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Review Article

Sorption of Heavy Metals from Aqueous Solutions by *Moringa* Biomass

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Abstract

Discharge of heavy metals into the aquatic systems is a global concern. Conventional methods for the removal of heavy metals are associated with several disadvantages such as unpredictable metal ion removal, high material costs and the generation of toxic sludge that is often more difficult to manage. Biomaterials offer many benefits such as easily accessible, show good adsorption capacity for metal pollutants. This review explores the efficiency of various species of *Moringa* and their biomass in the removal of heavy metals from aqueous solutions. Further, the effect of contact time, solution pH, biosorbent dosage, biosorbent preparation, equilibrium and kinetic studies during the removal of metal pollutants were also reviewed.

Keywords: *Moringa oleifera*; Heavy metal removal; Sorption; Green sorbent; Water pollutants

Introduction

Heavy metals are toxic pollutants and their discharge into surface waters, from natural geochemical and anthropogenic sources, is a global concern. They are released into through a variety of sources such as metal smelters, effluents from plastics, textiles, microelectronics, wood preservatives producing industries, usage of fertilizers and pesticides. Common anthropogenic sources include agricultural activities, atmospheric deposition, road run off, discharges from industrial plants and sewage works, acidic mine effluents and building of reservoirs. A large number of physico-chemical methods based on coagulation, ion-exchange, reverse osmosis and flocculation (with various synthetic coagulants such as aluminum, ferric salts, soda ash, polymers, etc.) have been developed for removal of heavy metals. However, these methods are associated with several disadvantages such as unpredictable metal ion removal, high material costs and the generation of toxic sludge that is often more difficult to manage. Therefore, a sustainable way for removing heavy metals from contaminated water is required and use of biomaterials offers great potential. Biomaterials offer many benefits such as easily accessible, show good adsorption capacity for a variety of pollutants (even at low concentrations), do not require any processing, being environmentally friendly and locally available at very low cost [1]. There has been an increasing trend to evaluate some indigenous cheaper biological materials for wastewater treatment.

Moringa oleifera plant belongs to the family *Moringaceae* is cultivated across whole of the tropical belt for different purposes. Common names of *M. oleifera* are Sahjan, *Moringa*, Drumstick tree, Horseradish tree, Surajana, etc. *M. oleifera* being native of the western and sub-Himalayan tracts, India, Pakistan, Asia Minor, Africa and Arabia, is now found in Cambodia, Philippines, North and South America, Central America and the Caribbean Islands [2]. There has been increased interest in the subject of natural coagulants for treatment of water and wastewater. *Moringa oleifera* seed proteins have been found to possess coagulating properties similar to those of alum. In this review, various species and biomass of *Moringa* were compared for the removal of heavy metals and other metal pollutants of aqueous solutions. The experimental conditions involving different parameters, viz. effect of contact time, solution pH, biosorbent dosage, biosorbent preparation, equilibrium and kinetic studies were also reviewed.

Heavy Metal Removal by Moringa Biomass

Cadmium

The sorption capacity of *M. oleifera* seeds for the removal of Ag(I) from water was described by Araujo et al., [3]. Further, the applicability of *M. oleifera* for removing various metal ions Cd(II), Pb(II), Co(II), Cu(II), and Ag(I) from aqueous solutions was also investigated. The seeds of *M. oleifera* were shown to be an efficient adsorbent material of natural origin for the pre-concentration of cadmium present in alcoholic matrices. The sample pH, eluent concentration and buffer concentration were studied to determine the influence on the extraction efficiency. pH 9.3 leads to better results and the eluent concentration of 0.5 mol L^{-1} was found optimum for the adsorption process [4]. The potential of *M. stenopetala* for cadmium removal was investigated by Mataka et al., [5]. With an initial cadmium concentration of 7 mg/l, *M. stenopetala* seed powder, at a dose of 2.50 g/100 ml, reduced the concentration of cadmium by 53.8%. Comparison of removal capacities between *M. stenopetala* and *M. oleifera* indicated that *M. stenopetala* was more effective than *M. oleifera* in removing cadmium from water. The percentage removal increased sharply to about 80.0% with increase in pH up to pH 5 and then gradually increased slowly to maximum removals of 93.8 and 88.4% for *M. oleifera* and *M. stenopetala* respectively.

The sorption properties of bioactive constituents of *M. oleifera* seeds for decontamination of cadmium at laboratory scale [6] and the maximum removal of cadmium was 72% by using 0.2 g/l of bioactive dosage. Optimum conditions for the percentage removal of Cd(II) ion using shelled *Moringa oleifera* seeds were described by Sharma et al., [7]. It includes biomass dosage (4.0 g), metal concentration (25 µg/

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ml), contact time (40 min) and volume of the test solution (200 ml) at pH 6.5 in which 85.1% Cd was removed from the aqueous solution. The potential of *Moringa oleifera* whole seed kernels in removing lead, iron, and cadmium ions from synthetic contaminated water was investigated. Metal ion removal was observed ranging from 70.86 ± 2.22% to 89.40 ± 0.00% for lead, 66.33 ± 3.38% to 92.14 ± 0.00 % for iron and 44.95 ± 3.95% to 47.73 ± 6.38 % for cadmium [8].

Lead

The removal potential of three parts of *Moringa* (seed husk, seed and pod), in lead (II) biosorption from contaminated water was studied by Tavares et al., [9]. Lead biosorption increased rapidly during the first 30 min and, after that, it remained practically constant. The lead removal percentage when reached equilibrium at 30 min was 97.9% for husk (0.084 mg L^{-1} residual), 96.3% for seed (0.148 mg L^{-1} residual) and 97.8% for pod (0.088 mg L^{-1} residual). The maximum removal obtained for lead biosorption, at pH 6, was 98.7%, 98.8% and 98.2% for husk, seed and pod respectively.

Biosorption of Pb(II) from aqueous solutions using the citric acid treated *M. oleifera* leaves was studied by Reddy et al., [10]. The biosorption from aqueous solution was found to be greatly dependent on solution pH (209.54 mg g^{-1} at pH 5.0). *M. oleifera* bark for the removal of lead from aqueous solution was investigated by Reddy et al., [11]. The equilibrium sorption capacity was minimum at pH 2 (23.3%) and reached maximum value (96.5%) at pH 5. Adsorption increased from 86.0 to 99.38% with increase in adsorbent dose with a maximum removal of Pb^{2+} was observed with an adsorbent dose of 400 mg. The time dependence studies demonstrated that the highest metal binding was obtained within 30 min of contact time. *M. stenopetala* has the capacity to remove heavy metals from water and the effectiveness of removal increased with increasing dosage of whole seed powder. In general *M. stenopetala* seed powders (52.05% and 72.52%) are more effective than *M. oleifera* (47.71% and 68.43%) in lead removal at a dosage of 1g 100 ml and 1.5 g/100 ml respectively [12].

Nickel

The operating parameters that affect the adsorption process of Ni(II) such as pH, agitation time and adsorbent dosage, were investigated by Marques et al., [13]. The influence of the adsorbent dosage on nickel sorption was studied by varying the amount of adsorbent from 0.5 to 2.0 g. The percentage adsorption of nickel increased with an increase in the adsorbent mass for up to 2.0 g. The results showed that *M. oleifera* seeds demonstrate good removal capacities for Ni(II) (29.6 mg/g). Reddy et al., [14] studied the sorption potential of *M. oleifera* bark for Ni(II) removal from water under equilibrium conditions. It has been observed that under highly acidic conditions (pH~2.0) the amount of Ni(II) removal was very small, while the sorption had been increased with the increase in pH from 3.0 to 6.0 and then decreased in the range 7.0 and 8.0. The maximum biosorption capacity of Ni(II) was 30.38 mg g^{-1} at an optimum pH 6.0. The calculated thermodynamic parameters showed the feasibility, endothermic and spontaneous nature of the biosorption of Ni(II) onto *M. oleifera* bark biomass. The removal efficiency of Ni(II) ions from aqueous solution using shelled *M. oleifera* seed powder was evaluated by Raj et al., [15]. Batch experiments resulted into standardization of optimum conditions of biomass dosage (4.0 g), Ni(II) concentration (25 mg/L) volume (200 ml) at pH 6.5.

Copper

The potential of using the *M. oleifera* biosorbent to treat gold mine wastewater having a Cu(II) concentration of up to 10 mg L^{-1} was studied by Acheampong et al., [16]. *M. oleifera* seeds removed 74% of the Cu(II) in 180 min and then continued slowly until equilibrium was attained. In another study by Acheampong et al., [17], the maximum sorption capacity of *M. oleifera* seeds for Cu(II) was 2.2 mg g^{-1}. The seeds removed Cu(II) efficiently, accomplishing low equilibrium concentrations in solution, even for the higher initial Cu(II) concentrations (up to 150 mg L^{-1}) used in the experiments. The seeds also showed good Cu(II) removal efficiency, reaching a metal uptake of approximately 2 mg g^{-1} for a Cu(II) equilibrium concentration of 7 mg L^{-1}.

Mercury

Moringa oleifera gum, a natural stem exudate was modified *via* acryloylation reaction and evaluated as adsorbent for Hg^{2+} ions as a function of contact time, temperature, pH and initial ion concentration. The optimum initial pH value for adsorption of Hg^{2+} ions from aqueous solution by NPAMG was determined as 5.5. It was observed that the % adsorption increased from 75.4% to 77.6% with change in temperature from 10 to 20°C. It has been observed to be an efficient adsorbent with the maximum adsorption capacity of 840.34 mg g^{-1} [18].

Chromium

Three different sizes of *M. oleifera* seed pods powder were used as green biosorbent for chromium (VI) ions [19]. Experimental results revealed that the maximum removal of Cr(VI) was observed at pH 1. The removal efficiency of Cr(VI) by fine, mixed and coarse fraction was 91.8, 74.9, 52.6% respectively. Adsorbent dosage of 2.5 g L^{-1} of *M. oleifera* pod powder removes up to 99% of Cr(VI).

Adsorption of chromium on to a bio-adsorbent, *M. oleifera* seed and the experimental results showed that maximum removal of Cr(III) and Cr(VI) was observed at pH 7 and pH 2, respectively. The percentage removals of Cr(III) by whole seed powder was 97% [20].

The sorption properties of shelled *Moringa oleifera* seeds for removal of chromium was explored by Sharma et al., [21]. A biomass dosage (4.0 g), metal concentration [25mg/L for Cr (III); 50mg/L for Cr (VI)], contact time (40 minutes) at pH 6.5 and 2.5 was optimum for the removal of 81.02%; Cr (III) and 88.15% Cr (VI) respectively. In another study, Sharma et al., [22] reported the adsorption of ternary mixture of heavy metal solution onto the surface of unmodified shelled *Moringa oleifera* seeds. It was found to be competitive where the adsorption capacity of the metals was lowered (10-20%) with those of single metal ions. The maximum percentage sorption calculated for each ion present in ternary mixture [Cd(II): 76.59%, Cr(III): 68.85% and Ni(II): 60.52%]. The seeds efficiently removed the ternary metal ions with the selectivity order of Cd(II) > Cr(III) > Ni(II).

Arsenic

In a study by Pramanik et al., [23], *M. oleifera* led to a reduction in arsenic and iron of 47% and 41%. The sorption behavior of the two oxidation states of Arsenic [As(III) and As(V)] species using *M. oleifera* was carried out by Kumari et al., [24]. Both As (III) and As

Table 1: Moringa biomass for the removal of Heavy Metals from Aqueous Solutions.

Heavy Metals	Biomass used	References
Cd^{2+}, Pb^{2+}, Cu^{2+}	*M. stenopetala* seed powder	Kebede et al., [27]
Cd (II), Pb (II), Cu (II)	*M. stenopetala* bark	Kebede et al., [28]
Hg^{2+}	*M. oleifera* gum	Ranote et al., [18]
Cr (VI)	*M. oleifera* seed pods	Shirani et al., [19]
Pb (II)	*M. oleifera* husk, pods, seeds	Tavares et al., [9]
As, Fe	*M. oleifera* seeds	Pramanik et al., [23]
Cd	*M. oleifera* leaf and bark extract	George et al., [29]
Cu, Ni, Cr	*M. aptera* pods	Matouq et al., [30]
Pb, Cr	*M. oleifera* seeds	Basra et al., [31]
Cd^{2+}, Zn^{2+}	*M. oleifera*	Kituyi et al., [26]
Cu (II)	*M. oleifera* seeds	Acheampong et al., [16]
Ni (II)	*M. oleifera* seeds	Marques et al., [13]
Pb, Cu, Cd, Ni, Mn	*M. oleifera* leaves powder	Obuseng et al., [32]
Cd (II), Cu(II), Ni(II)	*M. oleifera* leaves	Reddy et al., [33]
Co, Cu, Pb, Cd, Ag	*M. oleifera*	Papoh et al., [35]
Ni (II)	*M. oleifera* bark	Reddy et al., [14]
Cu (II)	*M. oleifera*	Acheampong et al., [17]
Cd	*M. oleifera* seeds	Alves et al., [4]
Ag (I)	*M. oleifera* seeds	Araujo et al., [3]
Cd (II)	*M. stenopetala* and *M. oleifera* seed powder	Mataka et al., [5]
Ni (II)	*M. oleifera* seed powder	Raj et al., [15]
Pb (II)	*M. oleifera* leaves	Reddy et al., [11]
Pb^{2+}	*M. oleifera* bark	Reddy et al., [10]
Cr	*M. oleifera*	Ghebremichael et al., [20]
Cd	*M. oleifera* seeds	Jamal et al., [6]
Ternary mixture of Cd(II), Cr(III), Ni(II)	*M. oleifera* seeds	Sharma et al., [21]
Cr (III), Cr (VI)	*M. oleifera* seeds	Sharma et al., [22]
Zn (II)	*M. oleifera*	Bhatti et al., [25]
Pb	*M. stenopetala* and *M. oleifera* seed powder	Mataka et al., [12]
Cd (II)	*M. oleifera* seed powder	Sharma et al., [7]
As (III), As (V)	*M. oleifera* seed powder	Kumari et al., [34]
Pb	*M. oleifera* whole seed kernel	Sajidu et al., [8]
As (III)	*M. oleifera* seed powder	Kumari et al., [24]

(V) sorption on shelled *M. oleifera* seeds increased with the increasing concentration of the metal ions reaching the optimum level 60.21 and 85.6%.

Zinc

An evaluation of the parameters important for the biosorption of Zn(II) by *M. oleifera* was carried out by Bhatti et al., [25]. The results revealed that the maximum adsorption of Zn(II) ions from aqueous solutions occurred at pH 7 using *M. oleifera* biomass pretreated with NaOH having particle size. Further, the results demonstrated that the biomass concentration strongly affected the amount of metal removed from aqueous solutions. Use of *M. oleifera* as a biosorbent for sequestration of Zn and Cd for both single and mixed systems was investigated by Kituyi et al., [26]. The biosorption was pH dependent and the highest uptakes of both metal ions occurred at an optimum of pH 4 and decreased with increasing pH. Metal biosorption decreased drastically with increasing pH and Zn^{2+} ions were more efficiently biosorbed than Cd^{2+}.

Other Heavy Metals

The use of *Moringa stenopetala* seed powder for the removal of Cd^{2+}, Pb^{2+} and Cu^{2+} ions from industrial effluent and synthetic waste water was investigated by Kebede et al., [27]. The maximum percentage adsorption under optimum conditions of Cd^{2+}, Pb^{2+} and Cu^{2+} ions from synthetic wastewater were 99.65, 99.66 and 99.42%, whereas that from industrial effluent were 94.17, 94.67 and 92.81%.

The maximum adsorption capacity was found to be 23.26, 16.13 and 10.20 mg/g for Cd^{2+}, Pb^{2+} and Cu^{2+} ions respectively. Similarly the bark powder of *Moringa stenopetala* was used as an absorbent for heavy metals from wastewater [28]. The maximum removal efficiency of Cd(II), Pb(II) and Cu(II) were 99.08, 99.68 and 99.60% from synthetic wastewater respectively. Whereas, the removal efficiency was 94.80, 95.50 and 94.23% for Cd(II), Pb(II) and Cu(II) respectively in real wastewater. The maximum adsorption capacity of 38.46 ± 0.21, 35.71 ± 0.86 and 34.48 ± 0.93 mg g^{-1} was observed for Cd(II), Pb(II) and Cu(II).

Biosorption percentage of modified bark extract is comparatively higher and thus efficient than the biosorption percentage of modified leaf extract [29]. It was seen that cadmium has highest adsorption percentage with both bark and leaf extracts (58% and 42%) of *M. oleifera*. Maximum adsorption of 70% was observed with zinc and nickel showed least adsorption percentage (15%) for bark extract.

The effectiveness of *Moringa* aptera Gaertn in the removal of heavy metals was evaluated by Matouq et al., [30]. Kinetic test demonstrates that biosorption equilibrium reached within 40 min for copper, 30 min for nickel and 40 min for chromium. The removal percentage increases with increasing the adsorbent dose in the solution, but the adsorption capacity of *Moringa* pods decreases. It was found that *Moringa* pods were not a good biosorbent for the removal of zinc from wastewater.

The potential of *Moringa oleifera* seed powder and its aqueous extract on pH, electrical conductivity to minimize heavy metals load of sewage waste water was investigated by Basra et al., [31]. The increase in pH was maximum after 1 h contact time when *Moringa* seed powder alone or used in combination with alum as compared to control or alum alone. However, increase in pH was constant after 3 or 6 h contact time for seed powder. The removal of metal ions increased gradually with contact time and individual effect of *Moringa* seed aqueous extract and seed powder adsorb and remove Pb and Cr after 1, 3 and 6 h was more significant in treated sewage water than untreated.

Obuseng et al., [32] investigated the uptake of different metal ions such as lead, copper, cadmium, nickel, and manganese from the single and multimetal solutions using *M. oleifera* seed biomass. Potential of the citric acid modified *M. oleifera* leaves powder in removing Cd(II), Cu(II) and Ni(II) ions from an aqueous solution by biosorption in the batch method was performed by Reddy et al., [33]. The maximum removal efficiency of three metals was observed in the pH range 4-6. The results revealed that the optimum biosorption pH value for Cd(II), Cu(II), and Ni(II) was 5.0. The maximum biosorption percentage reached >90% for all metal ions as biomass concentration was 0.04 g. Kinetic test demonstrated that sorption equilibrium is reached within 50 min and the metal sorption capacity was found to be in the general order of Cd(II) > Cu(II) > Ni(II) (Table 1).

M. oleifera seed demonstrated good removal of cobalt, copper, lead, cadmium and silver [35]. *M. oleifera* seeds were used for sorption studies using AgI standard solutions in batch experiments as functions of adsorbent mass, extraction time, particle size and pH [3]. The optimum conditions were found as 2.0 g of adsorbent with particle size of 75-500 µm, 100 mL of 25.0 mg L^{-1} AgI, extraction time of 20 min and pH at 6.5.

Conclusion

This review explored a new cheaper, economical and eco friendly biosorbent using *Moringa* biomass for the removal heavy metal ions. The sorption process depends on the initial metal concentration, pH, contact time and particle size, biomass type and species used. This paper summarizes the effective *Moringa* biomass capable of removing a wider range of heavy metals from aqueous solutions.

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