Ph Dependence Of Sorption Of Cd2+, Zn2+, Cu2+ And Cr3+ On Crude Water And Sodium Chloride Extracts Of *Moringa Stenopetala* And *Moringa Oleifera*

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pH dependence of sorption of Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+} on crude water and sodium chloride extracts of *Moringa stenopetala* and *Moringa oleifera*

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The ability of crude water and sodium chloride extracts of partially defatted powder of *Moringa stenopetala* (MS) and *Moringa oleifera* (MO) to remove heavy metals (Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+}) from single ion solution was investigated. 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. Cu2+ sorption increases slightly with pH to about 60% for MS at pH 6 and then becomes constant up to pH 8 when sorption rises to completion. Preliminary characterization of the actual powder by proton nuclear magnetic resonance showed clear presence of amide (-CO-N-H), benzenoid (Ar-H), saturated alkyl and unsaturated fragments in both MS and MO. The mass spectrum showed the presence of amino ($R-NH_2$) fragments. The remarkable heavy metal sorption ability of *M. stenopetala* and *M. oleifera* could thus be attributable to, among other mechanisms, coordination or complex formation between the metal cations and pH dependent oxygen and nitrogen anionic sites of the Moringa proteins.

Key words:*Moringa stenopetala*, *Moringa oleifera*, heavy metals, sorption, water.

INTRODUCTION

As part of our work on heavy metal remediation in contaminated water using locally available low cost effective methods (Sajidu et al., 2005a; Mataka et al., 2006), the present study explores heavy metal sorption property of crude water and sodium chloride extracts of *Moringa oleifera* and *Moringa stenopetala* seed powder. The metals studied are cadmium, zinc, copper and chromium. Cadmium is one of the most toxic heavy metals without any known biological function. Zinc and copper, which are essential nutrients for plants and animals, can be toxic at very high concentrations. Chromium occurs in two redox states, Cr(III) and Cr(VI) with the former occurring as a cation and the later as an anion (chromate). Cr(III) is less toxic than Cr(VI). Because of the toxicities of cadmium and chromium the World Health Organization's maximum contaminant levels in drinking water are 0.003 mg/L and 0.05 mg/L respectively (WHO, 2004).

However, levels of up to 0.015 mg/L and 0.48 mg/L have been detected in streams of Blantyre city in Malawi (Sajidu et al, 2005b). Methods traditionally employed for water remediation consist of heavy metal removal by chemical coagulation using aluminium and ferric salts (Fatoki and Ogunfowokan, 2002) and cationic surfactants (Evans, 2003); physical precipitation using ion exchange and sorbents (Singh et al., 2001); and phytoremediation that includes rhizofiltration, phytostabilisation, phytoextraction (Lyte et al., 1998; Lambert et al., 2003). However, because of the high costs of these methods it is necessary to develop a more cost effective remediation system particularly in developing countries such as Malawi. More

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over, research findings clearly report the serious drawbacks such as Alzheimer's disease, carcinogenic effects and health problems associated with aluminum sulphate, polyaluminum chloride, polyaluminum sulphate, iron hydroxide, iron chloride, soda ash and synthetic polymers used in water treatment.

Use of natural coagulants for treatment of water and wastewater in developing countries is an area that is gaining interest. Tropical plants of the family of *Moringacea*e, are amongst some of the natural coagulants that have been studied for clarification of turbid water. *M. oleifera* is the most widely distributed, well-known and studied species of the family *Moringaceae* because of its previous economic importance as a source of the commercially important 'Ben oil' and more recently, as a multipurpose tree for arid lands and a source of water purifying agents for developing countries (Morton, 1991). *M. oleifera* is native to sub-Himalayan North-Western India and Pakistan but the plant was distributed to other areas of tropical Asia in prehistoric times and to other parts of the world including Malawi during the British colonial era. *M. stenopetala*, often referred to as the African Moringa tree, originates from southern Ethiopia and Kenya (Jahn, 1991). The food, fodder, water clarifying and medicinal uses of the *Moringacea*e, especially oleifera are well documented and the trees are recommended for live fencing, inter-cropping, and pollution control (Morton, 1991; Moges, 2004; Coote et al., 1997; Pratt et al., 2002; Williamson, 1975; Palgrave, 1983).

The water-soluble *Moringa* seed proteins possess coagulating properties similar to those of alum and synthetic cationic polymers. The use of *Moringa* species for water clarification is a part of African indigenous knowledge. Jahn (1981) first studied and confirmed the coagulating properties of *Moringa* seeds after observing women in Sudan use the seeds to clarify the turbid Nile waters. *M. stenopetala* is less widely distributed than M. oleifera but stenopetala is reportedly more resistant to insect pests than other members of the family and its seeds are larger and easier to process than those of oleifera (Kayambazinthu, D., Forestry Research Institute of Malawi, personal communication). Although the water clarifying properties of *M. stenopetala* have not been as extensively studied as those of *M. oleifera*, Jahn (1986) reported that 100-150 mg/L of *M. stenopetala* was as effective in water clarification as 200 mg/L of *M. oleifera* which indicates that stenopetala is more effective than oleifera. The mechanism of coagulation by *Moringa* is not well understood and different authors have attributed it to existence of proteins and non-protein flocculating agents (Ndabigengesere et al., 1995; Gassenschmidt et al., 1994, Okuda et al., 2001).

Although a number of papers are found on the water clarification properties of *Moringa*, only a few deal with heavy metal removal potential of *Moringa*. Metal ion removal ranging from 70 to 89% for lead, 66 to 92% for iron and 44 to 47% for cadmium using *M. oleifera* seed kernels and ram press cakes with initial metal concentration of 7 ppm and sorbent dose of 120 mg/L has been reported by our group (Sajidu et al., 2005a). Kumari et al. (2006) studied the removal and recovery of arsenic from aqueous system using shelled *M. oleifera*. The study revealed removal capacities of 60.21% As^{3+} and 85.6% As^{5+} at a biomass dosage of 2.0 g in 200 ml of 25 mg/L of the metal. Sharma et al. (2006) reported favourable performance of biosorption of Cd^{2+}, Cr^{3+} and Ni^{2+} on shelled M. oleifera seeds. Our group has reported that *M. stenopetala* is better than *M. oleifera* at removing lead from contaminated water (Mataka et al., 2006). Lead removal of 96% from initial concentration of 7 mg/L at a dosage of 2.4 g of seed powder in 100 ml of the metal solution had been reported. In continuation of the work, the present investigation reports the pH dependence of sorption of Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{2+} cations on crude water and sodium chloride extracts of *M. stenopetala* and *M. oleifera*.

MATERIALS AND METHODS

Moringa seeds collection

Dry *M. oleifera* seeds were collected from naturally growing plants in villages around Chikwawa Boma in Southern Malawi. Dry *M. stenopetala* seeds were purchased from Whizpop Products Ltd, Nairobi in Kenya. The seeds were stored at room temperature. The seeds were deshelled by hand just before extraction of the coagulant. The deshelled seeds were washed in distilled water to remove any dirt, dried in air and then powdered using mortar and pestle. Partial defatting was done by mixing the powder in 95% ethanol (10% w/v) and shaking for 30 min. The solids were separated by centrifugation and dried at room temperature. Coagulant extraction was done by mixing the dried defatted powder with distilled water and 0.6 M NaCl at 5% (w/v) solutions. The solutions were stirred for 30 min and filtered, first, through Munktell filter paper No. 3 and then membrane filter No. 47 mm. The filtrates are termed crude extracts abbreviated as MOC-DW, MOC-SC, MSC-DW and MSC-SC for the *M. oleifera* crude extracts of distilled water, salt, *M. stenopetala* crude extracts of distilled water and salt, respectively.

Metal solution preparation

Cd^{2+} was prepared from analytical grade reagent $Cd(NO_3)_2.4H_2O$ (declared impurity of less than 1%) (BDH) to give a stock concentration of 0.6 mM (67.44 ppm). Cu^{2+} and Zn^{2+} were prepared from analytical grade reagent $Cu(NO_3)_2.3H_2O$ (declared impurity of less than 0.5%) (MERCK) and Zn(NO3)2.6H_2O (declared impurity of less than 0.2%) (Mallinckrodt Chemical Works) at a stock concentration of 1.25 mM (78.44 and 81.74 ppm respectively). Cr^3+ of 2.10 mM (109.2 ppm) was prepared by dilution of a 1.4 M stock solution of $Cr(ClO_4)_3.6H_2O$.

pH profile studies for Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+} binding

9.0 ml of 0.1 M $NaNO_3$ was pipetted into each of 10 centrifuge tubes. An appropriate amount of acid (20 mM HNO_3) or base (20 mM NaOH) was added to give a specified pH (pHinitial). 1.0 ml of the Moringa crude extract (MOC-DW, MOC-SC, MSC-DW or MSC-SC) and 0.5 mL of stock metal solution were added into each of the centrifuge tube. The solution mixtures were shaken for 48 h and then centrifuged for 15 min at 3000 rpm using KUBOTA KS-5200C centrifuge. About 4 ml of the supernatant was taken, acidified with a drop of concentrated nitric acid and analyzed for the given metal concentration on an atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100). The pH in the remaining supernatant in the centrifuge tubes was recorded as the equilibrium solution pH (pHequil). Percentage metal uptake (%E) was calculated by use of equation (1)

$$\%E = \frac{(C_o - C)x100}{C_o} \qquad (1)$$

Where C_o and C are the initial and final concentrations respectively of the metal ions in solution. Plots of % metal bound for a given metal and Moringa extract were made in order to study the pH dependence of the metal sorption reaction by the extract.

Seed powder characterization

In order to have an idea of available functional groups in the Moringa extracts, proton nuclear magnetic resonance data (^{1}H-NMR) of both MS and MO powder were recorded in a Bruker spectrometer DRX-400 operating at 400 MHz. About 10 mg of the powder was dissolved in 1 ml of D_2O and filtered to remove any undissolved suspending solids before running the NMR experiment.

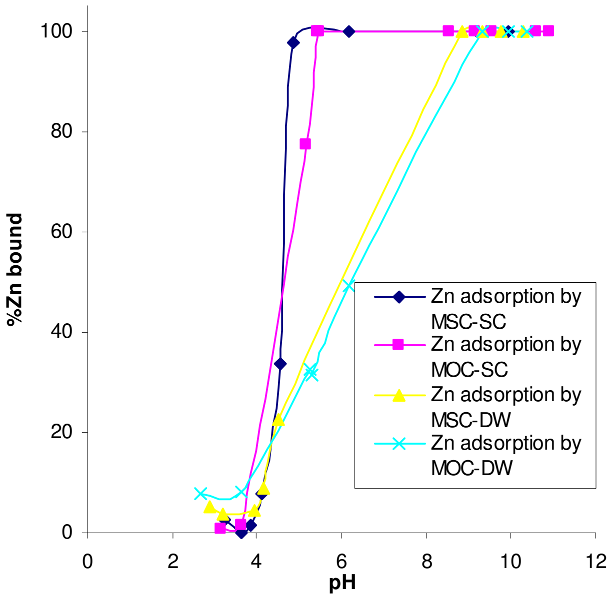

Figure 1. Effect of pH on the binding of Zn^{2+} by different *Moringa* crude extracts.

RESULTS AND DISCUSSION

Figures 1, 2, 3 and 4 show the binding of Zn^{2+}, Cd^{2+}, Cr^{3+} and Cu^{2+} respectively to different forms of Moringa crude extracts as a function of pH. In general, metal binding increased with increasing pH. Most of Zn binding by NaCl extracts of both M. stenopetala and *M. oleifera* occurred within a narrow pH range of 4 and 4.5 while Zn binding by the water extracts occurred between pH 4 and 7. Cd binding was observed to start at a high pH value of 6 with most of it occurring between pH 6 and 8. Cr binding mostly occurred between pH 3 and 5 with *M. stenopetala* extract showing better binding capacity at each pH value

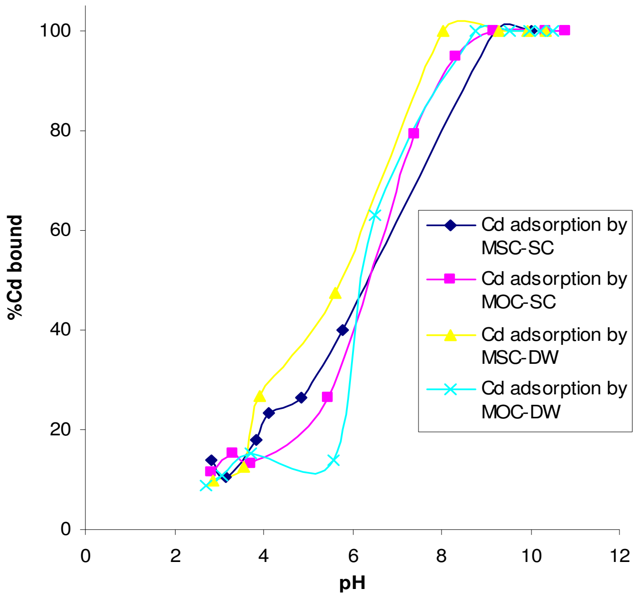

Figure 2. Effect of pH on the binding of Cd^{2+} by different *Moringa* crude extracts.

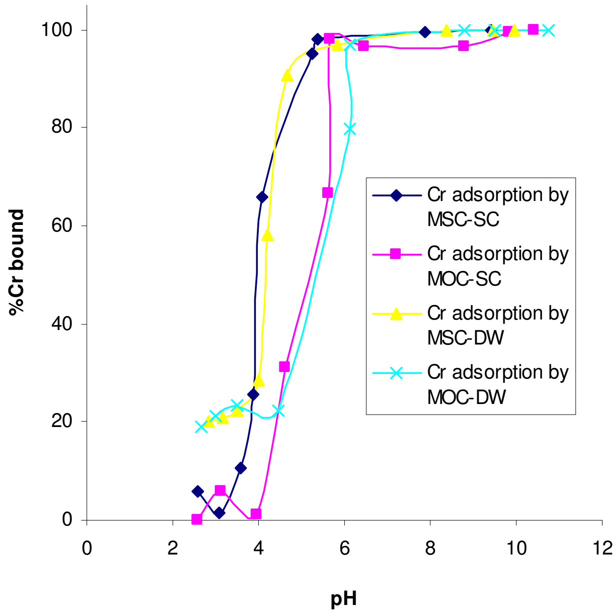

Figure 3. Effect of pH on the binding of Cr^{3+} by different *Moringa* crude extracts.

Table 1. pH values of the metal-MSC-SC mixture at the beginning of reaction ($pH_{initial}$) and at equilibrium (pH_{equil}) indicating the general pH decrease.

pH values in the MSC-SC metal systems							
Zn^{2+}		Cd^{2+}		Cr^{3+}		Cu^{2+}	
$pH_{initial}$	$pH_{equil.}$	$pH_{initial}$	$pH_{equil.}$	$pH_{initial}$	$pH_{equil.}$	$pH_{initial}$	$pH_{equil.}$
2.98	3.23	2.86	2.81	2.58	2.57	2.74	2.73
3.69	3.65	3.21	3.17	3.10	3.07	3.16	3.14
4.49	3.87	3.70	3.61	3.66	3.57	3.56	3.52
4.97	3.96	4.27	3.82	4.32	3.79	4.35	3.76
6.42	4.11	5.13	3.94	5.14	3.89	5.27	3.88
7.16	4.54	6.40	4.12	6.40	4.08	6.30	4.08
8.24	4.86	7.47	4.86	7.42	5.25	6.65	4.54
8.82	6.16	8.19	5.79	7.92	5.36	8.16	5.27
10.15	9.18	10.11	9.23	9.22	7.87	9.62	7.70
10.83	9.96	10.70	10.00	10.16	9.43	10.08	9.25

Table 2. pH values of the metal-MOC-SC mixture at the beginning of reaction ($pH_{initial}$) and at equilibrium (pH_{equil}) indicating the general pH decrease.

pH values in the MOC-SC metal systems							
Zn^{2+}		Cd^{2+}		Cr^{3+}		Cu^{2+}	
$pH_{initial}$	$pH_{equil.}$	$pH_{initial}$	$pH_{equil.}$	$pH_{initial}$	$pH_{equil.}$	$pH_{initial}$	$pH_{equil.}$
3.19	3.16	2.85	2.82	2.63	2.58	2.69	2.81
3.63	3.64	3.30	3.31	3.14	3.11	3.25	3.25
5.23	5.15	3.74	3.72	3.97	3.96	4.12	4.06
6.25	5.41	5.48	5.49	5.08	4.63	5.09	4.88
8.17	5.49	6.66	5.46	6.00	5.62	6.14	5.26
9.14	8.54	8.17	7.39	7.51	5.66	7.57	5.65
9.81	9.17	8.81	8.31	7.98	6.47	8.47	7.20
10.13	9.54	9.66	9.17	9.32	8.81	9.03	8.41
10.98	10.58	10.75	10.35	10.29	9.85	9.80	8.92
11.13	10.90	11.04	10.80	10.88	10.41	10.22	9.76

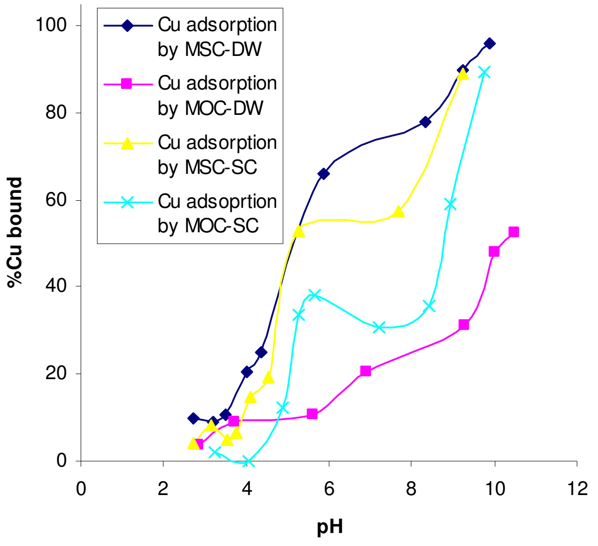

Figure 4. Effect of pH on the binding of Cu^{2+} by different *Moringa* crude extracts.

than the extracts of *M. oleifera.* It was also observed that Cr binding (about 20%) by water extracts of both *M. stenopetala* and *M. oleifera* also occurred at pH values below 3. The binding of Cu by all extracts was interesting.

In all cases some binding occurred between pH 4 and 6 and then no binding occurred until pH increased to above 8 when MSC-DW, MSC-SC and MOC-SC sorption of Cu increased to over 80% while that of MOC-DW still remained low. The uptake of the metal ions was accompanied by a decrease in the pH of the metal-extract mixture as shown in Tables 1 and 2, particularly at pH ranges where metal binding was observed. This is a general trend in metal ion uptake by most biomasses (Igwe et al., 2005). It suggests a mechanism of metal uptake which involves exchange of hydrogen ion at the substrate by the metal ion. Such an exchange reaction would therefore be influenced by the relative concentration of the exchangeable hydrogen ion on the substrate and the hydrogen ion concentration (as measured by pH) in the medium. The higher the concentration of hydrogen ion in the medium (lower pH) the more difficult it is for deprotonation of the substrate; consequently there would be insignificant binding of the metal.

Preliminary characterization of the actual powder by 1H-NMR gave chemical shifts at 1.2, 1.3, 1.9, 2.8, 4.8, 5.2, 5.4, 5.5 7.1 and 7.4 ppm indicating presence of amide (-CO-N-H), benzenoid (Ar-H), amino ($R-NH_2$), saturated and unsaturated alkyl fragments in both MS and MO. A singlet chemical shift at 1.5 ppm in MS which could be due to sulfhydryl (R-SH) fragment was observed. A forest of peaks between chemical shift 3.2 and 4.2 ppm was observed of which it was not easy to assign any molecular fragments to. This explains why MS showed slightly better metal sorption capacity (save in Cd^{2+}) than MO at most pH values. The remarkable heavy metal sorption ability of *M. stenopetala* and *M. oleifera* could thus be attributable to, among other mechanisms, coordination or complex formation between the metal cations and pH dependent oxygen and nitrogen anionic sites of the Moringa proteins or free amino acids. However, further studies need to be taken in order to elucidate the actual mechanisms. This pH metal binding dependence of the Moringa extracts also suggests that the bound metals can be recovered by lowering the pH (reversing the reaction) of the medium.

It can therefore be concluded that water and sodium chloride crude extracts of *M. stenopetala* and *M. oleifera* can successfully be used to remove cadmium (Cd^{2+}), chromium (Cr^{3+}), zinc (Zn^{2+}) and copper (Cu^{2+}). The removal of the metals is pH dependent with each metal having a characteristic pH range within which it is mostly removed. Reduction of pH in the systems suggests that hydrogen ion-metal cation exchange mechanism governs the metal removal process although at very high pH values metal hydroxide precipitation may also be involved.

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REFERENCES

Coote C, Bonongwe C, Stewart M (1997). The distribution, uses and potential of development of *Moringa oleifera* in Malawi. Forestry Research Record No.67. Forest Research Institute of Malawi, Zomba

Evans CV (2003). Removal of heavy metals and radionuclides from soils using cationic surfactant flushing. University of Wisconsin Water Resources Institute. pp.???

Fatoki OS, Ogunfowokan AO (2002). Effect of coagulant treatment on the metal composition of raw water. Water South Africa 28 (3): 293-298.

Gassenschmidt U, Jany DK, Tauscher NH (1994). Isolation and characterisation of a flocculating protein from *Moringa oleifera* Lam. Biochemica et Biophysica Acta Vol. 1243: 477-481.

Igwe JC, Nwokennaya EC, Abia AA (2005). The role of pH in heavy metal detoxification by bio-sorption from aqueous solutions containing chelating agents. Afr. J. Biotechnol. Vol. 4(10): 1109-112.

Jahn SA (1981). Traditional water purification in tropical and developing countries Existing methods and potential application. Publ 117. Deutsche Gesellschaft fur Technische Zusammenarbeit (GTZ) GmbH, Eschborn

Jahn SA (1986). Proper use of Natural coagulants for rural water supplies: Research in the Sudan and a guide for new projects. Deutsche Gesellschaft fur Technische Zusammenarbeit (GTZ) GmbH, Eschborn.

Jahn SA (1991). The Traditional Domestication of a multipurpose tree *Moringa stenopetala* (Bak. f.) Cuf. In the Ethiopian Rift Valley. Ambio Vol. 20: 244-247.

Kumari P, Sharma P, Srivastava S, Srivastava MM (2006). Biosorption studies on shelled Moringa oleifera Lamarck seed powder: Removal and recovery of arsenic from aqueous system. Int. J. Miner. Process. Vol. 78: 131-139.

Lambert M, Leven B, Green R (2003). New methods of cleaning up heavy metal in soils and water innovative solutions to an environmental problem http://www.envirotools.org/ 17/07/05.

Lyte CM, Lytle WF, Yang N, Quian J, Hansen B, Zayed A, Terry N (1998). Reduction of Cr(IV) to Cr(III) by wetland plants: Potential for situ heavy metal detoxification. Environ. Sci. Technol. Vol. 32: 3087-3093.

Mataka L, Henry EMT, Masamba WRL, Sajidu SM (2006). Lead remediation of contaminated water using *Moringa stenopetala* and *Moringa oleifera* seed powder. International Journal of Environmental Science and Technology (in press).

Moges Y (2004). Recommended agroforestry/multipurpose trees for Borana lowlands/midlands and their production techniques. Subreport No.4: FARM Africa/SOS Sahel, Tropical forestry.

Morton JF (1991). The Horseradish tree, *Moringa Pterygosperma* (Moringacae) – A Boon to Arid Lands. Econ. Bot. Vol. 45: 318-333.

Ndabigengesere A, Narasiah KS, Talbot GB (1995). Active agents and mechanism of coagulation of turbid waters using *Moringa oleifera*. Water Res. Vol 29: 703-710.

Okuda T, Baes AU, Nishijima W, Okada M (2001). Coagulation mechanism of salt solution-extracted active component in Moringa oleifera seeds. Water Res. Vol. 35: 830-834.

Palgrave KC (1983). Trees of southern Africa. Struik Publishers (Pty), Capetown.

Pratt JH, Henry EMT, Mbeza HF, Mlaka E, Satali LB (2002). Malawi Agroforestyry Extension Project Marketing & Enterprise Program Main Report Malawi Agroforestry Publication No.47.

Sajidu SM, Henry EMT, Kwamdera G, Mataka L (2005a). Removal of lead, iron and cadmium ions by means of polyelectrolytes of *Moringa Oleifera* whole seed kernel. WIT Trans. Ecol. Environ. Vol. 80: 251-258.

Sajidu SMI, Henry EMT, Masamba WRL (2005b). Review of heavy metal pollution in Malawi, Environmental Long-Term Observatories Network of Southern Africa – ELTOSA, 3rd ELTOSA Conference, 28 August- 1st September 2005, Mangochi, Malawi.

Sharma P, Kumari P, Srivastava MM, Srivastava S (2006). Ternary biosorption studies of Cd(II), Cr(III) and Ni(II) on shelled Moringa oleifera seeds. Bioresource Technology, In press.

Singh SP, Ma LQ, Harris WG (2001). Heavy metal interactions with phosphatic clay: sorption and desorption behaviour. J. Environ. Qual. Vol. 30: 1961-1968.

Williamson J (1975). Useful plants of Malawi. University of Malawi. Zomba.

WHO (World Health Organization),(2004). Guidelines for drinking water quality. 3rd Edition, Vol. 1, Recommendations, WHO: Geneva.