Assessment of Heavy Metal Accumulation Potential of Local Aquatic Macrophytes for Wastewater Phytoremediation

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ABSTRACT

Due to industrial discharge, agricultural runoff, and poorly managed waste, heavy metal contamination of water bodies has become a global problem. Existing methods of physicochemical treatment are effective but costly and produce hazardous waste. Aquatic macrophytes can be used in bioremediation as an alternative, sustainable, low-cost process that utilize the ability of macrophytes to accumulate, translocate and detoxify heavy metals.

This review examines the potential of six commonly studied species to accumulate heavy metals. These species include Eichhornia crassipes, Lemna minor, Pistia stratiotes, Hydrilla verticillata, Azolla pinnata and Typha latifolia with respect to lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn) and mercury (Hg). Scholars have evaluated important arguments such as rhizofiltration, phytoextraction, the process of phytochelatin synthesis, vacuolar sequestration, hindrance of reactive oxygen species (ROS) scavenging etc. In addition, they also studied on additional quantitative indices bioaccumulation factor (BAF) and translocation factor (TF). An analysis of the efficiency determinants (pH, temperature, and biomass productivity). A Broadest high-efficacy metal removal profile: crassipes. pinnata in L. Fridges are beneficial in selectivity and doubling rate of biomass. The seasonal performance of a highly competitive species in the station ecosystem is crippled by the post-harvest disposal of biomass. Future insights entail informing policy-makers and planners. We need to scale-up integrated waste management techniques to manage agri-food systems.

Keywords: *Aquatic macrophytes; Heavy metals; Phytoremediation; Bioaccumulation factor; Rhizofiltration; Wastewater treatment; Metal tolerance*

1. Introduction

The levels of heavy metals in surface and groundwater are increasing with increasing industrialization and urbanization. Heavy metals are naturally occurring and non-biodegradable substances that linger eternally in the environment. Because they do not undergo biological degradation, they accumulate in each food chain level. The damage to the earth from plastic pollution is not only severe but harmful for life. The USEPA and the EU Water Framework Directive has classified priority pollutants or priority substances as toxic and mutating as well as having a carcinogenic as well as endocrine disrupting capacity containing heavy metals like lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), nickel (Ni), copper (Cu) and zinc (Zn) (Ali et al. 2019).

Common methods like coagulation and flocculation, ion exchange, membrane filtration, and others, although efficient, have high capital costs and energy demand and they also produce toxic sludge, making them inapplicable in a resource constraint scenario (Fu & Wang, 2011). Consequently, there is interest in Phytoremediation by aquatic macrophytes.

Studies have been conducted on Eich hornia crassipes, Lemna minor, Pistia stratiotes and Hydrilla verticillata, Azolla pinnata and Typha latifolia for the uptakes of the heavy metals from the contaminated water which takes place in all tropicals, subtropical, and temperate. The goal of this review is to explain the accumulation mechanism, quantify the operation parameters that control the efficacy of remediation, and define key knowledge gaps that require investigation regarding the use of the biosurfactants and bio emulsifiers.

2. Sources and Environmental Impact of Heavy Metals in Wastewater

Heavy metals are released into water through industrial point sources such as electroplating, tanneries, battery manufacturing and dyeing industries and agricultural runoff from phosphate fertilisers (Pb, Cd) and pesticides (Cu, Zn) (Tchounwou et al. 2012). Municipal sewage adds Pb and Cu from plumbing along with Hg and Zn from personal care products. Methylmercury (MeHg), a highly toxic compound that accumulates in the aquatic food web, is produced by the microbial methylation of mercury in anaerobic sediments (Driscoll et al. 2013). Chromium(VI) is a toxic chemical released from chromite ore processing and leather tanning which is a carcinogen and is highly mobile in water.

Metal concentrations which are sublethal affect the enzyme activity of aquatic species and disturb DNA replication. This causes a change in the community structure as well as the ecosystem services. Acute toxicity events lead to mass death of aquatic fauna and also have repercussive effects on ecosystem functions (Vardhan et al., 2019). The urgency to treat wastewater is underscored by chronic human exposure that causes neurodevelopment deficits (Pb), renal tubular dysfunction, osteoporosis (Cd), neurological damage (Hg).

3. Aquatic Macrophytes and Their Role in Phytoremediation

There are a variety of growth forms of aquatic macrophytes such as free floating, emergent, submerged, etc. Each has its own advantage on phytoremediation. Free-floating species, such as E. crassipes, L. minor and P. stratiotes, suspend their roots in the water column to optimize rhizofiltration. Species such as T. The plants H. latinfolia use water from the sediment and the water column above the sediment through root-rhizome. Verticillata opens itself wholly to the dissolved metals. Azolla pinnata is a floating pteridophyte that partners with Anabaena azollae for nitrogen-fixing symbiosis, enabling biomass productivity limitations.

Plants can be employed for cleaning contaminated environments and for recovering valuable metals through two distinct methods: phytoextraction and rhizofiltration. Phytoextraction entails root uptake and the thorough translocation of metals to harvestable above-ground tissues. Rhizofiltration on the other hand, refers to the absorption, adsorption and precipitation of metals by roots with little or no transport to the shoots. (Zhu et al., 1999). Most aquatic systems function simultaneously through both mechanisms. The long history of using aquatic plants in wastewater treatment includes constructed wetlands with Phragmites australis and Typha spp. They have been in operation in Europe since the 1970s. However, meaningful deployment of hyperaccumulating macrophytes - informed by their mechanisms and comparative approach - is a more recent trend 1.

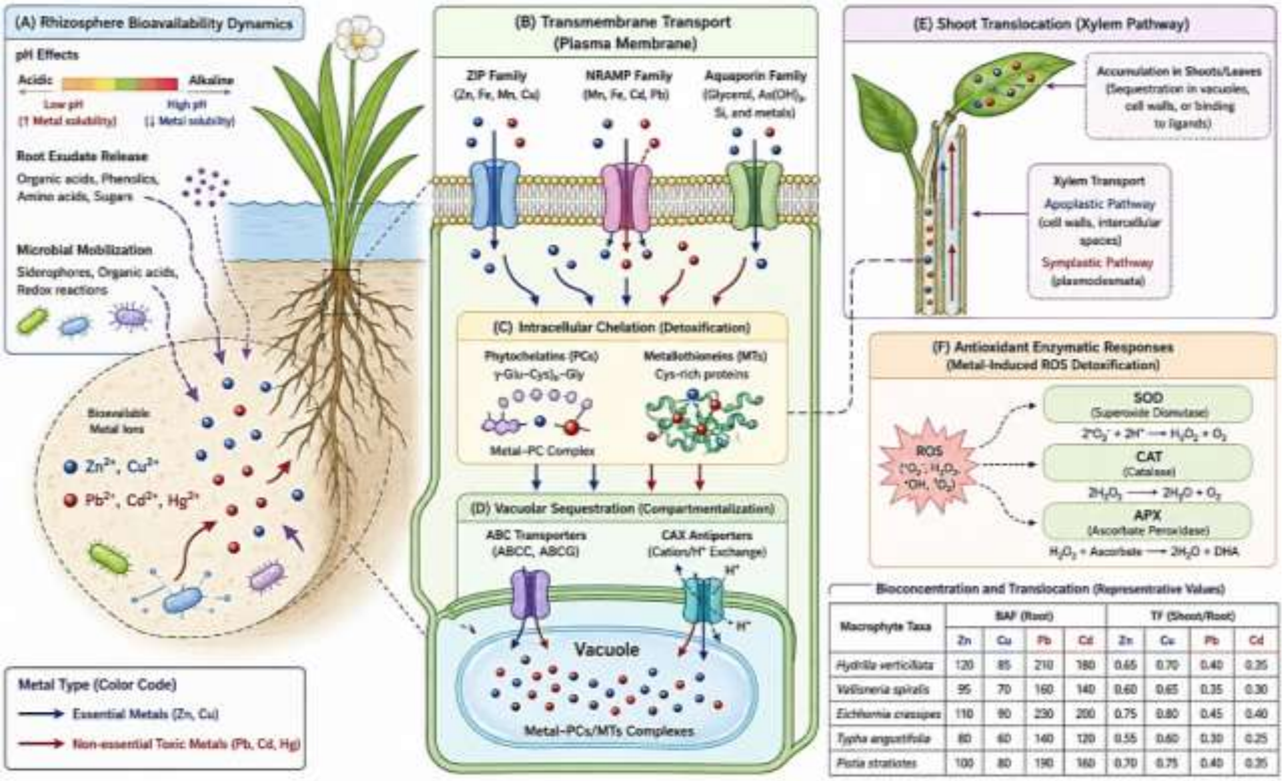
4. Mechanisms of Heavy Metal Uptake and Accumulation

4.1 Rhizosphere Dynamics and Transmembrane Transport

The rhizosphere is a zone of chemical reactions marked by root exudation (citrate, malate, oxalate), proton release and microbe activity which change metal speciation and bioavailability. The solubility of Pb^{2+}, Cd^{2+} and Zn^{2+} generally increase in the soil of plants due to acidification. Metal ions are taken up by the root plasma membrane via specific transporters. For example, the ZIP transporter family mediates the uptake of Zn2+, Cd2+, and Fe2+. NRAMP proteins are known to transport Mn2+, Fe2+, Cd2+, and Pb2+. Also, aquaporin channels mediate the entry of Hg2+ and methylmercury (Clemens, 2001). Transporters that respond to essential ions are often misled by excess non-essential metals. An early-response mechanism that inhibits feedback when the metal burden becomes excessive.

4.2 Intracellular Detoxification and ROS Response

an root growth cells, peptides of formula (γ-Glu-Cys)n-Gly (phytochelatins; PCs) chelate Cd, Pb, Hg and others metal and are transported into vacuoles by ATP-binding cassette (ABC) transporters (Cobbett & Goldsbrough, 2002) Cysteine-rich proteins (MTs) perform complementary chelation for Cu and Cd. The primary mechanism of hyperaccumulation involves vacuolar sequestration by CAX antiporters of metal-chelate complexes in vacuoles. Heavy metal exposure leads to the generation of reactive oxygen species, which are $O_2^{\bullet -}$, H_2O_2, •OH. These reactive species cause oxidative damage to lipids and DNA. The enzymatic antioxidants include SOD, CAT, APX, GR, etc., while non-enzymatic scavengers involve ascorbic acid, glutathione, carotenoids, and proline (Sharma and Dietz, 2009).



Bioconcentration and Translocation (Representative Values)

Macrophyte Taxa	BAF (Root)				TF (Shoot/Root)			
	Zn	Cu	Pb	Cd	Zn	Cu	Pb	Cd
Hydrilla verticillata	120	85	210	180	0.65	0.70	0.40	0.35
Vallisneria spiralis	95	70	160	140	0.60	0.65	0.35	0.30
Eichhornia crassipes	110	90	230	200	0.75	0.80	0.45	0.40
Typha angustifolia	80	60	140	120	0.55	0.60	0.30	0.25
Pistia stratiotes	100	80	190	160	0.70	0.75	0.40	0.35

FIGURE 1: Mechanism of Heavy Metal Uptake and Accumulation in Aquatic Macrophytes

5. Comparative Heavy Metal Accumulation Potential

Standard indices determining phytoremediation performance are the Bioaccumulation Factor (BAF) and the Translocation Factor (TF). According to Ali et al. 2019, BAF > 1000 confirms the hyperaccumulator status and TF > 1 confirms preferential shoot transfer for phytoextraction.

The model macrophyte, Eichhornia crassipes, has BAF values of 1200–2800 for Pb and 900–2100 for Cd (Rezania et al., 2016), removal efficiencies of 85–98% for Pb and 79–95% for Cd, and productivity in biomass of 20–30 t dry wt ha^{-1} yr^{-1}. The TF value for Pb < 0.4 indicates retention of the root while TF for Zn and Cu tend towards 1.0. This invasive species must be contained strictly.

Lemna minor has a BAF of > 2500 for Cd and TF of > 1 for Zn, which show a doubling time of 24–48 h for high throughput removal (Khellaf & Zerdaoui, 2010). Removal rates for cadmium are between 70 and 92 %, with the performance of the substance declining in the presence of more than 2 mg/L of lead. Its capacity to function within pH range of 4.5–8.5 and temperature range of 10–35 °C suitable for polishing of secondary effluents.

Utilization of P. stratiotes removes 78-94% Cr (VI) from tannery effluents with BAF 800-1500 for Cr (Arora et al., 2020). The tissue composed of aerenchyma forms an oxidizing rhizosphere which favors the precipitation of Cr(III). The most likely mechanism that was at play is root-zone immobilization as indicated by the low TF for Cr (less than 0.3). Submerged hydrilla verticillata achieves direct adsorption across all surfaces (BAF 900–1800 for Pb; Agunbiade et al., 2009) and serves as a sensitive aquatic bioindicator for Pb. Performance decreases in muddy water due limited light. The removal of 88–96% Cd by Azolla pinnata (BAF 1100–2200) is due to the adsorption of polysaccharides present in its cell wall and the increased synthesis of PCs (Rai 2008). The biomass in nitrogen-depleted effluents is maintained by its Anabaena symbiont, whereas its superior APX activity affords exceptional tolerance to Cd. According to Maine et al (2009), aquatic plants such as Typha latifolia, which are the main species used in constructed wetlands, exhibited 74–88% Zn and 60–82% Hg removal over years. Root-zone immobilization predominates (TF less than 0.3 for Pb and Hg); however, a Zn TF greater than 0.7 indicates active xylem loading.

Table 1. Comparative heavy metal accumulation and removal efficiency of selected aquatic macrophytes.

Plant Species	**Target Metals**	**Removal Efficiency (%)**	**Reference**	**Key Findings**
Eichhornia crassipes	Pb, Cd, Cr, Ni, Cu, Zn, Hg	85–98% (Pb); 79–95% (Cd)	Rezania et al., 2016	Highest BAF (>1000) for Pb/Cd; rapid biomass turnover; invasive — containment required
Lemna minor	Cd, Zn, Cu, Pb	70–92% (Cd); 65–88% (Zn)	Khellaf & Zerdaoui, 2010	24–48 h doubling time; TF > 1 for Zn; sensitive to Pb > 2 mg/L
Pistia stratiotes	Cr, Pb, Cd, Ni	78–94% (Cr); 72–89% (Pb)	Arora et al., 2020	Aerenchyma enhances root adsorption; low TF for Cr (< 0.3); suited to tannery effluent

Plant Species	**Target Metals**	**Removal Efficiency (%)**	**Reference**	**Key Findings**
Hydrilla verticillata	Pb, Cu, Zn, Cd	80–91% (Pb); 68–85% (Cu)	Agunbiade et al., 2009	Submerged; whole-body contact; bioindicator for aquatic Pb; light-dependent
Azolla pinnata	Cd, Cr, Cu, Ni	88–96% (Cd); 75–90% (Cr)	Rai, 2008	N-fixing symbiont boosts productivity; high APX activity; superior Cd scavenging
Typha latifolia	Pb, Zn, Ni, Hg	74–88% (Zn); 60–82% (Hg)	Maine et al., 2009	Root-zone immobilization; TF < 0.3 for Pb/Hg; ideal for constructed wetlands

BAF = Bioaccumulation Factor; TF = Translocation Factor. Removal efficiencies reported at initial metal concentrations of 1–10 mg/L.

6. Factors Affecting Phytoremediation Efficiency

Increase in solution pH is an important abiotic factor of reducing the solubility of Pb^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+}. The solubility of Pb^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} drastically reduces above pH 7 – 8 due to hydroxide and carbonate precipitation. The solubility of Cr(VI) species varies greatly with pH (Tangahu et al., 2011). The majority of macrophytes optimally take up metals between pH 5.5 and 6.5. Temperature significantly regulates the activity of enzymatic transporters. Two tropical species namely E. crassipes and P. stratiotes peaked at 25 to 35ºC. Furthermore, temperate species L. minor and T. Latifolia operated efficiently at 15 to 25ºC. Notably, transport uptake rates decreased by 50 to 80% at temperatures lower than 10ºC (Maine et al. 2009). Light availability indirectly modulates metal flux in submerged species like H. activity where light intensity appears to be directly linked to the removal level of Pb.

Following the initial metal concentration, the removal efficiency exhibited a sigmoidal response: low doses up to around 1–5 mg/L were approximately linear, followed by a maximal efficiency of this range and a decline thereafter for > 10–20 mg/L due to phytotoxicity. The different forms of metals in real industrial waste such as free ions, organic complexes and colloids are very different from controlled conditions that are used in laboratory tests. This is a key knowledge gap for scaling up studies in field conditions Ali et al (2019). E. emphasizes biomass productivity and harvesting frequency is equally important. crassipes (doubling time 11–

14 days) exhibits the highest mass-based rate of removal, while harvesting at 60–70% of peak standing biomass optimizes metal export and longevity.

7. Advantages, Limitations, and Future Prospects

The operational costs of macrophyte phytoremediation are estimated to be 5–20% of those of equivalent physicochemical systems, which makes it a cost-effective method. It is solar-powered and visually unobtrusive. It also has co-benefits such as the removal of nutrients, carbon sequestration and habitat provision (Rezania et al., 2016). The pyrolysis or acid leaching of harvested biomass could extract metals that have potential economic value. The method is however limited in terms of specificity towards metal (not all metals get detected) concentration dependence, seasonal performance (which may vary depending on season) and it poses ecological risks due to invasive species. Remaining controversial from a regulatory and environmental standpoint is post-harvest disposal of metal-laden biomass.

Future research should focus on polyculture systems. A. crassipes with A. the pinnata and T The emergence of new technologies that can be translated into commercial solutions would greatly enhance the reliability and viability of constructed wetlands. These include: (1) innovative polyculture systems using C4 plants such as Miscanthus×giganteus and Panicum virgatum, and wetland species such as Pontederia cordata and Arundo donax, which otherwise can achieve 15–35% higher removal than monocultures (Vymazal, 2011); (2) GE cultivars overexpressing PC synthase, improved ABC-transporters, or modified TF regulation; (3) techno-economic and life cycle analyses at pilot and full scale; (4) standardized protocols for safe biomass valorization or disposal; and (5) IoT-enabled, real-time management of constructed wetland systems to compensate for environmental variability.

8. Conclusion

The review shows that aquatic macrophytes are a scientifically proven, economically feasible, and ecologically sound strategy to remove heavy metals from wastewater. Eichhornia Crassipes has the highest rate of metal removal performance (BAF > 1000; 79–98% efficiencies) with high biomass productivity and high antioxidant defensive mechanism. Azolla pinnata and Lemna minor were the most efficient to remove the heavy metals Cd and Zn, respectively, with doubled biomass. The preferred species for a long-term constructed wetland targeting Zn, Hg, and Ni during the experimentation was Typha latifolia due to its root-zone immobilization.

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