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REVIEW PAPER OPEN ACCESS

Removal of heavy metals by natural adsorbent: review

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Abstract

Water pollution by heavy metals has been recorded as a major problem in the global context. It occurs due to the direct and indirect discharge of diverse chemicals into the water bodies without sufficient treatment to reduce and diminish the harmful compounds. Many methods and materials are used in heavy metal removal from water. Biosorption by plant leaves is a potent and environmentally alternative technique for heavy metals removal from water.

This review article revises the most recent studies of biosorbents such as plants" leaves, plants' seeds, barks, and agricultural wastes and their efficiency on heavy metals adsorption, like Lead. Cadmium, Mercury, Chromium, Arsenic, Copper, Zinc and Nickel. This literature revision draw the base line of our ongoing study which explores the removal efficiency of *Moringa oleifera* leaves on cadmium and the sorption properties of the plant *Moringa oleifera* Lam. leaves for decontamination of Cd at laboratory scale.

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Introduction

Pollution of surface and ground water caused by human and industrial activities has been recorded as a major problem in the global context (Satya *et al.,* 2011) Water pollution considered as the leading universal cause of 80 % of diseases (OECD, 2006). According to the United Nations organization reports there are 1.1 billion people still do not have access to safe supply of drinking water; the majority of them are among the world's poorest and developing countries (Abaliwano *et al.,* 2008), Table 1 shows some details of the sources and toxicity of some heavy metals.

Table 1. Heavy metals sources and its toxicity.

Metal	Source	Toxic effect	Reference
Cadmium	Electroplating, smelting, alloy manufacturing, pigments, plastic and mining	Itai–Itai disease, carcinogenic, renal disturbances, lung insufficiency, bone lesions, cancers, hypertension, weight loss	(Momodu and Anyakora, 2010; Sharma and Bhattacharyya, 2005; Singh, 2005)
Lead	Manufacturing of batteries, pigments Electroplating, ammunition	Anaemia, brain damage, anorexia, malaise, loss of appetite	(Ali *et al.,* 2013; Low *et al.,* 2000; Mataka *et al.,* 2006)
Chromium	Electroplating, paints and pigments, metal processing, steel fabrication and canning industry	Epigastric pain, nausea, vomiting, severe diarrhoea, lung tumors, Carcinogenic, mutagenic, teratogenic	(Ali *et al.,* 2013; Rao *et al.,* 2010; Singh, 2005)
copper	Electronics plating, paint manufacturing, wire drawing, copper polishing, and printing operations	Reproductive and developmental toxicity, neurotoxicity, and acute toxicity, dizziness, diarrhoea	(Ali *et al.,* 2013; Bilal *et al.,* 2013)
Arsenic	Smelting, mining, energy production from fossil fuels, rock sediment's	Bone marrow depression, haemolysis, liver tumors, gastrointestinal symptoms, cardiovascular and nervous system functions disturbances,	(Momodu and Anyakora, 2010)
Mercury	Volcanic eruptions, forest fires, battery	Corrosive to skin, eyes, muscles, neurological and renal disturbances,	(Farooq *et al.,* 2010)
Nickel	copper sulphate manufacture, electroplating, non-ferrous metal, mineral processing,	Reduced lung function, lung cancer, chronic bronchitis, dermatitis, chronic asthma.	(Febrianto *et al.,* 2009; Öztürk, 2007)
zinc	Mining and manufacturing processes	Causes short term "metal-fume fever," gastrointestinal distress, nausea and diarrhea	(Farooq *et al.,* 2010)

Every day, there are thousands of chemicals discharged directly and indirectly into water bodies without further treatment for elimination of the included harmful compounds (Salim *et al.,* 2008). Heavy metals are without doubt well thought-out as the most hazardous and harmful metals even if they present as traces, since they accumulate in the tissue of living organisms (Rao *et al.,* 2010).

The use of inorganic coagulants for water treatment is a wide-ranging. Aluminum sulphate and activated carbon are examples of the inorganic coagulants and aluminum sulphate is the most commonly used coagulant in the developing countries (Farooq *et al.,* 2010). However, aluminum sulphate reported to cause some neurological diseases for instance pre-senile dementia or Alzheimer's disease. The adsorption by activated carbon known to be the most efficient way for removing heavy metals (removes more than 99% of certain metal ions), but still uneconomic method and cannot be recycled (Othman *et al.,* 2010). Table 2 illustrates the advantages and disadvantages of some techniques to remove heavy metal.

Table 2. Advantages and disadvantages of some techniques to remove heavy metal.

Method	Advantages	Disadvantages
Chemical Precipitation	Inexpensive. Simple. Most of the metals can be removed.	Disposal problems. Large amounts of sludge produced. (Abaliwano *et al.,* 2008)
Ion-exchange	Metal selective. High regeneration of Materials.	Fewer numbers of metal ions removed. High cost. (Rao *et al.,* 2010)
Chemical coagulation	De watering. Sludge settling.	Large consumption of chemicals. High cost. (Abaliwano *et al.,* 2008)
Membrane process and ultrafilteration	High efficiency (>95% for single metal Less solid waste produced Less chemical consumption.	Removal (%) decreases with the presence of other metals. High initial and running cost. Low flow rates. (Fu and Wang, 2011)
Using natural zeolite	Relatively less costly materials. Most of the metals can be removed.	Low efficiency. (Fu and Wang, 2011)
Adsorption Using activated carbon	High efficiency (>99%). Most of the metals can be removed.	No regeneration. Cost of activated carbon. Performance depends upon adsorbent. (Abaliwano *et al.,* 2008)
Electrochemical methods	Pure metals can be achieved. Metal selective. No consumption of chemicals.	High running cost. High capital cost. Initial solution pH and Current density. (Rao *et al.,* 2010)

Though, currently used methods contain several restrictions in the removal of heavy metals from water (Abaliwano *et al.,* 2008). Such methods showed to be not effective and not economically possible for the treatment of low concentrations (Kelly-Vargas *et al.,* 2012).

Biosorption is a property of both living and dead organisms (and their components), and has been exploited as a promising biotechnology because of its simplicity (Bilal *et al.,* 2013). Accordingly, Biosorption can be defined as the removal of substances from solution by biological materials (Gadd, 2001); Table 3 represents the advantages and disadvantages of used biosorbents. Biosorption describes any system includes a sorbate (an atom, molecule, a molecular ion) work together with a biosorbent (a solid surface of a biological matrix) resulting in an accumulation at the sorbate–biosorbent interface, and therefore a decrease of sorbent concentration in the solution (Sasaki *et al.,* 2013). Several biosorption studies have been carried out using microbial systems such as bacteria, microalgae and fungi. Many proceedings have been studied and developed for the effective removal of heavy metals using biosorbents, such as microbial biomass (Beveridge and Murray, 1980) and agricultural waste materials like sugar cane bagasse, fly ash and peat (Gupta and Ali, 2000), rice husks and straws (Han *et al.,* 2013), soya bean, saw dust, walnut and cotton seeds hull, corn cobs, banana peels (Memon *et al.,* 2008).

Table 3. Advantages and disadvantages of biosorbents.

Advantages	Disadvantages
Low operation costs if low-cost sorbents are used. (Fu and Wang, 2011)	Shorter life time of biosorbents when compared with conventional sorbents. (Fu and Wang, 2011).
Low quantity of sewage sludge disposed. (Gadd, 2008).	Early saturation i.e. when metal interactive sites are occupied.(Gadd, 2008).
COD of wastewater does not increase. (Sahmoune *et al*., 2011).	Recyclable and decomposable properties of biomass are delaying their long-term applications in adsorption processes. (Sahmoune *et al*., 2011).
The process is simple in operation. (Sahmoune *et al*., 2011).	
Biosorbents are selective and regenerable. (Fu and Wang, 2011).	

Natural Biosorbents

Agricultural waste materials are usually composed of lignin and cellulose as the main constituents (Beveridge and Murray, 1980). Other components are hemicelluloses, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process, for example carboxyl, amino, alcohol and esters (Gupta and Ali, 2000). These groups assumed to have the ability to bind heavy metal by replacement of hydrogen ions for metal ions in solution or by donation of an electron pair from these groups to form complexes with the metal ions in solution. Many researchers reported the relation between the presence of various functional groups and their complexation with heavy metals during biosorption process (Tarley and Arruda, 2004). A number of studies have highlighted the potential of inexpensive adsorbents prepared from an agricultural by-product (Babel and Kurniawan, 2003). (Benaissa, 2006) has investigated the capacity of four inexpensive materials which are peels of peas, broad bean, medlar and fig leaves, to remove cadmium from aqueous solutions, it was noted that the broad bean peel has the maximum adsorption capacity for Cd (II). Furthermore, *Agave sisalana* (sisal fiber) was proposed as a biosorbent for Pb (II) and Cd (II) ions from natural waters (dos Santos *et al.,* 2011). In addition, adsorption of Ni (II) ion from water was studied using two strains of *Yarrowia lipolytica* (Shinde *et al.,* 2012). A newly developed deep-sea bacterium, Pseudo alteromonas was reported as a biosorbent for Cd (II) removal from water (Zhou *et al.,* 2013).

Saw dust as biosorbent

Saw dust has been widely studied to remove metal ions from waste water. A research group has carried out a comprehensive study on treated and untreated saw dust and the initial adsorption was observed to be very fast (Memon *et al.,* 2007). Popular Romanian fir tree sawdust (*Abies alba*) was investigated as biosorbant for Cd (II) removal from synthetic aqueous solution and showed good results (Nagy *et al.,* 2013).

Tree Barks, stems and straw as biosorbent

The capability of coniferous barks for removing toxic heavy metal ions was investigated too (Seki *et al.,* 1997).

Reddy *et al.* (2011) found that *Moringa oleifera* bark is very effective for the removal of Ni (II) from aqua solutions. In 2010, Acacia *nilotica stems* have been investigated by Baig *et al.* (2010) to remove As (II) from surface water. Moreover, Tan and Xiao, 2009 have examined the efficacy of ground wheat stems to remove Cd (II) and they noted that blocking of the functional groups decreased the binding capacity of Cd (II) whereas increasing functional groups improved the binding capacity. In addition,(Ghodbane *et al.,* 2007) studied the effectiveness of eucalyptus bark as an inexpensive adsorbent for removing Cd (II) ions from aqueous solution, and stated that the bark is an excellent adsorbent for removing metals ions from wastewater with efficiency as good as traditional adsorbents with less cost. The *Triticum aestivum* straw powdered has been examined by Farooq *et al.,* (2011) for Cd (II) removal. (Han *et al.,* 2013) has investigated rice straw for Cd (II) removal from water.

Shells and Husks as biosorbents

In 2006, Pino *et al.* have reported that coconut shell - *Coco's nucifera*- Powder is a potent and economical alternative for the biosorption removal of dissolved metals. Chromium adsorption in water was studied by Alves and Coelho, 2013 using *Moringa oleifera* husks. The husk of a black gram (*Cicer arientinum*) was investigated as a new biosorbent of Cd (II) from low concentration aqueous solutions (Saeed and Iqbal, 2003). Moreover, the removal and recovery of Cd (II) from waste waters using a rice husk have studied by Ajmal *et al.,* (2003).

Bran/grains as biosorbents

Rice bran was evaluated for its potential use as a biosorbent for Cd (II), Cu (II), Pb (II) and Zn (II) (Montanher *et al.,* 2005). A novel biosorbent rice polish has been successfully utilized for the removal of Cd (II) from wastewater by Singh, (2005). The use of spent grain a byproduct of the brewing industry was studied by Low *et al.*, (2000), as adsorbent to remove Cd (II) and Pb (II) from aqueous solutions.

Seeds as biosorbents

Litchi chinensis seeds were indicated as an effective biosorebent for Ni removal from aqueous solutions (Flores-Garnica *et al.,* 2013). Removal of Pb (II), Cu (II), Cd (II), Ni (II), As (II), Mn (II), and Zn (II) by *Moringa oleifera* seeds was examined (Obuseng *et al.,* 2012). J*antropha curcas L.* Seed's hull has been investigated for Cd (II) and Zn (II) metals ions' removal from aqueous solution (Mohammad *et al.,* 2010). In 2012, *Strychnos potatorum* seeds have been investigated by (Saif *et al.*, 2012) to remove Cd (II) from aqueous solution.

Leaves as biosorbents

Cinnamomum camphora leave's powder was investigated as a biosorbent for the removal of Cu (II) and Pb (II) ions from aqueous solutions (Chen *et al.,* 2010). Furthermore, it was reported that *Moringa oleifera* leaves extract is a good sorbent for Pb (II) from aqueous solution (Reddy *et al.,* 2010). A batch adsorption study of Cd (II) ions from aqueous solution by *Hevea brasiliensis* (HB) leaf powder has also been reported (Hanafiah *et al.,* 2006). Sharma and Bhattacharyya, (2005) have studied the adsorption of Cd (II) using neem leaf powder. In addition, the leaves of the olive tree (*Olea europaea*) were proposed as a novel adsorbent for the removal of Cd (II) from solutions (Hamdaoui, 2009). Recently, extensive studies on Cd (II) adsorption taking powdered leaves of a variety of trees have been carried out (Pandey *et al.,* 2008).

Factors affecting on biosorption of heavy metals

The effect of different operating parameters such as initial concentration of heavy metal, adsorbent dosage, temperature, particle size of adsorbent, effect of pH on the biosorption capacity and other factors are summarized in Table 4(Chojnacka, 2010).

Conclusion and remarks

Lately many research works have been conducted and numerous research groups are still running intensive experiments to find economical eco-friendly techniques and bio-materials to be exploited for heavy metal removal and water treatment before discharging it to the environment. Adsorption is one of the most studied techniques. The main categories of adsorbents are carbon, agricultural wastes, industrial wastes, clays and others. Some of the adsorbents with high loading capacities (>90 mg/g) for example broad been peel, fig leaves, Kraft lignin, Platanus orientalis, Medlar peel, peas peel, rice husk, modified sugarcane bagasse, modified wheat bran, aliginate carriers, alcaligenes eutrophus and baker's yeast are used (Rao *et al.,* 2010).

Table 4. Factor affecting biosorption.

Factors	Effects
Biosorbent dosage	It decreases the quantity of biosorbed pollutant per unit weight of biosorbent, but increases its removal efficiency
Initial pollutant concentration	It increases the quantity of biosorbed pollutant per unit weight of biosorbent, but decreases its removal efficiency
Solution pH	It enhances biosorptive removal of cationic metals or basic dyes, but reduces that of anionic metals or acidic dyes
Temperature	It usually enhances biosorptive removal of adsorptive pollutant by increasing surface activity and kinetic energy of the adsorbate, but may damage physical structure of biosorbent
Agitation speed	It enhances biosorptive removal rate of adsorptive pollutant by minimizing its mass transfer resistance, but may damage physical structure of biosorbent
Ionic strength	It reduces biosorptive removal of adsorptive pollutant by competing with the adsorbate for binding sites of biosorbent
Biosorbent size	It is favorable for batch process due to higher surface area of the biosorbent, but not for column process due to its low mechanical strength and clogging of the column
Other pollutant concentration	If coexisting pollutant competes with a target pollutant for binding sites or forms any complex with it, higher concentration of other pollutants will reduce biosorptive removal of the target pollutant

Cd (II) is amongst the most toxic and hazardous ions to living organism and its allowable limit in drinking water must be 0.005 mg/L. As a result removal and eliminating Cd (II) in the polluted water has become a vital mission and essential environmental goal to search for appropriate and alternative solutions. Removal of Cd (II) from aqueous solutions can be accomplished by several techniques such as chemical precipitation, ion exchange, membrane separation and adsorption.

However, it was found that up to this moment and according to the best of our knowledge, there are some studies on *Moringa oleifera* seeds and bark to remove heavy metals from water, meanwhile, there are no or not disclosed studies on the leaves of *Moringa oleifera* to remove Cd (II) from water, Therefore it was found that it is very useful and encouraging to use *Moringa oleifera* leaves to remove Cd (II) from water and wastewater and in our ongoing research we are examining the effect of *Moringa oleifera* leaves on Cd (II) removal and the optimum conditions that might give the best results in this work.

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