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Review on Phytoremediation Potential of Floating Aquatic Plants for Heavy Metals: A Promising Approach

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Abstract: Water pollution due to heavy metals has become a serious environmental concern due to their hazardous properties. Since conventional water remediation techniques are generally ineffective and non-environmentally friendly, phytoremediation has gained increasing attention from worldwide researchers and scientists due to its cost-effectiveness and environmental friendliness. Hence, this review first discussed soil and water remediations. Phytoremediation can be divided into five techniques to remove heavy metals from the polluted environment, namely, phytostabilization (phytosequestration), phytodegradation (phytotransformation), phytofiltration (rhizofiltration), phytoextraction (phytoaccumulation), and phytovolatilization. Four common floating aquatic plants (accumulator plants), such as duckweed (*Lemna minor*), water lettuce (*Pistia stratiotes*), water hyacinth (*Eichhornia crassipes*), and watermoss (*Salvinia*) were discussed in detail due to their great capability in absorbing the metal ions by their roots and further translocating the metal ions to the aerial parts. Furthermore, the parameter studies, such as optimum pH and temperature of the water, exposure duration, initial metal concentration, water salinity, and the addition of chelating agents, were evaluated. The absorption kinetics of the plants was discussed in detail. In short, phytoremediation is a promising green and sustainable water remediation approach. However, further research is necessary to enhance its practicability and performance at large-scale implementation.

Keywords: phytoremediation; hyperaccumulator plants; heavy metals pollution; accumulation; bioremediation

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1. Introduction

Due to rapid urbanization and industrialization, about 40% of the world's population is facing water scarcity problems [1,2]. Some contributing factors to these issues are climate change, food necessity, and the inefficient utilization of natural resources. In addition, a study revealed that the death of 1.8 million people was linked to water pollution in 2015 [3]. The progressive revision and assessment of water resource policy at all levels are indeed necessary. Water pollution has been linked to severe human health issues such as infectious diseases, nervous system damage, and even death [4]. Moreover, water pollutants are tremendously harmful to aquatic life. Therefore, the rehabilitation of wastewater is the only remediation solution to cope with the greater demand for water for industrial and agricultural use.

Nowadays, most of the surface waters are not achieving the optimal standard owing to a variety of stressors that affect freshwater quality, namely point source and non-point source pollution, the change in land use and climate, which further magnifies the challenge of supplying water security [5]. In detail, point sources of water pollution are those discharged from a single and identifiable origin. Contrarily, non-point sources of pollution are those pollutants eliminated from various sources and diverse non-identifiable sources [6].

In the United Kingdom, one of the primary stressors on water quality is an excessive nutrient released from a diffuse source of water pollution [5]. On the other hand, in China, other issues of heavy metal pollution are notable. The interactions between various stressors in time and space could lead to additional effects [5]. For instance, an increase in land-use change on account of vigorous agricultural activities and a potential rise in storm frequency might escalate the distribution of nutrients, such as phosphorus and nitrogen, and fine sediment to receiving water bodies. Eventually, the rapid expansion of industrial and residential activities would negatively impact the water quality of rivers, lakes, and oceans [4,7].

Phytoremediation is a promising green technology in wastewater remediation by using plants and microorganisms to eliminate, translocate, immobilize, or degrade the contaminants from the environment [8–12]. In other words, phytoremediation employs the fact that a living plant can act as a photosynthetic-driven pump proficient in eliminating pollutants such as metals and metalloids from the environment and water effectively [9,13]. Notably, aquatic plants play an essential role as a natural absorber in phytoremediation for heavy metals and contaminants with their extensive root systems, making them the best selection for the uptake of pollutants through their shoots and roots [1]. Phytoremediation technology has received global attention among scientists and administration bodies due to its effectiveness in lowering unparalleled environmental pollution via an environmentally friendly pathway. Figure 1 demonstrates the increasing trend for phytoremediation based on the data extracted from Scopus by using the keywords of "phytoremediation and phytoremediation and water" from 2002 to 2022.

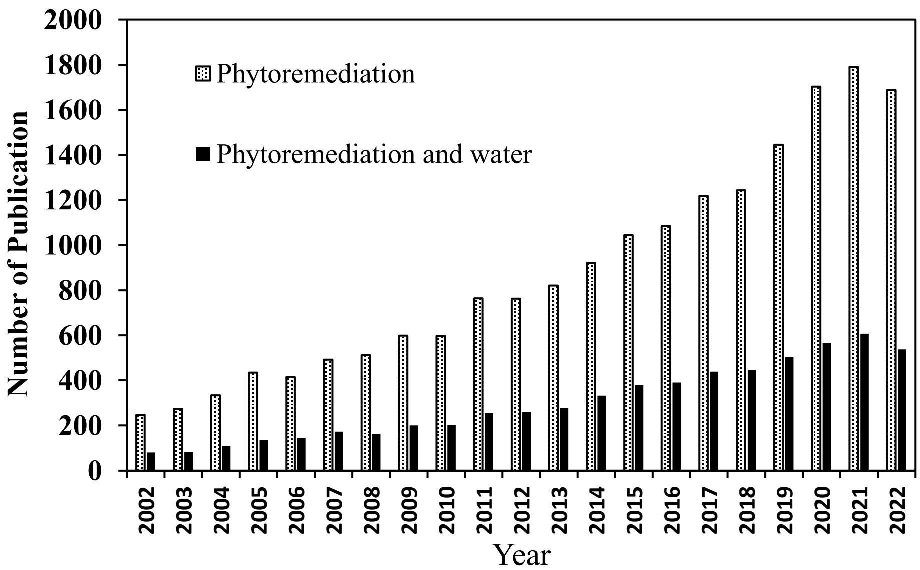

Figure 1. Increasing use of aquatic plants in phytoremediation.

This review intends to examine the phytoremediation of heavy metals within different accumulator plants. It focuses on the emerging phytoremediation results for the removal of heavy metals from contaminated water and the main mechanisms occurring between the heavy metals and the accumulator plants. The phytoremediation parameters and kinetic studies were also updated and discussed. Lastly, this review also proposed some useful prospects and challenges for further development to boost the development of phytoremediation that is capable of improving the efficiency of the process.

2. Types of Phytoremediation

Phytoremediation can be applied to remove heavy metals in contaminated soil or contaminated wastewater through the bioaccumulation process. The utilization of accumulator plants is the crucial element of phytoremediation, and its selection is based on the bioaccumulation capacity of the accumulator plants on the targeted heavy metal. Some studies have ascertained the bioaccumulation capability through a series of experiments.

2.1. Soil Remediation

Conventional soil remediation approaches such as chemical oxidation and solvent extraction used to treat the contaminated soil with heavy metals and residues are generally cost-intensive and destructive to soil nature. Additionally, these methods require the transportation of contaminated substances to the treatment site, introducing additional risks of secondary pollution [10]. Lately, phytoremediation has received attention in remediating soil contamination sites due to its profitability, environmental friendliness, and durable application. Phytoremediation employs plants and microorganisms to eliminate, isolate, or degrade toxic substances away from the environment. The reliable mechanisms for soil remediation are phytoextraction and phytostabilization [10]. Phytoextraction uses plants to extract and capture the contaminant, whereas phytostabilization contains the contaminant. Other workable phytoremediation mechanisms include rhizofiltration and phytovolatilization. Rhizofiltration works by absorbing and adsorbing the contaminant. On the other hand, phytovolatilization works by absorbing the contaminant from the medium via plant roots and discharging them into the atmosphere [14].

Bioavailability expresses the degree of contaminants readily absorbed by plants through exposure to them [14]. Plants will only absorb or uptake metals that are bioavailable to them. Metal bioavailability is vital in determining the success of phytoremediation by plants. Low metal bioavailability is the primary factor that restricts the phytoextraction of metal contaminants [15]. In addition, soil microbes play a crucial role in catalyzing redox reactions, altering the metal bioavailability in soil and the tendency for root uptake.

The factors affecting the metal bioavailability in soil are the pH, microorganisms, root exudates, soil organic matter, and competitive cations [10]. The acidity and alkalinity of the soil determines the metal solubility and mobility in the soil. At acidic or low pH conditions, plants liberate more metals into the soil solution to compete with hydrogen ions (H^+), thus enhancing the metal bioavailability. Under alkaline or neutral pH conditions, the immobilization of metals such as lead (Pb) and chromium (Cr) would happen. Therefore, the metals are not bioavailable to plants [16]. In addition, soil microorganism such as the strain of *Xanthomonas maltophyla* was proven to accelerate the precipitation of Cr^{6+} to trivalent chromium ions (Cr^{3+}) from a state of high mobility to low mobility and less toxic compounds [17].

Once taking up the heavy metals, the metals concentrate in the root tissues through immobilization or further translocate towards the aerial part of the plant via xylem vessels [14]. In shoots, the metal accumulation usually happens in vacuoles, which are cellular organelles that have a low metabolism. The hyperaccumulator plants are usually equipped with vital metal tolerance mechanisms, namely metal detoxification and metal exclusion, to cope with the toxic effects of metal ions at elevated concentrations [17]. For metal exclusion, the excluders prevent metal absorption by roots and preclude further translocation and accumulation in plant shoots.

The phytoextraction mechanism to eliminate soil contaminants includes five necessities: (1) mobilization of metal ions in the rhizosphere, (2) uptake of metal ions through plant roots, (3) translocation of metal ions internally to the shoots, stems, and leaves of the plant, (4) heavy metal tolerance, and (5) metal sequestration in plant tissues [18]. Among these requirements, heavy metal tolerance is an essential requirement for phytoremediation since higher plant tolerance to metal stress indicates that a higher number of metals could be accumulated in the plant tissues with the lowest detrimental impacts on plant health [18]. Metals such as cadmium (Cd) are easier to be absorbed from the soil via phytoextraction [16].

The potential metal tolerance in a plant relies on some mechanisms, such as metal binding in the plant cell wall, active transportation of metal ions into the plant vacuoles, the formation of metal complexes, and the chelation of metal ions with peptides and proteins.

Apart from the physiological processes dominating the plant tolerance, another crucial factor in predicting the phytoextraction potential is the yearly production of biomass, including the dry weight of shoots and the net composition of metal harvested [14].

2.2. Water Remediation

It has been reported that the application of aquatic plants in the remediation of wastewater was initiated about 300 years ago [19]. Several plant species have been examined and evaluated for their efficiencies in concentrating organic and inorganic contaminants from the water via hydroponic, constructed wetlands, or natural habitats. However, in wetland systems, the precipitated inorganic contaminants from the water often enter the sediments, leading to a complex recovery. Opposingly, floating plant systems could eliminate contaminants via biomass harvesting [20].

Among the diverse floating aquatic plant species, phytoremediators such as *Azolla*, *Eichhornia*, *Lemna*, *Spirodela*, *Wolfia*, and *Wolfialla* demonstrated high efficiency in removing water pollutants through bioaccumulation in their plant tissues [19]. Explicitly, *Lemna minor*, *Eichhornia crassipes*, and *Pistia stratiotes* are specifically employed to eliminate metal ions present in the aquatic system [20]. For instance, *Eichhornia crassipes* can biodegrade inorganic pollutants by concentrating various metal ions, such as copper (Cu), Cd, Cr, lead (Pb), and zinc (Zn).

Additionally, it could remove other contaminants such as total dissolved solids (TDS), total suspended solids (TSS), biological oxygen demand (BOD), and chemical oxygen demand (COD) from industrial wastewater [21]. The harvesting process is comparatively simple due to its floating and not-rooted structure [22]. Furthermore, the treatment by plants such as *Lemna minor* and *Pistia stratiotes* successfully reduced the TDS, BOD, COD, chloride, and sulphate in the wastewater.

3. Classification of Phytoremediation Technique

Several mechanisms are involved in phytoremediation to uptake heavy metals by using aquatic plants from the polluted water bodies and subsequently transforming them into a non-toxic form. These mechanisms are phytofiltration, phytoextraction, phytodegradation, phytostabilization, and phytovolatilization, as shown in Figure 2 [23]. The application of phytoremediation typically starts with the recognition and screening of suitable aquatic plants with great potency to concentrate metals, dissolved nutrients, and other pollutants [19,24]. Each mechanism has its unique characteristics, applications, and uptake routes, which are discussed in the following subsections. For example, in a water environment, rhizofiltration works well by overcoming the inherent biological limitation found in phytoextraction. Specifically, phytoextraction is more suitable for treating polluted soils at shallow depths. Table 1 shows the phytoremediation strategies that are applicable for the removal of different categories of contaminants present in the water bodies.

Table 1. Phytoremediation mechanisms for the removal of pollutants present in the aquatic environment [19].

Pollutants	Mechanisms	Descriptions
Inorganic	Phytoextraction	Eliminate the contaminants in the form of harvestable plant biomass.
	Phytostabilization	Minimize the contaminants mobility.
	Phytoaccumulation	Hyperaccumulation due to hypertolerance.
	Rhizofiltration	Roots filter water via absorption or adsorption.
Organic	Phytodegradation	Degrade the contaminants in the plant.
	Phytostimulation	Stimulate the microbial activity to degrade the contaminants.
	Phytoassimilation	Transport and metabolize the contaminants in plants.
	Phytovolatilization	Extract the contaminants from media and liberate them through air.
	Phytotransformation	Degrade contaminants into a simpler form.

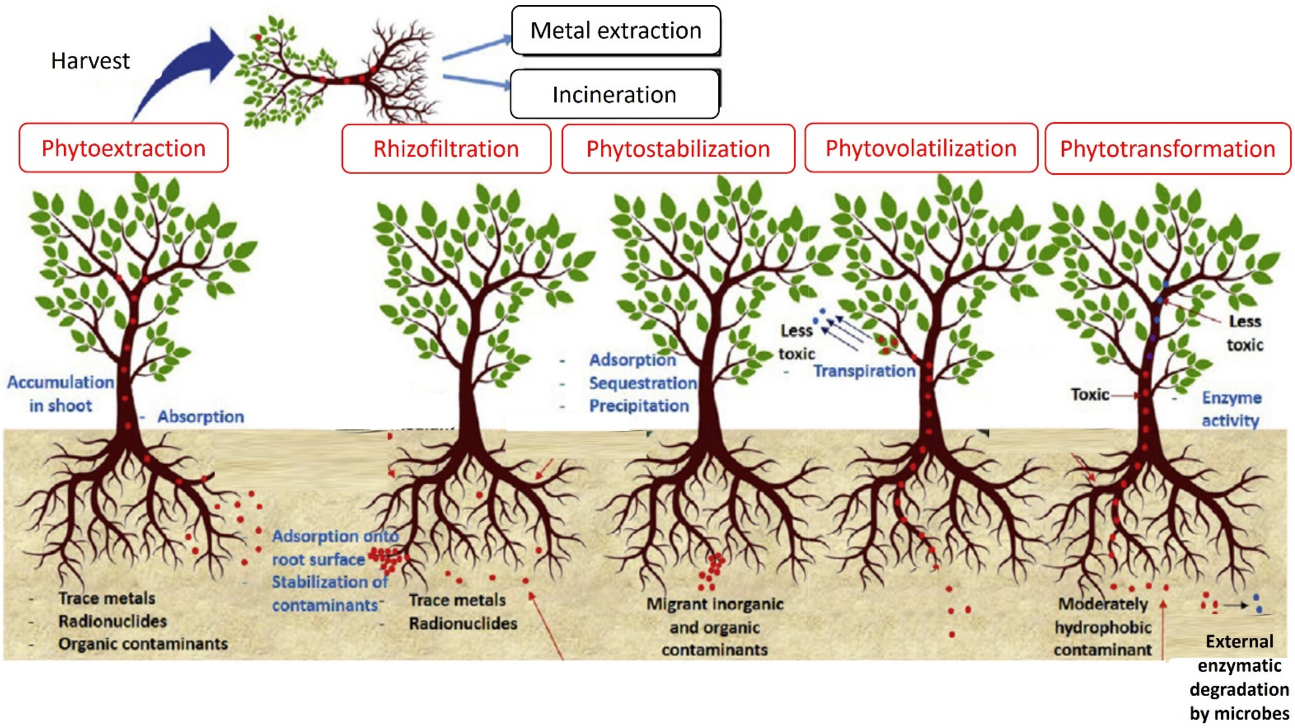

Figure 2. Phytoremediation mechanisms for various types of heavy metals mitigation. Reproduced with permission from [25]. Copyright 2020 Elsevier Ltd.

Rhizo- implies root; thus, rhizofiltration/phytofiltration involves the adsorption or absorption of pollutants in the solution adjacent to the plant roots. The working mechanism in rhizofiltration is similar to that of phytoextraction. However, the plants are mainly used to address the polluted water. The plant species for pollutant removal are cultivated in greenhouses, in which their roots are in contact with water [26]. It could only happen once the widespread fibrous root system has been successfully established. The plant species that grew in the polluted area will uptake the water containing pollutants by their roots. Once the plant roots reach the pollutant saturation limit, they will be harvested. Plants with dense root systems are preferred for rhizofiltration to concentrate the maximum concentration of the contaminants with the larger root adsorption area [20]. Some rootless or floating macrophytes demonstrate high efficiency and potential for the rhizofiltration of metal ions such as Cr, Pb, and Zn from an aqueous system. Nevertheless, the performance of rhizofiltration will depend on the types of metal and the plant's metabolism [21]. The plants selected for rhizofiltration must be resistant to metal, tolerant to hypoxia, and have a large surface area for absorption [14].

Meanwhile, phytoextraction could also be referred to as phytoaccumulation. The phytoextraction mechanism involves the heavy metal uptake from the soil through the root of crop species and further translocates into the aerial part of the plant [1]. The translocation process is regulated by employing leaf transpiration and root pressure. According to Shaari et al. [16], one of the strategies to improve metal solubility in the soil is through the addition of chelating agents. Upon completion of the phytoextraction, the plant will be harvested and disposed of with care [20]. In addition, the plant can be burned for energy generation and further recovery or recycle important metal from the ash. The hyperaccumulators selected should have high efficiency to accumulate high concentrations of crucial micronutrients and uptake considerable quantities of non-crucial metals, such as Cd [27]. Hyperaccumulators occupy environments rich in metals because of their greater necessity for metals than normal accumulator and non-accumulator plants. Additionally, plants with high biomass production are efficient in pollutant uptake. Lastly, plants with high translocation factors, elongated roots, and simple harvesting processes are suitable for phytoextraction [14].

On the other hand, phytostabilization/phytosequestration uses specific plant species to deactivate contaminants contained in the groundwater and soil. As its name implies, phytostabilization could be referred to as in-place immobilization or phytoimmobilization [1]. This process happens when the roots of plants absorb, accumulate, adsorb, or precipitate the pollutants to restrict their movement. Microbes restrict the mobility of contaminants by deliberating chelating substances, avoiding the upward migration of the contaminants to the groundwater, and lessen the bioavailability of metal in the food chain [26]. For example, *Arbuscular mycorrhizal* symbiosis could stabilize the metals in soil [20]. Furthermore, phytostabilization can restore vegetation cover at contaminated sites by employing metal-tolerant plants, especially when the natural vegetation is unable to sustain in the soils contaminated with metals or physically disturbing surface materials. Accordingly, plants could limit the migration of pollutants via wind destruction, delivery of the affected soil surface, and leaching of soil pollutants to groundwater. Apart from that, plants that are inefficient in translocating the absorbed metals from the root to the aerial part are preferable for phytostabilization [14].

In phytovolatilization, the plant absorbs contaminants from the soil and converts them into various volatile compounds, then discharges the metal in gaseous form into the adjacent environment or atmosphere through the plant's stomata via transpiration [1]. Phytovolatilization, primarily concerned with remediating organic acids, is also useful in treating mercury (Hg) and selenium (Se). For the phytovolatilization of Se, with a long half-life of 327,000 years, the suitable plant species are Indian mustard and canola. Phytovolatilization offers numerous advantages, including the unnecessary auxiliary management of vegetation, less soil corrosion, absence of soil interruption, unreturned harvesting, and dumping of plant biomass. Furthermore, the presence of bacteria in the plant's rhizosphere assists in biotransforming the contaminant and eventually bolsters the phytovolatilization rate. However, phytovolatilization is still an arguable method since it discharges toxic metals and returns them to the atmosphere [20]. The research undertaken by Jeevanantham et al. [23] suggested that the heavy metals taken up by plants could transform into a water-soluble and non-toxic form while being transported from the root to the leaves of the plant and being compartmented in the vacuole, followed by the volatilization of metal ions to the atmosphere. The accumulation of metal begins in the epidermis of leaves, followed by the accumulation in the mesophyll of leaves. However, a hyperaccumulator usually inhibits the accumulation of metals in mesophyll with its high evaporation rate of modified soluble metals. Therefore, no adverse effects could result on the plants.

Lastly, phytodegradation, also known as phytotransformation, involves the breakdown of contaminants into simpler molecules through the enzymatic metabolic activity in plants with their corresponding microorganisms [21]. In certain circumstances, selected plants possess the capability to uptake toxic compounds, followed by the detoxification and metabolization of toxic compounds as nutrients [27]. The detoxification of toxic compounds usually involves three stages, namely bioactivation, conjugation, and compartmentalization. Each phase requires various types of enzymes, such as oxygenizes and nitro reductases, classified by the properties and distribution of their reaction products. The enzymes generated by plants could catalyze and speed up the degradation process. The phytodegradation process could be classified into internal and external processes [23]. In particular, two mechanisms that work for the degradation are the plant's enzymatic activity and photosynthetic oxidation. In terms of external degradation, pollutants absorbed by plants will be hydrolyzed into smaller sizes, whereas, for internal degradation, the organic pollutants absorbed are further broken down into smaller sizes by plant enzymes and are eventually used as metabolites.

4. Accumulator Aquatic Plants

The selected plant species must have a high potential to take up various pollutants, rapid growth, be easy to cultivate, and be simple to harvest [8]. Moreover, an ideal plant species applied in phytoremediation should meet a few criteria: (1) plants that show a high accumulation rate for heavy metals even at low concentrations, (2) plants that are easy to harvest, (3) plants that have resistance towards pests and diseases, (4) plants that are capable to uptake several types of heavy metals, and (5) plants that display environmentally friendly and economical application [28]. In reality, aquatic plants such as water lettuce, water hyacinth, and vetiver grass have demonstrated excellent capability to eliminate different pollutants such as heavy metals, TDS, TSS, BOD, COD, and nutrients present in wastewater.

4.1. Duckweed (Lemna minor)

Duckweed, with the scientific name *Lemna minor*, is the fastest-growing and smallest plant species on the planet. The five aquatic genera under the *Lemnaceae* family are *Lemna*, *Landoltia*, *Spirodela*, *Wolffia*, and *Wolffiella* [1]. The *Lemnaceae* family has been the focus of recent research for phytoremediation due to their rapid growth, rapid biomass productivity, phytoplankton, microbial minimization, and high metal and nutrient accumulation capability [19]. These plant species usually appeared in the form of small leaf-like structures known as fronds. They can propagate under various environmental conditions, specifically in the pH ranges from 3.5 to 10.5 and the temperature range between 7 and 35 °C [27]. Furthermore, duckweed can be cultivated in different seasons owing to its cold tolerance characteristic. However, the growth of duckweed species needs special environmental considerations owing to its high sensitivity towards various contaminants. Moreover, diverse duckweed species have various metal tolerances depending on the ambient water conditions such as temperature, pH, metal concentration, and electrical conductivity.

Based on the recent study conducted by Rezania et al. [29], the findings revealed that duckweed has been widely used to recover the nutrients and heavy metals released from agricultural and domestic wastewaters. Referring to another study, the results demonstrated that *Lemna gibba* was more efficient than *Salvinia minima* and *Azolla caroliniana*, thus, was appraised as a hyperaccumulator plant. Additionally, *Lemna minor* could accumulate high concentrations of Cd, Cu, nickel (Ni), magnesium (Mn), Zn, arsenic (As), and uranium (U). *Wolffia globose* possesses a great tolerance to concentrate 400 mg As per kilogram of its dry weight and subsequently removes it effectively [19]. Nevertheless, the burning of metal-contaminated duckweed has become an issue for safe disposal [1,30]. In addition, their degradation through carbonization, incineration, hydrolyzation, or anaerobic digestion is necessary to avoid successive contamination in the environment.

4.2. Water Lettuce (Pistia stratiotes)

Water lettuce, with the scientific name *Pistia stratiotes*, is a free-floating macrophyte that can absorb and concentrate pollutants in the plant body [31]. *Pistia stratiotes*, which belongs to the Araceae family, is a floatable aquatic plant with a hanging root structure submerged in water [29]. Water lettuce is abundant in many regions, such as the tropical and subtropical areas of Asia and America, because of its simple growth requirements and ability to adapt to an extensive range of growth environments. Based on the study conducted by Gupta, Roy, and Mahindrakar [31], a considerable portion of iron (Fe), Mg, Mn, Cd, calcium (Ca), and cobalt (Co) were adsorbed or deposited on the outer root surfaces of water lettuce, whereas more aluminum (Al), Cu, Cr, Ni, and Pb were absorbed by the plant roots. *Pistia stratiotes* are also an effective phytoremediator plant species in treating Mn-polluted wastewater [32]. The advantages of water lettuce are that it is fast-growing, able to cover large water surfaces, and that it requires an uncomplicated harvesting process. Referring to Lu et al. [33], water lettuce possesses an excellent capability in accumulating metal ions from the water bodies with a high concentration factor greater than 10^2. By taking its bioconcentration factor as an indicator, this plant was regarded as a hyperaccumulator for Cu, Cr, Fe, Mn, Ni, Pb, and Zn. Therefore, it was feasible to apply it for surface water remediation.

4.3. Water Hyacinth (*Eichhornia crassipes*)

Water hyacinth, with the scientific name of *Eichhornia crassipes*, is a rooted macrophyte belonging to the families of *Pontederiaceae* and *Eichhornia*. Water hyacinth usually grows largely in polluted water systems and eutrophic lakes [34]. This fast-growing free-floating perennial aquatic weed appears with upright and rounded leaves with a dark blue root system, and it has been demonstrated to be highly competent in remediating domestic wastewater due to its highly resistant features [19]. It is one of the most prevailing invasive vascular plants in the aquatic system due to its tolerance to high concentrations of heavy metals, acetic acids, formaldehyde, formic acids, oxalic acids, and phenols. In addition, it can rapidly adapt to various aquatic physiochemical surroundings, such as those caused by drought and moist sediment conditions. Furthermore, it can uptake tremendous quantities of contaminants, especially heavy metals and nutrients. Various researchers have claimed that water hyacinth exhibited a modest accumulation efficiency towards Cd and Zn. Meanwhile, the plants were efficient in treating waters containing toxic Cr^{6+}. Moreover, water hyacinth was highly efficient in eliminating nitrogen and potassium from the aquatic system. The plant's pollutant removal efficiency was closely related to its maximum growth. The optimal growth conditions for water hyacinth were a pH of 6 to 8, a temperature between 10 and 40 °C, and a water salinity below 5 mg/L [29].

4.4. Watermoss (*Salvinia*)

Salvinia, which belongs to the Salviniaceae family, is a floating aquatic plant with a fast growth rate and a high tolerance towards metal toxicities [29]. *Salvinia* species is a popular plant for heavy metal remediation due to its inherent capacity to absorb and concentrate high compositions of different heavy metals. Essentially, the roots of the plants have shown an unreasonably high potential to accumulate metal ions, such as Cr, Ni, and Pb, higher than their leaves [34,35]. In particular, *Salvinia natans* is a hyperaccumulator for some specific heavy metals, and its leaves could accumulate more heavy metals compared to the other parts of the plant. Table 2 summarizes the heavy-metal removal efficiencies demonstrated by different aquatic plants in phytoremediation applications.

Table 2. Summary of heavy metals removal efficiency by floating aquatic plants in phytoremediation.

Aquatic Plants	Conditions	Heavy Metals Removal Efficiency	References
Duckweed (*Lemna minor*)	Sampling time: 25 days Temperature: 7 to 20 °C Initial concentration (ppb): 16.31 As, 1.47 Cd, 67.37 Cr, 25.84 Cu, 0.36 Hg, 347.8 Ni, 23.37 Pb, 49.59 Zn Framework: industrial wastewater	90.95% As, 97.79% Cd, 90.25% Cr, 98.46% Cu, 82.84% Hg, 98.08% Ni, 99.91% Pb, 98.00% Zn	[36]
	Sampling time: 7 days Temperature: 13 to 20 °C Relative humidity: 70% Photoperiod: 16 h light, 8 h dark Concentration: 10^{-6} mol/L metal solutions	95% Cd, 93% Pb, 81.2% Zn, 86.5% Cu	[36]
Water lettuce (*Pistia stratiotes*)	Sampling time: 15 days Initial concentration (mg/L): 0.08–0.46 Cu, 0.03–1.36 Ni, 0.09–0.86 Pb, 0.26–1.31 Zn Framework: field	39.72–72.58% Cu, 28.96–68.79% Ni, 43.02–76.66% Pb, 26.99–79.57% Zn	[3]
	Sampling time: 30 days Initial concentration (mg/L): 22.17 Al, 5.03 As, 0.028 Cd, 2.84 Cr, 0.16 Cu, 14.70 Fe, 20.37 Mn, 5.25 Pb, 2.01 Zn Framework: steel industry effluent	73% Al, 74% As, 82.8% Cd, 62.8% Cr, 78.6% Cu, 61% Fe, 39.5% Mn, 73% Pb, 65.2% Zn	[37]

Table 2. *Cont.*

Aquatic Plants	Conditions	Heavy Metals Removal Efficiency	References
Water hyacinth (*Eichhornia crassipes*)	Sampling time: 15 days Temperature: 25 ± 5 °C Humidity: 72 ± 15% Initial concentration (mg/L): 1.12 Fe, 0.62 Cu, 1.41 Ni, 0.77 Pb, 1.42 Zn Framework: landfill leachate	87.56% Fe, 87.09% Cu, 81.56% Ni, 84.41% Pb, 90.18% Zn	[38,39]
	Initial concentration (mg/L): 0.24 Pb, 1.20 Pb, 4.97 Hg, 3.34 Ni Framework: industrial wastewater	97.50% Cd, 95.10% Ni, 99.90% Hg, 83.40% Pb	[29]
Watermoss (*Salvinia*)	Sampling time: 28 days Initial concentration (mg/L): 0–12.39 Framework: field	72–91% Cd, 80% Cu, 72–91% Ni, 72–91% Zn	[3]
	Sampling time: 12 days Temperature: 25 °C Humidity: 70–75% Photoperiod: 16 h light, 8 h dark Initial concentration: 1.0 mg/dm^3 Cr, 1.0 mg/dm^3 Hg	74% Cr, 93% Hg	[40]

5. Phytoremediation Mechanisms Using Accumulator Aquatic Plants

In general, heavy metal accumulation in plants involves the uptake of metals into the plant tissue and the liberation of the absorbed metals back to the external medium. In aquatic ecosystems, the adsorption of heavy metals onto the sediment takes place. However, these adsorbed metals could be freed from the sediment and remobilized in the water system if the sediment is disturbed or the water chemistry changes [41]. The potential sediment disturbances could be due to bioturbation, resuspension, the presence of organic matter, and an alteration in water salinity, thereby manipulating the equilibrium concentration between the metal ions in the water and the sediment [42]. Heavy metal remobilization is unwanted since this would contaminate clean areas when conveyed by the water current. Free-floating plants take up metals from the water by their roots. Despite uptake, the metals could be released back into the water and soil environments from the plant tissue. Aside from that, metals could be liberated into the air in a gaseous form from the surfaces of the leaves.

For instance, water lettuce must be harvested periodically not only to maintain growth density at an optimal level but also to remove metals and nutrients efficiently from water bodies. This is because the pollutants taken up by the plants will be released into the aquatic environment following the death and decomposition of the plants [33]. In the cases where a higher metal removal rate is desirable, the plant biomass should be harvested more frequently and on time. Moreover, the residence time of metals in different mediums will directly manipulate the metal concentration available in that particular medium [43]. Most metals tend to accumulate in the soil and sediment, which are known as sinks. Contrarily, metals usually have a shorter retention time in water and air since these mediums only usually serve as transport mediums. Explicitly, the retention time of metals in water varies depending on the type of heavy metals. For instance, Pb^{2+} exhibits a shorter residence time compared to Zn^{2+} [43].

5.1. Absorption, Adsorption, and Efflux of Metals by Plants

Plants can function as accumulators and excluders in phytoremediation. Accumulator plants can survive without being affected by a large number of metals concentrated within their aerial tissues owing to their ability to biodegrade and biotransform the metals into non-toxic forms. Opposingly, excluders limit the metal uptake into their plant biomass due to the presence of barriers [43]. As a result, excluders demonstrate low metal uptake even at high external metal concentrations. Normal plants commonly accumulate metals in quantities that do not exceed their short-term metabolic needs. Lower metal concentrations between 10 and 15 ppm are sufficient for the basic functioning of normal plants. Nevertheless, an exception is hyperaccumulators, which can absorb and tolerate thousands of ppm of metal concentrations within their tissues. The reason for this is that hyperaccumulators possess more than one detoxification mechanism for preventing metal toxicity, such as metal storage into vacuoles, metal chelation, and metal efflux [44].

According to Huynh, Chen, and Tran [45], there are two different mechanisms of heavy metal absorption in plants, namely root absorption and foliar absorption. Concerning root absorption, plant roots absorb heavy metals into the apoplast while absorbing water. The presence of –COOH groups in the pectin of the plant roots allows the exchange of cations within the cell membrane [46]. In turn, it becomes a transportation means for heavy metals to move into the cell wall from the external medium through diffusion or mass flow, where absorption actively takes place. The total concentration of metal uptake could be bound to the anions in the cell wall, transported apoplastically, and into the cells [43]. The distribution of the absorbed metals among these three locations relies on the types of metal species and the genotype of the plants.

Since water hyacinths possess dense and fibrous root systems, aerobic bacteria are well established in these aquatic environments. These bacteria gather the nutrients and inorganic pollutants that serve as food for plant nourishment [45]. Hence, the plants grow faster and are harvestable as phytoremediation plant biomass after storing the heavy metals in their tissues. Aside from root absorption, foliar absorption might occur in the plants, where the passive absorption of heavy metals occurs through stomata cells and cuticle fissures on the plant's leaves [46]. A high density of stomata cells stimulates greater ion uptake capacity as most of the uptake process is initiated in the ectodesmata. However, cuticle fissures could only act as weak ion exchangers owing to their non-esterified cutin polymers and cationic pectin substances. Specifically, the penetration of ions occurs from a low-charge density outer surface to high-charge density cell walls through the cuticle. Correspondingly, cation absorption is more likely to happen over anion absorption in this mechanism [43].

Furthermore, heavy metals could be adsorbed by plants with the aid of the bacteria attached to the feathery and fibrous roots. Meanwhile, the ionic imbalance could happen within the cell membrane [45]. In aquatic macrophytes, the usual metal transportation mechanism is rhizofiltration, in which the metal is contained, immobilized, and accumulated within the plant's roots [34]. The roots exudate within the rhizosphere, allowing the adsorption of metals on the root surfaces of the plant.

A different discovery was reported by Lissy and Madhu [46]; they suggested that phytoextraction was the process accounting for the uptake of heavy metals from a contaminated aquatic system. Despite metal absorption, metal efflux could happen. Metal efflux is a process of releasing the metal from the vacuole to the cytoplasm, from the cytoplasm to the apoplast, and seepage from the apoplast to the external medium. Various liberation and seepages are probably non-metabolic processes [43]. In addition, the efflux of metals from the cuticular layer of leaves might happen when metal ions are exchanged with hydrogen ions (H^+) during acid rainfall. Metal ions, such as Hg in a gaseous form, might also be liberated to the atmosphere through open stomata.

5.2. Bioconcentration, Translocation, and Distribution of Metals

The two important parameters for evaluating the heavy metal uptake by aquatic plants are the concentration factor (CF) and the bioconcentration factor (BCF). The CF is an indicator that assesses the total metal accumulation by plants through absorption and adsorption, whereas the BCF is an index that accounts for the metal absorption by plants from the external medium [15]. The BCF values are usually smaller than the CF values, and the difference between both values is small if the absorption of metal ions is dominant in plants. Furthermore, BCF values greater than 1000 are commonly regarded as a sign of great phytoremediation potential [47]. The BCF is a more suitable indicator for distinguishing the hyperaccumulator from the normal plants since the concentration of metals accumulated in the plant through absorption is more significant [33].

Furthermore, Greger [43] found that the majority of metals tend to bind to the cell walls during their transportation. The findings revealed that there was about 75 to 90% metal uptake by the plant's roots while only 10 to 25% were further translocated in the shoots. For instance, the distribution of Cd was lower in higher parts of the plants, following the descending order: dense fibrous roots > storage roots > stems > leaves. Vesely et al. [48] also found that more Pb was accumulated in water lettuce roots compared to that in the leaves. Additionally, a higher accumulation of Pb in the roots of water hyacinth than that in the stems and leaves was reported by [49]. On top of that, the addition of chelating agents could increase the metal bioavailability in the soil and facilitate the transportation of metal ions within the plant [14]. For example, the introduction of ethylenediamine tetraacetic acid promotes plant Cd uptake.

The translocation factor (TF) is the ratio between the concentration of metal ions accumulated in the plant shoot to that in the plant root. Ideally, a hyperaccumulator plant should have a TF value greater than one [47]. A TF value larger than one indicates that the heavy metals absorbed by the plants have been translocated effectively to the aerial parts of the plant [31]. In contrast, a TF value lesser than one implies that the heavy metals tend to accumulate and store in the plant's roots with less translocation to the aerial parts. A low TF value might be due to the exclusion strategy and restriction of metal movement towards the plant's aerial parts [47].

Generally, the TF value increased with an increased contamination level in the tributary. The translocation mechanism is crucial for the plant as it could prevent the excessive accumulation of toxic metal ions in the plant's roots [42]. The detoxification of metal ions might happen within the leaves of the plants through evapotranspiration. Evapotranspiration is an evaporation process of water from the plant leaves, promoting the absorption of nutrients and other substances from the medium into the plant's roots. Meantime, it accounts for the movement of heavy metals into the plant's shoots [13].

Another study reported on the metal distribution within the shoots and roots of plants, indicated by the root/shoot (R/S) ratio. The R/S ratio implies the metal concentration accumulated in the plant root over the shoot. For exemplification, approximately 80% of Cr, Cu, Fe, and Ni accumulated in the plant root with an R/S ratio equal to or greater than 6, while Fe has an R/S ratio greater than 17 [33]. Concretely, plant roots are the final destination of the absorbed metals since the roots can concentrate a greater amount of metal ions than their shoots. However, hyperaccumulator plants should have a shoot-to-root ratio of greater than one, reflecting the effective transportation of metals from the plant's roots to the harvestable parts of plants. Nevertheless, non-accumulator plants have a shoot-to-root ratio much smaller than one [13].

5.3. Phytotoxicity of Heavy Metals in Plants

Undesirable effects on the plant's growth and development were observed due to the accumulation of toxic metals in their roots, stems, and leaves. Bioactive metals could be classified into two groups: redox-active and non-redox-active metals. Redox-active metals, such as Cr, Cu, Mn, and Fe, could directly disrupt the plant cell homeostasis, break DNA strands, defragment proteins or cell membranes, destroy photosynthesis pigments, and cause cell death. Opposingly, non-redox active metals could impose oxidative stress on plants [50]. Moreover, Kumar, Singh, and Chopra [31] reported that phytoremediation using water lettuce to remediate sugar mill effluent containing Cd, Cu, Cr, Fe, Pb, Mn, and Zn, induced the yellowing of the plant's leaves as well as chlorosis and necrosis.

The phytotoxic responses of various plants to heavy metals are presented in Table 3. For example, Mishra and Tripathi [34] reported that the exposure of water hyacinth to Cr ions at 10.0 and 20.0 mg/L concentrations could result in the yellowing of plant leaves, chlorosis, and root exfoliating. In addition, the chlorophyll, protein, and sugar content in the plants were found to reduce along with the escalating metal concentration and exposure time. They also found that Cr demonstrated a higher degree of metal toxicity as compared with Zn. In addition, Hasan, Talat, and Rai [51] revealed that Cd was more toxic than Zn. The increase in Cd concentration affected the relative growth rate and demonstrated a negative growth rate when the Cd concentration in the growth culture medium was 4.0 ppm and above. A similar declining plant growth trend was observed as increasing Zn concentration from 2.0 to 12.0 ppm but without showing a negative growth rate.

Table 3. Phytotoxicity of heavy metals in plants.

Plants	Heavy Metals	Concentration	Experimental Layout and Duration	Phytotoxic Responses	References
Water hyacinth	Cr	10.0 to 20.0 mg/L	15 L experimental tanks filled with 10 L of tap water and investigated up to day 11	Yellowing of leaves, leaf chlorosis, and growth retardation.	[34]
	Zn	2.0 to 12.0 ppm	2 L container filled with 1 L tap water and investigated up to day 16	Growth reduction, leaf chlorosis, metabolism disruption.	[51]
	Cd	1.0 to 4.0 ppm		Growth reduction, growth retardation, new root growth inhibition, root function disruption, leaf chlorosis.	
Duckweed	Cd Cu	>10 mM >50 µM	10 L plastic reactors with 5 L of lake water and investigated up to day 15	Pigment degradation and photosynthesis restriction.	[52]
Water lettuce	Pb	1 to 2 mmol/L	60 L PE containers filled with 10 L of Hoagland nutrient solution and investigated up to day 8	Chlorophyll synthesis inhibition, chlorophyll reduction, loss of photosynthesis activity.	[48]
	Ni	1.0 and 10.0 ppm	Unknown size for hydroponic tubs filled with 10% Hoagland's solution and investigated up to day 6	Plant wilting, chlorosis in leaves, chlorophyll reduction, carotenoid reduction, water loss, browning of root tips, and root damage.	[53]

At a Cd concentration of 3.3 ppm, the metal toxicity led to the retardation of plant growth by hindering the growth of new roots and disrupting the function of the roots. The leaf chlorosis was fast, implying the decaying of plant tissue due to acute metal toxicity. This could eventually hinder the metabolism of plants [51]. Furthermore, exposure to excessive Cr concentration could result in a loss of photosynthesis pigments, protein, and sugar in plants. For instance, the presence of Cr in duckweed could result in a slower growth rate due to the restriction in photosynthesis [52]. Kumar, Singh, and Chopra [31] also found that higher heavy metal concentrations in wastewater could restrict aquatic plant growth and limit plant metabolism and physiological processes.

Nevertheless, the exposure of water hyacinth to Zn could cause oxidative impairments and alter the metalloenzymes of the plant. Moreover, the loss of chlorophyll could interfere with photosynthesis because of the interrupted chloroplasts. The reduction of sugar might slow down photochemical activities and chlorophyll initiation. Eventually, the loss of protein content resulting from the production of protein complexes might impede enzymatic activity [34]. The study presented by Buta et al. [49] suggested that the chlorophyll contents declined after six days of exposure to multi-metallic systems. Generally, the carotenoid content in plants decreased in all plants. For water lettuce, the uptake of Zn and Cu could restrict the biosynthesis of chlorophyll and carotenoids, resulting in an obvious discoloration of the plant leaves [54].

6. Phytoremediation Parameters and Kinetic Studies

There are several influencing factors that enhance or inhibit the performance of phytoremediation of heavy metals, as shown in Table 4. The selection of appropriate types of plants is the key to the success of phytoremediation technology; additionally, the factors such as solution pH, solution temperature, exposure duration, water salinity, initial metal concentration and chelating agents' concentration can also directly influence phytoremediation efficiency.

Table 4. Factors affecting on the phytoremediation performance in previous studies.

Plant Species	Heavy Metals	Influence/Enhancement Factor and Details	Significant Results	Reference
Thlaspi caerulescens	Cd, Zn	pH	The soluble metal form of both Cd and Zn was greatly increased with decreasing pH.	[55]
Eichhornia crassipes	Cd, As, Pb, Zn, and Cu	Temperature	The ideal water temperature for growth is between 28 °C and 30 °C. Temperatures exceeding 33 °C stifle further development.	[45]
Elodea canadensis, *Potamogeton natans*	Cu, Zn, Cd, Pb		The metal concentration and accumulations increased with increasing water temperature.	[56]
		Salinity	The metal concentration increased with decreasing salinity.	[56]
Eichchornia crassipes	Zn, Cd	Exposure duration	The overall metal uptake by the plant increased with the duration of the exposure time.	[51]
		Initial solution concentration	The uptake of heavy metals increased with an increase in the initial solution concentration.	[51]
Sasa argenteostriata (Regel) E.G. Camus	Pb	Chelating agents (Ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA))	The combined application of EDTA and NTA brought the accumulation of Pb availability to a more reasonable level than EDTA alone.	[57]
Zea mays L.	Cd	Chelating agents (ethylenediamine tetraacetic acid (EDTA), diethylenetriacetic acid (NTA), tetrasodium N, N-diacetate (GLDA), aspartate dibutyric acid ether (AES), and iminodisuccinic acid (IDSA))	Total Cd extraction followed the order AES (6 mmol kg^{-1}) > GLDA > NTA > EDTA > IDSA (3 mmol kg^{-1})	[58]

6.1. Effect of Solution pH

The uptake of metal ions by aquatic macrophytes is reliant on the solution's pH. According to Obinnaa and Ebere [3], the metal uptake was usually higher at a lower solution pH of about 4, thus reducing the metal concentration in the external culture medium. Notably, the pH of the medium would alter the metal speciation and metal bioavailability [43]. In low pH or acidic environments, most heavy metal ions exist as free positively charged species because of the higher H^+ concentration in the water, implying that more metals are soluble and bioavailable to biota. Therefore, plants could absorb the heavy metal ions easily, resulting in higher metal uptake. According to Soltan and Rashed [59], the pH of the water medium decreased with escalating metal concentrations from 50 to 100 mg^{-1} owing to the ionic exchange potential and the discharge of proton from the water hyacinth root while accumulating the metal ions.

Based on the study conducted by Singh, Gupta, and Tiwari [60], the author suggested that plants showed a better accumulation of Pb^{2+} at pH 6 than that at pH 9. As evidence, 89% metal removal was attained at pH 6, while only 56% metal removal was achieved at pH 9. Different findings were reported by Uysal and Taner [61], in which the highest Pb^{2+}

uptake by plants occurred at pH 4.5, followed by a decreasing metal accumulation within pH ranges from 4.5 to 6 and a constant uptake rate within pH 6 to 8.

In addition to that, the pH level affects the growth of plants. Generally, the plant cytoplasm environment was best maintained at pH 7 to ensure optimal plant growth and survival. In addition, Hardy and Raber [62] found that the Cd^{2+} uptake by plants increased within the pH ranges between 2 and 4. At pH 2, the acidic growth environment caused the blenching of the plant's roots and plant death, inhibiting metal uptake. In other words, the heavy metal uptake by plants reduced significantly when the pH decreased from 4 to 2 due to the fact that there were fewer anionic sites available for the ion exchange and more competitive metal binding between the protons and the metal ions to the plant's cell walls [63]. However, it was noteworthy that the presence of other contaminants in the medium could affect the metal-uptake efficiency [64]. For example, a solution with pH ranges between 6 and 9 might only be feasible for the remediation of wastewater without heavy metal contamination.

6.2. Effect of Solution Temperature

Solution temperature is another crucial ecological factor affecting the performance of metal uptake by aquatic macrophytes. The uptake of most metal ions by plants relies upon the temperature of the medium. This is because the change in temperature might influence the solubility and kinetic energy of the metal ions [65]. Based on the findings presented by Singh, Gupta, and Tiwari [60], the removal percentage of Pb^{2+} by plants increased by 22% when raising the temperatures from 20 °C to 28 °C. This finding was in agreement with Rai [66], illustrating an increasing metal uptake trend by plants with increasing temperatures. Uysal and Taner [61] also revealed that the Pb^{2+} accumulation by plants was the highest at 30 °C and the lowest at 15 °C. However, at a temperature beyond 30 °C, the metal uptake reduced again. The sudden decrease in the metal accumulation by plants might be due to the stress effects imposed on plants at the higher temperature of 35 °C, thus lowering the metal-uptake efficiency.

Similarly, Giri [67] reported that the removal of As and Cr metal ions by plants gradually decreased when increasing the temperature from 25 °C to 45 °C. The author suggested that the fast absorption rate and maximum metal removal by plants had taken place at 25 °C, which might be owing to the wide availability of metal binding sites on the plant roots during the initial ion exchange process. Hence, it was deduced that the metal absorption processes of plants were regulated by an exothermic process. Additionally, Rakhshaee, Khosravi, and Ganji [63] revealed that the metal uptake by plants increased with increasing temperatures from 10 to 25 °C.

Apart from affecting the metal-uptake efficiency, the solution's temperature influences the growth of plants. The behavior of aquatic accumulators varies depending on the temperature. Temperatures between 20 °C and 30 °C could result in the optimal cultivation of most aquatic plants. Conversely, a temperature equivalent to or lower than 10 °C could hinder the metabolic activities of most aquatic plants [64]. Additionally, it would hinder the growth of plants and inactivate microbial activity, leading to a low metal removal efficiency by plants [65]. Instead, a minimum temperature of 15 °C should be maintained to ensure optimal pollutant removal by microbes. The study also suggested that the optimal water temperature for the growth of water hyacinth was between 28 and 30 °C, while the optimum air temperature was between 21 and 30 °C. Nevertheless, at greater than 33 °C, it would suppress the successive growth of the plant [45]. Unfavorable culture medium temperatures restricted the growth of plants and caused plants to cease the uptake. As a result, the plants were incapable of accumulating the metals [68]. However, in some cases, plants can grow at colder temperatures.

6.3. Effect of Exposure Duration

Various exposure durations of aquatic plants to the metal concentrations in the culture medium resulted in various metal uptake performances. Lu et al. [33] reported that the total metal accumulation in the roots and shoots of the plant generally increased with increasing exposure durations. In addition, Soltan and Rashed [59] discovered that the plants cultivated in 100 mg/L of metal solution portrayed a declining metal uptake trend at increasing exposure durations due to the wilting of the plants resulting from the high toxicity of the metal accumulated in the plant tissue. Consequently, the metal uptake by plants via diffusion and osmosis reduced significantly with increasing exposure times.

Furthermore, Hardy and Raber [62] found that the Cd^{2+} uptake rate by plants was fast at the first 4 h but decreased linearly for the subsequent 72 h, implying that the percentage of metal uptake declined with increasing exposure durations. The trend of Cd^{2+} and Zn^{2+} absorption by the plants as the function of exposure time at various concentrations has been studied by [51]. The uptake of Cd^{2+} by the plants took place in two stages at higher metal concentrations of 4.0 and 6.0 ppm. A greater uptake efficiency was observed during the second stage, from the 6th to the 16th day, implying that the metal uptake rate increased with increasing exposure times. However, at lower Cd^{2+} concentrations of 1.0 and 2.0 ppm, the metal-uptake rate reduced with increasing exposure duration. The Zn^{2+} uptake trend by plants only showed a single stage of biphasic at any exposure concentration.

6.4. Effect of Water Salinity

Another crucial parameter affecting the metal uptake by plants is water salinity. The salt concentration of water affects the growth and reproductive potential of aquatic plants. Different plants had varying degrees of salinity tolerance, which regulates the capability of the plants to remove pollutants from the water environment. It revealed that floating macrophytes, such as water hyacinth and water lettuce, were likely influenced by the low water salinity at about 2.50% [69]. In the case of high salt concentrations in the water, it slowed down the transpiration rates and reduced the total dry weight of the plants [64]. Moreover, high water salinity might induce the complexation of metal–chloride, making the metal uptake process more complex, hence reducing the metal uptake by plants [43]. Correspondingly, the aquatic plants would die owing to the decreased osmotic potential levels as the water molecules had a lower potential to flow from a less solute region to a high solute region.

6.5. Effect of Initial Metal Concentration

The initial concentration of metal in the culture medium would also manipulate the metal-uptake efficiency of the plant's roots and leaves. The heavy metal uptake by plants usually increases with increased initial metal concentrations [59]. A similar observation was reported by Lu et al. [33], suggesting that the removal capacity of metal was higher when the aquatic plants were cultivated in wastewater with higher metal contamination levels. For instance, Pb^{2+} accumulated in the roots and leaves of plants increased with the escalating Pb^{2+} concentration in the growth medium [48].

Moreover, Uysal and Taner [61] found that the amount of metal accumulated in the plants increased with escalating initial metal concentrations ranging between 0 and 50 mg/L. However, it decreased when increasing the metal concentration from 50 to 100 mg/L. At higher initial metal concentrations, the plants wilted due to the metal toxicity imposed on the plant tissues. The decreased metal accumulation might also be attributable to the transpiration of the metal ions in the roots to the surrounding solution, imposing adverse effects on the survival of the plants. The common phytotoxicity effect on the plants was truncated plant growth resulting from hindered photosynthesis [59]. Furthermore, the higher concentrations of metal ions in the medium imposed inhibitory consequences on plant metabolism, alternately minimize plant growth, cause leaf necrosis, and destroy the plant's physiological systems [67]. In general, the high correlation coefficient of 0.9801 confirmed the positive relationship between the metal uptake by plants and the initial metal concentration in the culture medium.

The metal concentrations in the sediment and the metal accumulated in the roots of the plant reflected a positive linear correlation for most heavy metals, such as Co, Mn, Ni, and Sn, with R^2 values of 0.3559, 0.4216, and 0.7616, respectively. This implied that the plant could accumulate and remove more heavy metals at higher contamination levels [42]. However, the linear correlation between the metal concentration in the sediment and that accumulated in the plant's roots was weaker for the accumulation of Cu and Pb, with R^2 values of 0.3338 and 0.3011, respectively. For instance, when the plant was treated with escalating Pb concentrations from 30 to 50 mg/L, it demonstrated a declining metal accumulation rate [60].

Nevertheless, the accumulation of Cd, Sb, and Zn in the plant's roots became constant with escalating concentrations of metals in the medium upon reaching its absorption limit. This was because the plant might restrict the metal uptake by immobilizing or activating selective barriers in the plasma membrane when reaching the uptake limit of metal accumulation [42]. A similar finding was reported by Greger [43], where the metal uptake was not linearly correlated to the increasing initial metal concentration. The over-accumulation of metal ions in the plant tissue saturated the limited binding sites, subsequently reducing the metal removal rate. Therefore, it could be inferred that the metal uptake from the soil, sediment, and water was the greatest at lower external metal concentrations due to the less competitive ionic exchange process.

6.6. Effect of Other Metals Concentration

The presence of other metals in the culture medium also affected the metal uptake by aquatic plants because of the metal binding competition at the plant cell wall [43]. For example, the absorption of Cd^{2+} by the plant's roots declined when other cations of escalating ionic radii or valency are present. Specifically, the Cd^{2+} uptake by plants declined when increasing the concentration of Zn^{2+} in the medium [62]. Apart from that, a slower rate of metal uptake in the multi-metallic system than the single metal system was portrayed due to the competition between Cd^{2+} and Zn^{2+} metals for the similar metal exchange sites of plants, limiting the metal-uptake efficiency during metabolism. Moreover, Zn^{2+} could protect against Cd^{2+}, giving rise to the loss of potassium ions at the plant-membrane level [51].

6.7. Effect of Chelating Agent Addition

Another crucial factor affecting phytoremediation is the bioavailability of metals in the soil that facilitates the transportation of metal ions within the plant [14]. Most metals were not readily bioavailable to the plant due to their high binding abilities to the soil [70]. According to Prasad [71], heavy metals or metalloids, such as As, Cd, Cu, Ni, Se, and Zn, were more bioavailable to plants. In contrast, Cr and Pb were the least bioavailable metals, implying that these metals were more resistant to phytoextraction. Hence, the addition of a chelating agent became an effective way to enhance the metal bioavailability in the soil and improve the metal uptake by the plants. Upon the introduction of a chelating agent to the soil, it formed water-soluble metal–chelant complexes, which were further taken up by the plants via the apoplastic route [72]. The formation of complexes, in turn, restricted the precipitation of the heavy metal, increased their mobility, enhanced the bioavailability of the heavy metals, and promoted metal desorption [73].

Chelating agents could be generally classified into synthetic and organic types. Synthetic chelating agents include ethylenediamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid, and ethylene glycol tetra-acetic acid [14]. According to Dhaliwal et al. [74], the addition of a chelating agent to the soil improved the phytoextraction of Cd^{2+} uptake by plants. The results showed that the metal uptake was increased by about 15% with increasing amounts of EDTA in the soil from 1 to 2 mg/kg levels. This might be attributed to the higher bioavailability and mobility of the metal ions in the soil, thus boosting the metal uptake and translocation by the plants. Additionally, a dosage of EDTA at 2.7 mmol/kg enhanced phytoextraction [75].

EDTA was regarded as an efficient chelate, yet it had unfavorable toxic effects on plants, soils, and ecosystems, which might introduce risks to the environment [76]. Accordingly, natural, biodegradable, non-toxic, and environmental-friendly organic chelators such as citric, acetic, oxalic, and malic acids have been proposed to overcome the toxic effects that resulted from the use of EDTA. Shinta, Zaman, and Sumiyati [75] suggested that citric acid was more effective than EDTA as it acidified and lowered the pH level of the soil, created a microbial community in the soil, and promoted the growth of plant roots. As a result, the plants showed higher metal absorption due to faster growth. On the other hand, Souza et al. [15] recommended that organic chelating agents might be employed during the plant harvesting process to enhance the metal desorption and metal bioavailability in soil.

6.8. Kinetics of Phytoremediation

The kinetic model of phytoremediation is important to determine the efficiency, effectiveness, and natural behavior of aquatic plants during heavy metal removal from water or soil [77]. In addition, the kinetic model is useful for investigating the mass transfer rate of metals from a medium to plant tissues. On top of that, the kinetic study provides insightful information regarding the design and optimization of biological treatment technology at a large scale. Based on the findings reported by Naaz [78], the bioaccumulation kinetics of the heavy metals in the entire plant of water hyacinth were investigated. The results showed that the experimental data could fit into a linearized first-order kinetic equation with minimal adjustments, as presented in Equation (1). Moreover, Ingole and Bhole [79] proposed linearized first-order kinetics for heavy metal removal by the plant, as shown in Equation (2). Notably, the uptake rate constant (k) for the plants is an important parameter for evaluating the metal uptake performance by plants. The linear relationship observed from the plot of log (C_t) versus time (t) confirmed the first-order behavior of heavy metals uptake by plants.

First-order kinetic equation with slight adjustment:

$$\log(C_t) = -\frac{k}{2.303}t + \log(C_0) \quad (1)$$

First-order kinetic equation:

$$\log(C_t) = -kt + \log(C_0) \quad (2)$$

where

C_0 = initial concentration of metal in water, mg/L
C_t = concentration of metal in water at time t, mg/L
k = first-order uptake rate constant, day^{-1}
t = sampling time, days

The kinetic parameters of several heavy metal removals by accumulator plants are summarized in Tables 5 and 6. According to Singh et al. [77], the first-order kinetics of heavy metals uptake by the plants demonstrated the best-fit results with a high determination coefficient (R^2) greater than 0.82 and a rate constant larger than 0.023 mg/L·day. Similarly, Ingole and Bhole [79] found that the heavy metal uptake by the plant fitted well to the first-order behavior. The plant demonstrated the highest uptake rate of 0.1027 day^{-1} during the removal of Pb compared to other metals such as Ni, Hg, Zn, As, and Cr. Overall, it attained high R^2 values larger than 0.789, confirming the fitness to the straight-line plot of log (C_t) and t. Apart from that, Rakhshaee, Khosravi, and Ganji [63] revealed that the removal of heavy metals by living plants corresponded to the first-order kinetic, following the descending sequence of the first-order kinetic constant: $Zn^{2+} > Ni^{2+} > Pb^{2+} > Cd^{2+}$. The highest removal rate of 0.94 min^{-1} was attained for the removal of Zn^{2+} by the living plant, while the lowest of 0.118 min^{-1} was achieved for the removal of Cd^{2+}.

Table 5. Summary of kinetic model and equilibrium isotherm model.

Plant	Heavy Metal	Research Highlight	References
Dendrocalamus asper	Cu	The removal rate of Cu from the contaminated source had an order of 2.71 and a kinetic constant of 0.0013 $ppm^{-1.71}$ day^{-1}	[80]
Bambusa merilliana, *Bambusa blumeana*, *Dendrocalamus asper*	Cu	The zero-order model has well described the uptake of metal ions per mass of plant with a correlation value R^2 of 0.954 and a rate constant of 3.136 mg/(kg·day).	[81]
Eichhornia sp., *Pistia* sp.	Cr	Pseudo-first-order (0.910) and pseudo-second model (0.665) are more suitable for bioaccumulation kinetic in *Pistia* sp. rather than *Eichhornia* sp.	[82]
Eichhornia crassipes, *Lemma valdniana*	As	Pseudo-first-order gave a good correlation for both plants, with a correlation value R^2 > 0.8 for all the concentrations involved.	[83]

Table 6. Kinetic parameters of heavy metals removal by plants.

Heavy Metal	k (day^{-1})	R^2	References
Cd	0.0625	0.930	[77]
Cu	0.0700	0.890	
Fe	0.0800	0.920	
Mn	0.0825	0.870	
Pb	0.0575	0.980	
Zn	0.0875	0.890	
As	0.0693	0.825	[79]
Cr	0.0548	0.968	
Hg	0.0879	0.885	
Ni	0.0937	0.950	
Pb	0.1027	0.789	
Zn	0.0749	0.990	

According to Kamalu et al. [84], Richards's pseudo-first-order (PFO) and pseudo-second-order (PSO) models had been adopted through the verification with experimental results. The kinetic model of a common plant hyperaccumulator was established by studying the pathways starting from its rhizosphere to the atmosphere via the stem. By solving the two systems of phloem and xylem ordinary differential equations for the upward and downward transportation of the metal through the plant xylem and the phloem, the kinetic models for both PFO and PSO were developed, as illustrated in Equations (3) and (4), respectively. By deriving Equation (4), the PSO kinetic equation generated a dumb-bell shape profile and eventually optimized the model, as displayed in Equation (5).

PFO kinetic model:

$$q = q_m - (q_m - q_0)e^{k_1(t_0 - t)} \quad (3)$$

PSO kinetic model:

$$q = \frac{q_0 - q_m(q_m - q_0)e^{k_2(t_0 - t)}}{1 - (q_m - q_0)e^{k_2(t_0 - t)}} \quad (4)$$

Derivation of PSO kinetic model:

$$D_q = \frac{{k_2}^2(q_m - q_0)^2 e^{k_2(t_0 - t)}}{1 - (q_m - q_0)e^{k_2(t_0 - t)}} \quad (5)$$

where

q = metal concentration at time t, mg/L
q_m = maximum concentration of absorbed metal, mg/L
q_0 = initial metal concentration, mg/L
k_1 = PFO kinetic rate constant, day^{-1}

k_2 = PSO kinetic rate constant, mg/L·day
t = sampling time, day
t_0 = initial sampling time, day

The results showed that the phytoremediation process followed the PSO relationship of Richard's model, achieving high R^2 values ranging between 0.9979 and 0.9991, implying that the prediction obtained from the model were highly consistent with the experimental data. Opposingly, the phytoremediation process showed a low degree of compatibility with the PFO kinetic model [84]. Hence, it can be inferred that the natural phenomenal process of phytoremediation demonstrated a sigmoidal profile. Moreover, the concentration of metal uptake by the plants via the xylem tissue generally decreased with time. On the other hand, the uptake of heavy metals via the phloem exhibited an increasing trend or a free-fall profile along with time, which means that the sigmoidal profile might set in at longer exposure times due to its natural behavior.

7. Conclusions

Water plays an irreplaceable role in sustaining the life of living beings, including humans, animals, and plants. Increasing water contamination with heavy metals has become a serious concern nowadays due to rapid industrial development, growing population, and frequent anthropogenic activities. Therefore, phytoremediation using floating plants is regarded as a promising green technology to remediate the heavy-metal-contaminated water in an environmentally-friendly and cost-effective way. This research study investigated various process parameters affecting the phytoremediation behavior by aquatic macrophytes, such as the solution pH, solution temperature, exposure duration, water salinity, initial metal concentration, presence of other metals concentration, and the addition of chelating agent. The findings revealed that the optimal solution pH and temperature were pH 4 and 30 °C. In addition, it was found that the metal uptake by aquatic macrophytes generally enhanced with increasing temperature, exposure duration, and initial metal concentration in the growth culture medium. Additionally, the metal uptake was enhanced with the addition of chelating agents on the soil. However, it decreased with increasing water salinity and the presence of other metals concentration.

The kinetics of phytoremediation were studied to determine the effectiveness and natural behavior of plants during heavy metal uptake. The finding revealed that aquatic plants obeyed the first-order kinetic model, illustrating a linear relationship between the metal uptake concentration with time. On the other hand, some plants demonstrated good fitness to the PSO of Richard's model, reflecting a natural sigmoidal profile of heavy metal uptake by plants. Apart from that, various post-harvested biomass disposal methods were studied. These disposal methods included composting, compaction, direct disposal, leaching, pyrolysis, incineration, and nanoparticle synthesis. Each method had different working principles and demonstrated various performances and limitations. Among these methods, incineration was regarded as the most feasible technology due to its ability to significantly reduce biomass volume, save transportation costs, and decompose almost all the organic matter in the contaminated plant biomass.

In a nutshell, all of the research objectives were attained. The aquatic plants, especially water hyacinth, demonstrated great efficiency in absorbing various metal ions. Most of the metal absorption processes by aquatic plants followed the first-order kinetic model. In short, phytoremediation is a promising green water remediation technique. However, further research and studies are required to enhance its feasibility and practicability at large-scale implementation.

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