Research Article

Use of *Moringa oleifera* (Moringa) Seed Pods and *Sclerocarya birrea* (Morula) Nut Shells for Removal of Heavy Metals from Wastewater and Borehole Water

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Use of nonedible seed pods of *Moringa oleifera* (Moringa) tree and nutshells of *Sclerocarya birrea* (Morula) tree for removal of selected metal ions (lead, cadmium, copper, manganese, iron, zinc, and magnesium) from wastewater and borehole water samples was investigated. Removal parameters such as contact time, pH, temperature, particle size, sorbent dose, and initial metal concentration were optimized. Determination of residual metal ions after employing sorbent was done using flame atomic absorption spectroscopy (FAAS). Using 200 ng synthetic metal ion mixture in 50 mL of water sample, the optimized parameters for Moringa seed pods were 60 min contact time, 1.0 g of sorbent dose, pH 8, 100 μm sorbent particle size, and extraction temp 35°C. While using Morula nutshells, the optimized conditions were 120 min contact time, 2.0 g sorbent dose, pH 8, 100 μm sorbent particle size, and extraction temp of 35°C. The removal efficiency of acid treated sorbents was compared to that of untreated sorbents and it was found to be higher for acid treated sorbents. These nonedible plant parts for Morula and Moringa plants are proposed as a cheap, simple, and an effective alternative for purification of water contaminated with heavy metals.

1. Introduction

Demands on water resources for households, commercial, industrial, and agricultural activities are increasing on daily basis. Agriculture and domestic sectors account for more than 70% of global freshwater withdrawals [1]. Wastewater resulting from homes and industries is often discharged into rivers after treatment. Recycling and reuse of wastewater can be a supplementary source to already existing water sources, especially in arid and semiarid regions where water is scarce. Municipal wastewater comes mainly from sewage treatment plants, which may contain pathogens and potentially toxic elements and organic compounds. Before discharge into rivers, removal of most pollutants can be achieved by treatment technologies such as screening, primary treatment, and secondary and tertiary treatment in wastewater treatment plants. Despite the usage of treated wastewater in several parts of the world, the safety and quality of wastewater reuse still remain a problem [2]. Trace inorganic compounds such

as heavy metals could be present in treated water due to treatment failure or inability to remove them [3]. Besides occurring naturally, heavy metals may leach from industrial and consumer waste into the groundwater. Therefore, there is a high probability that the water discharged to the rivers after treatment in oxidation ponds and potable and ground water as well could contain heavy metals not benign to the environment.

Therefore, the biggest predicament is to optimize the benefits of wastewater as water sources and the nutrients it contains while minimizing negative impacts on human health. Fu and Wang [4] reported that the trend in heavy metals pollution in the ecosystem was increasing consistently throughout the world especially among developing countries. Hence, there is a need to come up with a way of purifying water, which is effective and also cost effective even at very low metal concentrations. Removal of heavy metals from wastewaters has been achieved through chemical precipitation [4, 5], ion exchange [6, 7], ion flotation [8, 9],

TABLE 1: Metal concentration (mgg^{-1}) in Moringa seed pods and Morula nut shells.

| | Concentration of metal (mgg^{-1}) and ± standard deviation | | | | | | |
	Pb	Cu	Cd	Fe	Zn	Mn	Mg
Moringa seed pods	0.018 ± 0.002	0.012 ± 0.009	Not detected	0.111 ± 0.026	0.036 ± 0.015	0.047 ± 0.007	2.578 ± 0.041
Morula nut shells	0.015 ± 0.004	0.012 ± 0.005	Not detected	0.088 ± 0.031	0.026 ± 0.033	0.029 ± 0.007	2.274 ± 0.006

adsorption [5, 10–12], reverse osmosis [13–17], and membrane filtration [8–10, 18]. Although these conventional methods have higher capacity for the removal of toxic heavy metals, their utilization may require several pretreatments as well as additional treatments, thereby incurring high installation and operating cost [19, 20]. Due to these challenges, there is need for safer, economical, and effective ways for elimination of heavy metals from waters.

Recently, use of low cost sorbents has focused attention on use of biological materials as a considerable potential solution for removal and recovery of pollutants from industrial effluents [21–27]. These materials have the following advantages: they (i) are readily available, (ii) require little or no processing, (iii) possess good adsorption capacity even for low-level metal concentrations, (iv) have got selective adsorption for heavy metal ions, and (v) can be easily regenerated [28–30]. Such materials include use of plant parts from indigenous trees like *Moringa Oleifera* and *Sclerocarya birrea*. These tropical multipurpose trees can be easily cultivated and adaptable in semiarid climates; hence, they can be beneficial to developing world. Most parts of these trees are edible and very beneficial to human beings and have a lot of applications. Essential oils and essential minerals are extracted from Morula kernel [31] while Moringa biomass has been used as coagulant agent in water purification [32], for heavy metal removal [33] and removal of organic pollutants from aqueous solutions [34]. However, some parts of these trees that are not edible are normally considered as waste material and often thrown away: for example, seed pods from Moringa and nut shells from Morula. However, limited work has been done on the application of *Moringa oleifera* seed pods (MSP) and *Sclerocarya birrea* nut shells (MNS) since these parts are often taken to be useless.

The work reported here seeks to explore the unexploited property of Moringa seed pod (MSP) and Morula nut shells (MNS) as a bioremedial approach for removal of metals (copper, zinc, lead, manganese, cadmium, magnesium, and iron) from wastewater and borehole water. The removal efficiency of the two materials is compared. Metal removal by employing acid treated MSP and MNS sorbents was also investigated.

2. Materials and Methods

2.1. Materials. All reagents were of analytical grade. Acids were used for digesting and adjusting pH. HNO$_3$ (69%, Skylabs), HCl (32%), Minema Chemicals, and double deionized water (Millipore-Q Millipore 18.2 MΩ/cm resistivity) were also used for dilutions of samples to be analyzed with FAAS. Elemental standards solutions used for calibration were prepared from 1000 ppm of stock solutions supplied by Minema Chemicals (Pb and Fe), Merck Pty Ltd. (Cu, Mn, Mg, and Zn), and Sumitomo Metal Mining Instruments (pty) Ltd, (Cd). NaOH (≥97.0%, Rochelle Chemicals) was used to adjust pH, (Hanna Instruments HI 991001 pH); orbital shaker (Scigenics), agate pestle, and mortar were also used for reducing the particles further. 100 μm, 200 μm, and 500 μm stainless steel sieves were used for sieving the sorbents. The filter papers used were ashless Whatman filter paper number 1 from England. The filter papers were used to filter the mixtures of sorbents and solution.

2.2. Preparation and Characterization of MSP and MNS. The *Moringa oleifera* (Moringa) seed pods (deseeded) and *Sclerocarya birrea* (Morula) nut shells were obtained from various sampling points in Artesia, Botswana. Dried Moringa seed pods (MSP) and Morula nut shells (MNS) were washed with double deionized water, further dried in an oven at 65°C for 24 hrs. The dried samples were ground and then sieved to different mesh sizes (100, 200, and 500 μm) and stored in glass bottles until further analysis. The MNS and MSP powder were also characterized by Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope (SEM) as described in Section 2.5.

2.3. Determination of Metal Concentration in Sorbent Material. About 2 g of each ground sorbent was weighed and then digested with an aqua regia solution of HCl : HNO$_3$ in a ratio of 3 : 1 v/v. Each mixture was placed in 100 mL conical flasks and heated at 85°C until the volume was reduced to 1 mL. The resulting volume was filtered using a Whatman number 1 filter paper and put into 50 mL volumetric flasks. Deionized water was added to the flasks and filled up to the mark. The samples were analyzed using FAAS following a modified method [35]. Table 1 reflects the concentration of the selected metals.

2.4. Acid Treatment of MSP and MNS Sorbents. 15 g of each sorbent was weighed and put in a conical flask, 200 mL of 0.1 M HNO$_3$ was added, and the mixture was soaked for 24 hrs. The mixture was then filtered and the sorbent was washed several times with deionized water until the pH of the sorbent was neutral (around pH 7). The sorbent was then dried in an oven at 50°C overnight and then put in glass bottle until further use.

Using the optimized sorption parameters (Section 2.6), the ability to remove heavy metals from waste water samples by the acid treated and untreated sorbents were compared.

TABLE 2: Concentration (mgL^{-1}) of selected metals in water samples.

| | Average concentration (mgL^{-1}) of selected metals in water samples and ± standard deviations. | | | | | | |
	Fe	Zn	Cu	Cd	Pb	Mn	Mg
Inlet	1.361 ± 0.020	0.251 ± 0.010	0.086 ± 0.005	0.013 ± 0.001	0.285 ± 0.021	0.309 ± 0.001	12.867 ± 0.009
Primary	1.074 ± 0.023	0.206 ± 0.012	0.078 ± 0.001	0.013 ± 0.001	0.245 ± 0.007	0.304 ± 0.001	11.596 ± 0.003
Secondary	0.288 ± 0.046	0.142 ± 0.063	0.029 ± 0.002	0.015 ± 0.001	0.230 ± 0.042	0.222 ± 0.001	13.487 ± 0.002
Aeration	2.432 ± 0.045	0.405 ± 0.087	0.127 ± 0.012	0.016 ± 0.001	0.390 ± 0.003	0.380 ± 0.001	13.478 ± 0.001
Effluent	0.255 ± 0.028	0.116 ± 0.018	0.028 ± 0.002	0.015 ± 0.001	0.265 ± 0.021	0.211 ± 0.005	13.671 ± 0.003
Borehole	0.334 ± 0.004	0.011 ± 0.002	0.012 ± 0.001	0.002 ± 0.001	0.113 ± 0.008	0.002 ± 0.000	1.288 ± 0.032

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

FTIR spectroscopy was used to characterize the sorbents to determine the functional groups responsible for metal removal. The FTIR spectra were recorded in the wavenumber range $400–4000\,cm^{-1}$ on a Perkin Elmer system 2000 FTIR. The sorbents were kept at ambient temperature. 1 mg seed powder per 200 mg of KBr was weighed. The powder was pressed into pellets by using a 15 ton hydraulic press. The data were collected at $2.0\,cm^{-1}$ resolution, and each spectrum was a result of 256 scans.

In order to observe the surface morphology of the sorbents, a Philips XL 30 ESEM model environmental scanning electron microscope (ESEM) was used.

2.6. *Biosorption of Heavy Metal Ions.* Batch experiments were used for the biosorption of Cd, Cu, Fe, Zn, Mg, Mn, and Pb. Stock solutions at various concentrations were prepared from $1000\,mgL^{-1}$ of each metal standard. Solution of known metal ion concentration was prepared and known amount of sorbent (MSP or MNS) was added. The mixture was shaken with a controlled orbital shaker and the concentrations of the unadsorbed metal ions in solutions were determined after separation of the sorbent by filtration using Whatman paper number1 filter papers. The effects of contact time (0–240 min), initial metal concentration ($1–20\,mgL^{-1}$), pH (2.0–10.0), sorbent dose ($0.5–2.5\,g$, in $50\,mL^{-1}$), particle size (100–$500\,\mu m$), and temperature (298–333 K) were studied as shown in Figure 1. Analysis and instrumentation were done using FAAS with air/acetylene. The amount of the metal adsorbed (% removal) by the sorbent was calculated using

$$\% \,Removal = \frac{C_i - C_f}{C_i} \times 100, \tag{1}$$

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

2.7. *Sampling and Storage of Water Samples.* Water samples were obtained from Gaborone waste water treatment plant, Gaborone, Botswana. At the treatment plant five sampling sites were identified (inlet point, primary settling, secondary settling point, aeration point, and effluent point). Grab sampling technique was employed to obtain the water samples from individual sampling sites. Each sample was put in labelled brown glass bottle and acidified to pH < 2 in order to prevent further microbial activity which could eventually affect the composition of metal in the sample. Also acidifying the samples ensured that all metals were dissolved.

The water samples were placed in the cold room at 4°C; this was to help immobilize any microbial activity or degradation of the sample. Samples were stored for seven days until analysis.

2.8. *Determination of Metal Concentration in the Wastewater and Borehole Samples.* 50 mL of waste water from inlet, primary, secondary, aeration, effluent points, and borehole samples was put in six different 250 mL conical flasks. The samples were digested by adding 1.0 mL of 55% HNO_3 and 0.5 mL of 37% HCl was added to each flask. The mixture was heated until the initial volume reduced to approximately 0.5 mL. The mixture was then filtered into a 50 mL volumetric flask and deionized water added to the mark. The sample was then analyzed with AAS to determine the concentration of seven selected metals (Pb, Zn, Fe, Cu, Mg, Mn, and Cd). Table 2 shows the concentrations of the metals.

2.9. *Application of the Optimized Biosorption Method to Real Samples.* The extraction efficiency for the acid treated sorbents and the untreated sorbents was compared by applying the optimized parameters (Section 2.6) to water samples collected from sewage treatment plant and borehole water collected from a borehole in Artesia, Botswana. Both Moringa seed pods and Morula nut shells biomass were used for the metal removal in the samples. 50 mL of water samples was used and the optimized conditions were applied to both water samples. The analysis was done in triplicate, and the analytes remaining in the water sample after sorption were determined with FAAS.
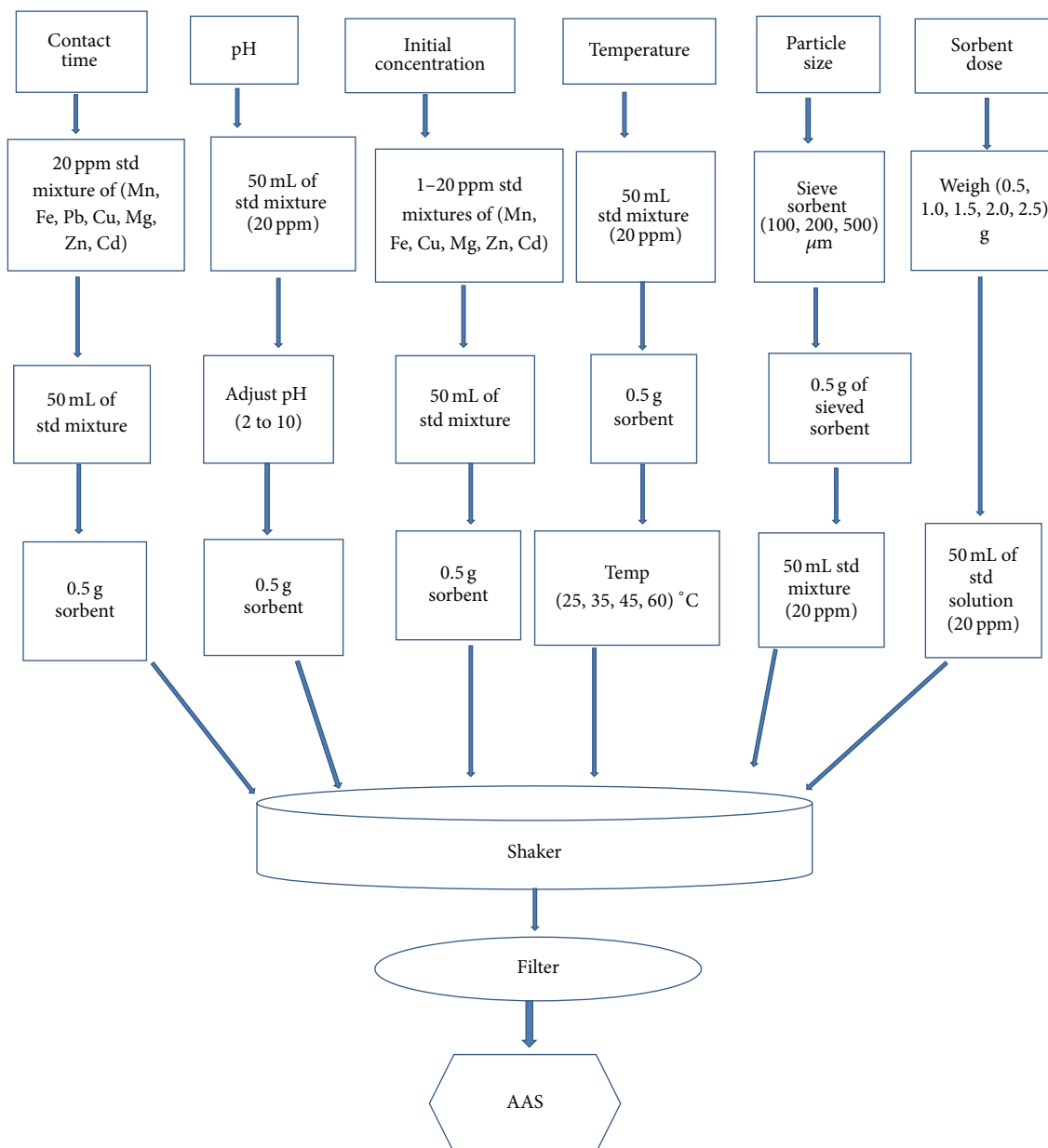
FIGURE 1: Summary of the optimization procedures for biosorption of metals on Morula nut shells and Moringa seed pods.

3. Results and Discussion

3.1. Characterization of the Sorbents. The SEM images (Figures 2(a) and 2(b)) reveal the surface texture and morphology of the sorbents. The micrographs of MSP (Figure 2(a)) reveal mesoporous structures with different pore sizes. These surface characteristics would result in high metal binding due to available binding cavities for the metal ions. MNS micrographs also show that the structures consist of different shapes and have pores on the surface offering binding sites for higher adsorption capacity of metal on the sorbent.

Other sorbents have shown similar characteristics, for example, almond shells [36], *Moringa oleifera* wood [37], and fruit peels [22]. However, the efficiency of the sorbent can be increased by increasing the number of pores and the surface area. This is done by treating the sorbents with acids or activated with carbons [33, 34].

3.1.1. Fourier Transform Infrared (FTIR) Spectroscopy. The IR spectra of MSP as shown on Figure 3(a) show broad bands around $3333\,cm^{-1}$ attributed to the surface hydroxyl group. The bands at 2917 and $2849\,cm^{-1}$ are due to C-H group of the alkenes, at $1741\,cm^{-1}$ the C=O from esters, at $1593\,cm^{-1}$ the C=C aromatics, and C-O from carboxylic acids at 1104 to $1027\,cm^{-1}$. Decrease in intensity and shift of the above-mentioned peaks as shown in Figure 3(b) could be due to interaction of the metal with the specific functional groups.
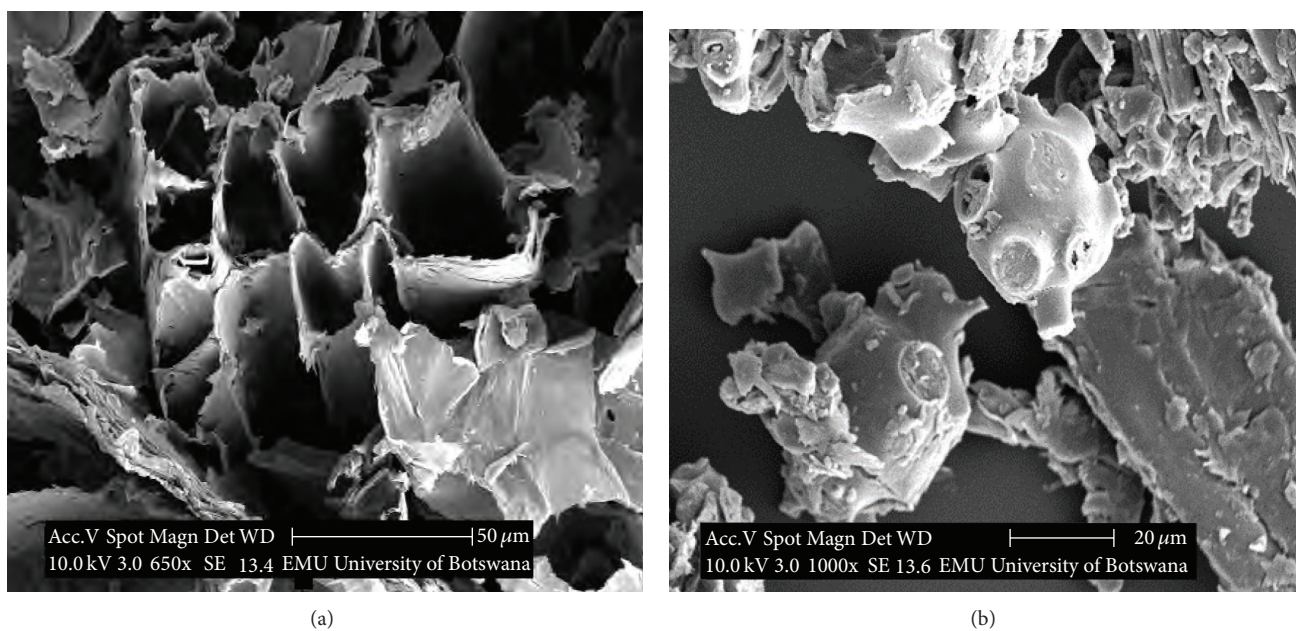
(a)

(b)

FIGURE 2: SEM micrographs: (a) Moringa seed pods and (b) Morula nut shells.
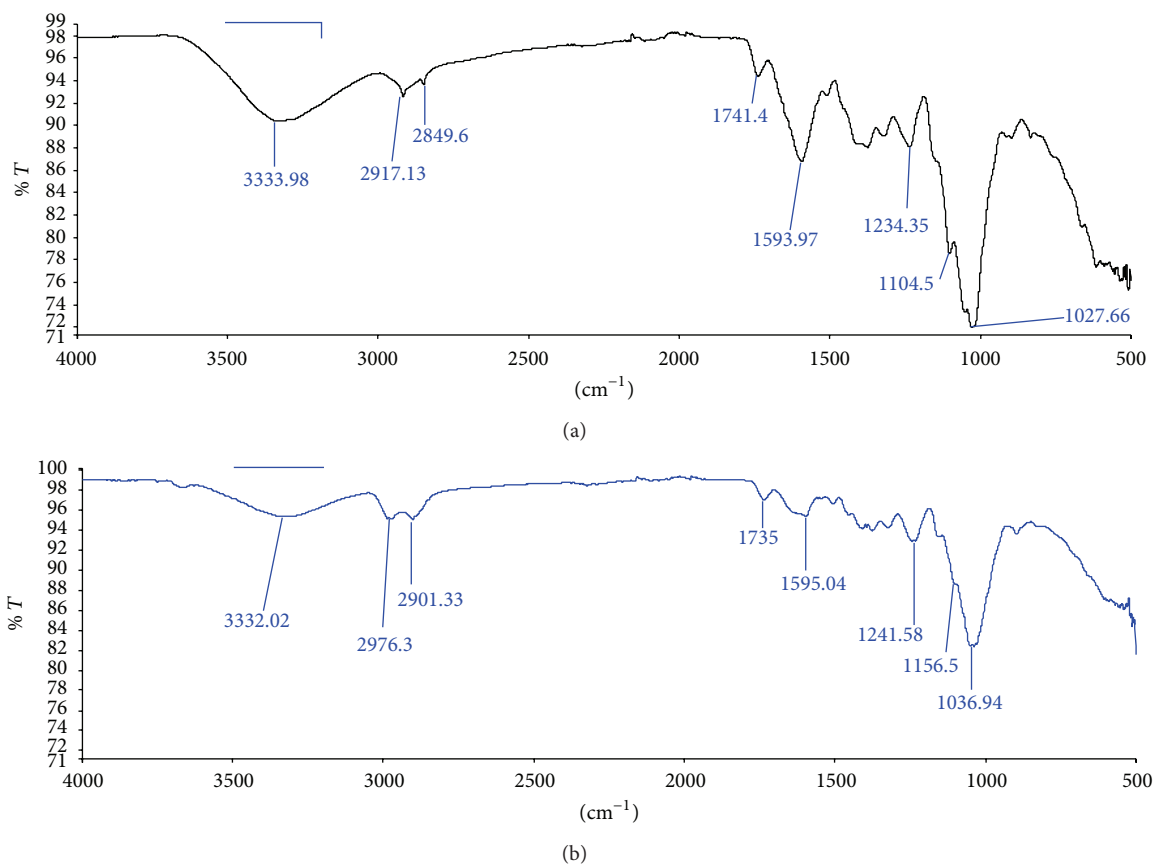

(a)

(b)

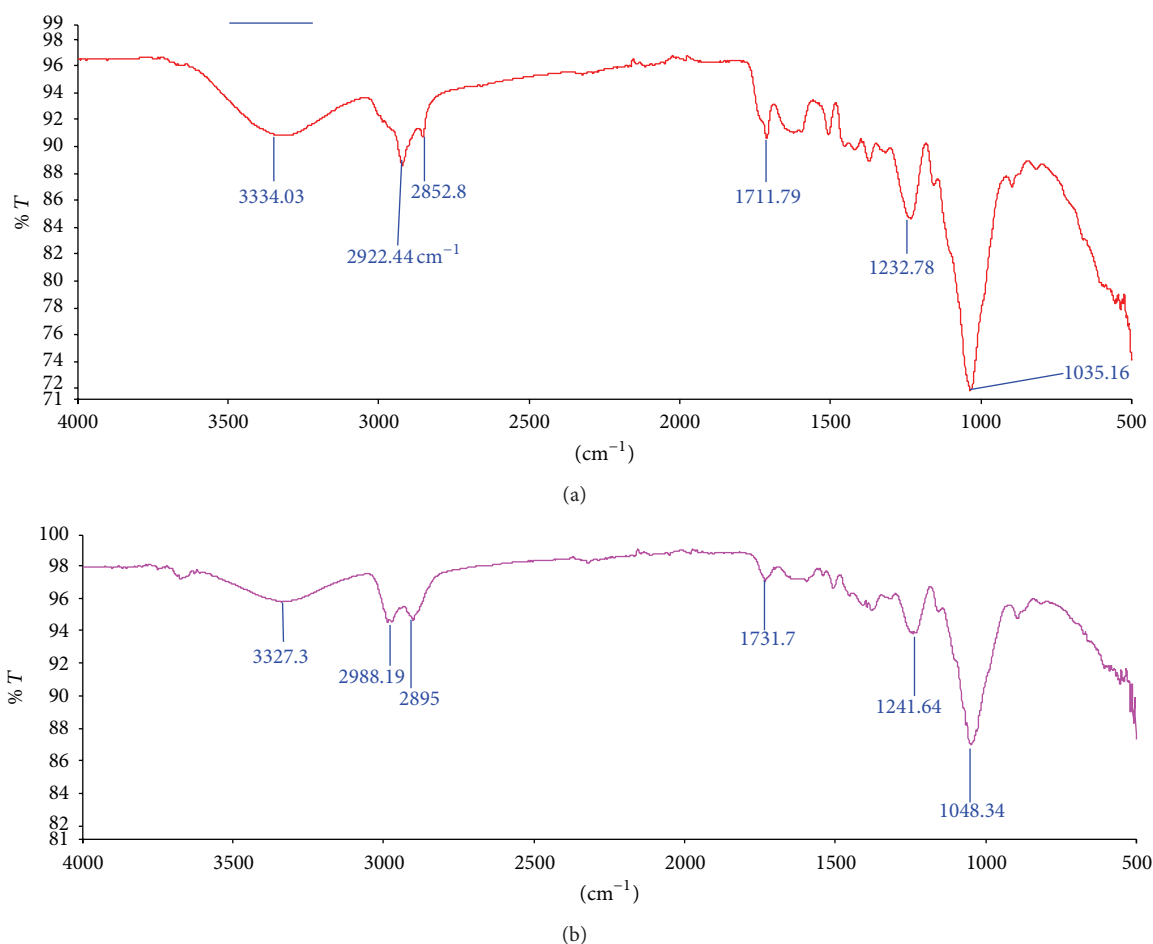FIGURE 3: Unnormalized spectra of MSP (a) before metal ion removal and (b) after metal ion removal.

FIGURE 4: Unnormalized spectra of MNS (a) before metal sorption and (b) after metal sorption from water sample.

The metal adsorption capacity is influenced strongly by the surface structures of carbon-oxygen and surface behavior of carbon [38]. Studies done with other biomass sorbents have shown similar functional groups responsible for metal removal [36, 37, 39]. The functional groups responsible for metal removal in MSP are therefore hydroxyl (OH), C-H of the alkenes, C=C alkenes, and C-O from the carboxylic acids.

Morula nut shell (MNS) IR spectra are shown in Figures 4(a) and 4(b). Figure 4(a) is for MNS before sorption while Figure 4(b) is after sorption of metals. The observed peaks on Figure 4(a) were identified as hydroxyl (O-H) broad group at 3334 cm^{-1}, C-H from alkenes at 2922–2852 cm^{-1}, carbonyls (C=O) at 1711 cm^{-1}, amines at 1232 cm^{-1}, and C-O from either carboxylic acid, esters, or ethers at 1035 cm^{-1}.

Figure 4(b) shows FTIR spectra of metal loaded MNS. The shift and reduction of the peaks such as O-H (3327 cm^{-1}), C-H (2895–2988 cm^{-1}), C=O (1735 cm^{-1}), C-N (1241 cm^{-1}), and C-O (1048 cm^{-1}) are due to interaction of the functional group with the metal ions. The functional groups such as amines, carboxylic, hydroxyl, and carbonyls form anionic sites as pH is raised from acidic to basic conditions. The anionic sites could be responsible for binding with the metal cations. It can be speculated that combination of the following could be the principal mechanism for metal removal [40]:

(i) electrostatic interactions between the conjugate base of either carboxyl group or amine group (at pH 8) reacting with metal ions, (ii) coordination or complex formation (using empty d-orbitals of metal ions) to interact with the electron pairs from the oxygen in the carboxyl, hydroxyl, and nitrogen of the amine groups, (iii) ion exchange processes in which the ionizable hydrogen on the carboxyl and amine groups exchange with metal cations, (iv) microprecipitation (especially at higher pH) where the OH- ions form insoluble hydroxides with the metal ions and the sorbent here then acts as a filter, (v) acid-base interactions (most of these metal ions are hard acids and interact with atoms on the functional groups such as oxygen on the carboxyl and hydroxyl group and nitrogen on the amine groups), and (vi) adsorption: for example, with the presence of alkenes, the concentration of electron density on them actually creates dipole moments with negative dipole moment concentrated on the center of the double bond and the positively charged metal ions will sit on these areas with high electron density.

It can be concluded that, in the MSP, the functional groups significant for metal removal are the carbonyl, alcohol, and alkenes groups, while with MNS, the active groups for metal removal are the alcohols, carbonyls, alkenes, amines, and carboxylic acids.
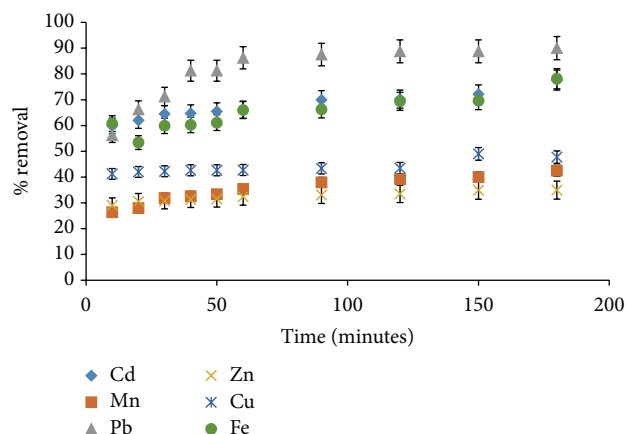
FIGURE 5: Effect of contact time on metal removal using MSP (all other variables in Section 2.6 constant).

FIGURE 6: Effect of contact time on selected metal removal using Morula nut (MNS) sorbent (all other variables constant).

3.2. Effect of Operating Variables

3.2.1. Effect of Contact Time. Contact time is an important parameter for determining the equilibrium time required for the sorption of metal ions on a sorbent as it is directly proportional to amount of metal ions removed from aqueous solution. It was observed that when MSP sorbent was used for metal removal, the highest removal was reached within 60 minutes (Figure 5) and for MNS sorbent it was 120 minutes (Figure 6), the equilibrium was reached, and further increase in time did not show any significant change. The extraction efficiency of the selected metals by MSP was directly proportional to the sizes of the metal ions: that is, the order was Pb > Cd > Fe > Cu > Mn > Zn > Mg (largest to smallest), with exception of copper and magnesium. This trend could be attributed to the fact that the sorbents have pores of different sizes as seen from SEM micrographs and therefore offer different binding sites to the different metal ions [41]. However, larger metal ions were removed efficiently compared to smaller ions. Similar trend has been observed in previous studies [33]. The trend in metals removal by MNS from the aqueous samples was in the order Cu > Fe > Pb > Zn > Cd > Mn > Mg. Percentage removal of the metal ions on the MNS increases with increase in contact time. More time allows the adsorbent particle to interact with the metal ion and increase chances of more adsorption [42]. MNS has greater affinity for the metal with higher electronegative values [43], that is, Cu (2.00 Pauling), Fe (1.91 Pauling), Pb (2.33 Pauling), Zn (1.65 Pauling), Cd (1.69), Mn (1.55 Pauling), and Mg (1.31 Pauling). Higher biosorption of the metals on the sorbents can also be explained by hard-soft-base theory [44]. Metals belonging to hard acid like Fe may be removed effectively.

3.2.2. Effect of pH. The pH of aqueous solution is very important in sorption processes since it affects the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbent, and the degree of ionization of the sorbate during the reaction [45]. An increase in pH of solution while keeping all other factors (time, temperature,
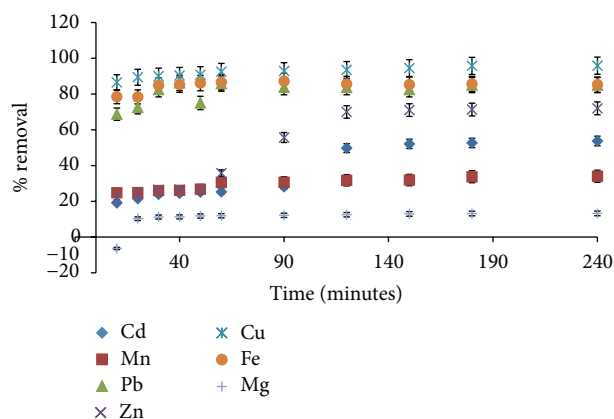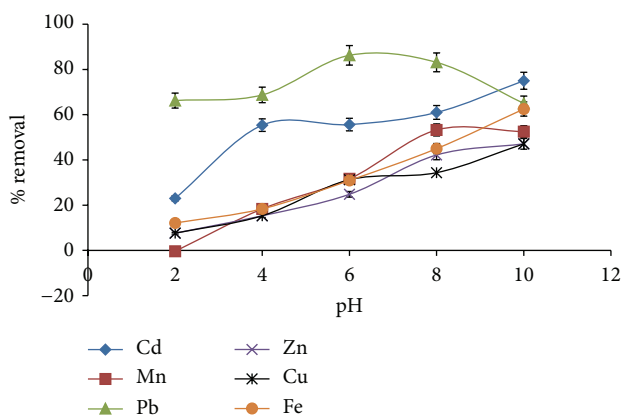

FIGURE 7: Effect of adjusting pH on metal removal by Moringa seed pods (MSP). Other conditions kept constant.

metal concentration, sorbent dose, and particle size) constant increased the percentage removal of the selected metal ions using the MSP (Figure 7) and MNS (Figure 8). This could be due to the surface charge on the sorbents. At low pH, the cations compete with the hydrogen ion in the solution for the active sites and therefore lower adsorption. But at higher pH, the surface of the adsorbent has a higher negative charge which attracts more cations [37]. At pH > 8, precipitation of metal hydroxide is likely to occur and hence could enhance metal removal, resulting in the sorbents acting like filtering materials. Removal of Pb was highest at pH 6; however, ANOVA showed that there was an insignificant decrease in percentage removal as the pH was increased to pH 8. Therefore, the optimum pH was taken to be 8 for all metals using both sorbents since there was highest percentage removal before the precipitates could form.

3.2.3. Effect of Initial Metal Concentration. The initial concentration provides essential driving force to overcome all mass transfer resistance of metal ions between the aqueous and the solid sorbent. As the initial metal concentration is increased, the removal efficiency is increased and after saturation, the
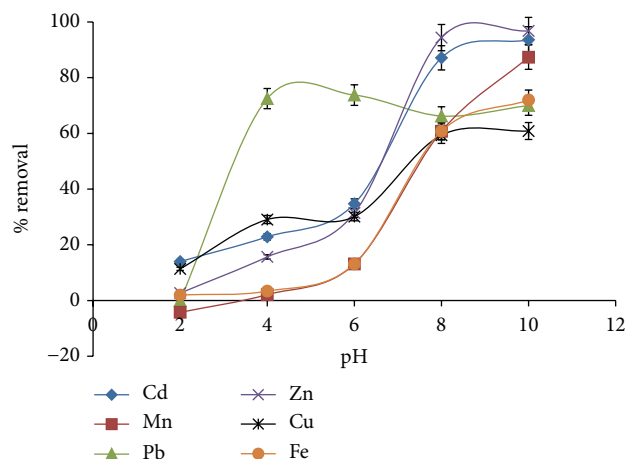
FIGURE 8: Effect of pH on metal removal using morula nut shells (MNS) while keeping other conditions constant.
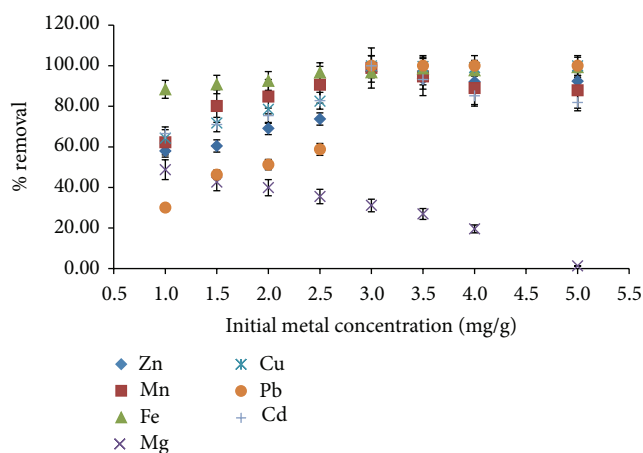

FIGURE 9: Effect of initial metal concentration on metal removal by MNS.

FIGURE 10: Effect of initial metal concentration on metal removal by MSP.
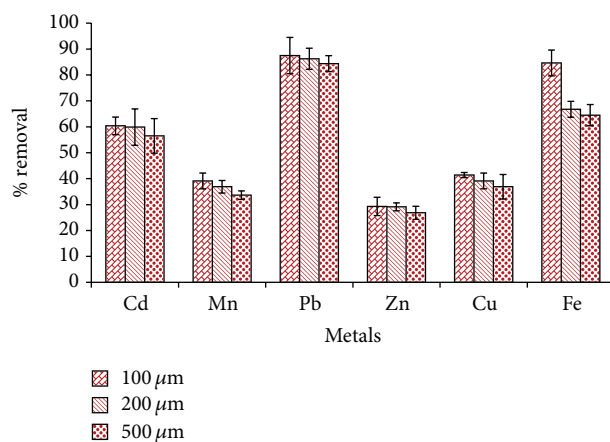
FIGURE 11: Effect of particle size on metal removal using MSP.

percentage removal is constant as shown in Figure 9 while using MNS. This could also be attributed to the saturation of the binding sites as more ions are added in the solution. As the concentration of metal ion increases, the number of metal ions competing for available binding sites on the sorbent increases. Therefore, binding sites become quickly saturated as the biomass amount remained constant [38, 46]. The same was observed using MSP; at lower concentration there was an increase in removal efficiency; however, after a threshold (different for each metal) any further increase in the metal concentration resulted in reduced removal efficiency for Zn, Mn, Fe, Cu, and Cd (see Figure 10). Removal of magnesium by both sorbents was poor and this was attributed to limited loading capacity of the sorbents due to saturation of magnesium binding sites. This is because the concentration of magnesium ions in the sorbent was higher (see Table 1) in comparison to the other metals. Therefore, increase in initial concentration led to a decrease in percentage removal of magnesium.
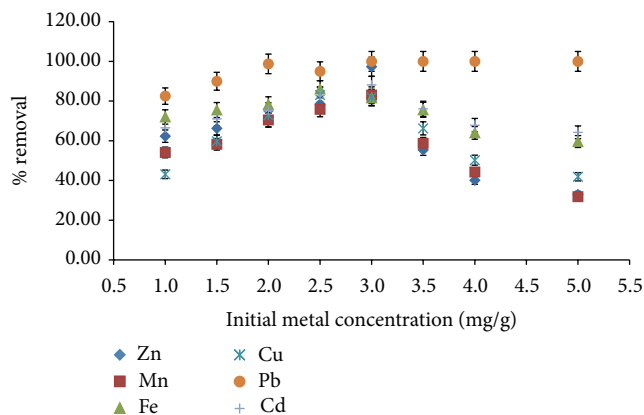
3.2.4. Effect of Particle Size. Surface area of the sorbent is significant for sorption process. Exposure of the sorbent sites for solid-metal ion interaction is high if the surface area of the sorbent is high. As shown in Figures 11 and 12 using MSP and MNS, respectively, the percentage removal of the metal was effective at sorbent particles size less than $100\,\mu m$ as compared to larger particles. The smaller the particle size the higher the surface area per unit weight of sorbent and hence higher percentage removal is expected [47]. Similar trends have been observed by other researchers [45, 48]. An exception was the magnesium that showed higher removal at $500\,\mu m$ while using MNS (Figure 12) and this may be attributed to the fact that magnesium may prefer to adsorb internally as opposed to external adsorption. Beside adsorption at the outer surface of the sorbent, there is a possibility of intraparticle diffusion from the outer surface into the internal surface of the sorbent [40]. A large particle size has larger internal surface area than a small one, and hence magnesium showed higher removal at $500\,\mu m$ than at $100\,\mu m$. However, ANOVA significant test was conducted and showed that using $100\,\mu m$ had no significant difference, hence resulting in using $100\,\mu m$ to be the optimum particle

FIGURE 12: Effect of particle size on metal removal using MNS.

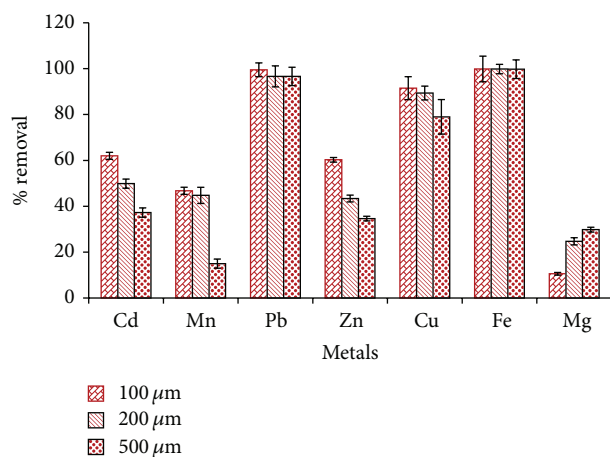FIGURE 13: Effect of temperature on metal removal using MSP.

FIGURE 14: Effect of temperature on metal removal using MNS.

size using both sorbents. It was also observed that while using MSP, there was no removal of magnesium due to the fact that MSP had higher amounts of magnesium (see Table 1) and therefore the adsorbing sites for magnesium were saturated.

The ionic sizes trend of the metals is Pb > Cd > Zn > Cu > Mg > Fe > Mn for divalent cations. The larger ions are expected to be removed first and the order of removal should decrease from Pb to Mn [49], but in some case it will be different depending on the environment of the interacting sites. This trend was not observed completely and this could be attributed to the fact that the metals were interacting differently with the MNS and MSP adsorbing sites.

3.2.5. Effect of Temperature. An increase of removal efficiency with increase in temperature has been attributed to two factors. Increase in temperature increases the mobility of the metal ions towards the sorbent and also it may cause a swelling effect within the internal structure of the sorbents and therefore enabling the metal ions to penetrate further or increases the surface area for the binding of the metal ions [48]. Temperature effect on metal removal by the sorbents was investigated using batch experiments conducted in water bath with temperature range from 25°C to 60°C. There was no significant change in percentage removal for other metals except for lead where there was increase at 35°C as depicted in Figure 13 when using MSP. It was also observed that there was no significant change when higher temperatures up to 60°C were used; hence, 35°C was used as optimum temperature. Araújo et al. [50] discussed that use of Moringa seed pods for removal of Zn and Pb worked well at a temperature of 30°C to 35°C. Figure 14 shows an increase in percentage removal from 25°C up to 35°C for removal of Zn, Cd, Mn, and Mg using MNS. When removing Fe, Cu, and Pb, there was no significant difference even when temperature was altered. Hence, 35∘C was taken to be the optimum extraction temperature.

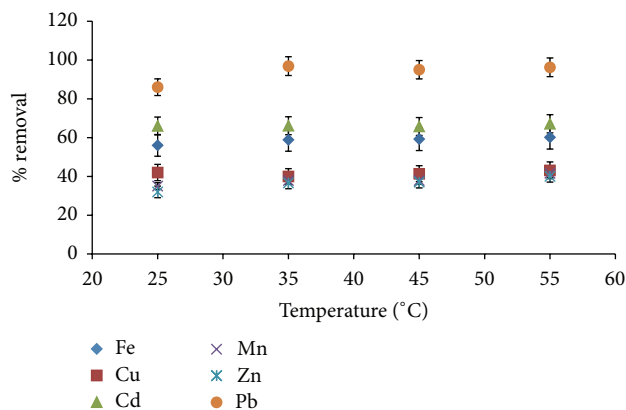*3.2.6. Effect of Sorbent Dose.* It is expected that, as the sorbent amount increases, the number of sorbent particles
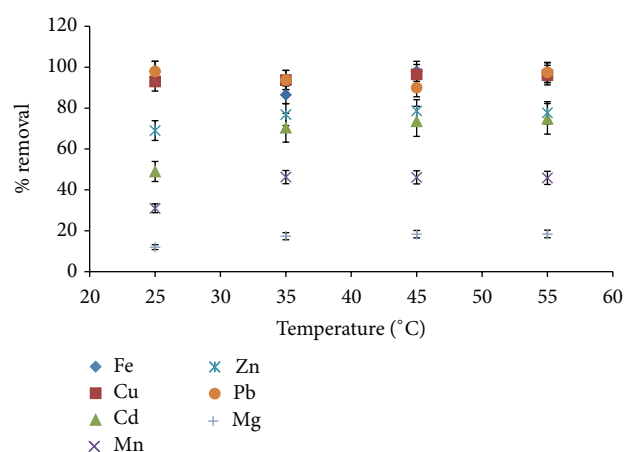
surrounding the metal ion or ratio of sorbent particle to metal ion increases [51]. This increases the surface area on which the metal ions bind to the surface of the sorbents, hence increasing the removal efficiency. However, a further increase beyond the optimum sorbent dose decreases the percentage removal and this is attributed to the fact that there is possibility of the particle overlapping and overcrowding resulting in a reduction of the total adsorbent surface area and hence decreases the percentage removal [38]. Figure 15 shows that as the sorbent dose was increased from 0.5 g to 1.0 g of MSP sorbent, the percentage removal of metal ions increased and the optimum sorbent dose for the removal of Cd, Mn, Zn, Cu, and Fe was 1 g except Pb which had its highest removal using 1.5 g sorbent. However, ANOVA showed that there was no significant difference when 1 g was used to remove Pb ions. The results for metal removal using MNS adsorbent at different dosing levels (0.5 g to 2.5 g) showed a slight increase for cadmium, manganese, and zinc up to 2 g dosing level (Figure 16), but no significant difference was observed for copper, lead, and iron at all dosing levels. Similar studies have been reported with other low cost sorbents [29, 43]. Therefore, 1 g of MSP and 2.0 g of MNS was taken to be the optimum sorbent dose for the experiments.

TABLE 3: Summary of the optimized parameters.

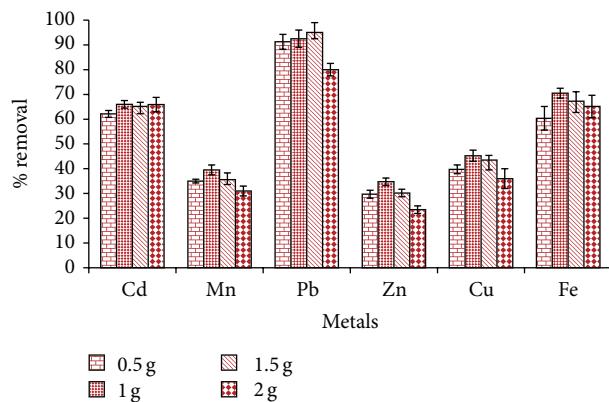| Material	Contact time (min)	PH	Temp (°C)	Adsorbent dose (g)	Particle size (μm)
Morula nut shells	120	8	35	2	100
Moringa seed pods	60	8	35	1	100

FIGURE 15: Effect of adsorbent dose on metal removal using Moringa seed pods.
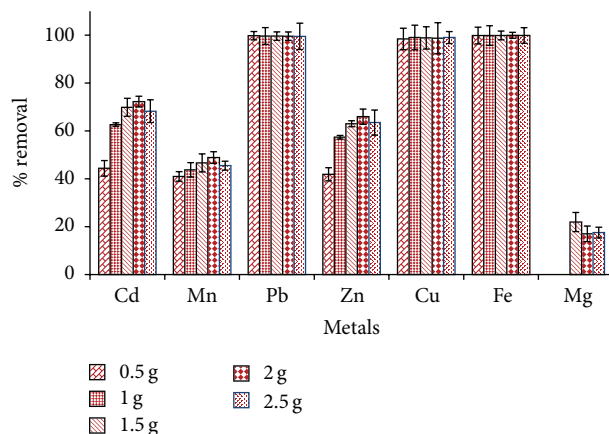
FIGURE 16: Effect of adsorbent dose on metal removal using MNS.

FIGURE 17: Percentage removal of metals from wastewater using MNS.
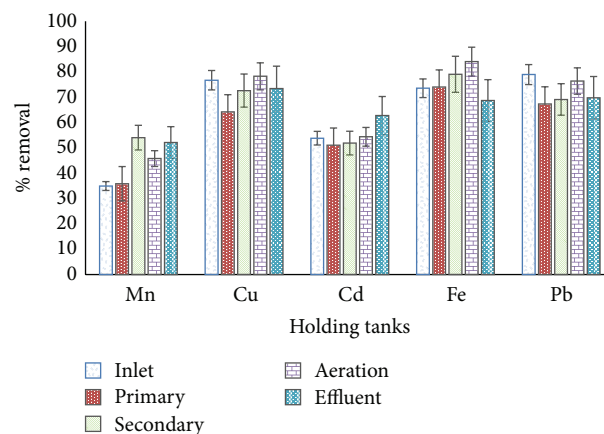
FIGURE 18: Percentage removal of metals from wastewater using MSP.

Table 3 shows the summary of the optimized parameters. They were then applied in real samples (wastewater and borehole water) as discussed in Section 3.3.

3.3. Metal Removal from Wastewater and Borehole Water.
Figures 17 and 18 show the percentage removal of metals from wastewater holding tanks using Morula nutshells and Moringa seed pods, respectively.

The metals were removed from the wastewater efficiently using MNS as shown in Figure 17. At effluent tanks the percentage trend was Fe > Cu > Pb > Mn > Zn > Cd > Mg. This was a little different from optimization process and this could be attributed to the fact that in real samples there are other competitive ions competing for the same binding sites and reducing and altering the removal efficiency. MSP also removed five elements Mn, Cu, Cd, Fe, and Pb. The trend was
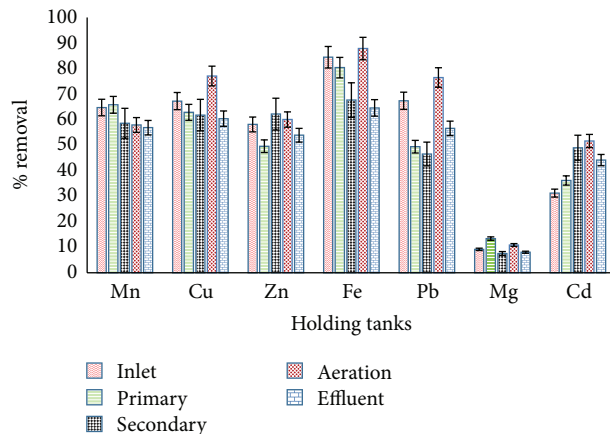
Cu > Pb > Fe > Cd > Mn. However, MSP could not remove Zn and Mg due to desorption of the ions from sorbent into the sample solution and probably due to saturation of binding sites on the sorbent.

Removal efficiency was also investigated in borehole samples as shown in Figures 19 and 20. MSP removed Pb > Cd > Cu > Fe efficiently in that order. However, for the reason stated above, Zn, Mg, and Mn were not removed. However, MNS removed all the metal efficiently with an exception of Zn as shown in Figure 20.

Due to poor removal efficiency of some metals, sorbents were chemically treated to determine if the removal efficiency can be increased as discussed in Section 3.4.
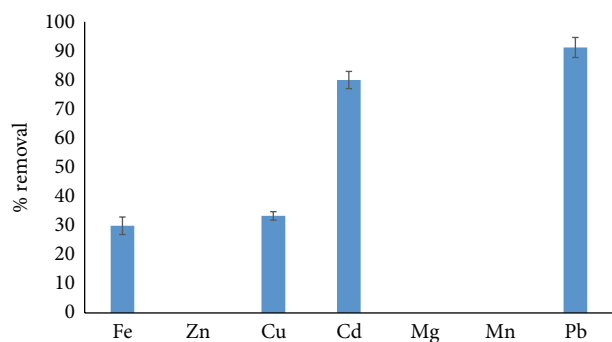
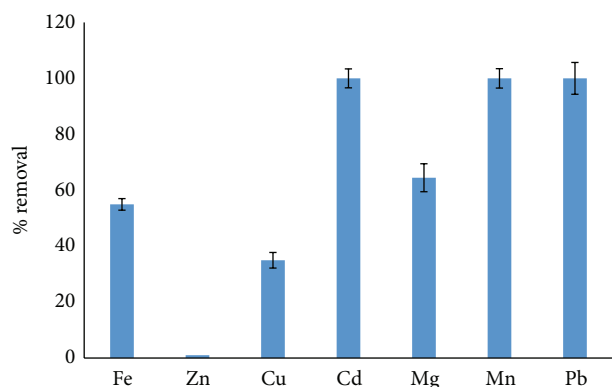FIGURE 19: Percentage removal of metals from borehole water using MSP.

FIGURE 21: Comparison of treated and untreated MSP for removal of metal from wastewaters at final effluent point.

FIGURE 20: Percentage removal of metals from borehole water using MNS.

FIGURE 22: Comparison of treated and untreated MNS for removal of metal from wastewaters at final effluent point.

3.4. Use of Treated MNS and MSP for Metal Removal from Wastewater Samples.

Use of untreated plant biomass is capable of directly removing metal ionic species from aqueous solutions. This has been confirmed in this work. To further enhance metal removal efficiency, sorbents can be chemically pretreated before metal sorption. Commonly employed treatments include using alkaline solutions and acids. This treatment normally removes organic and inorganic matter from the sorbent surface [27]. Treating the sorbents with acid helps to extract any metal cations on the sorbents, thereby creating new sorption sites and increasing the surface area of the sorbent and hence increasing the metal removal efficiency. In this current work, acid (0.4 M of HNO_3) and untreated MNS and MSP sorbents were compared in terms of extraction of heavy metals from the inlet and effluent wastewater samples. It was observed that treated sorbents showed better removal efficiency as compared to the untreated sorbents as shown by Figures 21 and 22 using treated MSP and MNS, respectively.

The percentage removal of Fe, Zn, Cu, Cd, Mg, Mn, and Pb from water samples using treated MNS was 79.6, 52.9, 78.2, 58.6, 90.3, 100.0, and 93.4 while using treated MSP it was 80.9, 57.6, 89.0, 65.5, 88.2, 100.0, and 94.7, respectively.

Other sorbent materials have been used to effectively remove heavy metals from aqueous solution, for example, use of carbon materials for removal of metals from aqueous solutions [45, 48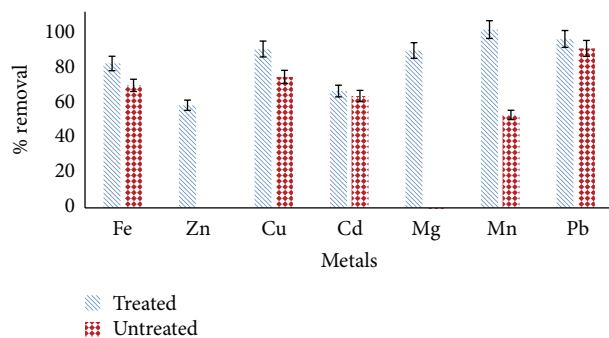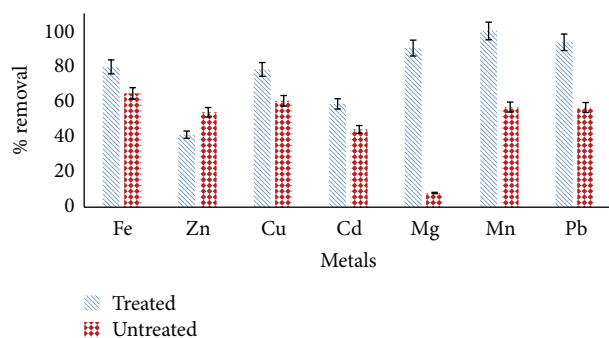, 52, 53]. The removal efficiencies were reported to be in the range of 65% to 90%. However, some of the disadvantages associated with use of such sorbents are the high costs and cannot be regenerated and the adsorption efficiency of carbon materials also depends on the nature of carbon used. Synthetic adsorbents such as zeolites have been reported to remove metals effectively. However, it was demonstrated that the capability of these minerals depends on the pretreatment method and that conditioning improves the ion exchange ability and removal efficiency [54]. Low cost sorbents have been reported to effectively remove heavy metals such as soybean hulls [55], tea waste [24], fruit peels [22], egg shells [56], and other agricultural wastes [57, 58].

3.5. Method Validation.

The linearity of the method was tested by using standards in the range of $0.0 \, mgL^{-1}$ to $5.0 \, mgL^{-1}$ of the selected metal (Pb, Mn, Fe, Zn, Mg, Cu, and Cd). The developed method was validated and the % metal removal by sorbents was between 86.49 ± 4.33 and $99.63 \pm 3.36\%$. The method indicated good linearity ($R^2 > 0.99$) for all selected metals and also proved to be sensitive as low LODs were achieved ranging from 0.010 ± 0.003 to $0.067 \pm 0.02 \, mgL^{-1}$. Equation (2) below was used to calculate for the % removal:

$$\% \text{ Removal} = \frac{\text{amount added} - \text{amount found}}{\text{amount added}} \times 100. \quad (2)$$

4. Conclusion

Moringa oleifera seed pods and *Sclerocarya birrea* nut shells were used to successfully remove selected heavy metals from water samples. This work explored the possibility of adding value to waste material by recycling and reusing for purification of contaminated water. FTIR analysis of the sorbents showed different functional groups indicating complex nature and capability of the sorbents. The pH, initial metal concentration, sorbent dose, particle size, and temperature were found to affect the sorption process. Removal efficiencies were improved after treating sorbents with acids. The developed method was found to be simple, cheap, environmental friendly, and does not need trained personnel to use it. Hence, it can be a remedial solution for water scarcity in rural areas where there are no resources to obtain the expensive conventional techniques.

Competing Interests

The authors declare that they have no competing interests.

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