar trend for the biosorption of Pb(II) on fungi *Botrytis cinerea* and attributed the enhancement of metal uptake to an increase in electrostatic interactions (relative to covalent interactions) which involve sites of progressively lower affinity for metal ions. The results in Fig. 2 further show that there was no significant observed reduction in the sorption of metal ions in binary and ternary mixtures (i.e. the presence of other ions). Several studies reported in literature observed significant reductions in metal uptake capacities of the biosorbents in multi-metal systems and this has often been attributed to competition between metal ions for the available binding sites on the biomass surface [19–21].

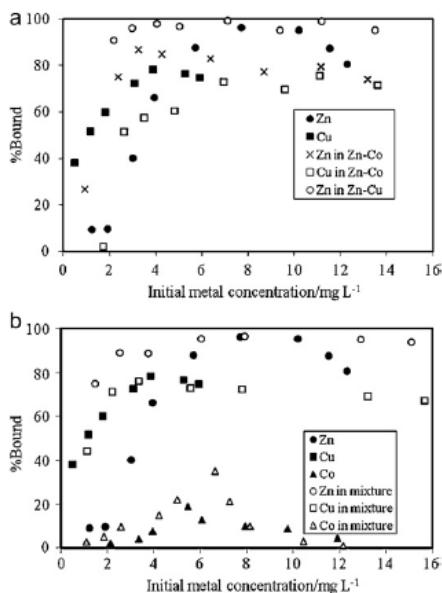


Fig. 2. Effect of metal ion concentration and the presence of other ions (mixture in (b) refers to a mixture of Zn, Cu and Co).

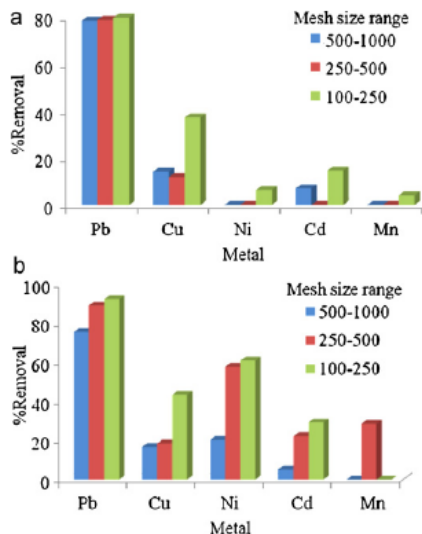


Fig. 3. Effect of MOSB particle size and mixing method, i.e. (a) shaker and (b) sonicator in removal of metals.

3.1.3. Effect of shaking method and particle size on heavy metal ion removal by MOSB

Fig. 3 shows that the general % removal of heavy metals in this method followed the trend Pb(II) > Cu(II) > Cd(II) > Ni(II) > Mn(II). For orbiter shaking, all the metals were better removed at seed particle size of 106 μm in the order Pb(II) > Cu(II) > Cd(II) > Ni(II) > Mn(II). For 250 μm , only Pb(II) and Cu(II) were better removed with Pb(II) being removed more than Cu(II) whereas Ni(II), Cd(II) and Mn(II) being the least removed metals. Also at 500 μm , the percentage metal ion removal followed the order Pb(II) > Cu(II) > Cd(II) while Ni(II) and Mn(II) metals had the least % removal.

The overall trend of heavy metal removal (%) using sonication method followed the order Pb(II) > Ni(II) > Cu(II) > Cd(II) > Mn(II) (Fig. 3). This removal was found to be directly proportional to the size of the metal ions, Pb(II) being the largest metal ion among the metals studied was highly removed and Mn²⁺ is the smallest metal ion, hence was removed the least. % removal of Pb(II), Cu(II), Ni(II), and Cd(II) in water by MOSB as biosorbent increased as the particle size of the powder reduces, in the order 106 μm > 250 μm > 500 μm , whereas for Mn(II) metal, the % removal was highest for particle size of 250 μm . The fact that metal removal was inversely proportional to particle size might be due to increased surface area for adsorption of metals as the particle size reduces.

Generally, the extraction efficiency was directly proportional to the sizes of the metal ions (from largest to smallest) Pb(II) > Cd(II) > Cu(II) > Ni(II) > Mn(II). Metals of larger sizes were highly removed whereas those of smaller sizes were the least removed except for Cd(II), Ni(II) and Cu(II), which were reversed, which could be due to diagonal relationship between Cd and Cu, hence similar sizes.

The extraction by shaking was less efficient than extraction by sonication since it showed less removal of the metals under study as compared to the sonication method. In fact, sonication can be carried out within a shorter period of time unlike the shaking method which is carried out for a long period of time yet it has less efficiency in metal ion removal.

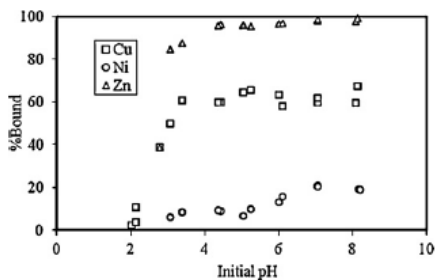


Fig. 4. Effect of initial pH.

3.1.4. Effect of initial pH

It is well documented that pH of the biosorption medium is an important parameter affecting the uptake of heavy metals from aqueous solutions by biosorbent. Fig. 4 summarizes the removal of Cu(II), Ni(II) and Zn(II) by MOSB from aqueous solutions as a function of pH. It is observed that the biosorption of the metal ions Cu(II) and Zn(II) increased dramatically with increase in initial solution pH, reaching an optimum value at 3.5, i.e. sorption capacity then tends to level off. The increase in biosorbed for Ni(II) is more gentle initially and begins to increase sharply at pH 5 reaching maximum at pH 7 (this trend is not so obvious in Fig. 4 unless the Ni(II) data is plotted alone). The lower removal of the studied metal ions at below optimum pH values can be attributed to the effective competition between higher concentration of H^+ or H_3O^+ and metal ions present in the form of M^{2+} or $M(OH)^+$ according to their speciation diagrams [21]. From these results, the MOSB is effective in removing metal ions in wide pH range. The results have shown that the powder of the MO seeds keeps its adsorption power at neutral pH (i.e. pH 7). The elimination of the pH adjusting step for the adsorption process on a large scale is favorable because it simplifies the process and results total costs. Previous studies have shown that the main component for water treatment in the MO seeds is protein whose isoelectric point is about pH 10 and the properties such as fluorescence [22], circular dichroism [23] and zeta potential [24] are independent of pH in the range 4–9. Based on these results and FTIR data reported, it is not surprising that the MOSB is effective in such a wide pH range.

3.2. Metal removal by the ligand

The extraction efficiency for the metal ions Cd(II), Cu(II), Pb(II), Ni(II) and Mn(II) was done with an inorganic ligand (1,4-bis[N,N-bis(2-picoyl)amino]butane). The results are shown in Fig. 5, the general trend of the heavy metal ions uptake by the ligand followed decreased in the order Mn(II) > Cd(II) > Cu(II) > Ni(II) > Pb(II). This was found to be the reverse of the trend for MOSB. The ligand was found to be more effective in metal uptake at the most alkaline

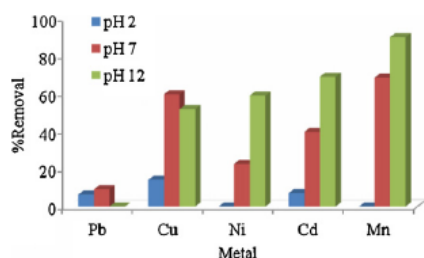


Fig. 5. Effect of ligand in removal of metals at different pH.

pH (i.e. pH 12) for Cd(II), Mn(II) and Ni(II) and whereas pH 7 (neutral pH) was effective for Cu(II) and Pb(II). Metal ions removal followed the decreasing orders Mn > Cd > Ni > Cu > Pb at pH 12 and Mn(II) > Cu(II) > Cd(II) > Ni(II) > Pb(II) at pH 7. At pH 2 (acidic pH), the % metal removal was higher for Cu(II), Pb(II) and Cd(II) and lower for Ni(II) and Mn(II) metal ions.

Generally, the extraction efficiency was inversely proportional to the sizes of the metal ions (from largest to smallest) Pb(II) > Cd(II) > Cu(II) > Ni(II) > Mn(II). That is, the ligand's efficiency in metal removal increased with the decrease in ionic metal size, and decreased with increase in size, e.g. Mn(II) is the smallest metal ion of all the metals studied in this report and Pb(II) being the largest, therefore Mn(II) was highly removed from water than all the metals and Pb(II) was the least removed metal. The reason for this order might be that the smaller the metal ion, the tighter it is bound to the ligand since there is shorter nucleic distance therefore there will be more attraction as compared to larger metal ions. The series for heavy metal removal by the ligand was the reverse order of the removal by extraction by shaking for MO seeds. The order was found to be Mn(II) > Cu(II) > Cd(II) > Ni(II) > Pb(II).

4. Conclusions

The present work explored a new cheaper, economical and selective biosorbent from MO seeds as an alternative to costly adsorbents for the removal heavy metal ions. The main advantages include its low cost (inexpensive), effective, rapid attainment phase equilibration, wide effective pH range and capability to adsorb a mixture of metal ions without being affecting the sorption effectiveness (i.e. no reduction in sorption capacity as result of competitive). The sorption process has been shown to be affected from experimental conditions such as initial metal concentration, pH, contact time and particle size. FTIR analysis of the MOSB showed the presence of various functional groups indicating the complex nature and capability of the biosorbent. The metal removal by MOSB was compared to that of a synthesized inorganic ligand. The work has also demonstrated that the biosorbent and ligand differ in the type of metal ions they are effective in removing in water. This means that using a composite adsorbent of MOSB and ligand may result in more effective material capable of removing a wider range of heavy metals from environmental and industrial wastewater samples.

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References

- [1] A.L. Hinwood, M.R. Sim, D. Jolley, N. de Klerk, E.B. Bastone, J. Gerostamoulos, *Environ. Geochem. Health* 26 (2004) 27–36.
- [2] I. Thornton, D.J.A. Davies, J.M. Watt, M.J. Quinn, *Environ. Health Perspect.* 89 (1990) 55–60.
- [3] P.X. Sheng, Y.-P. Ting, J.P. Chen, L. Hong, *J. Colloid Interface Sci.* 275 (2004) 131–141.
- [4] S. Oshima, N. Hirayama, K. Kubono, H. Kokusen, T. Hunjo, *Anal. Sci.* 18 (2002) 1351–1355.
- [5] A. Svenson, L. Kaj, H. Bjorndal, *Chemosphere* 18 (1989) 1805–1808.
- [6] A. Hong, T.C. Chen, E. Macauley, *Can. J. Civil Eng.* 22 (1995) 1185–1197.
- [7] Y. Kamykova, A.-M. Strömval, B.-M. Steenari, *J. Hazard. Mater.* 152 (2007) 885–891.
- [8] B. Matuschka, G. Strauba, *J. Chem. Technol. Biotechnol.* 37 (1993) 412–417.
- [9] R. Cibulka, F. Hampel, J. Smidrkal, F. Liska, *Tetrahedron Lett.* 40 (1999) 6849–6852.
- [10] E. Lachowicz, B. Rozanska, F. Teixidor, H. Meliani, M. Barboiu, N. Hovnanian, *J. Membr. Sci.* 210 (2002) 279–290.
- [11] N. Hirayama, N. Ichitani, K. Kubono, Y. Mastuoka, H. Kokusena, T. Honjo, *Talanta* 44 (1997) 2019–2025.

- [12] M.G.B Drew, M.R.St.J. Foreman, A. Geist, M.J. Hudson, F. Marken, V. Norman, M. Weigl, *Polyhedron* 25 (2006) 888–900.
- [13] H.-S. Wang, W. Shi, B. Zhai, J.-G. Ma, J. Xia, P. Cheng, *J. Mol. Struct.* 833 (2007) 102–107.
- [14] A. Olsen, *Water Res.* 21 (1987) 517–522.
- [15] S.A. Muyibi, L.M. Evison, *Water Res.* 29 (1995) 1099–1105.
- [16] J. Beltrán-Heredia, J. Sánchez-Martín, *J. Hazard. Mater.* 164 (2009) 713–719.
- [17] M. Helen Kalavathy, L.R. Miranda, *Chem. Eng. J.* 158 (2010) 188–199.
- [18] B.B. Marvey, Y. Gultneh, R. Butcher, *Int. J. Mol. Sci.* 7 (2006) 179–185.
- [19] P. Sharma, P. Kumari, M.M. Srivastava, S. Srivastava, *Bioresour. Technol.* 97 (2006) 299–305.
- [20] T. Akar, S. Tunali, I. Kiran, *Biochem. Eng. J.* 25 (2005) 227–235.
- [21] M.M. Rao, D.K. Ramana, K. Seshiah, M.C. Wang, S.W.C. Chien, *J. Hazard. Mater.* 166 (2009) 1006–1013.
- [22] H.M. Kwaambwa, R. Maikokera, *Colloids Surf. B J.* 60 (2007) 213–220.
- [23] H.M. Kwaambwa, R. Maikokera, *Colloids Surf. B J.* 64 (2008) 118–125.
- [24] H.M. Kwaambwa, A.R. Rennie, *Biopolymers* (2012), doi:10.1002/bip.22014.