MORINGA OLEIFERA SEEDS AS A LOW-COST BIOSORBENT FOR REMOVING HEAVY METALS FROM WASTEWATER

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ABSTRACT

Heavy metals are considered to be one of the major contaminants of water in recent years due to their non-biodegradable property; hence making them toxic and bioaccumulate to living organisms. Conventional methods such us chemical precipitation, physical treatment through ion exchange are used for removing heavy metal ions from water. These methods are expensive and attributed to incomplete metals removal and high cost of treatment. In recent years, researchers have found alternative low cost and effective method for removal of toxic metals through biosorption process using biological materials. Moringa oleifera seeds is one of the biological materials which has effective adsorption capacity for removal of heavy metals from water and wastewater. In this article, the seeds of Moringa oleifera seeds as a low-cost biosorbent for removal of heavy metals is presented. Moringa oleifera seeds is inexpensive material that contains amino acids. The amino acid is a major constituent of the functional groups that aids in greater ability of heavy metals removal through metal ion exchange or complexation, which is mainly affected by pH, biosorbent dosage, and contact time. *Moringa oleifera* seeds residues have a greater capacity to absorb heavy metals in a single solution compared to multi ion solution.

Keywords: *Moringa oleifera* seeds, biosorbent, heavy metals, amino acids, waste water.

INTRODUCTION

Heavy metals constitute a major group of contaminants of water. They arise from different sources such as natural geochemical and anthropogenic activities (Kumari, Sharma, Srivastava, & Srivastava, 2006). Heavy metals are defined as metallic substances that have a relatively high density (at least 5 gcm^{-3}) compared to water (Tchounwou, Yedjou, Patlolla, Sutton, & Luch, 2012). The bases of anthropogenic activities originate from agricultural activities, atmospheric deposition, road run off, discharges from industrial plants and sewage works, acidic mine effluents and building of reservoirs (Sajidu, Henry, Kwamdera, & Mataka, 2005). Heavy metals are a danger to human life and the environment due to its non-biodegradability compare to organic pollutants making them toxic and persistent in the environment and increasing their concentrations in living systems-bioaccumulation (Adhiambo, Lusweti, & Morang'a, 2015). Metals such as cadmium (Cd), arsenic (As), chromium (Cr), manganese (Mn), copper (Cu), mercury (Hg), nickel (Ni), iron (Fe), zinc (Zn) and lead (Pb) (Jarup, 2003) are found to be toxic to humans and ecological environments even in low concentrations. Table 1 shows some heavy metals and their maximum acceptable concentrations in drinking water set by the Environmental Protection Agency (EPA). Some of these heavy metals have the potential of being assimilated, stored and concentrated in the human body, resulting in several diseases to the human body. (E.g. central nervous system impairment, kidneys failure, liver disorder) (Verbost, Flik, Pang, Lock, & Bonga, 1989). Therefore, it is of extreme importance to prevent heavy metals from entering drinking water sources by ensuring their removal from wastewater before it is disposed of into the environment. This is a crucial step towards meeting the acceptable concentrations of metals in drinking water such as those set by the EPA and, hence, prevent any potential adverse effects on human health and aquatic life. Over the years, many treatment options like physical, chemical, and biological were implied to remediate heavy metal contaminated soil, water, and sediments. Such methods include thermal treatment, adsorption, chlorination, chemical extraction, ion-exchange, membrane separation, electrokinetics, bioleaching etc (Aruliah et al., 2019). Moringa Oleifera is increasingly becoming a biosorbent in the removal of heavy metal from waste and polluted water. However, some key findings such as dosage, pH and time kinetics have not been explicit. Therefore, this review is to elucidate on these key gaps identified in the literature in order to provide clear and unambiguous end to these issues.

Table 1. Maximum acceptable concentrations of some heavy metals in drinking water

Element	EPA Limit (mgL^{-1})
Antimony	0.006
Arsenic	0.010
Beryllium	0.004
Chromium (total)	0.100
Cadmium	0.005
Cupper	1.300
Lead	0.015
Mercury	0.002
Selenium	0.050
Silver	0.100

BIOSORPTION-PREFERRED METHOD FOR HEAVY METALS REMEDIATION OF WASTEWATER

Many methods for heavy metals removal from water and wastewater including chemical precipitation and physical treatment (Singh, Rupainwar, Prasad, & Jayaprakas, 1998) have been studied. These methods are costly and have disadvantages such as incomplete removal of heavy metals, high treatment cost, and generation of secondary waste which are very toxic hence, requiring cautious disposal (Congeevaram, Dhanarani, Park, Dexilin, & Thamaraiselvi, 2007; Apori, Hanyabui, & Asiamah, 2018). Researchers have found an alternative method which is very cheap and efficient in removal of toxic metals through biosorption. Biosorption, which is the removal of heavy metals from water and waste water using biological materials are less costly compared to chemical and physical treatments methods. The Biosorption method depends on the capability of biological materials to remove heavy metals through metal binding by multiple mechanisms such as ion exchange, electrostatic forces and precipitation. Some of the biological methods used for the removal of heavy metals includes trickling filter, biosorption, activated sludge process, and various anaerobic methods. Studies have indicated that *Moringa oleifera* seed used as a biological material for heavy metals removal from water and waste water has a potent adsorption capacity (Kumari et al., 2006). This review looks at the botanical classification, morphological, geographical distribution and climatic conditions favoring growth and performance of moringa. Further, mechanisms and models explaining the sorption properties of moringa seeds as biosorbent are discussed in this review.

MORINGA OLEIFERA

Moringa oleifera is one of the 14 species of *Moringa* which is the sole genus of the plant family *Moringaceae*. *Moringa oleifera* is originated from western and sub-Himalayan tracts, India, Pakistan, Asia Minor, Africa and Arabia (Mughal, Ali, Srivastava, & Iqbal, 1999) and is a fast-growing shrub or small tree, attaining a height of 12 meters. It consists of a crown and trunk which is always single. It is well adapted to the semi-arid tropics and subtropics conditions and are highly tolerant to poor soils (da Silva & Kerr, 1999). It is drought tolerant and has nutritional and water purification attributes (Muyibi, Noor, Ong, & Kai, 2001). *Moringa oleifera* seeds (Figure 1) have been used as adsorbents for removing metal ions due to their good adsorption capacity. Moringa has a wide range of uses including as food, traditional medicine, fodder, and as a living fence (Morton, 1991; Coote, Stewart, & Bonongwe, 1997; Pratt, Henry, Mbeza, Mlaka, & Satali, 2002). *Moringa oleifera* is an important food which is now considered to be a 'natural' nutrition of the tropics. It is highly nutritive and used as vegetable in many countries, particularly in India, Pakistan, Philippines, Hawaii and many parts of Africa (Anwar, & Bhanger, 2003; Anwar, Ashraf, & Bhanger, 2005). The roots are used as a horseradish substitute and the young green pods are a delicacy in India. The leaves are edible and good sources of Vitamins A and C, and protein concentrate. The tree appears in the pharmacopoeia of Africa, Asia, South America and the Caribbean for the traditional treatment of many illnesses including asthma, diarrhea, fever, cough, stomach pains, blood pressure, heart problems, epilepsy and joint diseases (Sajidu et al., 2005).

Moringa oleifera Seed

The seeds of *Moringa oleifera* can be considered as a lignocellulosic adsorbent due to their cellulose; hemicellulose and lignin constituent. Seeds which contain 30 % and 30 % lipids are made up of functional groups such as O–H, C=O, C–N, which comprise macromolecules (Pagnanelli, Mainelli, Vegliò, & Toro, 2003). Amino acids are a major constituent of the functional groups (Araújo et al., 2010). The proteinases amino acids have diverse structure in relation to pH dependent properties and consist of physiological groupings of varying binding agents. The binding agents have great ability to interact with a metal either by metal ion exchange or complexation to form organo-metallic complex. *Moringa oleifera* seed (MOS)-metal ion binding appears to be an ion exchange process involving electrostatic attraction between negatively charged groups of amino acids and metallic cations (Kumari et al., 2006).

Fig. 1: Seeds of Moringa oleifera

FACTORS INFLUENCING HEAVY METAL SORPTION OF UNMODIFIED *MORINGA OLEIFERA* SEEDS IN WASTEWATER TREATMENT

Phenomenon of adsorption is widely used because of its relatively high performance, environmental friendliness and less operational difficulty. A number of researchers have used various adsorbent systems for the removal of heavy metals from waste water, produced from various industrial waste materials. Many of these low-cost sorbents include bark, lignin, farm waste, fly ash and clay minerals (Kalavathy, & Miranda, 2010; Galiatsatou, Metaxas, & Kasselouri-Rigopoulou, 2002). Among the many variables that affect metal adsorption process is pH. pH is the most critical parameter that affecting any adsorption studies (Araújo et al., 2010) due to their interference in the solid–solution interface, effecting the charges of the active sites of the MOS and the metal behavior in the solution (Gao, & Wang, 2007).

Table 2. Heavy metals removal in waste water using unmodified *Moringa Oleifera* seed (LM-Langmuir model, Q_{max}- Adsorption capacity, FM-Freundlich mode NR-Not reported)

Heavy metals	pH	Biomass Dosage (g)	Contact time (min)	Q_{max} (mg g^{-1})	Types of Metal solution	Model	% Removal	Mechanism	Sources
Cd^{2+}	6.5	4.0	40	1.06	Ternary	LM	NR	Amino acid-metal interaction	(Sharma, Kumari, Srivastava, & Srivastava, 2007)
Cr^{3+}	6.5	4.0	40	1.01		LM	NR		
Ni^{2+}	7.5	4.0	40	0.94		LM	NR		
Ag	6.5	2.0	20	NR	single	NR	100	Electrostatic attraction	(Araújo et al., 2010)
Cd^{2+}	6.5	2.0	20	NR		NR	70		
Co^{2+}	6.5	2.0	20	NR		NR	28		
Cu^{2+}	6.5	2.0	20	NR		NR	82		
Pb^{2+}	6.5	2.0	20	NR		NR	98		
Cd^{2+}	7	0.4	160	7.864	Single	FM	NR	Ion exchange	(Meneghel et al., 2013)
Cd^{2+}	6.5	4	40	-	Single	NR	85.10		Kumari, et al., 2006
Cd^{2+}	NR	0.5-1.5	60	0.168	single	LM	NR	Ion exchange	(Madzvamuse, Kugara, Shumba, 2015)
Cr^{3+}	NR	0.5-1.5	60	-		NR	NR		
Pb^{2+}	NR	0.5-1.5	60	1.281		LM	NR		
Cd^{2+}	NR	0.2	30	93.30	single	FM	97	Ion exchange	(Aziz, Jayasuriya, & Fan, 2015)
Pb^{2+}	NR	0.2	30	59.63		LM	81		
$Ni^{2+\ d}$	NR	0.2	30	101.83		LM	74		
Pb^{2+}	NR	0.2	NR	NR		NR	90	Amino acid-metal interaction	(Ali, 2017)
Ni^{2+}	NR	0.2	NR	NR		NR	85		
Cd^{2+}	NR	0.2	NR	NR		NR	99		
Mg^{2+}	4.0-6.4	0.5	5	5.61	Single	LM	100	Ion exchange	(Marques, Alves, Coelho, & Coelho, 2013)
Cd^{2+}	NR	2	NR	NR	single	NR	89	Ion exchange	(Sajidu et al., 2005)
Pb^{2}	NR	2	NR	NR		NR	92		
Ni^{2+}	NR	2	NR	NR		NR	48		
Cu^{2+}	6.5	2	30	3.83	single	FM	NR	Amino acid-metal interaction	(Kowanga, Mauti, & Mbaka, 2016)
Pb^{2+}	5.5	2	40	1.50		FM	NR		
Cr^{3+}	7	1	60	12.6	single	FM	97.94	Amino acid-metal interaction	(Ghebremichael, Gebremedhin, & Amy, 2010)
Cr^{4+}	2	2	60	-		NR	99.9		

The next parameter is the dosage or quantities of adsorbing material. Increase in the dosage of adsorbent increases the amount of metal ions adsorbed onto the surface of the adsorbent (Adelaja, Amoo, & Aderibigbe, 2011). The increase is attributed to the fact that more adsorption sites will be available when the mass of the adsorbent is increased. The period in which the adsorbate and absorbent are in contact with each other influences the efficiency of heavy metal removal. The efficacy is attributed to the rapid uptake of heavy metals onto the surface of the biosorbent in a shorter time followed by slow release of the ions back in the solution with time until an equilibrium is attained. This is due to the saturation of the available adsorption sites present on the MOS (Table 2).

ADSORPTION CAPACITY AND MECHANISM FOR REMOVAL OF HEAVY METAL IONS USING UNMODIFIED MORINGA SEED AS BIOSORBENT

Many studies have reported that metal sequestration occurs through complex mechanisms, including ion-exchange and complexation depending on several factors including biomass dosage, type of metal ion and contact time (Araújo, Melo, Alves, & Coelho, 2010). Seeds of *Moringa oleifera* have a great sorption capacity for heavy metal removal. The seeds consist of many forms of functional group such as O–H, C=O, C–N, and others physiological diverse group of binding agents. The binding agents consist mainly of negative charges, coming from their surface functional groups, which exchanges with the positive charge of the heavy metal ion through ion-exchange mechanism. Kumari et al. has reported on significant Cd (II) removal from aqueous solution by *Moringa oleifera* seed (Kumari, et al., 2006). In their study it was shown that the biosorption of Cd by MOS is attributed to the availability of carboxyl groups especially of amino acids functionality interacting with Cd (II) ions to form ligands. According to Kalavathy and Miranda, arsenic, copper, cadmium, lead, nickel and zinc are the most significant contaminants (Kalavathy, & Miranda, 2010). It is well known that the presence of heavy metals in the atmosphere is responsible for a number of diseases associated with the risk of dermal injury, respiratory problems and various forms of cancer, even in moderate concentrations.

The most commonly used isotherm models for adsorption study are Langmuir, Freundlich, Dubinin-Radushkevich and Temkin. It can be clearly observed in Table 2 that metal ions removal has been shown to both fit Langmuir and Freundlich model but majority they are best fitted to Langmuir model (e.g. Cd^{2+}, Cr^{3+} and Ni^{2+}) which is based on the assumption that adsorption is limited to monolayer coverage, all surface adsorption sites are the same with each site accommodating one adsorbed particle and there is no interaction between neighboring adsorbed molecules or atoms; and there are no phase transition (Ghebremichael et al., 2010). Madzvamuse et al. (2015), compared adsorption properties of MOS and activated MOS as low- cost adsorbent for the uptake of lead, chromium, mercury and Cadmium as mono component system. They found that the data for *Moringa oleifera* seeds fit well with Langmuir isotherm model for lead and cadmium ion removal. Also, increase in the dosage of Moringa *oleifera* seed from 86.0 % to 99.38 % increases the amount of metal ion adsorbed onto the surface of the adsorbent (Adelaja et al., 2011; Madzvamuse et al., 2015; Shama et al., 2007). Araújo et al. (2010b) recorded 98% removal of lead using 2.0 grams dosage of *Moringa oleifera* compared to 81% of lead removal with same dosage of MOS (Aziz et al., 2015), the differences are as a result of the environment in which the experiment were conducted. The mechanism underlying increased sorption of these heavy metals was attributed to in increased amount of adsorption site for greater removal of the heavy metals (Koetlisi and Mucgaonyerwa, 2019).

Moringa oleifera seeds residues have a greater capacity to absorb heavy metals in a single solution compared to multi ion solution. However, in single metal solutions, ions with larger ionic radii are better adsorbed than those with less ionic radii (Igwe and Abia, 2007). Sharma et al., conducted biosorption of multi-solution composed of Cd (II), Cr (III), and Ni (II) on unmodified shelled *Moringa Oleifera* seed in ternary mixture and compared it to a single metal ion solution (Sharma et al., 2007). The results of the study suggest that sorption capacity for each of the metal ions present in the multi metal ion solution was less compared to the ions in the single metal solution which was attributed to reduction in the availability of the binding sites (Igberase, Osifo, & Ofomaja, 2017). Also, seeds of plant species like *Moringa oleifera* (MO) contain natural polyelectrolyte mainly of potential nitrogen and oxygen ligands that are known to have an affinity for coordinating to heavy metals. Sajidu et al., studied the removal of lead, iron and cadmium ions by polyelectrolytes of the Moringa Oleifera whole seed kernel and results indicated that, Moringa Oleifera seed polyelectrolytes showed considerable lead, cadmium and iron removal property with percentage reduction in solutions of 89%, 48% and 92%, respectively (Sajidu et al., 2005).

CONCLUSION

The present articles reviews Moringa Oleifera Seeds as a Low-Cost Biosorbent for removing heavy metals from wastewater. Waterbodies are polluted with heavy metals through various activities, the various technologies used to treat wastewater is very expensive and resource demanding. The seeds of Moringa oleifera has been proved and established as a cost-effective process for the treatment of wastewater. *Moringa oleifera* seed residue is an inexpensive material that contains amino acid which is a major constituent of the functional groups that aids in heavy metal removal in waste or contaminated water. The binding agents have great ability to interact with the metal either by metal ion exchange or complexation to form organo-metallic complex. *Moringa oleifera* seed - metal ion binding seems to be an ion exchange mechanism involving electrostatic attraction between negatively charged groups of amino acids and metallic cations. *Moringa oleifera* seed have the potential to remove heavy metals in single solution than multi ions solution and is mainly affected by pH "between" 5-8, biosorbent dosage, and contact time.

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