INDIAN JOURNAL OF SCIENCE AND TECHNOLOGY

REVIEW ARTICLE

OPEN ACCESS

Received: 11-01-2022

Accepted: 21-03-2022

Published: 02.05.2022

Citation: Singh A, Kumar S (2022) Application of Aquatic Plants Dead Biomass in Remediation of Heavy Metals Pollution by Adsorption: A Review. Indian Journal of Science and Technology 15(16): 729-735. https://doi.org/10.17485/IJST/v15i16.82

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Funding: None

Competing Interests: None

Published By Indian Society for Education and Environment (iSee)

ISSN
Print: 0974-6846
Electronic: 0974-5645

Application of Aquatic Plants Dead Biomass in Remediation of Heavy Metals Pollution by Adsorption: A Review

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Abstract

Objectives: To figure out the sources of heavy metals pollution in water bodies, their toxicity, and utilization of aquatic plants' dead biomass as adsorbents for heavy metals removal. In addition, this review also explains the adsorption mechanism through adsorption isotherms and kinetics. **Methods:** Various research papers related to aquatic plant adsorbents from various sources have been compiled to assess the adsorption capacity of heavy metals from synthetic solutions as well as from the wastewater. **Findings:** The adsorption using aquatic plants as adsorbents were found to be an economic and environment-friendly method for heavy metal adsorption from wastewater as aquatic plants grow rapidly and are found abundantly. The efficacy of these adsorbents has been increased by various researchers by modifying them via chemical treatment and nanotechnology. It was found that adsorbent derived from various aquatic plants like *Eichhornia crassipes*, *Pistia stratiotes*, *Ceratophyllum demersum*, *Spirodela polyrhiza*, *Lemna minor*, etc. shows good adsorption potential for heavy metal removal. **Novelty:** The research data on adsorption shows that the dead biomass of these plants can be capable for elimination of heavy metals from aqueous solutions. As some of the aquatic plants are invasive and compete with the native species, not desirable for the aquatic ecosystem, so utilization of aquatic plants provides double benefits.

Keywords: Adsorption; Heavy metal; Aquatic plant; Adsorbent; Adsorption capacity

1 Introduction

Water is the lifeline of Earth and it is the foundation of the rich environmental cycle as it is responsible for the great diversity and abundance of life on earth [1]. Water supports all living things, but its quality is damaging due to the rapid increase in population, urbanization, and industrialization. Water pollution is the introduction of unwanted substances that alter the quality of water and impairs its usefulness and affects aquatic life. The results of rapid industrialization include the emission of metal-containing wastes which are ultimately disposed into water bodies, altering their usefulness and quality. Some of the most common heavy metals are lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg), etc. They are discharged from various industrial activities such as mines operation, electroplating, pigments, textiles, ore refining, fertilizers, tanneries, batteries manufacturing, smelting, paper, and pulp industries and pesticides, etc[2–4]. The term "Heavy metal" is an element having a specific gravity higher than 5.0 g cm^{-3} and an atomic weight between 63.5 and 200[5]. The heavy metals are non-biodegradable and can be accumulated through the food chain in human beings as they are at the top level of the food chain and cause serious health problems in them. When the concentration of heavy metal exceeds permissible limits, they become toxic and carcinogenic too. Heavy metals are toxic and must be removed from wastewater before they can be dumped into the environment.

Many different conventional methods like chemical precipitation, coagulation, ultra-filtration, electro-dialysis, reverse osmosis, and ion exchange have been employed for removing heavy metals. These procedures are not always effective and linked to the discharge of waste and by-products with large capital and operating expenses, incomplete processing, high energy and, chemical requirements, and require safe disposal[6]. This requires a low-cost, high-efficiency means of overcoming the shortcomings of traditional methods. Because the adsorption process includes high metal removal effectiveness, adsorbents must be available locally, ease of use, low capital cost, low sludge formation, no need for additional nutrients, metal recovery, and adsorbent reproducibility has been studied to be more reliable and promising[7,8]. The main objectives of this review are to study various aquatic adsorbents (in raw and modified form) and their feasibility in heavy metal removal from wastewater. In addition, various factors affecting adsorption, isotherms, and kinetics are discussed here.

2 Adsorption Process

Adsorption is easy, simple, and cost-effective method for heavy metals removal from industrial effluents[9]. Nowadays, various easily available materials like plant parts, plant waste, food waste, industrial by-products, agricultural waste, and aquatic plants are also used as an adsorbent for heavy metals removal. The adsorbent may be used in raw form or modified with some chemicals to increase the efficiency of the adsorption process. The transport of mass on the solid's surface (adsorbent) from the liquid phase to form a film (adsorbate) is referred to as adsorption. The adsorbent used should be cost-effective to make the process cost-efficient. A 'low-cost adsorbent' refers to the adsorbent which presents abundantly in nature, requires less processing cost, could be a by-product or waste product from other processes. Modification of adsorbents with acids, bases, and other chemicals increases their adsorption efficiency as modification increases the surface area and sorption sites to adsorb more metal ions.

Aquatic plants are being experimentally used to mitigate organic and inorganic pollutants from the aquatic system through adsorption. Aquatic plants grow rapidly and produce a huge amount of biomass, which can be used for various useful purposes. Generally, living plants are used for metal removal as metal ions are accumulated in the living tissues but adsorption does not require living plants, it requires dehydrated biomass of plants and removes metal toxicity. The main advantages of using dead biomass over living biomass are as follows: Avoiding the problems of metal toxicity on plants, the dried biomass is easy in handling, transport, and conservation, and recovery of sorbed heavy metals is possible.

2.1 Adsorption affecting parameters

The adsorbent performance depends on biomass characteristics and various parameters which affect the adsorption process including pH, contact time, initial metal concentration, temperature, adsorbent dose, and agitation speed[10]. Table 1 shows the impacts of various factors on the adsorption process.

2.2 Study of isotherm and kinetic models

Isotherm (Langmuir and Freundlich) and kinetic (pseudo-first-order and pseudo-second-order) studies help us to understand the mechanism of adsorption. These models have been applied to the adsorption data which shows the suitability of isotherm or kinetic equation better to the data. Here are some studies by various investigators showing the applicability of isotherm and kinetics are listed in Table 2.

3 Aquatic plants as metals removing agents

Aquatic plants grow in or near a water body and are also called macrophytes. Aquatic plants are classified based on their habitats. Aquatic plants are broadly grouped into floating plants, submerged plants, and emergent plants. Floating plants float

Table 1. Effect of various parameters on adsorption capacity of heavy metal [11]

Adsorption parameters	Effects on adsorption of heavy metals
pH	It increases the adsorptive removal of cationic heavy metals and decreases the adsorption removal of anionic heavy metals.
Initial ion concentration	It decreases the removal efficiency but enhances the adsorption capacity, i.e. the amount of adsorbed metal on the surface of the adsorbent.
Adsorbent dose	It reduces the adsorption capacity while increasing removal efficiency.
Temperature	It usually improves heavy metal adsorptive removal by raising the adsorbate's surface activity and kinetic energy, but it can harm the adsorbent's physical structure.
Agitation speed	It improves the adsorption rate of heavy metals by reducing mass transfer resistance, however, it may harm the adsorbent's physical structure.
Contact time	Adsorption increases with increasing contact time.

Table 2. Various isotherm and kinetic studies of heavy metal adsorption by aquatic plants adsorbents

Adsorbent	Heavy metal	Maximum adsorption capacity	Isotherm model	Kinetic study	References
Myriophyllum spicatum L.	Co^{2+} Ni^{2+} Zn^{2+} Cu^{2+}	2.3 mg g^{-1} 3 mg g^{-1} 6.8 mg g^{-1} 29 mg g^{-1}	Langmuir Freundlich	—– —–	[12]
Hydrilla verticillata	Cr^{6+} Ni^{2+}	29.43 mg g^{-1} 48.72 mg g^{-1}	Freundlich	Pseudo-second-order	[13]
Azolla filiculoides	Cr^{6+}	10.6 mg g^{-1}	Langmuir, Freundlich	Pseudo-second-order	[14]
Salvinia sp.	Pb^{2+}	210.1 mg g^{-1}	Langmuir	Pseudo-second-order	[15]
Eichhornia crassipes (modified nano-EC)	Cr^{6+} Ni^{2+}	79.04 mg g^{-1} 85.09 mg g^{-1}	Langmuir	Pseudo-second-order	[16]
Salvinia natans	Pb^{2+}	0.614 mmol g^{-1}	Langmuir	——-	[17]
Nymphea lotus	Pb^{2+} Cd^{2+}	49.07 mg g^{-1} 25.46 mg g^{-1}	Langmuir	——	[18]
Ceratophyllum demersum	Cd^{2+}	35.71 mg g^{-1}	Langmuir	Pseudo-second-order	[19]
Lemna perpusilla Torr.	Pb^{2+}	86.96 mg g^{-1}	Langmuir	Pseudo-second-order	[20]

on the surface of the water and are not attached to the bottom of water like *Eichhornia*, *Lemna*, *Azolla*, *Salvinia*, *Trapa*, etc. Submerged plants include various classes like submerged free-floating plants (*Ceratophyllum*, *Hydrilla*), submerged rooted plants (*Potamogeton*, *Najas*, *Ruppia*, etc.), surface living forms with submerged roots (*Nymphaea*, *Nelumbo*), emergent plants attached to the sediments (*Ranunculus*, *Typha*, *Carex*, etc). Aquatic plants are also considered as a plague for many ecosystems and even as a residue for some activities, therefore, their use implies positive environmental effects as well [21]. The dead biomass of various aquatic plants have been used as adsorbents by researchers showed that aquatic plants played a successful role in heavy metals adsorption from wastewater or aqueous solution like *Salvinia*, *Lemna*, *Eichhorniacrassipes*, *Pistia*, *Ruppia*, *Ceratophyllum*, *Myriophyllum*, *Spirodela*, *Nymphaea*, *Nymphea alba*, and *Azolla*.

The removal process using aquatic plants contains two uptake processes [22]: An initial fast, reversible, metal-binding process (biosorption) on dried plant material and an irreversible, slow, ion-removal step (bioaccumulation). Here, we discuss some aquatic plants for the adsorption process in the removal of heavy metals. The adsorption potential of various aquatic plants in their raw form has been discussed in Table 3.

3.1 *Eichhornia crassipes*

Eichhornia crassipes is a major aquatic weed, fast-growing and free-floating in nature. It is known for extremely high metal tolerance. The dried biomass of *Eichhornia crassipes* was used for the adsorption of Pb^{2+} from liquid effluents. The adsorption process was found to be pH-dependent and the irregular surface of the adsorbent might aid in the adsorption of Pb^{2+} on the

Table 3. Adsorption of heavy metals by different aquatic plants adsorbents

Adsorbent	Raw adsorbent	Metals adsorbed	% removal or q_e (mg g^{-1})	References
Eichhornia crassipes	Whole plant Dried roots	Pb^{2+} Co^{2+}	75.44 86.9%	[23] [24]
Ceratophyllum demersum	Raw	Cd^{2+}	95%	[25]
A. filiculoides	Raw	Ni Cu	0.77 mmol g^{-1} 0.54 mmol g^{-1}	[26]
Lemna minor	Raw	Pb^{2+}	95%	[27]
Spirodela polyrhiza	Raw	Mn^{2+} Cu^{2+} Zn^{2+}	35.7 52.6 28.5	[28]
Pistia stratiotes	Raw	Cr^{3+} Pb^{2+}	0.317mmol g^{-1} 0.225mmol g^{-1}	[29]
Salvinia molesta	Raw	Cr^{6+}	33.33	[30]

surface of the adsorbent[23]. The maximum adsorption was observed at pH 5. Arafat[24] studied the adsorption potential of dried Eichhornia roots in the adsorption of Co^{2+} from an aqueous solution. The adsorption experiment was carried out as a function of pH, initial conc., contact time, and root weight. The maximum adsorption was observed in the first 15 minutes at pH 8.

3.2 *Ceratophyllum demersum*

C. demersum is a submerged free-floating rootless and perennial aquatic macrophyte. It grows in stagnant water and is distributed all over the world. It forms modified leaves, sometimes forms dense mats just below the surface. The dead biomass of *Ceratophyllum demersum* was used as an adsorbent to remove Cd^{2+}. The percentage removal was 95 at pH 5 in 20 minutes using 1.0 g of biomass. The cadmium removal increases with increasing dosage of adsorbent[25].

3.3 *Azolla filiculoides*

Azolla filiculoides are floating water ferns, commonly found in ditches, ponds, and slow-flowing streams. The best use of this plant is as a biofertilizer, alternatively, it can be used for other useful applications. This may be possible to use in the form of adsorbent for removing pollutants both organic and inorganic from wastewater. *A. filiculoides* has also been used for the elimination of precious metals like gold, silver from wastewater containing effluents from gold or silver plating industries. Ahmady-Asbchin and Omran[26] used the dried *Azolla filiculoides* biomass for heavy metal removal using batch experiments. The adsorption capacities for Ni and Cu using *A. filiculoides* were approximately 0.77 and 0.54 mmol g^{-1} (dry Azolla), respectively.

3.4 *Lemna minor*

Lemna minor belongs to Lemnaceae family and is a small, and free-swimming aquatic plant.Excessive growth of *Lemna minor* shows detrimental effects on aquatic life. So, it was found to be used as an adsorbent to solve the problem of water contamination due to organic and inorganic pollutants. Tang et al.[27] in their experiment investigated the maximum removal efficiency was above 95% for Pb^{2+} using Lemna perpusila. The batch experiment was conducted to remove Pb^{2+} by using dried adsorbent (4g L^{-1}) at pH 4.6, initial concentration of 50 mg L^{-1} Pb^{2+}, and contact time of 210 min. This study showed the effectiveness of *L. Perpusila* in the treatment of wastewater as it is locally available and inexpensive.

3.5 *Spirodela polyrhiza*

Spirodela polyrhiza (L.) Schleiden (Greater duckweed) belongs to Araceae family and free-floating aquatic plant. It is distributed in freshwater habitats worldwide. They are rapidly growing and highly abundant macrophytes due to which they can be used in the adsorption of pollutants. Meitei and Prasad[28] studied the use of *Spirodela polyrhiza* to adsorb heavy metals like Mn^{2+}, Cu^{2+}, and Zn^{2+} from single, binary, and ternary metal solution systems. The contact time to attain equilibrium was within 120 minutes. The maximum adsorption capacities observed were 52.6 mg g^{-1} for Cu^{2+}, 35.7mg g^{-1} for Mn^{2+} and 28.5 mg g^{-1} for Zn^{2+} ions. The adsorption capacity was reduced in binary and ternary metal solution systems. It was better fitted in the case of a single metal system. This plant showed greater potential in removing heavy metals from their aqueous solutions.

3.6 *Pistia stratiotes*

Pistia stratiotes belong to the Arum family, Araceae. It is a free-floating aquatic plant having feathery roots and fleshy leaves. It also has application in medicines, but alternatively, it can be used for pollutant removal in adsorption. *Pistia stratiotes* was used for adsorption of heavy metals like lead and chromium by Lima et al.[29]. They found that the adsorbent made from this plant is renewable, biodegradable, fast and easy growing, supports a broad temperature range and pH. The adsorption of Cr^{3+} and Pb^{2+} were examined using adsorption experiments. The maximum adsorption capacities for the removal of Cr^{3+} and Pb^{2+} were recorded as 0.317 and 0.225 mmol g^{-1}, respectively.

3.7 *Salvinia molesta*

S. molesta is a floating fern that grows on slow-moving fresh water and grows rapidly like a dense mat on the surface of rivers, lakes, and ponds. Singh et al.[30] used dead biomass of *S.molesta* for adsorption of Cr^{6+} from the aqueous solution. The experiments were carried out as a function of pH, adsorbent dose, temp., initial conc., agitation speed, and contact time. The maximum adsorption capacity was found to be 33.33mg g^{-1} which shows that biomass of *S. molesta* can be used as an adsorbent for the removal of heavy metals.

4 Advancement in aquatic plant-based adsorption

Some advancements have been made in the field of adsorption using aquatic plants. They have been transformed into biochar or modified by different chemicals and converted into nano-adsorbents. These changes were applied to increase the efficiency of adsorbents in heavy metal adsorption. This review paper reveals some studies of adsorbent modification which shows how adsorbent is modified and helpful in increasing adsorption potential. The modification of adsorbents with their adsorption potential is discussed in Table 4.

Table 4. Adsorption of heavy metals by modified aquatic plants adsorbents

Adsorbent	Modification	Metals adsorbed	% removal or q_e (mg g^{-1})	References
Eichhornia crassipes	Biochar WH300 WH500 WH700 Magnetic biochar Nano-EC Microspheres	Cd Cu^{2+} Zn^{2+} Cr^{6+} Ni^{2+} Cr^{6+}	49.83 36.89 25.82 3.53 9.42 79.04 85.09 7.7	[31] [32] [33] [34]
Lemna minor	0.2M NaOH Biochar	Cr^{6+} Ni^{2+}	98% 41.68	[35] [36]
Pistia stratiotes	0.1 M NaOH	Pb^{2+}	202	[37]
Spirodela polyrhiza	diethylenetriamine-grafted *Spirodela polyrhiza* (DSP)	Ni^{2+} Pb^{2+}	33.02 36.50	[38]

Li et al.[31] studied the preparation and characterization of water hyacinth biochars for the removal of cadmium (Cd) at temperatures ranging from 300°C to 700°C. Biochar made from water hyacinth was classified as WH300, WH500, and WH700 according to treatment at different temperatures. Nearly 90% of Cd was removed at pH 5 which was observed as optimum pH. The maximum Cd adsorption capacities were observed as 49.837, 36.899, and 25.826 mg g^{-1} for WH300, WH500, and WH700, respectively. *E. crassipes* biochar can be a good adsorbent for the treatment of wastewater that has the potential to transform environmental problems into new purification technologies.

Nyamunda et al.[32] evaluated the potential by making magnetic biochar (Fe_2O_3-EC) from water hyacinth by the chemical precipitation of a mixture of $FeCl_2$ and $FeCl_3$ on the biomass of water hyacinth followed by pyrolysis in the removal of Cu^{2+} and Zn^{2+}. The maximum adsorption capacities obtained for Cu^{2+} and Zn^{2+} were 3.53 mg g^{-1} and 9.42 mg g^{-1}, respectively. All these studies showed that *Eichhornia crassipes* was found to be a good adsorbent for heavy metal removal. The synthesis of nano-EC and nano-LM were prepared by *Eichhornia crassipes* (raw EC) and *Lemna minor* (raw LM) using the sol-gel method[33]. These were employed to eliminate Ni^{2+} and Cr^{6+} ions from the aqueous solution effectively. The optimal pH for maximum Cr^{6+} ion removal by nano-EC and nano-LM was 2, and the adsorbent dosage was 0.5g L^{-1} with 50 and 120 min, respectively. Carreño-Sayago[34] developed the microspheres with dry and pulverized biomass of the roots *E. crassipes*, combining them with sodium tripolyphosphate for the removal of chromium from tanneries water. The pH, the initial concentration, and the ideal amount of these microspheres were evaluated together with the adsorption isotherms and the maximum adsorption capacity of Cr^{6+} was observed to be 7.7 mg/g.

An experiment was done to study the removal of Cr^{6+} by increasing the efficiency of lemna by modifying it with 0.2 M NaOH. The best metal removal was observed at pH 3 and it increases with increasing dose and contact time. A decline in removal has been observed with increasing initial concentration [35]. Yan et al. [36] studied the utilization of biochar made from pyrolysis of *lemna minor* at 400°C in the treatment of Ni-electroplating wastewater. The maximum adsorption for removal of Ni was observed to be 41.68 mg g^{-1}.

Ferreira et al. [37] used the dried biomass of Pistia stratiotes and *Salvinia* sp. for adsorption of lead which was modified by treating with 0.1M NaOH solution and stirring for 2h. The adsorption capacity observed to remove Pb^{2+} was 202 and 210.1 mg g^{-1} by a modified mixture of *Pistia stratiotes* and Salvinia sp. and modified *Salvinia* sp., respectively. Adsorption tests indicate that modification enhances the biomass adsorptive ability. A novel adsorbent, diethylenetriamine-grafted *Spirodela polyrhiza* (DSP), was prepared by modifying natural *S. polyrhiza* (SP) with diethylenetriamine by cross-linking with epichlorohydrin and utilized for adsorption of Ni^{2+} and Pb^{2+} from water [38]. The maximum adsorption capacities of DSP for Ni^{2+} and Pb^{2+} were 33.02 and 36.50 mg g^{-1} respectively.

5 Conclusion

In this study, adsorption is being demonstrated over other conventional methods for heavy metals removal. The use of aquatic plant adsorbents has a negligible cost, renewable, biodegradable materials, and is found as a promising method for contaminant removal. Aquatic plants being used also show their potential to remove heavy metals as they grow rapidly and are found abundantly. Various modifications are being used to increase their efficiency to remove or adsorb pollutants in the form of heavy metals, organic and inorganic materials also. Various aquatic plants like *Eichhornia crassipes*, *Ceratophyllum*, *Lemna*, *pistia stratiotes*, *Spirodela polyrhiza*, *Azolla*, and many others have been used for adsorption purposes. Some of the aquatic plants are invasive and deteriorate the water quality of the water body, using these plants in the adsorption process delivers double benefits. This review shows that aquatic plants have more ability to adsorb heavy metals and these fast-growing invasive aquatic species can be utilized for wastewater treatment. Adsorption efficiency can be increased by modifying adsorbents with various chemical species. Further studies can be employed by using nano-adsorbents derived from aquatic plants and making the process cost-effective.

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