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Review

Utilization of *E. crassipes* in the biosorption and recovery of metals from aquatic environments

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Water hyacinth (*Eichhornia crassipes*), has attracted significant attention as the world's worst invasive aquatic plant due to its extremely rapid proliferation and congest growth, presenting serious challenges in navigation, irrigation, and power generation. Attempts to control the weed have proved to be costly with minimum results. However, the same plant has demonstrated an amazing ability to absorb and concentrate many toxic metals from aquatic environments. Consequently, research activity on utilization of the plant has been registered over the last few decades. This article reviews literature related to the utilization of *E. crassipes* in the biosorption and recovery of metals from aquatic environments. Availability in large quantities, high biosorption capacity, renewability and low cost determine the extent to which biosorbents can be adapted technologically. Sorption dynamics through classical and competitive models, effect of physical and chemical treatment, pH, temperature, initial metal concentration and biosorbent dose on metal removal by water hyacinth is discussed.

Key words: Biosorption, heavy metals, precious metals, recovery, water hyacinth.

INTRODUCTION

The toxicity and health hazards associated with heavy metals have been established beyond any doubts. Considerable attention has been paid to methods for metal removal and those commonly used include; electrochemical methods, reverse osmosis, chemical precipitation, ion exchange, biological processes, flotation and membrane processes (Park et al., 2010). Unfortunately, limitations synonymous with these methods have been understood to include incomplete metal removal, high energy or reagent requirements or the generation of toxic sludge and other waste products which require disposal. In addition, these methods are also limited when used for the decontamination of aquatic systems with adsorbates in a low concentration range (Vieira and Volesky, 2000; Volesky, 2007). As a result of these challenges, there has been considerable interest in the use of other sorbent materials, particularly bio-sorbents (Volesky and Holan, 1995; Vasudevan et al., 2001; Vijayaraghavan and Yun, 2008).

'Biosorption' has been defined by Volesky (2007), a pioneer in the field, as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions. As opposed to a much more complex phenomenon of bioaccumulation based on active metabolic transport, biosorption by dead biomass (or by some molecules and/or their active groups) is passive and based mainly on the "affinity" between the (bio) sorbent and sorbate (Volesky, 2007). The biosorption process involves a solid phase (sorbent or biosorbent) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ion). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution (Hussain et al., 2010). The biosorbent materials possess metal-sequestering property and can be used to decrease the concentration of heavy metal ions in solution from ppm to ppb level. Advantages of this technology over conventional ones include its low cost, high efficiency, minimisation of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery following adsorption (Gadd, 1993).

In their recent review paper, Park et al. (2010), observed that biosorbents that have been sought for the removal of metal ions primarily fall into the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes, natural residues and other biomaterials, the former two perhaps giving broader choices. Some mycelia available in large quantities as waste materials from large scale fermentation processes have been used as a source of biosorbents conveniently (Kapoor and Virraghavan, 1995). Seaweeds, which can be obtained in large quantities from ocean and inexpensive, have also attracted attention as possible biosorbents (Suzuki et al., 2005). Other abundant natural materials which have been investigated for their heavy metal removal potential are the aquatic macrophytes such as *Pistia stratiotes* and *Lemna minor*, which are present at high growth rate (Wang, 1990; Klumpp et al., 2002). Recently, water hyacinth (*E. crassipes*) has attracted significant attention as a possible biosorbent for the removal of heavy metals (Mahamadi and Nharingo, 2007; 2010a; 2010b).

Water hyacinth is a wild fern belonging to the family pontederiaceae found abundantly in various tropical and sub-tropical countries of Latin America and the Caribbean, Africa, Southeast Asia and the Pacific (Mailu, 2001; Thomson et al., 2002; Mironga, 2004; Plummer, 2005). Generally, the level of reproduction of water hyacinth has been very high in countries where the plant has recently been introduced and this has been attributed, to a large extent, to the eutrophication in water bodies and the absence of natural enemies of the plant. The weed has attracted significant attention as the world’s worst invasive aquatic plant due to its extremely rapid proliferation and congests growth. In many places, the weed presents serious challenges in navigation, irrigation, and power generation (Malik, 2007). The explosive nature of water hyacinth growth and its related problems have called for serious efforts to control its spread. Management strategies have taken a physical, chemical or biological approach (Westerdahl and Getsinger, 1988; Ram and Moolani, 2000; Julien and Griffiths, 1998; Julien and Orapa, 1999; Mbati and Neuenschwander, 2005; Kathiresan, 2000; Zhang et al., 2005; Shabana and Mohamed, 2005; Babu et al., 2004; Ogwang and Molo, 2004).

UNLOCKING VALUE OF WATER HYACINTH

As attempts to control the weed have caused high costs and labour requirements, leading to nothing but temporary removal of the water hyacinths, considerable research effort has been directed towards exploration of various ways of unlocking value in the otherwise troublesome weed. A number of possible uses of the plant, some of which have been developed and others are still in their infancy have been suggested. These include possible utilization of the weed as a phytoremediation agent (Sajn et al., 2005), as a biosorbent for toxic metals (Malik, 2007), for power alcohol and biogas production (Mshandete et al., 2004; Ali et al., 2004), as a compost (Szczeck, 1999), and for animal fodder/ fish feed (Aboud et al., 2005). Other potential uses of the weed include its use as pulp material for producing greaseproof paper (Goswami and Saikia, 1994) and the production of fibreboards for a variety of end uses such as bituminized board for low-cost roofing material, indoor partitioning, etc. Formulations of water hyacinth-based medicines to treat certain diseases have been reported in India (Oudhia, 1999a, b).

Applications of water hyacinth in metal removal

Water hyacinth, among other aquatic macrophytes, has been shown to possess a great potential to remove pollutants when being used as a biological filtration system (Muramoto et al., 1991). It contains many polyfunctional metal-binding sites for both cationic and anionic metal complexes. Potential metal cation-binding sites of algal cell components include carboxyl, amine, imidazole, phosphate, sulphate, sulfhydryl, hydroxyl and chemical functional groups contained in cell proteins and sugars (Mahmood et al., 2010c). The weed could remove several heavy metals and other pollutants (Pinto et al., 1987; Delgado et al., 1993; Zaranyika et al., 1994; Mahamadi and Nharingo, 2007, 2010a, 2010b). Recorded achievements triggered efforts directed towards the utilization of water hyacinth in phytoremediation.

Application of raw, dried water hyacinth roots in metal removal

Dried roots from water hyacinth have been used to study its removal behaviour from monocomponent aqueous metal solutions (Table 1). Schneider et al. (1995) studied the feasibility of dried water hyacinth roots for the removal of Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} ions from aqueous solution. The authors showed that in terms of lead and copper uptake per dried mass of biosorbent, dried roots and aerial parts of water hyacinth are better biosorbents than the biomass of the bacterium *Mycobacterium phlei*, the yeast *Candida parapsilosis*, fungal *Rhizopus oryzae* strains, and acacia bark. Sorption data for the metal ions fitted a Langmuir isotherm with the accumulation following the order $Pb^{2+}>Cd^{2+}\approx Zn^{2+}$ on a weight basis. It was deduced that the mechanism of adsorption involved the carboxylate group on the surface of the biomass. The authors further suggested that dried biomass of the plant might be placed in simple bags and used in a very low-cost metal ion removal system for decontamination of chemical and mining industrial wastewater. In an oncoming publication, Schneider et al. (2001), it was shown that the biomass of macrophytes *Potomoyenten luscens*, *Salvinia herzogii* and *E. crassipes* can be subjected to a number of elution cycles without losing their adsorption capacity. Al Rmalli et al. (2005) showed that a biomaterial produced from dried water hyacinth roots, can provided a simple, effective, yet cheap method for removing arsenic from contaminated water. Elangovan et al., (2008) reported a study for the removal of Cr^{6+} and Cr^{3+} using dried aquatic weeds; reed mat (*Cannomois virgata),* water lettuce (*Pistia stratiotes*), arrow-leaved tear thumb (*Polygonum sagittatum*), lotus flower (*Nelumbo nucifera*), gree taro (*Colocasia esculenta*), water lily flower (*Nymphaea* sp.) mangrove leaves (*Rhizophora mangle* L.) and water hyacinth. It was found that the removal of Cr^{3+} followed the order: reed mat>water hyacinth>mangrove leaves>water lily>green taro, whereas for the removal of Cr^{6+}, mangrove leaves showed the greatest uptake.

On the removal of Cu^{2+} from aqueous solution by dried water roots, Zheng et al. (2010) showed that the biomass have a high affinity and large sorption capacity for the removal of the metal ion. Sorption equilibrium data obtained fitted the Langmuir isotherm and magnitude of the activation energy of the biosorption pointed towards a chemisorption process. The authors concluded that the water hyacinth roots are efficient and inexpensive biosorbent for Cu^{2+} removal. In a more recent publication, Hasan et al. (2010) utilized dried water hyacinth powder of the aerial part of the weed (stem and leaves) for the removal of Cr^{6+} and found that the sorption was negatively affected by pH whereas temperature had a positive effect.

Application of activated carbon and ash derived from water hyacinth in metal sorption

A growing number of researchers have explored the possibility of removing metal ions using activated carbon and ash derived from water hyacinth (Table 2). Shekinah et al. (2002) showed that removal of Pb^{2+} from aqueous solution using activated carbon prepared from water hyacinth increased with increase in pH. In a similar study utilizing activated carbon derived from water hyacinth, Kadirvelu et al. (2004) reported that the sorption of Hg^{2+} depended on contact time, pH, Hg^{2+} and carbon concentration. The sorption data obtained fitted the Langmuir and Freundlich models.

Mahmood et al. (2010c) reported that ash of water hyacinth satisfied the criteria for a hyperaccumulator of Pb^{2+}, Zn^{2+}, Cr^{6+}, Zn^{2+} and Ni^{2+}. Furthermore, it was possible to recover the metals from industrial waste water through desorption experiments. The authors concluded that water hyacinth-derived ash offers several advantages including cost effectiveness, high efficiency, minimization of chemical/biological sludge, and regeneration of biosorbent with possibility of metal recovery.

Application of acid/alkali treated water hyacinth in metal sorption

Biosorption usually contains organic functional groups

Table 1. Batch sorption of metal ions using raw dried roots derived from water hyacinth.

Experimental parameter	Removal/maximum sorption capacity	Reference	Comment
2 mg ml^{-1} biosorbent, initial pH 5.5, with agitation, initial metal concentration 6.3-20 mg l^{-1}.	Pb (47 mg g^{-1}) Cu (23.0 mg g^{-1}) Cd (27.0 mg g^{-1}) Zn (20 mg g^{-1})	Schneider et al. (1995)	Biosorption capacity of water hyacinth found to be greater than that of yeast, bacterial and fungal strains.
30 mg l^{-1} biosorbent dose, 200 µg l^{-1} As(III) or As(v), pH 6, 120 min shaking time.	93% of As(III) 95% of As(v)	Al Rmalli et al. (2005)	As concentration in treated solution < 10 µg l^{-1} (WHO guideline limit value).
10 mg ml^{-1} absorbent, initial pH 5, 150 rpm agitation rate, 303 K temperature, initial concentration 10-150 mg l^{-1}, 6 hr sorption time.	Cr(III) (6.6 mg g^{-1}), Cr(VI) (0.3 mg g^{-1}).	Elangovan et al. (2008)	Biosorption capacity of water hyacinth found to be comparable to that of water lily, green taro, mangrove and reed mat.
0.4 mg ml^{-1} biosorbent, initial pH 5.5, 150 rpm agitation rate, 298 K temperature.	Cu (22.7 mg g^{-1})	Zheng et al. (2009)	Sorption of Cu appeared to involve ion exchange and complex formation.
2 mg ml^{-1} biosorbent, pH 2, 200 rpm agitation rate, 140 min sorption time 40°C.	Cr(VI) (91.6 mg g^{-1})	Hasan et al. (2010)	Chromium uptake decreased with an increase in pH, but increased with temperature and initial metal concentration.

such as alcohols, aldehydes, ketones, carboxylic, phenolic, and other groups on their surface. Ionization of these groups in aqueous solution enables them to participate in cation binding (Ofomaja and Ho, 2008). The ionization of functional groups on the biomass surface depends on pH of the solution: at $pH>pK_a$, most of these functional groups are mainly in ionized form and can exchange H^+ with metal ions ion solution, at $pH<pK_a$, complexation phenomenon occurs (Fourest and Volesky, 1996). Several researchers have therefore studied biosorption of metal ions by acid/alkali-treated biomass (Table 3). Yao and Ramelow (1997) showed that up to 100% metal uptake was possible for Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Ag^{1+}, with acidic and basic treatment enhancing the metal uptake. Acidic treatment was shown to increase the Cr^{6+} uptake capacity of water hyacinth roots whereas the removal of Cr^{3+} was lowered (Elangovan et al., 2008). Ibrahim et al. (2009) combined various spectroscopic techniques and quantum *ab intio* calculations to study the potential of water hyacinth dry matter for the removal of heavy metals from wastewater. It was shown that water hyacinth which is subjected to acetic acid is able to absorb acetate which finds its way to the cellulose of the plant. The dried and treated system acts like carboxylated cellulose and in particular, it can accelerate the removal of Cd from the aquatic environment. It was further suggested that treated water hyacinth has the additional advantage that it reduces or even eliminates the diverse impact of the weed on the environment.

In a more recent publication, Mahamadi and Nharingo (2010b) carried out a competitive adsorption study using acid treated water hyacinth. The sorption dynamics the Pb^{2+}, Cd^{2+}, Zn^{2+} mixture were probed using q_e'/q_e ratios, where the prime denotes the presence of other metal ions. The equilibrium data showed that the uptake of ions from binary and ternary systems followed the order Pb>>Cd>Zn. The multielement effect was found to be antagonistic and the Pb-Zn,

Table 2. Batch sorption of metal ions using activated carbon and ash derived from water hyacinth.

Source/form of water hyacinth biosorbent	Experimental parameter	Removal/maximum sorption capacity	Reference	Comment
Water hyacinth-derived activated carbon	20 to 25 mg l^{-1} Pb(II), pH 3, 100-125 min sorption time.	16.6 mg g^{-1}	Shekina et al. (2002)	Increasing pH from 2 to 4 resulted in increased Pb removal
Water hyacinth-derived ash	100 mg/ml adsorbent dose, pH 1.6-6.5, 5-30 mg l^{-1} Ni(II), Zn(II), Cd(II), Pb(II), Cr(VI) and Cu(II), 24 hr sorption time.	29.8 mg g^{-1} Pb(II), 24.0 mg g^{-1} Zn(II), 28.4 mg g^{-1} Cd(II), 29.8 mg g^{-1} Cu(II), 29.8 mg g^{-1} Ni (II).	Mahmood et al. (2010c)	Adsorption-desorption of the metals showed potential for their recovery.
Water hyacinth-drived activated carbon	10-40 mg l^{-1} Hg(II) concentration, pH 5, biosorbents particle size of 125-180 µm, 200 to 360 min sorption time.	28.4 mg g^{-1}	Kadirvelu et al. (2004)	Sorption dependent on contact time, pH, Hg(II) and adsorbent concentration. Equilibrium data fitted both the Langmuir and Freundlich isotherm models.
Water hyacinth-derived ash	5-30 µg ml^{-1} Ni^{2+}, pH 6.54, 25 °C temperature.	1.978 µg/g	Hussain et al. (2010)	Desorption capacity found to be 3.71 µg/g

Pb-Cd and Pb-Cd-Zn systems showed good fitting to the Langmuir competitive model. The authors make important conclusions that the removal of Pb^{2+} ions in the presence of comparable amounts of either Cd^{2+} or Zn^{2+} or both, showed greater potential than the removal of Cd^{2+} and Zn^{2+} in the presence of Pb^{2+}.

METAL DESORPTION AND RECOVERY

An important consideration for the industrial application of water hyacinth is the question of metal recovery and biomass regeneration. Metal recovery is important especially when it involves valuable metals and desorption also becomes very much necessary when the biomass preparation/generation is costly. The economic application of a given biosorbent therefore depends not only on its biosorptive capacity, but also on the ease of its generation and reuse. It has also been noted that a successful desorption process requires the proper selection of the eluants, which are a function of the biosorbent type and mechanism of biosorption (Das et al., 2010). Some workers have reported significant studies on the recovery of precious metals as well as those of industrial significance (Table 4).

Using *Sargassum* as the biosorbent, Sathishkumar et al. (2010), observed that the biosorbed ionic gold in metallic form through pyro-crystallization technique showed the possibility of 91.44% recovery of the metal in pure form. In conclusion, the authors noted that gold from dilute solutions could be recovered through green processes in ionic, nanocrystalline, or metallic form as described by the end-consumer using *Sargassum* as biomaterial. On the desorption of gold from egg shell membrane, Ishikawa et al. (2002) showed that NaOH solution (0.1 mol/l) was capable of desorbing more than 95% of the gold (I) and NaCN (0.1 mol/l) was capable of desorbing more than 92% of gold(III). On application of an egg shell membrane column, 98% recovery of gold was reported. Kuyucak and Volesky (1989) observed that elution of gold adsorbed on brown marine alga, *Saragsum natans* could be achieved using a solution of 0.1 mol/l thiourea with 0.02 mol/l ferric ammonium sulphate. A limitation noted in the approach was the long desorption time (17 h). Recovery of ionic gold from exhausted decarboxylated biosorbent through elution (93%) was more efficient than incineration (61.89%) (Kwak and Yun, 2010). It was also reported that the combined method of biosorption and incineration could be effective for concentration and recovery of gold from the cyanide solutions.

Table 3. Batch sorption of metal ions using treated water hyacinth roots.

Experimental parameter	Removal (%)/maximum sorption capacity for single, binary and ternary component systems	Reference	Comment
5 mg l^{-1} initial metal concentration, initial pH 2-6. Acidic and basic treatment.	Up to 100% metal uptake was achieved for Pb, Cu, Cd, Cr, Mn , Ni, Co , Au, Ag, Cd –(single component)	Yao and Ramelow (1997)	Acidic and basic treatments increased the metal uptake for the metals.
2 mg ml^{-1} absorbent, initial pH 4.8, 150 rpm agitation rate, 303 K temperature, initial concentration 10-60 mg l^{-1}, 3 h sorption time. Acidic treatment.	Pb (26.3 mg g^{-1})-single Zn (12.6 mg g^{-1})-single Cd (12.6 mg g^{-1})-single Pb (25.4 mg g^{-1})-binary (Pb-Cd) Pb (22.1 mg g^{-1})-binary (Pb-Zn) Cd (4.1 mg g^{-1})-binary (Cd-Zn) Zn (3.0 mg g^{-1})-binary (Zn-Pb) Pb (14.3 mg g^{-1})-ternary (Pb-Cd-Zn) Cd (3.0 mg g^{-1})-ternary (Cd-Zn-Pb) Zn (3.7 mg g^{-1})-ternary (Zn-Cd-Pb)	Mahamadi and Nharingo (2010a,b)	Pb ions were effectively removed from aqueous solution in the presence of both Cd and Zn, but removal of Cd^{2+} and Zn^{2+} ions was suppressed in the presence of Pb^{2+}.
10 mg ml^{-1} adsorbent, initial pH 5, 150 rpm agitation rate, 303 K temperature, initial concentration 10-150 mg l^{-1}, 6 h sorption time. Acidic treatment	Cr(III) (6.2 mg g^{-1})-single Cr(VI) (6.4 mg g^{-1})-single	Elangovan et al. (2008)	Acid treatment significantly increased the Cr(VI) removal capacity whereas the removal of Cr(III) was lowered.
0.2; 1.2 mg ml^{-1} initial Cd concentration, 2 h sorption time.	55% uptake (low initial metal conc.) 80% uptake (high initial metal conc.)	Ibrahim et al. (2009)	Coordination of acetate to the plant found to occur via the cellulose of the plant where also Cd uptake takes place.

Silver recovery from $AgNO_3$ and $Ag(S_2O_3)_2^{3-}$ showed that the second strain of microalgae *Chlorella vulgaris* gave a higher uptake percentage (Cordery et al., 1994). Ishikawa et al. (2002) reported no loss biosorbent capacity when egg shell membrane was taken through five sorption/desorption cycles during the sorption of Au (I) and Au (III). Ma et al*.* (2006) showed that acidic thiourea was effective for the desorption and recovery of platinum and palladium from bayberry tannin immobilized collagen fiber. Reuse of the biosorbent was not possible due to lost biosorbent capacity when Cu (II) and Zn (II) were eluted from immobilized *Mentha arvensis* distillation waste using HC*l* (Hanif et al., 2009). Zhao et al. (1999) showed that biosorption using *Azolla filiculoides* could be used to treat wastewater for recycling and the recovered metal fed back to the planting bath. Ishikawa et al. (2002) identified Cu (II) and Pb (II) as metal ions which were sorbed for a time and later desorbed from egg shell membrane. On investigating the desorption of heavy metals from water hyacinth ash, Mahmood et al. (2010) reported that desorption was useful for the recovery of cadmium, copper and lead. However, a survey of the literature shows that limited work has been done so far on the biosorptive recovery of precious metals using water hyacinth.

Conclusion

The use of water hyacinth for metal biosorption

Table 4. Desorption and recovery of selected metals.

Adsorbent	Eluant	Desorption	Recovery	Reference	Comment
Egg shell membrane	NaOH NaCN	>95% Au(I), >92% Au(III)	98%	Ishikawa et al. (2002)	No loss of biosorbent capacity was observed through five consecutive sorption/desorption cycles.
Sargassum	NaOH	97.8% Au(III)	91.4%	Sathishkumar et al. (2010)	Gold from dilute solutions could be recovered through green processes in ionic, nanocrystalline, or metallic form using *Sargassum* biomass.
Bayberry tannin immobilized collagen fiber	Acidic thiourea	90.7% Pt(IV) 58.4% Pt(II)		Ma et al. (2006)	Acidic thiourea was found to be more effective for the desorption and recovery of platinum and palladium.
Immobilized *Mentha arvensis* distillation waste	HC*l*	90% Cu(II) and Zn(II)		Hanif et al. (2009)	Re-use of the biomass was not possible due to lost biosorbent capacity
Myriophyllum spicatum L.	HC*l*	55% Cu(II), 60% Ni(II), 71 to 72% Co(II) and Zn(II)		Lesage et al. (2007)	Desorption by HC*l* was not suggested as a useful strategy in recovering the metals and regenerating the biomass
Azolla filiculoides	HC*l* H_2SO_4		86 to 88% Zn(II) 96 to 99% Zn(II)	Zhao et al. (1999)	The technique showed that treated waste water could be recycled and the recovered zinc fed back to the planting bath.
Egg shell membrane	NaOH	17% Cu(II) 15% Pb(II) 4% Ni(II) 3% Zn(II)			Cu(II) and Pb(II) identified as metal ions which are sorbed for a time, and later desorbed.
Water hyacinth ash	HNO_3	61 to 98% Pb(II) 70 to 97% Cd(II) 71 to 79% Cu(II) 25 to 42% Cr(III) 24 to 40% Zn(II) 12 to 21% Ni(II)		Mahmood et al. (2010)	Desorption was found to be useful for the recovery of cadmium, copper and lead.

has been reviewed. Excellent removal capabilities of the biomass for several metals of environmental concern were apparent. Factors, such as pH, temperature, adsorbent dose, etc significantly affect the biosorption capacities. On considering the invasive nature of the weed and environmental problems associated with its control, biosorption offers an attractive application of the plant. However, utilization of the biomass in industrial-scale applications is still far from being realized. More investigation is still required on structural properties of the biosorbent, multi-metal studies, mechanistic modeling, possible metal recovery, biosorbent modification and adaptation to continuous flow utilization.

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