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RESEARCH ARTICLE

WATER HYACINTH (EICHHORNIA CRASSIPES) AS A PROMISING BIOSORBENT IN REMOVAL OF HEAVY METALS.

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Abstract

Water hyacinth (*Eichhornia crassipes*) is a naturally abundant plant having substantial heavy metal adsorptive capacity. *E. crassipes* is considered to be a noxious weed in many parts of the world due to its proficiency to grow and depletion of nutrients and oxygen from water bodies. Nonetheless, several studies have shown *E. crassipes* as a candidate for the treatment of wastewater contaminated with heavy metals. The present review aims to compile in a single paper the numerous studies conducted on the use of water hyacinth species for the removal of heavy metals in solution. The methods include a binder material produced either from the roots, shoots, fibers, pellets, the whole biomass, biochar or activated carbon derived from the water hyacinth biomass, and involve a process of binding such as biosorption, pyrolysis, immobilization with micro algae, or modification with nanoparticles. The paper also specifies with each method the extent of removal of metal ions and discusses about a specific disposal method of the metal contaminated biomass. Regardless the ability to act as an invasive aquatic species, *E. crassipes* has a great potential to be used as an in situ cost effective biosorbent phytotechnology for the amelioration of contaminated wastewaters with heavy metals.

Introduction:

Increasing industrial activities had caused a concomitant increase in the use of heavy metals over the last few decades (Reddy et al., 2012). Consequently, water bodies are the main preferences for the ultimate and final disposal of these industrial effluents causing its serious pollution. Moreover, this specifies to an alarming risk to global environment owing to the persistence, abundance and significant toxicity of these metals (Ahmed et al., 2015a; Ahmed et al., 2015b; Islam et al., 2015). Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment.

The most commonly applied physical and chemical treatment methods for heavy metal removal are chemical precipitation as hydroxides, carbonates or sulfides and subsequent liquid-solids separation by gravity settling, and flotation or filtration; sorption (adsorption, ion exchange); membrane processes; electrolytic recovery and liquid-liquid extraction. However, beside the merits, each method has been limited in its application due to some significant disadvantages, for instance, incomplete removal, high-energy requirements, production of toxic sludge or

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waste products that also require disposal and become economically unviable for the removal of heavy metals at lower concentrations (Wang and Chen, 2009).

The adsorption process is arguably one of the most popular methods for the removal of heavy-metal ions because of its simplicity, convenience, and high removal efficiency (Afkhami et al., 2007). In common sorption processes, commercial activated carbon and synthetic resins are usually used to gain high removal efficiency. However, due to their high production cost these two sorbents have not gained widespread use and popularity. There is a need for effective, cost-efficient and environment-friendly technology for the removal of heavy metal (Zheng et al., 2009).

Phytoremediation is such a remediation technique which can be used for the effective removal of heavy metals from the large polluted site where other chemical and physical remediation technologies prove to be not applicable and costly (Garbisu and Alkorta, 2003). Aquatic macrophytes have greater potential to accumulate heavy metals present inside their plant bodies (Priya and Selvan, 2014). In view of this, considerable attention has been focused on the development of adsorbents from various types of aquatic plants as these are inexpensive and locally available (Munagapati et al., 2010). The basic component of these low-cost organic biomass includes cellulose, lignin, hemicellulose, extractives, lipids, proteins, simple sugars, starch, etc. containing variety of functional groups that facilitates metal complexation and helps for the sequestration of heavy metals (Hashem et al., 2005; Hashem et al., 2007).

Water hyacinth (*Eichhornia crassipes*) (Family: Pontederiaceae) is a free-floating perennial aquatic plant originated from tropical and subtropical South America and is now widespread in all tropical climates. It is ranked as one of worst invasive weed globally (Bhattacharya et al. 2015; Villamagna and Murphy 2016). The genus *Eichhornia* comprises seven species of water hyacinth among which *E. crassipes* is the most dominant regarding distribution and have been reported to produce biomass faster than the other *E.* sp. (Rahman and Hasegawa 2011). Owing to its superior tolerance to a contaminated environment, rapid growth (Zhang et al., 2014) and high economic value with diverse potential applications (Rezania et al., 2015a), water hyacinth has gained widespread interest in environmental phytoremediation applications (Rezania et al., 2015b).

Water hyacinth shows high removal rates for manganese (Mn), iron (Fe), cadmium (Cd), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), arsenic (As) and mercury (Hg) (Mokhtar et al., 2011) from wastewater solutions along with absorbing organic substances such as formaldehyde, phenol, oxalic, acetic and formic acid. Water hyacinth is the best plant species for the accumulation of Cd (Liao and Chang, 2004). Leaf tissues of water hyacinth show great accumulation ability for the mercury, harvesting of such plant species could help to remove the mercury contamination (Wang et al. 2002). Kumar et al. (2016) reported that water hyacinth is the best candidate as compared to other aquatic plants for the phytoremediation of pulp and paper mill effluents load with different heavy metals Cr, Cu, Mn, Cd, Pb, Fe, Zn, Ni, and organic load EC (electrical conductivity), TDS, COD, BOD, TKN (total Kjeldahl nitrogen). Liao and Cheng (2004) ranked the heavy metal removal rate based on the ability of water hyacinth to remove (Cu > Zn > Ni > Pb > Cd) and showed that higher and lower removal efficiency belonged to Cu and Cd, respectively. Xiaomei et al. (2004) used water hyacinth for the removal of Zn and Cd from wastewater and also measured the concentration of Cd and Zn absorbed in different parts of water hyacinth (stem, leaves, roots, flowers). It was observed for the presence of 2040 mg/kg of Cd and 9650 mg/kg of Zn accumulated in the roots of water hyacinth. According to Shaban et al. (2005) to treat one liter of wastewater contaminated with 1500 mg/L arsenic requires 30 g of dried water hyacinth root for a period of 24 hours. Emerhi (2011) estimated chromium (III) removal from the aqueous solution and found the removal rate to be 87.52% with 10 mg Cr/1 solution. The objective of this review was to assemble the different usage methods of water hyacinth as a biosorbent in removal of heavy metals from aquatic systems.

Methods:

Literature search was conducted by searching for scholarly articles in PubMed, Google scholar, and Scopus by using search term “heavy metal removal”, “techniques of heavy metal removal”, “water hyacinth”, “*Eichhornia crassipes*”, “water hyacinth as a biosorbent”, “Lead removal + water hyacinth”, “Cadmium removal+water hyacinth”, “Chromium removal+water hyacinth”. Further searches were done after finding the relevant articles and references therein.

Results:

Based on the literature search, the methods through which water hyacinth plant is used as a biosorbent in heavy metal removal could be divided into eight groups. These are presented here in this result section.

Floating Bed Technique:

In this method done by Abbas et al. (2019), the effectiveness of water hyacinth was tested for the phytoremediation of landfill leachate for a period of 15 days. Fifteen plastic containers were used in experimental setup where aquatic plants were fitted as a floating bed with the help of thermo-pole sheet. It was observed that both plants significantly ($p < 0.05/p < 0.01/p < 0.001$) reduce the physicochemical parameters pH, TDS, BOD, COD and heavy metals like Zn, Pb, Fe, Cu and Ni from landfill leachate. Maximum reduction in these parameters was obtained at 50% and 75% landfill leachate treatment and their removal rate gradually increased from day 3 to day 15 of the experiment. The maximum removal rate for heavy metals was for Zn (80–90%), Fe (83–87%) and Pb (76–84%). Value of bioconcentration and translocation factor was less than 1 which indicates the low transport of heavy metals from roots to the above-ground parts of the plant. Besides, water hyacinth accumulates these heavy metals inside its body without showing much reduction in growth and showing tolerance to all the present metals.

Another comprehensive study on arsenic removal from water by *E. crassipes* was performed by Alvarado et al. (2008), and the results showed that it had a removal rate of 600 mg arsenic ha^{-1} d^{-1} under field conditions and a removal recovery of 18% under laboratory conditions. The removal efficiency of water hyacinth was higher due to its high biomass production and favorable climatic conditions. Mishra et al. (2008) compared arsenic removal efficiency of *E. crassipes*, *L. minor* and *S. polyrhiza* from tropical opencast coal mine effluent and observed that *E. crassipes* had the highest removal efficiency (80%) compared to other aquatic macrophytes over a 25 d course. This was supposed to be due to faster growth rate (Muramoto and Oki, 1983; Kelley et al., 1999), greater biomass production, and higher uptake ability of arsenic. Therefore, the results obtained from both studies suggest that *Eichhornia crassipes* is a suitable candidate for the removal of pollution load from landfill leachate.

Vertical Surface Flow Constructed Wetlands:

A study was led by Agarry et al. (2018) to evaluate the potential of a vertical surface flow constructed wetland (VSF-CW) vegetated with *Eichhornia crassipes* in treating petroleum refinery secondary wastewater under tropical conditions. Also, to provide a comparative evaluation of biotreatment kinetic models (traditional first order and other alternative kinetic models) proposed to describe the removal kinetics of organics (biochemical oxygen demand (BOD) and chemical oxygen demand (COD)), nitrate-nitrogen and total petroleum hydrocarbons (TPH) in wetland systems. The refinery secondary wastewater was characterized and treated in five VSF-CWs. *Eichhornia crassipes* were planted in three VSF-CWs and the remaining two VSF-CWs served as the unvegetated control. The wastewater relatively had high levels of turbidity (18.30 ± 3.88 NTU), BOD (20.40 ± 2.20 mg/L), COD (86 ± 6.0 mg/L), TPH (16.6 ± 1.76 mg/L), oil and grease (18.4 ± 2.00 mg/L), heavy metals(Cadmium (0.034 ± 0.01 mg/L), Lead (0.12 ± 0.05 mg/L), Chromium (0.47 ± 0.01 mg/L), Iron (1.54 ± 0.25 mg/L) and Nickel (0.09 ± 0.01 mg/L)) and Chloride (1412 ± 9.6 mg/L). The vegetated VSF-CWs significantly performed better than the unvegetated control and resulted in the removal efficiencies of 91.5% turbidity, 94.6% BOD5, 80.2% COD, 92.6% TPH, 90.4% oil and grease, 94% cadmium, 92.5% lead, 93% chromium, 94.8% iron, 92.2% nickel, and 57.7% chloride. Thus, *Eichhornia crassipes* planted VSF-CW has the potential of treating refinery secondary wastewater to discharge permissible limits.

Using Dried powder of root and shoot:

Dried water hyacinth as biosorbent for metal ions were also investigated in many literatures by powder of its roots and shoots. The chemical analysis and FTIR shows that water hyacinth is a mixture of cellulose and lignin (Ibrahim et al., 2012). Dried shoot and root were found as good sorbent for removal of more than 75% for Cd and more than 90% for Pb at optimum dosage of 5.0 g/l, pH 5.0; equilibrium time within 30–60 min by Ibrahim et al. (2012) where the removal using root and shoot were nearly equal. Besides, using dried roots at optimum dosage of 2.0 g/l, pH 5.0; equilibrium time within 90 min, Jahangiri et al. (2018) obtained a removal of 92% Pb(II) and 54% Cd(II). In both the cases, second-order kinetics was the applicable model.

The mechanisms for this sorption by the WMass should be related firstly to abundant functional groups (–OH, –NH, C–O, C–N and CO) on the biomass surface that could bind metal ions through complexation (Abdolali et al., 2016, Li and Yu, 2014), as shown as the strong bands at 3415 cm−1 (–OH or –NH), 1640 cm−1 (CO), 1319 cm−1(C–N) and 1055 cm−1 (C–O) observed in the IR spectrum of the WMass. Secondly, the SEM-EDX analysis indicated that some metal elements (K and Mg) inherently existed in the WMass was eliminated after sorption of metal ions, suggesting the replacement of K and Mg elements by metal ions through cation exchange, which played an important role for sorption of heavy metals by many mineral-containing biosorbents (Yuvaraja et al., 2014).

Schneider et al. (1995) also 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 found that the dried roots and aerial parts of the water hyacinth are better biosorbents than the biomass of the bacterium *Mycobacterium phlei*, the yeast *Candida parapsilosis*, fungal *Rhizopus oryzae* strains, and acacia bark in terms of lead and copper uptake per dried mass of biosorbent.

As Fibre

A study was led by Buasri et al. (2012) in which fibres from water hyacinth were used to remove Cu(II) and Zn(II) ions from aqueous solutions. The fibres were prepared through reaction of cellulose with phosphoric acid according to the method described by Suflet et al. (2006). In a 500 mL, three-necked flask equipped with a nitrogen inlet, a condenser, a thermometer, and a stirrer, 224 g urea was added, heated at 140°C and flushed with nitrogen. Water hyacinth (30g) and 168 mL phosphorous acid were added alternatively portionwise to the molten urea in order to reduce the foaming. The reaction was allowed to proceed at 150°C for 2 h. The fiber was washed with distilled water and acetone. A sample of fiber was treated with 0.5 M hydrochloric acid for 24 h under slow stirring. The modified cellulose was washed several times with deionized water to remove excess acid from biosorbent. It was dried for 24 h at 60°C in an oven. Biosorption experiments where then carried out with prepared biosorbent and metal solutions of $Cu(NO_3)_2$ and $Zn(NO_3)_2$. The equilibrium biosorption isotherms showed that water hyacinth possess high affinity and sorption capacity for Cu(II) and Zn(II) ions, with sorption capacities of 99.42 mg $Cu^{2+}$and 83.01 mg Zn^{2+} per gram biomass, respectively. All results showed that water hyacinth fiber is an alternative low cost biosorbent for removal of heavy metal ions from aqueous media.

Preparing Biochar by Pyrolysis

Biochar derived from biomass, especially from waste biomass, is recognized as one of the most available adsorbents due to their specific properties such as large surface area, highly porous structure and enriched surface functional groups (Lonappan et al., 2016). Several literatures have reported the conversion of water hyacinth into biochar followed by application in the treatment of wastewater (Zhang et al., 2015, 2016; Xu et al., 2016).

A study was led by Li et al. (2018) in which biochars were produced from long-root *Eichhornia crassipes* at four temperatures: 200, 300, 400 and 500°C, referred to as LEC200, LEC300, LEC400 and LEC500, respectively. The sorption ability of lead, zinc, copper and cadmium from aqueous solutions by four kinds of biochars was investigated. All the biochars had lower values of CEC and higher values of pH. LEC500 was the best one to bind toxic metals which can be reflected in the results of SEM, BET and elemental analyser. It was also found that alkyl, carboxyl, phosphate and cyano groups in the biochars can play a role in binding metals. In addition, the sorption processes of four metals by the biochars in different metal concentration R^2> 0.95 were all excellently represented by the pseudo-second-order model with all correlation coefficients. It could also be described satisfactorily by the Langmuir isotherms. According to calculated results by the Langmuir equation, the maximum removal capacities of Pb(II), Zn(II), Cu(II) and Cd(II) at 298 K were 39.09 mg g^{-1}, 45.40 mg g^{-1}, 48.20 mg g^{-1} and 44.04 mg g^{-1}, respectively. The positive value of ΔH_0 confirmed the adsorption process was endothermic and the negative value of ΔG_0 confirmed the adsorption process was spontaneous. The sorption capacities were compared with several other lignocellulosic materials which implied the potential of long-root *Eichhornia crassipes* waste as an economic and excellent biosorbent for eliminating metal ions from contaminated waters.

Furthermore, to enhance the adsorption capacity of biochar, literatures have shown the following chemical or physical modification of biochar:

Fe_3O_4 modified biochar:

Zhang et al. (2016). prepared magnetite-modified water hyacinth biochar for arsenate removal and found that 100% As(V) was depleted by magnetite-modified biochar compared to 8.9% by no Fe-modified biochar.

Modification with nanoparticles:

The adsorbing material relating to zinc nanostructures have also aroused increasing interest. CuO-ZnO composite nanofibers (Malwal and Gopinath, 2017), ZnO microspheres (Lei et al., 2017), Al-doped ZnO rods (Chouchene et al., 2017) and ZnO nanorods (Ansari et al., 2016) exhibited excellent adsorption capacity. In particular, ZnO loaded on activated carbon and ZnO thin films showed effective adsorption for Pb(II) (Kikuchi et al., 2006) and Cu(II) (Bagheri et al., 2014) removal, respectively. These researches suggest it may be feasible to load ZnO nanoparticles on water hyacinth biochar for efficient Cr(VI) removal.

In a study by Yu et al. (2018), biochar derived from waste water hyacinth was prepared and modified by ZnO nanoparticles for Cr(VI) removal from aqueous solution with the aim of Cr(VI) removal and management of waste biomass. The effect of carbonization temperature (500-800 °C), ZnO content (10-50 wt%) loaded on biochar and contact time (0.17-14 h) on the Cr(VI) removal were investigated. It was found that higher than 95% removal efficiency of Cr(VI) can be achieved with the biochar loaded 30 wt% ZnO. The adsorption kinetics of the sorbent is consistent with the pseudo-second-order kinetic model and adsorption isotherm follows the Langmuir model with maximum adsorption capacity of 43.48 mg g^{-1} for Cr(VI). Multiple techniques such as XRD, XPS, SEM, EDX and FT-IR were performed to investigate the possible mechanisms involved in the Cr (VI) adsorption. The results show that there is precipitation between chromium ions and Zn oxide. Furthermore, the ZnO nanoparticles acts as photo-catalyst to generate photo-generated electrons to enhance the reduction of Cr(VI) to Cr(III). The as-prepared ZnO/BC possess good recyclability and the removal ratio remained at about 70% in the fifth cycle, which suggests that both contaminants removal and effective management of water hyacinth can be achieved by the approach.

Using *Eichhornia crassipes*-derived Activated Carbon (AEC)

Activated carbon was prepared by Kadirvelu et al. (2004) from *Eichhornia crassipes* by cutting the plant material into small pieces, dried in sunlight until the moisture had partially evaporated and then further dried in a hot air oven for 24 h at 60°C. The completely dry material was packed into an iron vessel and covered with a tight-fitting lid to avoid contact with atmospheric air except for that entrapped within the voids in the material being activated. This arrangement was placed in a muffle furnace and heated at a temperature of 500°C for 1 h. After cooling, the resulting product was removed, ground and passed through 125–180 µm sieve. At last, batch sorption experiments were run with the AEC and aqueous solution as well as synthetic wastewaters to study its capability in Hg(II) removal.

In the batch sorption experiments with aqueous solutions, the contact time fixed at 6 h ensured that equilibrium had been attained. The equilibrium time for carbonized waste newsprint fibre whereas was 16 h for 100 mg/l Hg(II). This indicates that AEC required a lesser contact time for the complete elimination of Hg(II) from solution compared to activated carbon derived from newsprint fibre and commercial activated carbon (CAC) (Namasivayam and Periasamy, 1993; Aoyama et al., 2000). Besides, an adsorbent dosage of 1.6 g/l carbon was required to effect the quantitative removal of Hg(II) from 1000 ml of both 20 mg/l and 40 mg/l Hg(II) solutions. Pulido et al. (1998) found that 5 g/l CAC was required to effect the same removal of Hg(II), i.e. ca. three-times greater than that observed with our carbon. This demonstrates the higher efficiency of AEC relative to CAC. The optimum pH was found to be 5.

It was then applied to synthetic wastewaters which were prepared using literature methods by Kadirvelu (1998), adjusted at different pH values and agitated with 50 mg carbon for 6 h. The removal of Hg(II) from synthetic wastewater was dependent upon the composition, nature and the pH of the system. Increasing the carbon content led to an increase in the percentage removal of Hg(II) and the minimum dosage of carbon required for the removal of Hg(II) was 200 mg/50 ml solution. The percentage removal of Hg(II) also increased with increasing pH and attained a maximum value of 73% at a pH value of 5. The experiments conducted on the removal of Hg(II) from synthetic wastewater confirmed the validity of the results obtained from the batch mode studies, i.e. AEC can be used effectively for the removal of Hg(II) from synthetic wastewater.

Immobilizing microalgal cells on water hyacinth derived pellets:

In this experiment done by Shen et al. (2018), a complex of water-hyacinth derived pellets immobilized with Chlorella sp. was applied, for the first time, in the bioremediation of Cadmium (Cd). The Cd(II) removal efficiency of the complex was optimized by investigating several parameters, including the pellet materials, algal culture age, and light intensity. Results showed that the Cd(II) removal efficiency was positively related to the algal immobilization efficiency and the algal bioaccumulation capacity. Since higher surface hydrophilicity leads to higher immobilization efficiency, the water hyacinth leaf biochar pellet (WLBp) was selected as the optimal carrier. A maximum Cd(II) removal efficiency of 92.45% was obtained by the complex of WLBp immobilized with algal cells in stationary growth phase and illuminated with a light intensity of 119 µmolm^{-2} s^{-1}. Recovery tests on both microalgal cells and the WLBp demonstrated that the algal cells and the biochar pellet can be economically recycled and reused.

Disposal of Water Hyacinth Biomass Contaminated by Biosorption of Heavy Metals

Heavy metals accumulated in biomass may be released back to the environment if they were not properly disposed of, because most biomass are readily degradable. Pyrolysis can transform biomass into stable biochars that could be applied as a soil amendment, and such a transformation is also considered a promising strategy for carbon sequestration (Mao et al., 2012). For the purpose of safe disposal of biomass contaminated by biosorption of heavy metals, phosphate assisted pyrolysis of water hyacinth biomass contaminated by lead (Pb) was tried by Shi et al. (2017) to reduce the bioavailability and leaching potential of Pb, using direct pyrolysis without additive as a control method. Direct pyrolysis of the contaminated biomass at low temperatures (300 and 400 °C) could reduce the bioavailability of Pb, but the leaching potential of Pb was increased with the rising pyrolysis temperature. While phosphate-assisted pyrolysis significantly enhanced the recovery and stability of Pb in the char. Specifically, the percentages of bioavailable Pb and leachable Pb in the chars obtained by phosphate assisted pyrolysis at low temperatures were reduced to less than 5% and 7%, respectively. The sequential extraction test indicated the transformation of Pb into more stable fractions after phosphate-assisted pyrolysis, which was related to the formation of Pb phosphate minerals including pyromorphite and lead-substituted hydroxyapatite.

Conclusion:

This paper has discussed the different possibilities of using water hyacinth for the removal of heavy metals. It has also been evident that among the aquatic plants, water hyacinth has got more heavy metals uptake capability and improving the water quality. As heavy metals are up taken by the roots of the plant, concentrated in them, or translocated and concentrated to the shoots and other plant tissues, harvesting the plant can permanently remove the contaminants. Moreover, in terms of expense, it is also cheaper than different advanced technologies which needs more cost to work for the evacuation of pollutants from the wastewater. There are also possible scopes for recovery of valuable heavy metals from the plants by burning and extracting the metals from the ash. Thus, with the advanced use of phytotechnology, water hyacinth can be a viable tool for bioremediation.

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