HEAVY METALS UPTAKE BY FLOATING AQUATIC PLANTS AND ITS RECOVERING PATHWAYS

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"HEAVY METALS UPTAKE BY FLOATING AQUATIC PLANTS AND ITS RECOVERING PATHWAYS"** was prepared by **QUEK YEN YING** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Recently, water pollution with heavy metals has become a serious environmental concern due to their hazardous properties. Since conventional water remediation techniques are generally expensive and non-environmental-friendly, phytoremediation has gained increasing attention from worldwide researchers and scientists due to its cost-effectiveness and environmental friendliness. This study included reviewing numerous journal articles to demonstrate the efficiency of phytoremediation by aquatic plants. Phytoextraction and phytofiltration were the two main mechanisms accounting for soil and water remediations. Moreover, floating aquatic plants such as duckweed, water lettuce, water hyacinth, and watermoss were regarded as accumulator plants due to their great capability in absorbing the metal ions by their roots and further translocating the metal ions to the aerial parts. This study was performed in six steps: review planning, literature searching, literature screening and scanning, data collection, data analysis, and report writing. Furthermore, the parameter study findings revealed that the optimum solution pH and temperature range that favoured the metal uptake by plants were pH 4 and 30 °C, respectively. The metal uptake increased with increasing exposure duration, initial metal concentration, and the addition of chelating agents. Opposingly, it decreased with increasing water salinity and the presence of other metals such as zinc (Zn) in the solution. The absorption kinetics of the plants fitted well to the first order kinetic, demonstrating a linear relationship between metal uptake with time. Besides, the post-harvested biomass disposal methods were studied. The advantages of biomass disposal methods are to reduce water content, volume, and weight of the biomass, minimize transportation costs, and recover toxic metals from the biomass. Lastly, biosorption of heavy metals by most dead aquatic plants demonstrated the pseudo-second order kinetic and fitted well to the Freundlich model, indicating that multilayer chemisorption of metal ions was governing. In short, phytoremediation is a promising green water remediation approach. However, further research is necessary to enhance its practicability and performance at large-scale implementation.

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C_e	equilibrium constant of metal ions, mg/L
C_o	initial concentration of metal in water, mg/L
C_t	concentration of metal in water at time *t*, mg/L
K_F	Freundlich constant, mg/g
K_L	Langmuir constant, L/mg
K_R	separation factor
k_1	PFO kinetic rate constant, day^{-1}
k_2	PSO kinetic rate constant, mg/(L·day)
k_i	interparticle diffusion rate constant, mg/(g·min$^{1/2}$)
q_e	amounts of metal sorbed at equilibrium, mg/g
q_m	maximum concentration of absorbed metal, mg/L
q_o	initial metal concentration, mg/L
q_t	amounts of metal sorbed at time *t*, mg/g
t_0	initial sampling time, day
R^2	correlation values
C	the degree of deviation from the interparticle diffusion kinetics, mg/g
k	first order rate constant, day^{-1}
n	Freundlich intensity
q	metal concentration absorbed at time *t*, mg/L
t	sampling time, day

Al	aluminium
$Al(OH)_3$	aluminium hydroxide
Al^{3+}	aluminium (III) ion
As	arsenic
BCF	bioconcentration factor
BOD	biological oxygen demand
C	carbon
Ca	calcium
Ca^{2+}	calcium (II) ion

Cd	cadmium
Cd^{2+}	cadmium (II) ion
CF	concentration factor
Cl^-	chloride
Cl	chlorine
Co	cobalt
Co^{2+}	cobalt (II) ion
COD	chemical oxygen demand
-COOH	carboxyl group
Cr	chromium
$Cr(OH)_2$	chromium hydroxide
Cr^{2+}	chromium (II) ions
Cr^{3+}	trivalent chromium ions
Cr^{4+}	tetravalent chromium ions
Cr^{6+}	chromium hexavalent ion
Cu	copper
$Cu(OH)_2$	copper hydroxide
Cu^{2+}	copper (II) ion
$CuAl_2O_4$	copper aluminate
DNA	deoxyribonucleic acid
e^-	electron
EC	electrocoagulation
EDTA	ethylenediamine tetraacetic acid
EDX	energy-dispersive X-ray
FAS	fixed activated sludge
Fe	iron
$Fe(OH)_2$	iron hydroxide
Fe^{2+}	iron (II) ion
Fe^{3+}	iron (III) ion
FTIR	Fourier transform infrared
H^+	hydrogen ion
H_2	hydrogen
H_2O	water
Hg	mercury

K	potassium
K^+	potassium ion
$M(OH)_2$	metal hydroxide precipitate
M^{2+}	dissolved metals
Mg	magnesium
Mg^{2+}	magnesium (II) ion
Mn	manganese
Mo	molybdenum
N	nitrogen
Na	sodium
Na^+	sodium ion
Ni	nickel
$Ni(OH)_2$	nickel hydroxide
Ni^{2+}	nickel (II) ion
NO_2	nitrogen oxide
O	oxygen
OH^-	hydroxide ion
-OH	hydroxyl group
P	phosphorus
PAHs	polycyclic aromatic hydrocarbons
Pb	lead
Pb^{2+}	lead (II) ion
$PbAl_2Si_2O_8$	lead feldspar
PCBs	polychlorinated biphenyls
PFO	pseudo-first order
PPCPs	pharmaceutical and personal care products
PSO	pseudo-second order
R/S	root to shoot ratio
RO	reverse osmosis
Sb	antimony
Se	selenium
SEM	scanning of electron microscopy
Si	silicon
Sn	tin

TDS	total dissolved solids
TF	translocation factor
TSS	total suspended solids
U	uranium
XPS	X-ray photoelectron spectroscopy
Zn	zinc
Zn^{2+}	zinc (II) ion

CHAPTER 1

INTRODUCTION

1.1 Water Pollution

Due to rapid urbanization and industrialization, about 40 % of the world's population is facing water scarcity problems. Some contributing factors to these issues are climate change, food necessity, and inefficient utilization of natural resources (Ali, et al., 2020). Besides, a study revealed that the death of 1.8 million people have been linked to water pollution in 2015 (Obinna and Ebere, 2019). Thereby, giving rise to water pollution a worldwide concern. Thus, progressive revision and assessment of water resource policy at all levels are indeed necessary.

However, in the case of the United Nations Millenium Development Goal target is attained, it expects a significant decrease of 393 million people without an improved water source as compared between the year 1990 and the year 2015. Figure 1.1 reflects the world population with and without an enhanced drinking water source in 1990, 2004, and 2015 (World Health Organization and UNICEF, 2016). It shows an increasing trend of world population and a decreasing trend of people without access to improved drinking water over the year. Nonetheless, referring to the World Water Council, an estimation of about 3.9 billion people will be facing water scarceness by the year 2030 (Obinna and Ebere, 2019).

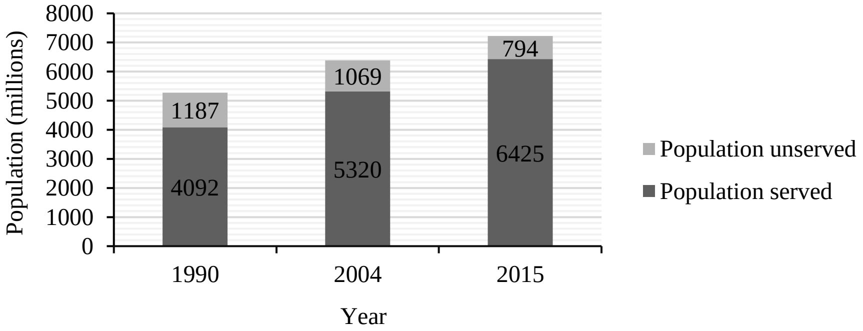

Figure 1.1: World Population (millions) With and Without Approach to Enhanced Drinking Water Source (World Health Organization and UNICEF, 2016).

The discharge of contaminants into the aquatic ecosystem has increased considerably over the years because of the rising number of farming activities, generation of geothermic water, and wastewater (Ali, et al., 2020). Water pollution has been linking to severe human health issues such as infectious diseases, nervous system damage, and even death (Afroz, et al., 2014). 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 affecting 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 (Fletcher, et al., 2020). 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 (Singh and Gupta, 2017).

In the United Kingdom, one of the primary stressors on water quality is an excessive nutrient released from a diffuse source of water pollution. 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 (Fletcher, et al., 2020). 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 like 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 river, lake, and ocean (Afroz, et al., 2014).

1.2 Problem Statement

Due to substantial industrialization, urbanization, and increased global population, the problems encountered in water and wastewater management are increasingly critical (Akpor, et al., 2014). The high concentrations of inorganic pollutants in water, specifically heavy metals could threaten human health and cause harm to the aquatic ecosystems. This is because heavy metals are not spontaneously biodegradable and persistent in the environment (Sharma, 2014). Besides, most metals could be delivered beyond trophic levels and stored in the biota (Rezania, et al., 2016). Owing to the high toxicities of heavy metals, water remediation is necessary to guarantee a clean and safe drinking water supply. The existing conventional water remediation technologies are membrane filtration, ion exchange, electrocoagulation, oxidation, and photocatalytic degradation (Fu and Wang, 2011). Still, these technologies are costly and could impact the environment adversely due to the formation of by-products like toxic sludges. As a result, the current attention is intended towards the less expensive and environmental-friendly technology, known as phytoremediation, that uses living plants to remediate the polluted water bodies (Sharma, et al., 2018).

Nonetheless, the application of phytoremediation at the commercial scale is still dissatisfying, owing to its time-consuming remediation process (Witters, et al., 2012). Moreover, phytoremediation could produce toxic post-harvested plant biomass contaminated with metals. Therefore, biomass disposal methods are required to recover the toxic metals in the plant biomass before disposing of them to the environment to prevent secondary environmental pollution.

Lastly, the waste plant biomass generated from the phytoremediation could be used as a biosorbent in water remediation. The potential use of plant biomass in heavy metal biosorption could be evaluated through characterization, kinetic, and isotherm studies. Hence, the ability and behaviour of plant biomass in metal accumulation through biosorption could be accessed.

1.3 Research Objectives

The main aim of the study was to review the application of floating aquatic plants in the removal of pollutants from the wastewater and its recovering pathways with the following objectives to be attained:

i. To elucidate the operating parameters and kinetic studies for phytoremediation of heavy metals using floating aquatic plants.
ii. To investigate the heavy metals recovery pathways from the post-harvested phytoremediation aquatic plants.
iii. To investigate the biosorption of heavy metals using the dead aquatic plants in terms of characterization, kinetics and isotherms.

1.4 Scope and Limitation of Study

In this study, the scope covered the classification of the various pollutants in the water bodies, such as organic pollutants, inorganic pollutants, and heavy metals. Besides, this report involved the study of the existing conventional heavy metals remediation technologies, namely membrane processes, electrocoagulation, ion exchange, chemical precipitation, and biological treatment, along with their working principles and limitations. This research also focused on phytoremediation mechanisms for soil and water medium. In addition, the types of floating aquatic macrophytes, such as duckweed, water lettuce, water hyacinth, and watermoss were reviewed in terms of their plant characteristics and capabilities in removing the heavy metal ions from the water bodies. Furthermore, the heavy metals uptake routes by aquatic plants via absorption, adsorption, metal efflux, and the chemometrics of phytoremediation such as bioconcentration factor, translocation factor, and root-to-shoot ratio were studied. The phytotoxic effects of metals at different concentrations on aquatic plants were further discussed.

Aside from that, the process parameters affecting the phytoremediation of heavy metals by aquatic macrophytes such as solution pH, solution temperature, exposure time, water salinity, initial metal concentration, presence of other metals concentration, and the addition of chelating agent were studied. Additionally, the kinetic studies of heavy metal uptake by live aquatic plants were conducted to observe the metal absorption behaviour of plants. Subsequently, the heavy metal recovery pathways from the post-harvested phytoremediation aquatic plant were reviewed. Seven biomass disposal methods, specifically composting, compaction, direct disposal, leaching, pyrolysis, incineration, and nanoparticle synthesis were further explored.

Moreover, the changes in the physicochemical characteristics of the dead aquatic plant before the after the biosorption of heavy metals were observed and compared via several characterization techniques such as scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. Eventually, biosorption kinetics and isotherms models were analysed and discussed to determine the biosorption behaviour of aquatic plants and evaluate the potential use of aquatic plant biosorbent in water remediation.

This research study, however, was subjected to some potential limitations. The first limitation was the lack of previous research studies and limited access to data relevant to the process parameters studied in this paper. Secondly, different experimental settings conducted by researchers might lead to different results and findings, leading to constraints during research findings generalization. Therefore, the preparation of this review paper required self-analysis and self-interpretation of the information and experiment data extracted from the prevailing literature papers to overcome these limitations in this study.

1.5 Outline of the Report

This study consists of five chapters. In Chapter 1, a general introduction regarding worldwide water pollution and the effect of water pollution on human health and the aquatic ecosystem are discussed. The problem statement and objectives of this study are highlighted in Chapter 1 to address the intention of this study based on the problem statement outlined.

Chapter 2 begins with the classification of various types of water pollutants, for example, organic, inorganic, and heavy metals. At the same time, literature reviews on the existing water remediation techniques are discussed. The main highlight in Chapter 2 would be the findings on the phytoremediation technology with their respective mechanisms. Moreover, this chapter provides information regarding the characteristics of the floating aquatic macrophytes suitable to be chosen as the accumulator plants in phytoremediation. Apart from that, the metals uptake routes by the aquatic plants and the phytotoxic effects of heavy metals accumulated in the plant tissues are reviewed.

Next, Chapter 3 summarizes the methodology and work plan while completing the review paper. Overall, the literature review paper is performed through several steps: the review planning, literature searching, literature screening and scanning, data collection, data analysis and interpretation, and report writing.

In Chapter 4, the process parameters affecting the phytoremediation behaviour by aquatic plants are highlighted. Several kinetic models describing the behaviour of metal ions absorption by aquatic plants are reviewed. Besides, the heavy metal recovery pathways from the post-harvested phytoremediation plants are discussed. Subsequently, the characterization of dead aquatic plant biomasses before and after biosorption of heavy metals are compared and analysed. Moreover, the biosorption kinetics and isotherms of plant biomasses are studied. Lastly, Chapter 5 concludes the key findings presented in the previous chapters and highlights the issues encountered in phytoremediation with some recommendations for improvement and future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Types of Pollutants

Water pollutants can be classified into organic and inorganic types. Organic pollutants include phenols, chlorobenzene, hydrocarbons, biological oxygen demand and chemical oxygen demand, while inorganic pollutants are nitrogen, phosphorus, sulphides, chlorides, and heavy metals (Bansode, 2002).

2.1.1 Organic Pollutants

Organic pollutants comprise carbon, hydrogen, oxygen, nitrogen, and other elements. Usually, the carbon bonds are attached to other compounds covalently. Besides, they might be carbohydrates, protein, or fat, which could biodegrade naturally (Akpor, et al., 2014). Other examples of organic pollutants are endocrine-disrupting chemicals, phenols, azo dyes, polyaromatic hydrocarbons, polychlorinated biphenyls, pesticides, etcetera (Bharagava, et al., 2018). In fact, the existence of organic pollutants in water has led to widespread concern. For example, rivers in lowland areas have become the hotspot for organic water pollutant filling (Obinnaa and Ebere, 2019).

The organic materials mainly originate from the pollution sources of agricultural, cosmetics, detergents, food processing waste, paper products, commercial, and industrial, fuel-burning by-products, herbicides and insecticides, volatile organic compounds, and drug pollution (Akpor, et al., 2014; Obinnaa and Ebere, 2019). Additionally, part of these organic water pollutants consists of persistent organic pollutants, which are carcinogenic and toxic to the environment. Indeed, the organic matter contained in water could exploit the oxygen requirements on the microorganisms that aid in the degradation and eventually use up the readily accessible dissolved oxygen for other aquatic species. As a result, it would cause an unfavourable impact on the metabolism and physiology of aquatic beings and death of plant cells (Zhang, et al., 2017). Table 2.1 summarizes the sources of pollution for various organic pollutants with their toxicity effects.

Table 2.1: Different Types of Organic Pollutants with Their Sources of Pollution and Toxicities.

Organic Pollutants	Sources of Pollution	Toxicities	References
Polycyclic Aromatic Hydrocarbons (PAHs)	Open burning, volcanic activities, coal deposits, electroplating, aluminium smelting, catalytic cracking towers, and activities related to petrochemical industry.	- Carcinogenic and mutagenic, posing significant threat to human health and well-beings. - Potentially suppress the immune system. - Could interfere the function of cellular and enzyme membranes.	(Abdel-Shafy and Mansour, 2016).
Polychlorinated Biphenyls (PCBs)	Production of capacitor and transformer, hydraulic lubricants and fluids disposal, heat transfer fluids, investment casting industries.	- Cause chronic effects to human such as damaged immune system, less efficient pulmonary function, and bronchitis. - Disrupt the endocrine function, maturation, physical growth, and behavioural or cognitive development of children.	(Burca and Watson, 2014; Jing, Fusi and Kjellerup, 2018; Obinnaa and Ebere, 2019; Schell, Knutson and Bailey, 2012)
Pharmaceutical and personal care products (PPCPs)	Sewage treatment plants, wastewater treatment plants, and manufacturing factories.	- Cause permanent harm to human beings and wildlife. - Serve as endocrine disruptors.	(Liu and Wong, 2013)

Table 2.1 (Continued)

Organic Pollutants	**Sources of Pollution**	**Toxicities**	**References**
Pesticides	Run-off from agriculture lands, carpet mothproofing, domestic application, pesticide production, and timber treatment.	- Toxic, mutagenic, and carcinogenic. - May impair immune system and endocrine system. - Affect children’s cognitive or behavioural development of the central nervous system - Cause residue issues.	(Özkara, Akyil and Konuk, 2016)
Phthalate esters	Fine or heavy chemicals industry wastes, plastics, resins, synthetic fibers, paints, and rubber making, artificial polymer delivery pipes, and body-care products.	- Acts as endocrine disrupting chemicals. - Toxic to developmental and reproductive system. - Carcinogenic to human.	(Adelagun, et al., 2021)

The uptake of organic pollutants by plants occurs via root absorption from soil or plant leaves absorption through air contact. The absorbed organic pollutants will be further translocated to the shoots and leaves of plant. The translocation of organic pollutants in the above-roots parts of plants can be categorized into short-distance and long-distance transport. Short-distance transport refers to the intracellular and intercellular transport, whereas long-distance transport regards to conducting tissue transport (Zhang, et al., 2017). The tolerance of aquatic species to take up organic materials corresponds to their capability to accumulate high concentration of pollutant metabolites in the 'bound' remainder section of the plant cell walls as differentiated to the vacuole, in which enzymatic and metabolic activities might happen (Obinnaa and Ebere, 2019).

The toxicity of organic pollutants varies depending on different parts of plant such as roots and leaves. On roots, organic pollutants contribute to the excessive mitotic division. On leaves, organic pollutants might disrupt cell biosynthesis, membrane stability, and deoxyribonucleic acid (DNA), as well as result in abnormal cell ultrastructure (Zhang, et al., 2017). The toxicities would also affect plant biochemical and physiological reactions. For example, linear alkylbenzene sulphonate could affect the growth and defence system of some plant species, such as *Lemna minor, Chara vulgaris, and Potamogeton perfoliatus*, respectively (Obinnaa and Ebere, 2019).

2.1.2 Inorganic Pollutants

Heavy metals and metalloids are the main concern among the other inorganic pollutants due to their high toxicity even in small amounts. Apart from heavy metals and metalloids, the inorganic contaminants comprise manure-based fertilizers consisting of excessive nutrients like phosphorus and nitrogen, toxic organics, suspended solids, phenols, cyanide, turbidity, and colour (Rezania, et al., 2016). Table 2.2 summarizes the different categories of inorganic pollutants, for example, nutrients, heavy metals, metalloids, and radionuclides with their sources of pollution.

Table 2.2: Classification of Inorganic Pollutants and Their Pollution Sources.

Inorganic Pollutants	Pollution Sources	References
Nutrients: Phosphorus, nitrogen, potassium	Agriculture, aquaculture, and septic tank inputs	(Fletcher, et al., 2020)
Heavy metals: Cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), mercury (Hg), magnesium (Mg), manganese (Mn), molybdenum (Mo), lead (Pb), nickel (Ni), zinc (Zn), tin (Sn)	Agriculture, mining and fossil fuels combustion, petroleum contamination, and sewage disposal	
Metalloids: Arsenic (As), selenium (Se), antimony (Sb)	Anthropogenic activities and geological processes	(Ahmad, et al., 2017)
Radionuclides: Uranium (U), strontium, caesium, plutonium, americium, radium	Waste disposal sites of nuclear power plants and nuclear power plants	

In general, metals with density greater than 5 g/cm^3 and an atomic number above 20 are often referred to as heavy metals (Gakwisiri, et al., 2012). Also, chemists have classified them as elements that are at a minimum five times denser than water (Dyjak, 2017). There are various heavy metals or metalloids, such as Co, Cu, Cr, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Zn, As, and Se. The primary source of heavy metal pollution originates from anthropogenic and geological activities. The activities that lead to the metal contamination including farming, mining, urban discharge, vehicle exhaust emissions, waste burning, fuel manufacturing, and smelting (Ali, et al., 2020). Additionally, volcanic eruption, weathering of rocks, and erosion are known to be the natural origin of heavy metal contamination. Table 2.3 displays the pollution sources for each type of metals or metalloids.

Table 2.3: Sources of Heavy Metals/Metalloids Contamination.

Metals/ Metalloids	Pollution Sources	References
As	Animal feed additives, wood preservatives, coal power plant, petroleum refining, mining, semiconductors, glass industries, pharmaceutical products, and fertilizers.	(Phearkeo, 2015)
Cd	Automotive tires, electroplating, mining, paints and pigments, plastic fertilizers, phosphate fertilizers.	
Cr	Electroplating, mining, tanneries, printing, photographic, and medicinal industries.	(GracePavithra, et al., 2019)
Cu	Electroplating industries, mining.	(Obinnaa and Ebere, 2019)
Hg	Volcanic activities, geothermal springs, geologic deposits of mercury, volatilization from the ocean, or weathering of rock, industrial waste disposal, coal combustion, mining, and electrical power generation.	(Wentz, et al., 2014)
Ni	Leaching from metals like pipe and fittings, dissolution from nickel ore-bearing rocks.	(World Health Organization, 2005)
Pb	Household plumbing systems including pipe, fittings, and solder.	
Zn	Industries such as batteries, paint, pigment, polymer stabilizers, smelting, and fossil fuel combustion.	(Gakwisiri, et al., 2012)

Surface water and groundwater pollutions by heavy metals have recently become a global concern. The severity of pollution differs immensely and is primarily regulated by local activities (Obinnaa and Ebere, 2019). The contamination of heavy metals has negatively impacted humans and wildlife health through the bioaccumulation in the ecological food chain with the persisting effect of metal tolerance evolution among specific organisms (Sharma, 2014). Moreover, detrimental effects of metals are info-disruption, which affects inter and intraspecies among organisms and microbes living in the freshwater. The toxicology of heavy metals on an individual relies upon the bioavailability of the metals, pH, organism toleration, and the existence of other ions that impede the metal bioavailability. Table 2.4 summarizes the toxic effects of each heavy metal on living beings.

Table 2.4: Metal Toxicities on the Living Beings.

Metals	Toxic Effects	Sources
Cd	- Mutagenic and carcinogenic. - Hypercalciuria damages bone and causes kidney failure and kidney stone. - Higher risk of osteoporosis, renal tubular, and lung damage, by infecting cardiovascular, digestive, urinary, reproductive, respiratory, nervous, and developmental systems. - Influence the calcium metabolism in animals, lead to calcium deficiency in fish, can cause larval mortality and impermanent growth reduction for long-term exposure.	(Akpor, et al., 2014; Obinnaa and Ebere, 2019; Sarwar, et al., 2017)
Cr	- May cause skin irritation and cancer at high concentrations. Hexavalent Cr is more toxic as compared to trivalent Cr with its capability to cause cancer and irritation. - Cause low birth weight, allergic dermatitis, impacting cardiovascular, immune, urinary, and respiratory systems, as well as fast hair loss.	(Akpor, et al., 2014; Sarwar, et al., 2017)

Table 2.4 (Continued)

Metals	Toxic Effects	Sources
Co	- Result in nausea, vomiting, and dermatitis.	(Akpor, et al., 2014)
Cu	- Cause damage in liver and kidney, eventually death and immunotoxin.	
Ni	- Can result in chronic bronchitis, dermatitis, allergic reaction, and kidney and brain damage.	(Sarwar, et al., 2017)
Hg	- Lead to anxiety, fatigue, depression, hair loss, vision disturbances, kidney damage, and ulcers.	
Pb	- Cause kidney damage, impact on synthesis of haemoglobin, leading to anaemia. - Can result in temporarily or permanent decrease in the functioning of kidney if expose chronically, which could cause probable renal failure.	(Akpor, et al., 2014)
Zn	- Lead to stomach cramps, vomiting, nausea, skin irritations, anaemia, injured pancreas, disrupted protein metabolism, respiratory disorders, and metal fever. - Constitute considerable danger to new-born and embryonic, especially when their mother absorbed high concentrations of it during pregnancy.	

2.2 Removal Methods for Water Pollutants

Before discussing the topic of phytoremediation, the existing conventional water remediation technologies such as membrane processes, electrocoagulation, ion exchange, chemical precipitation, and biological treatment are further discussed in terms of their working principles, advantages, and limitations.

2.2.1 Membrane Processes

The membrane process is a physical separation method that isolates and eliminates chemical compounds such as suspended solids, colloid particles, polymers, bacteria, viruses, heavy metals, and polar organics from aqueous wastes utilizing semipermeable membranes (Unadkat and Parikh, 2017). The common membrane technology consists of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (RO). Each membrane technology showed different separation abilities against various pollutants, as demonstrated in Figure 2.1 (Logisticon Water Treatment, 2022). Comparing these membrane technologies, RO is the most efficient membrane separation technique that can remove 95 to 99 % of dissolved species such as charged organic and inorganic salts (Reinsel, 2016).

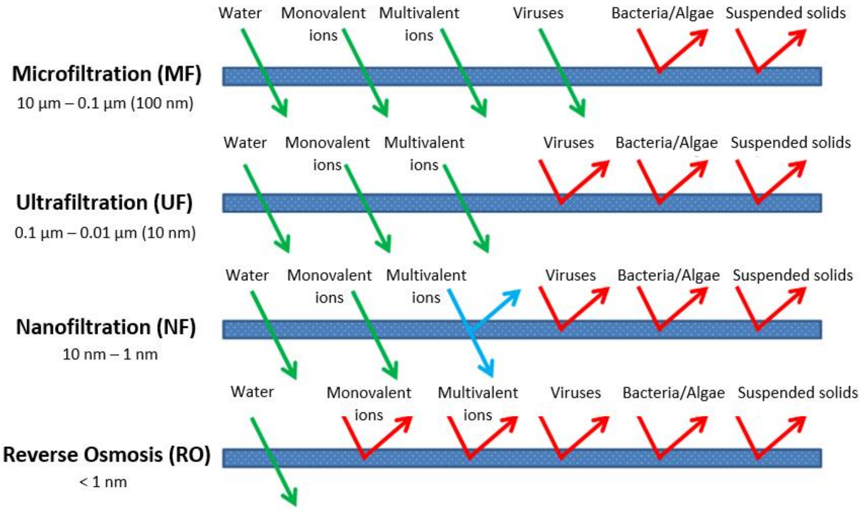

Figure 2.1: Separation Efficiency of Different Membrane Processes against Diverse Pollutants (Logisticon Water Treatment, 2022).

RO is a process that applies pressure more than the osmotic pressure to force the wastewater passing through a membrane from the high solute concentration area to the low solute concentration area while retaining the pollutants on one side (Reinsel, 2016). The membrane comprises a semipermeable layer with a pore sizes between 0.5 to 1.5 nm, allowing the movement of solvent and only smaller solutes to pass through (Qasem and Mohammed, 2018). Thus, the solutes with molecular size between 0.00025 to 0.003 µm are unable to pass through the membrane layer.

According to Qasem and Mohammed (2018), the RO process demonstrated high removal efficiency of greater than 98.75 % of metal ions such as nickel (II) ions (Ni^{2+}), chromium hexavalent ions (Cr^{6+}), and copper (II) ions (Cu^{2+}) in the wastewater discharged from the electroplating industry. Additionally, the RO process demonstrated a high removal efficiency of 98 % for Cu^{2+} and 99 % for cadmium (II) ions (Cd^{2+}) from the synthetic wastewater samples. Despite its high removal efficiency for heavy metals, RO poses some limitations such as membrane fouling and degradation due to the precipitation of salts on the membrane pores, high power demand due to the high operating pressures, the need for membranes recovery, and generation of a high waste stream volume (Fu and Wang, 2011). In addition, the application of RO is limited as it can only partially remove monovalent ions like nitrate and is unable to remove dissolved gases like ammonia (Reinsel, 2016).

2.2.2 Electrocoagulation

Electrocoagulation (EC) is a new method to purify water and wastewater through the combination of coagulation, precipitation, and adsorption. This electrochemical treatment process is gaining much attention due to its high efficiency in removing numerous organic and inorganic pollutants with little or nearly zero production of by-product waste (Ayub, et al., 2020). Moreover, it is easy to operate, low operational cost, and environmental-friendly. EC is especially effective in eliminating ionic species like heavy metal ions, suspended particles, phenolic wastes, arsenic, dyes from wastewater (Chandra, 2020). In the EC process, oxidation happened at the anode to produce coagulant, and reduction happened at the cathode to produce hydroxide ions (OH^-). The equations for the reduction and oxidation reactions are represented in Equations (2.1) and (2.2). Equation (2.3) demonstrates that with aluminium (Al) as the sacrificial anode, oxidation reaction produced aluminium (III) ions (Al^{3+}). In alkaline solution, precipitation of aluminium hydroxide, $Al(OH)_3$ as colloidal suspended particles happened as shown in Equation (2.4) (Huang, et al., 2020).

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (2.1)$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \tag{2.2}$$

$$Al \rightarrow Al^{3+} + 3e^- \tag{2.3}$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \tag{2.4}$$

Material like Al or Fe is usually applied as the sacrificial anode because of its low price and wide availability. The non-toxic coagulants with high contaminants removal capacity like iron hydroxides or aluminum hydroxides, $Fe(OH)_2$ or $Al(OH)_3$ are generated in-situ under alkaline pH conditions. The hydroxides precipitate formed when the OH^- produced at the cathode combined with the Al^{3+} or iron (II) ions (Fe^{2+}) in the solutions (Chandra, 2020). Under pH ranges between 5.5 to 8, the metal precipitate of $Al(OH)_3$ functions as an adsorbent to adsorb toxic metal ions in the wastewater. At above pH 8, it serves as a coagulant to aid in the coagulation process and remove the metal ions. Under such high pH condition, precipitation of various metal hydroxides like $Ni(OH)_2$, $Cu(OH)_2$, and $Cr(OH)_2$ would happen (Huang, et al., 2020). Nevertheless, the EC process has some drawbacks like energy-intensive, the need for periodic anode replacement due to its dissolution in solution, generation of hazardous secondary pollutants, and high potential of cathode passivation that lead to a low efficiency (Qasem and Mohammed, 2021).

2.2.3 Ion Exchange

The ion exchange process involves the exchange of the hazardous mobile metal ions in a liquid phase with the harmless and eco-friendly ions that are held electrostatically to the functional group incorporated in a solid matrix. The solid resin showed a higher affinity for specific dissolved ionic species such as heavy metals, arsenic, and nitrate than other ions, hence separating these species from another (Cobzaru and Inglezakis, 2015). For instance, the removal of lead (II) ions (Pb^{2+}) in a batch mode employing the chelating resin Lewatit TP-207 via reversible ion exchange process can be illustrated in Equation (2.5). In addition, the resins attached to the strongly acidic sulfonic groups and the weakly acidic carboxylic acid groups tend to become the conventional ion exchange resin (Fu and Wang, 2011).

$$R - 2Na + Pb^{2+} \leftrightarrow R - Pb + 2Na^{+} \qquad (2.5)$$

where

R = organic part of the resin

Recent attention is favored toward inorganic ion-exchange materials owing to their high thermal stability, high resistivity to radiation, and effective sorption capacity. Zeolites were the first conventional inorganic cation exchangers applied in wastewater treatment (Cobzaru and Inglezakis, 2015). The synthetic and natural-occurring zeolites acted as cation exchangers by allowing the exchange between their cations with the metal ions in wastewater (Fu and Wang, 2011). Adsorption capacities of natural zeolite called clinoptilolite for both single and multiple metal ions solution from wastewater showed the descending order of Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} (Bashir, et al., 2019). Moreover, the adsorption of Pb^{2+} and Cu^{2+} on thermally treated synthetic zeolite demonstrated the maximum capacities of 135.5 and 115.5 mg/g, respectively. The Pb^{2+} and Cu^{2+} will subsequently stabilize into lead feldspar ($PbAl_2Si_2O_8$) and copper aluminate ($CuAl_2O_4$), as illustrated in Figure 2.2. Generally, synthetic zeolite was superior to natural zeolite since it could be engineered with various chemical properties and pore sizes. Additionally, higher selectivity was demonstrated.

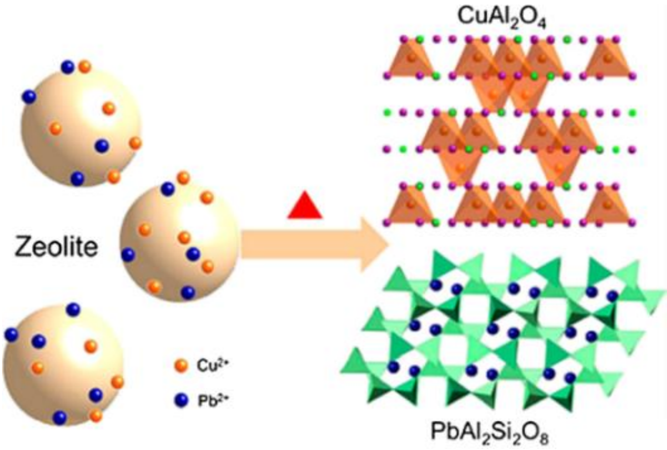

Figure 2.2: Adsorption of Pb^{2+} and Cu^{2+} on Zeolite (Bashir, et al., 2019).

The ion exchange process is popular since it offers numerous advantages like high metals removal efficiency, high remediation capacity, and rapid kinetics (Fu and Wang, 2011). Besides, it could recycle the pollutants with selective solid resins that are durable and reusable through on-site or off-site regeneration. Moreover, fewer waste products like spent solid resin and regenerant solutions are produced through the ion exchange process compared to the RO process. However, the resin bed is easily clogged and exhausted when treating the waste streams with greater than 2500 ppm and 50 ppm dissolved ions and suspended solids. Similar to adsorption, this method requires further research and study to improve reusability and stability (Reinsel, 2017).

2.2.4 Chemical Precipitation

Chemical precipitation is used for the removal of metallic ions and anions like cyanide, fluoride, and phosphate in wastewater. It separates the ionic compounds by adding the counter-ions to lower the solubility (Wang, et al., 2005). A reagent is introduced to the mixture would stimulate a chemical reaction to transform the dissolved metals (M^{2+}) into a solid metal hydroxide ($M(OH)_2$) which can be eliminated by filtration, flocculation, and sedimentation (Akpor, et al., 2014; Fu and Wang, 2011). The precipitation mechanism can be illustrated in Equation (2.6), whereby the hydroxide such as lime is introduced into the agitated wastewater to produce insoluble metal hydroxides precipitate (Sharma, et al., 2018).

$$M^{2+} + 2\,(OH^{-}) \rightarrow M(OH)_2 \tag{2.6}$$

where

M^{2+} = dissolved metal ions

OH^{-} = hydroxide precipitant

$M(OH)_2$ = insoluble metal hydroxides precipitate

In chemical precipitation, the type of metal ions to be removed and the type of coagulant used will directly affect the efficiency of precipitation. During chemical coagulation, the particles in the wastewater undergo destabilization by introducing positively charged coagulants such alum that subsequently lower the charges on the negatively charged ions. The particles would then agglomerate during chemical flotation (Akpor, et al., 2014). Hydroxide precipitation is favourable since it is relatively cheap, straightforward, and changeable pH level. Still, this method has some disadvantages, such as the need for high pH values for optimal precipitation efficiency, generate a large volume of hazardous waste like residual sludge to be dewatered, cause disposal problems, and the settlement of metal hydroxide precipitation with the existing complexing agents (Qasem and Mohammed, 2021).

2.2.5 Biological Treatment

Suspended growth systems like activated sludge processes are typically employed to treat municipal wastewater and industrial wastewater containing ammonia, nitrate, selenium, sulfate, and dissolved metals. This treatment process is frequently utilized to remove nutrients such as nitrogen and phosphorus. Besides, it could be used to remove both ammonia and nitrate via aerobic nitrification and anaerobic denitrification process. Suspended growth systems showed the best performance while treating the contaminants in relatively low concentrations (Reinsel, 2017). Yet, these systems became inefficient when remediating the wastewater stream with high metal concentration owing to the toxic effect of the cation on the biomass. The toxicity of metals could adversely affect the growth of microbial biomass and the efficiency of the treatment process. Certain metals acted as a micronutrient at low concentrations but might cause the break off cell at high concentrations (Buaisha, Balku and Özalp-Yaman, 2020). All heavy metals at moderate or high concentrations could impede microbiological processes owing to their toxicity. For instance, Cu showed higher toxicity compared to Pb, Zn, and Ni as it hindered heterotrophic biomass even at low concentrations and showed a negative impact on the bacteria in the activated sludge system.

2.3 Phytoremediation Technology

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 (Rezania, et al., 2015). In other words, phytoremediation employs the fact that a living plant can act as a photosynthetic driven pump proficient in eliminating pollutants like metals and metalloids from the environment and water effectively (Prasad, 2018). Notably, aquatic plants play an essential role as a natural absorber in phytoremediation for heavy metals and contaminants with their extensive roots system, making them the best selection for the uptake of pollutants through their shoots and roots (Ali, et al., 2020). Phytoremediation technology has gained global attention among scientists and administration bodies due to its effectiveness in lowering unparalleled environmental pollution via an environmental-friendly pathway. Figure 2.3 demonstrates the increasing trend for the use of aquatic plants in phytoremediation.

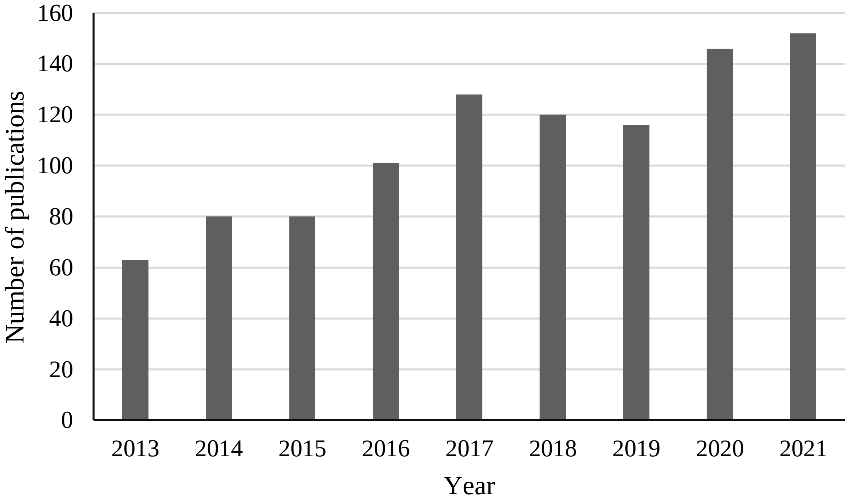

Figure 2.3: Increasing Use of Aquatic Plants in Phytoremediation.

Referring to Rezania, et al. (2015), aquatic plants like floating, submerged, and emergent plants are broadly applied in the phytoremediation for the wastewater treatment process to eliminate pollutants like heavy metals for the past five decades. Several researchers have also demonstrated the remediation of various wastewater discharged from industrial, commercial, or domestic sectors via phytoremediation technologies. Several mechanisms are involved in the phytoremediation to uptake the heavy metals by using the 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 (Jeevanantham, et al., 2019). 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 (Ansari, et al., 2020).

The selected plant species must have a high potential to take up various pollutants, own a rapid growth, easy to cultivate, and simple to harvest (Rezania, et al., 2015). Moreover, an ideal plant species applied in phytoremediation should pose a few criteria: 1) plants that show a high accumulation rate on heavy metals even at low concentration, 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 environmental-friendly and economic application (Phearkeo, 2015). In reality, aquatic plants like water lettuce, water hyacinth, and vetiver grass have demonstrated excellent capability to eliminate different pollutants like heavy metals, total dissolved solids (TDS), total suspended solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD), and nutrients containing in wastewater.

2.3.1 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 (Sarwar, et al., 2017). Lately, phytoremediation has gained attention in remediating the soil contamination sites due to its profitability, environmental-friendly, and durable application. Phytoremediation employs plants and microorganisms to eliminate, isolate, or degrade the toxic substances away from the environment. The reliable mechanisms for soil remediation are phytoextraction and phytostabilization. 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 (Laghlimi, et al., 2015).

Bioavailability expresses the degree of contaminants readily absorbed by plants through exposure to them (Laghlimi, et al., 2015). 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 (Souza, et al., 2013). Besides, soil microbes play a crucial role in catalysing 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 (Sarwar, et al., 2017). The acidity and alkalinity of soil would determine 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. At alkaline or neutral pH conditions, immobilization of metals like Pb and Cr would happen. Therefore, the metals are not bioavailable to plants (Laghlimi, et al., 2015). Besides, soil microorganism like 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 (Lasat, 2002).

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 (Sarwar, et al., 2017). In shoots, the metal accumulation usually happens in vacuoles, which are cellular organelles containing 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 concentration (Lasat, 2002). For metal exclusion, the excluders prevent the metal absorption by roots and preclude further translocation and accumulation in plant shoots.

Figure 2.4 displays the steps involved in the phytoextraction of metal from soil by plant. 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 (Sarwar, et al., 2017). Among these requirements, heavy metal tolerance is an essential requirement for phytoremediation since higher plant tolerance to metal stress indicates a higher number of metals could be accumulated in the plant tissues with the lowest detrimental impacts on the plant health (Verma, et al., 2022). Metals like Cd, are easier to be absorbed from the soil via phytoextraction (Shaari, et al., 2021).

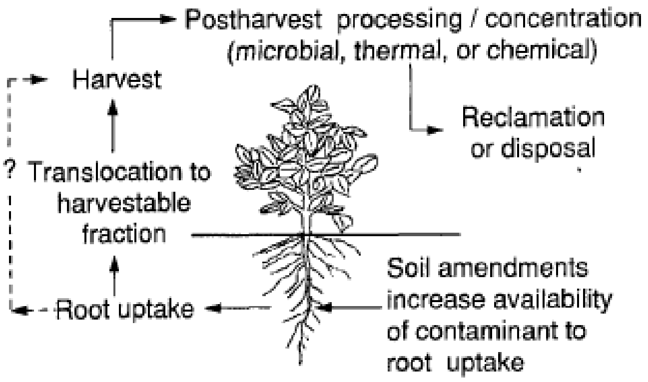

Figure 2.4: Steps Involved in Phytoextraction (Cunningham and Ow, 1996).

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, formation of metal complexes, and chelation of metal ions with peptides and proteins. Apart from the physiological processes dominating the plant tolerance, another crucial factor to predict the phytoextraction potential is the yearly production of biomass including the dry weight of shoots and the net composition of metal harvested (Sarwar, et al., 2017). Figure 2.5 demonstrates the phytoremediation mechanisms for metal uptake from soil covering from the metal bioavailability, phytoimmobilization, phytovolatilization to metal tolerance of the plant (Verma, et al., 2022).

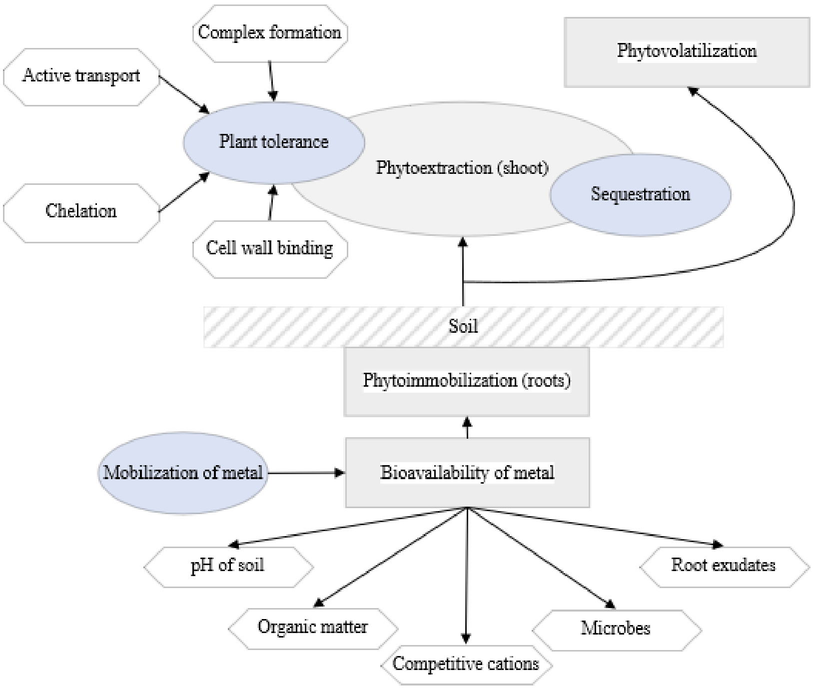

Figure 2.5: Phytoremediation Mechanisms for Heavy Metals Uptake by Plants from Soil (Verma, et al., 2022).

2.3.2 Water Remediation

According to Ansari, et al. (2020), the application of plants in the remediation of wastewater has been initiated about 300 years ago. 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 go into the sediments, leading to a complex recovery. Opposingly, floating plant systems could eliminate contaminants via biomass harvesting (Sharma, et al., 2018).

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 (Ansari, et al., 2020). Explicitly, *Lemna minor*, *Eichhornia crassipes*, and *Pistia stratiotes* are specifically employed to eliminate metal ions present in the aquatic system (Sharma, et al., 2018). For instance, *Eichhornia crassipes* can biodegrade inorganic pollutants by concentrating various metal ions like Cu, Cd, Cr, Pb, and Zn.

Additionally, it could remove other contaminants like TSS, TDS, BOD, and COD from industrial wastewater (Lakshmi, et al., 2017). The harvesting process is comparatively simple due to its floating and not rooted structure (Dixit, Dixit and Goswami, 2011). Furthermore, the treatment by plants like *Lemna minor* and *Pistia stratiotes* has successfully reduced the TDS, BOD, COD, chloride, and sulphate in the wastewater. In water environment, rhizofiltration works well by overcoming the inherent biological limitation found in phytoextraction. Specifically, phytoextraction is more suitable to treat polluted soils at shallow depths. Table 2.5 shows the phytoremediation strategies that applicable for the removal of different category of contaminants present in the water bodies.

Table 2.5: Phytoremediation Mechanisms for the Removal of Pollutants Present in the Aquatic Environment (Ansari, et al., 2020).

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 plant.
	Phytovolatilization	Extract the contaminants from media and liberate them through air.
	Phytotransformation	Degrade contaminants into a simpler form.

2.4 Accumulator Aquatic Plants

Accumulator plants usually have a fast growth rate, ability to absorb multiple metal ions at high concentrations, and tolerant towards metal toxicity. The characteristics, growth conditions, and pollutant removal ability of each plant are discussed in the following subsections.

2.4.1 Duckweed (*Lemna minor*)

Duckweed 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* (Ali, et al., 2015). *Lemnaceae* family have been the focus in recent research for phytoremediation due to their rapid growth, rapid biomass productivity, phytoplankton, microbial minimization, high metal and nutrient accumulation capability (Ansari, et al., 2020). 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 to 35 ℃ (Rezania, et al., 2016). Furthermore, duckweed can cultivate 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 tolerance depending on the ambient water conditions such as temperature, pH, metal concentrations, and electrical conductivity.

Based on the recent study conducted by Rezania, et al. (2016), the findings revealed that duckweed had been widely used to recover nutrients and heavy metals released from the agricultural and domestic wastewater. 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 Cd, Cu, Ni, Mn, Zn, As, and U. *Wolffia globose* owned great tolerance to concentrate 400 mg As per kilogram of its dry weight and subsequently removing them effectively (Ansari, et al., 2020).

The factors determining the metal uptake efficacy and bioaccumulation potential of duckweed are the exposure duration and metal concentration. From the experimental result, the metal bioaccumulation decreased with longer exposure duration due to the death of less endurable duckweeds (Ubuza, et al., 2020). Nevertheless, the burning of metal contaminated duckweeds has become an issue for safe disposal (Ali, et al., 2015). In addition, their degradation through carbonization, incineration, hydrolyzation, or anaerobic digestion is necessary to avoid successive contamination in the environment.

2.4.2 Water Lettuce (*Pistia stratiotes*)

Water lettuce, with the scientific name *Pistia stratiotes*, is a free-floating macrophytes that can absorb and concentrate the pollutants in their plant body (Kumar, et al., 2017). *Pistia stratiotes* which belongs to the *Araceae* family is a floatable aquatic plant in the water with a hanging root structure submerged in the water (Rezania, et al., 2016). Water lettuce is lavish in many regions such as the tropical and subtropical of Asia and America because of its simple growth requirements and ability to adapt to extensive range of growth environment. Based on the study conducted by Gupta, Roy and Mahindrakar (2012), a considerable portion of Fe, Mg, Mn, Cd, Ca, and Co were adsorbed or deposited on the outer root surfaces of water lettuce, whereas more Al, Cu, Cr, Ni, and Pb were absorbed by plant roots. *Pistia stratiotes* are also an effective phytoremediator plant species in treating Mn polluted wastewater (Hua, et al., 2012). The advantages of water lettuce are fast-growing, able to cover the large water surfaces, and require an uncomplicated harvesting process. Referring to Lu, et al. (2011), water lettuce possessed an excellent capability in accumulating metal ions from the water bodies with a high concentration factor of 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 in surface water remediation.

2.4.3 Water Hyacinth (*Eichhornia crassipes*)

Water hyacinth with the scientific name of *Eichhornia crassipes* is a rooted macrophyte belong to the family of *Pontederiaceae* and *Eichhornia.* Water hyacinth usually grows largely in the polluted water systems and eutrophic lakes (Mishra and Tripathi, 2009). This fast growing free-floating perennial aquatic weed appeared in upright and rounded leaves with a dark blue root system, demonstrated to be highly competent in remediating the domestic wastewater due to its highly resistant feature (Ansari, et al., 2020). 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. Besides, it could adapt to various aquatic physiochemical surroundings like drought and moist sediments condition rapidly. Furthermore, it could uptake tremendous quantities of contaminants especially heavy metals and nutrients. Various researchers claimed that water hyacinth showed 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 efficiency of pollutants removal by the plant was closely related to its maximum growth. The optimal growth conditions for water hyacinth were at pH 6 to 8, at a temperature between 10 to 40 °C, and the water salinity below 5 mg/L (Rezania, et al., 2016).

2.4.4 Watermoss (*Salvinia)*

Salvinia, which belongs to the *Salviniaceae* family, is a floating aquatic plant with fast growth rate and high tolerance towards metal toxicities (Rezania, et al. 2016). *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 plants had shown an unreasonably high potential to accumulate metal ions like Cr, Ni, and Pb than their leaves (Dhir, Sharmila, and Saradhi, 2008; Dhir, et al., 2011). In particular, *Salvinia natans* was the hyperaccumulator for some specific heavy metals, and its leaves could accumulate more heavy metals compared to other parts. Table 2.6 summarizes the heavy metals removal efficiency demonstrated by different aquatic plants in phytoremediation.

Table 2.6: Summary of Heavy Metals Removal Efficiency by Floating Aquatic Plants in Phytoremediation.

Plant Species	Conditions	Heavy Metals Removal Efficiency	References
Duckweed (*Lemna species*)	Sampling time: 25 days; pH: 7; Temperature: 7 to 20 ℃ 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 (multiple metals solution) Framework: laboratory scale	90.95 % As, 97.79 % Cd, 90.25 % Cr, 98.46 % Cu, 82.84 % Hg, 98.08 % Ni, 99.91 % Pb, 98.00 % Zn	(Tufaner, 2018)
	Sampling time: 7 days; Temperature: 13 to 20 ℃ Relative humidity: 70 % Photoperiod: 16 hours light, 8 hours dark Concentration (mol/L): 10^{-6} (single metal solution) Framework: laboratory scale	95 % Cd, 93 % Pb, 81.2 % Zn, 86.5 % Cu	(Basile, et al., 2012)
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 (multiple metals solution) Framework: field	39.72-72.58 % Cu, 28.96-68.79 % Ni, 43.02-76.66 % Pb, 26.99-79.57 % Zn	(Obinnaa and Ebere, 2019)
	Sampling time: 30 days; pH: 9.1; Temperature: 30.3 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 (multiple metals steel industry effluent) Framework: laboratory scale	73 % Al, 74 % As, 82.8 % Cd, 62.8 % Cr, 78.6 % Cu, 61 % Fe, 39.5 % Mn, 73 % Pb, 65.2 % Zn	(Aurangzeb, et al., 2014)

Table 2.6 (Continued)

Plant Species	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 (multiple metals landfill leachate) Framework: laboratory scale	87.56 % Fe, 87.09 % Cu, 81.56 % Ni, 84.41 % Pb, 90.18 % Zn	(Abbas, et al., 2019; Saha, Shinde and Sarkar, 2017)
	Sampling time: 30 days; pH: 7.74 Initial concentration (mg/L): 0.24 Pb, 1.20 Pb, 4.97 Hg, 3.34 Ni (multiple metals industrial wastewater) Framework: field	97.50 % Cd, 95.10 % Ni, 99.90 % Hg, 83.40 % Pb	(Rezania, et al., 2016)
Watermoss (*Salvinia species*)	Sampling time: 28 days; pH: 6.5-7.5 Initial concentration (mg/L): 0-12.39 (multiple metals wastewater sample) Framework: field	61 % Cd, 65 % Co, 92 % Cu, 70 % Fe, 87 % Mn	(Obinnaa and Ebere, 2019)
	Sampling time: 12 days; Temperature: 25 °C Humidity: 70-75 % Photoperiod: 16 hours light, 8 hours dark Initial concentration (mg/dm^3): 1.0 Cr, 1.0 Hg (single metal solution) Framework: laboratory scale	74 % Cr, 93 % Hg	(Bennicelli, et al., 2004)

2.5 Phytoremediation Mechanisms

There are various phytoremediation mechanisms such as phytofiltration, phytoextraction, phytostabilization, phytovolatilization, and phytotransformation, as illustrated in Figure 2.6. Each mechanism has its unique characteristics, applications, and uptake routes, which are discussed in the following subsections.

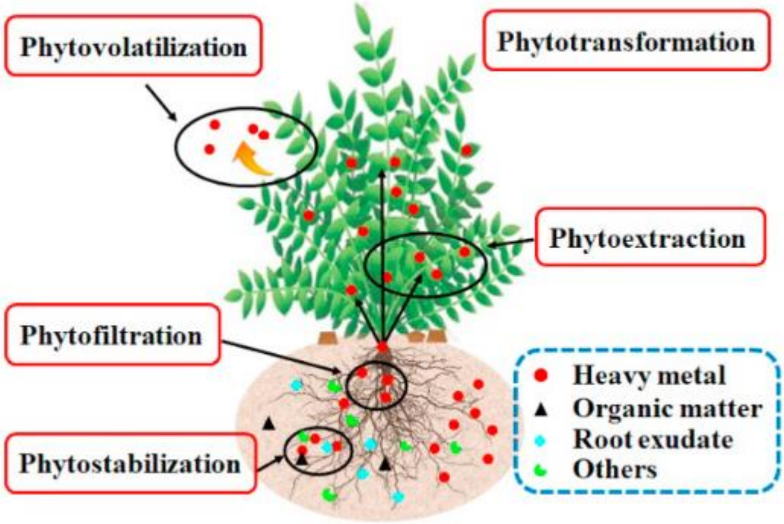

Figure 2.6: Phytoremediation Mechanisms for Various Types of Pollutants (Shen, et al., 2022).

2.5.1 Phytofiltration/ Rhizofiltration

Rhizo- implies root, thus, rhizofiltration involves the adsorption or absorption of pollutants in the solution adjacent to the plant roots. The working mechanism in rhizofiltration is likewise to 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 (Ramachandra and Ahalya, 2014). For the accommodation of plants, polluted water is gathered from a pollution source and took to the plants as a water source substitution. 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 reaching the pollutant saturation limit in plant roots, 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 (Sharma, et al., 2018). Some rootless or floating macrophytes demonstrate high efficiency and potential for 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 (Lakshmi, Sailaja and Reddy, 2017). The plants selected for rhizofiltration must be resistant to metal, tolerant to hypoxia, and have a large surface area for absorption (Laghlimi, et al., 2015).

2.5.2 Phytoextraction/ Phytoaccumulation

Phytoextraction could be referred as phytoaccumulation. The phytoextraction mechanism involves the heavy metal uptake from soil through the root of crop species and further translocate into the aerial part of the plant (Ali, et al., 2020). The translocation process is regulated by employing leaf transpiration and root pressure, as demonstrated in Figure 2.7. According to Shaari, et al. (2021), one of the strategy to improve the metal solubility in soil is through the addition of chelating agents. Upon completion of the phytoextraction, the plant will be harvested and disposed of with care (Sharma, et al., 2018). Besides, 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 like Cd (Akpor, et al., 2014). Hyperaccumulators have been occupying 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 (Laghlimi, et al., 2015).

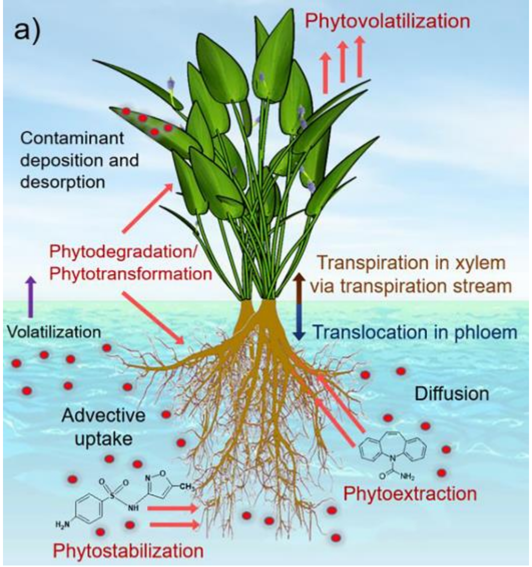

Figure 2.7: Phytoextraction, Translocation, and Transpiration in Plants (Kurade, et al., 2021).

2.5.3 Phytostabilization/ Phytosequestration

Phytostabilization uses specific plant species to deactivate contaminants contained in the groundwater and soil. As its name implied, phytostabilization could be referred as in-place immobilization or phytoimmobilization (Ali, et al., 2020). 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, avoid the upward migration of the contaminants to the groundwater, and lessen the bioavailability of metal into the food chain (Ramachandra and Ahalya, 2014). For example, *arbuscular mycorrhizal* symbiosis could stabilize the metals in soil (Sharma, et al., 2018). 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 (Laghlimi, et al., 2015).

2.5.4 Phytovolatilization

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 (Ali, et al., 2020). Phytovolatilization, primarily concerned with remediating organic acids, is also useful in treating Hg and 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 into the atmosphere (Sharma, et al., 2018). The research done by Jeevanantham, et al. (2019) 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, 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.

2.5.5 Phytodegradation/ Phytotransformation

Phytodegradation also known as phytotransformation involves the breakdown of contaminants into a simpler form of molecules through the enzymatic metabolic activity in plants with their corresponding microorganisms (Lakshmi, et al., 2017). In certain circumstances, selected plants own the capability to uptake toxic compounds, followed by detoxification and metabolization of toxic compounds as nutrients (Akpor, et al., 2014). The detoxification of toxic compounds usually involves three stages, namely bioactivation, conjugation, and compartmentalization. Each phase requires various types of enzymes such as oxygenises and nitro reductases, classified by the properties and distribution of their reaction products. The enzymes generated by plants could catalyse and speed up the degradation process. The phytodegradation process could be classified into internal and external processes (Jeevanantham, et al., 2019). 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 hydrolysed into smaller sizes whereas, for internal degradation, the organic pollutants absorbed are further broken down into smaller sizes by plant enzymes and eventually used as metabolites.

2.6 Heavy Metals Uptake Routes in Plants

Heavy metals are present in plants at various mediums such as water, sediment, and soil. In general, heavy metals accumulation in plants involves the uptake of metals into the plant tissue and liberation of absorbed metals back to the external medium. In aquatic ecosystem, 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 there is a disturbance on the sediment or a change in water chemistry (Du, et al., 2020). The potential disturbances on the sediment could be bioturbation, resuspension, presence of organic matter, and alteration in water salinity, thereby manipulating the equilibrium concentrations between the metal ions in water and sediment (Greger, 1999). The event of heavy metals remobilization is unwanted since they would contaminate clean areas when conveying by the water current. Free-floating plants take up metals by their roots from water. 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 gaseous form from the surfaces of 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 the water bodies. This is because the pollutants taken up by plants will release into the aquatic environment following the death and decomposition of plants (Lu, et al., 2011). In case of 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 concentrations available in that particular medium (Greger, 1999). 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 usually serve as transport mediums only. 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+}.

2.6.1 Absorption, Adsorption, and Efflux of Metals by Plants

Plants could function as accumulators and excluders in phytoremediation. Accumulator plants could survive without being affected by the large amount 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 (Tangahu, et al., 2011). As a result, excluders demonstrated low metals uptake even at high external metal concentrations. The normal plant commonly accumulates metal not exceeding their short-term metabolic needs. Lower metal concentrations between 10 to 15 ppm are sufficient for the basic functioning of normal plant. Nevertheless, an exception is given for hyperaccumulators that could absorb and tolerate thousands ppm of metal concentrations within their tissues. The reason for this is because hyperaccumulators own more than one detoxification mechanisms that prevent metal toxicity, such as metal storage into vacuoles, metal chelation, and metal efflux (Chaudhary, Jan and Khan, 2015).

According to Huynh, Chen and Tran (2021), there are two different mechanisms of heavy metals absorption by plants, namely root absorption and foliar absorption. Concerning root absorption, plant roots absorb heavy metals into the apoplast while absorbing the water. The presence of -COOH groups in the pectin of plant roots allow the exchange of cations within the cell membrane (Lissy and Madhu, 2011). In turn, it becomes transportation means for heavy metals to move into the cell wall from the external medium through diffusion or mass flow, where absorption takes place actively. The total concentration of metals being uptake could be bound to the anions in the cell wall, transported apoplastically, and into the cells, respectively, as illustrated in Figure 2.8. The distribution of absorbed metals among these three locations relies on the types of metal species and genotype of the plants.

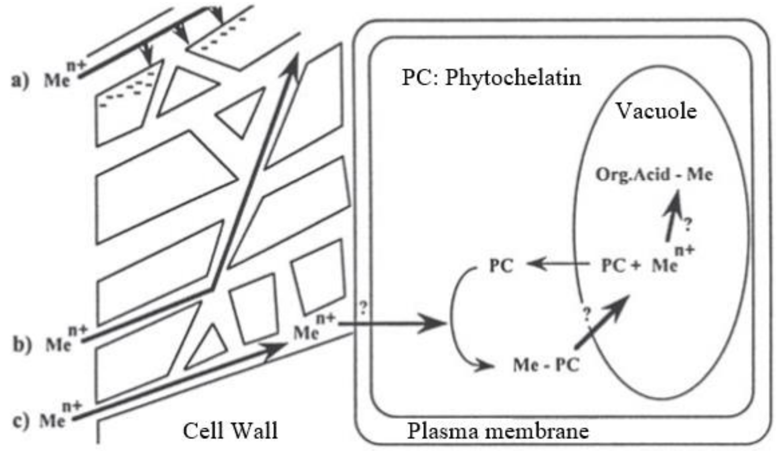

Figure 2.8: Metals (Me^{n+}) Uptake by the Plant Roots through (a) Binding with the Cell Wall, (b) Apoplastic Transportation, and (c) Transportation into Cells (Greger, 1999).

Since water hyacinth owns a dense and fibrous root system, aerobic bacteria are well established in aquatic environments. These bacteria gather the nutrients and inorganic pollutants, which serve as food for plants to keep nourishing (Huynh, Chen and Tran, 2021). Hence, plants grow faster and are harvestable as phytoremediation plant biomass after storing the heavy metals into their tissues. Aside from root absorption, foliar absorption might occur in the plants, where passive absorption of heavy metals occurs through stomata cells and cuticle fissures on the plant leaves (Lissy and Madhu, 2011). A high density of stomata cells stimulates greater ions uptake capacity as most of the uptake process initiates in ectodesmata. Yet, 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 a high charge density cell walls through the cuticle. Correspondingly, cation absorption is more likely to happen over anions absorption in this mechanism (Greger, 1999).

Furthermore, the 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 (Huynh, Chen and Tran, 2021). In aquatic macrophytes, the usual metal transportation mechanism is rhizofiltration, in which the metal is contained, immobilized, and accumulated within the plant’s root (Mishra and Tripathi, 2009). The root exudates within the rhizosphere allow the adsorption of metals on the plant root surface.

A different discovery was reported by Lissy and Madhu (2011), suggested that phytoextraction was the process accounting for the uptake of heavy metals from the 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 (Greger, 1999). Besides, the efflux of metals from the cuticular layer of leaves might happen when metal ions are exchanged with H^+ during acid rainfall. The metal ions, like Hg in gaseous form, might also be liberated to the atmosphere through opened stomata.

2.6.2 Bioconcentration, Translocation, and Distribution of Metals

The two important parameters evaluating the heavy metals uptake by aquatic plants are concentration factor (CF) and bioconcentration factor (BCF). CF is an indicator that assesses the total metal accumulation by plants through absorption and adsorption, whereas BCF is an index that accounts for the metal absorption by plants from the external medium (Souza, et al., 2019). BCF values are usually smaller than the CF values and the difference between both values is small if the absorption of metal ions are dominant in plants. Furthermore, BCF values greater than 1000 are commonly regarded as the sign of great phytoremediation potential (Das, Goswami and Talukdar, 2014). BCF is a more suitable indicator to distinguish the hyperaccumulator from the normal plants since the concentration of metals accumulated in the plant through absorption is more significantly (Lu, et al., 2011).

Furthermore, Greger (1999) found that the majority of the metals tend to bind to the cell walls during their transportation. The finding revealed that about 75 to 90 % of metals were uptake by the plant’s roots while only 10 to

25 % were further translocated in the shoot. For instance, the distribution of Cd was lower at a higher part of plants, following the descending order: dense fibrous roots > storage roots > stems > leaves. Vesely, et al. (2012) also found that more Pb was accumulated in water lettuce roots compared to that in leaves. Additionally, a higher accumulation of Pb in the root of water hyacinth than that in stems and leaves was reported by Buta, et al. (2011). 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 (Sarwar, et al., 2017). For example, the introduction of ethylenediamine tetraacetic acid promotes the Cd uptake by plants.

Translocation factor 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 TF value greater than one (Das, Goswami and Talukdar, 2014). TF value larger than one indicates that heavy metals absorbed by plants are translocated effectively to the aerial parts of plant (Kumar, Singh and Chopra, 2018). In contrast, TF value lesser than one implies that heavy metals tend to accumulate and store in the plant roots with less translocation to the aerial parts. Low TF value might be due to the exclusion strategy and restriction of metal movement towards the plant aerial parts (Das, Goswami and Talukdar, 2014).

Generally, TF value increased with an increased contamination level in the tributary. The translocation mechanism is crucial for the plant as it could prevent excessive accumulation of toxic metal ions in the plant root (Du, et al., 2020). The detoxification of metal ions might happen within the leaves of 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 roots. Meantime, it accounts for the movement of heavy metals into the plant shoot (Tangahu, et al., 2011).

Another study reported about the metal distribution within the shoot and root of plants, indicated by a root/shoot (R/S) ratio. The R/S ratio implies the metal concentrations accumulated in the plant root over the shoot. For exemplification, approximately 80 % of Cr, Cu, Fe, and Ni accumulated in the plant root with the R/S ratio equal to or greater than 6, while Fe has a R/S ratio greater than 17 (Lu, et al., 2011). Concretely, plant roots are the final destination of the absorbed metals since the roots could 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 an effective transportation of metals from plant roots to the harvestable part of plants. Nevertheless, non-accumulator plants own a shoot-to-root ratio much smaller than one (Tangahu, et al., 2011).

2.6.3 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 like Cr, Cu, Mn, and Fe could directly disrupt the plant cell homeostasis, break DNA strands, defragment proteins or cell membrane, destroy photosynthesis pigments, and cause cell death. Opposingly, non-redox active metals could impose oxidative stress on plants (Emamverdian, et al., 2015). Moreover, Kumar, Singh and Chopra (2018) reported that after phytoremediation using water lettuce to remediate sugar mill effluent containing Cd, Cu, Cr, Fe, Pb, Mn, and Zn, it induced yellowing of plant leaves, chlorosis, and necrosis.

The phytotoxic responses of various plants to heavy metals are presented in Table 2.7. For example, Mishra and Tripathi (2009) reported that the exposure of water hyacinth to Cr ions at 10.0 and 20.0 mg/L concentrations could result in plant leaves yellowing, chlorosis, and roots exfoliating. Besides, the chlorophyll, protein, and sugar content in the plant was found to reduce along with the escalating metal concentrations 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 (2007) revealed that Cd was more toxic than Zn. The increase in Cd concentrations 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. Similar declining plant growth trend was observed as increasing Zn concentrations from 2.0 to 12.0 ppm but without showing a negative growth rate.

Table 2.7: Phytotoxicity of Different Metals on the Plants.

Plant Species	Heavy Metals	Exposure Concentrations	Phytotoxic Responses	References
Water hyacinth	Cr	10.0 to 20.0 mg/L	Yellowing of leaves, leaves chlorosis, and growth retardation.	(Mishra and Tripathi, 2009)
	Zn	2.0 to 12.0 ppm	Growth reduction, leaf chlorosis, metabolism disruption.	(Hasan, Talat and Rai, 2007)
	Cd	1.0 to 4.0 ppm	Growth reduction, growth retardation, new root growth inhibition, root function disruption, leaf chlorosis.	
Duckweed	Cd	$>$ 10 mM	Pigment degradation and photosynthesis restriction.	(Miretzky, Saralegui and Cirelli, 2004)
	Cu	$>$ 50 μM		
Water lettuce	Pb	1 to 2 mmol/L	Chlorophyll synthesis inhibition, chlorophyll reduction, loss of photosynthesis activity.	(Vesely, et al., 2012)
	Ni	1.0 and 10.0 ppm	Plant wilting, chlorosis in leaves, chlorophyll reduction, carotenoid reduction, water loss, browning of root tips, and root damage.	(Singh and Pandey, 2011)

At a Cd concentration of 3.3 ppm, the metal toxicity could cause retardation in the plant growth by hindering the growth of new roots and disrupting the root function. The leaf chlorosis was fast, implying the decaying of plant tissue due to acute metal toxicity. This could eventually hinder the metabolism of plants (Hasan, Talat and Rai, 2007). Furthermore, exposure to excessive Cr concentrations 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 (Miretzky, Saralegui and Cirelli, 2004). Kumar, Singh and Chopra (2018) also found that higher heavy metal concentrations in wastewater could restrict the aquatic plant growth, 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 the photosynthesis because of the interrupted chloroplast. 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 the enzymatic activity (Mishra and Tripathi, 2009). The study presented by Buta, et al. (2014) 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 (Hegazy, Kabiel and Fawzy, 2009).

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Introduction

The overall methodology processes involved review planning, literature searching, literature screening and scanning, data collection, data analysis and interpretation, and report writing. Figure 3.1 represents the overall flow of methodological steps to achieve comprehensive studies on the topic of heavy metals uptake by floating aquatic plants and its recovering pathways.

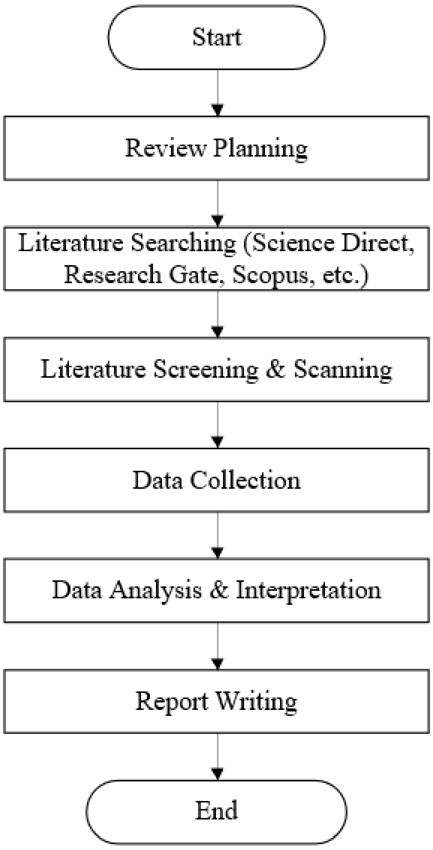

Figure 3.1: Overall Flow of Methodology Steps.

3.2 Planning

At the start of this review paper, review criteria such as the organic and inorganic pollutants in wastewater, phytoremediation mechanisms, the potential floating aquatic macrophytes for phytoremediation were developed to dispute the main concepts for appropriate searches and the requirements for this review. The research questions were designated based on the five whys and one how approach (Chen, et al., 2020). Figure 3.2 demonstrates the difference between conventional water remediation technologies and phytoremediation technology.

Q1: What are the common water pollutants in wastewater?
Q2: What are the sources of water pollutants?
Q3: What are the existing conventional water treatment technologies used to remediate water pollution?
Q4: What are the limitations of these conventional technologies?
Q5: How does phytoremediation overcome the limitations of conventional water remediation technologies?
Q6: How does phytoremediation work?
Q7: What are the characteristics of aquatic macrophytes for phytoremediation?
Q8: How do the different mechanisms in phytoremediation work?
Q9: What are the parameters affecting heavy metals uptake by plants?
Q10: How to manage the plant biomasses after heavy metals absorption?

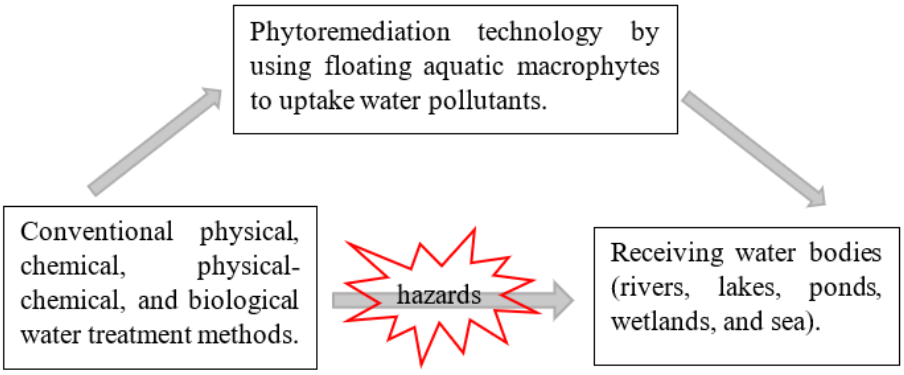

Figure 3.2: Conventional versus Phytoremediation Technologies for Water Pollutants Remediation (Chen, et al., 2020).

3.3 Eligibility Search Criteria

The eligibility criteria and inclusion criteria served as the central guide and priority design for the completion of this systematic review. The inclusion and exclusion criteria would aid in the selection of suitable research paper to be incorporated in the study by reviweing the titles, abstracts, and full-text

(Comer, 2021). The research questions and objectives would direct the criteria selection. Besides, the measurable outcomes with regards to the research questions, encompassing the design of study, methodology, and approach of analysis would guide the search criteria since it might affect the feasibility of the overall study and data analysis. Inclusion criteria are the elements apropriate to be included in the review paper, whereas exclusion criteria are the elements to be excluded from the review paper (MUSC Libraries, 2021).

Inclusion criteria:

1) Articles that related to the research subject of organic and inorganic pollutants in wastewater, water pollutants treatment methods, concepts of phytoremediation, and others with appropriateness and usefulness.
2) Articles published between 2002 and 2022 were used for data search.
3) Articles revealed in-depth information and results.
4) Papers published in English.
5) Works published as books, conference papers, and research articles.

Exclusion criteria:

1) Unorganized and inappropriate description review.
2) Works published in other languages besides English.
3) Editorial material.
4) Eliminate analogues.
5) Articles focused on irrelevant context to phytoremediation by floating aquatic macrophytes such as microorganisms assisted phytoremediation, terrestrial and rooted plant, and etcetera.

3.4 Information Sources

Various databases were screened and searched to make sure that all the related studies were in coverage (Ortiz-Martínez, et al., 2019). In this respect, bibliography was explored over diverse inclusive databases to minimize the potential bias. All the empirical facts that fulfill the pre-determined eligibility criteria through the development of the systematic review offered more proven findings (Lasserson, Thomas, and Higgins, 2021). The three main comprehensive databases used are Science Direct, Research Gate, and

Springer. The remaining databases encompassed American Chemical Society Publication, American Journal of Engineering Research, International Journal of Engineering Research and Methodology, MDPI Journal, Wiley, and other search engines.

150 articles were identified through database searching, skimmed, and scanned by the titles and abstracts after eliminating the duplicates. Subsequently, 115 full-text articles were accessed for eligibility before selecting the relevant papers to guarantee the comprehensiveness and fidelity of this review. The other 35 records were excluded due to the irrelevant and non-systematic contents. Finally, 110 studies with appropriate usefulness were included in the systematic review. With reference to the subject, the chosen articles were mainly addressing the examination of the remediation of organic and inorganic water pollutants using floating macrophytes via different mechanisms of phytoremediation technology.

3.5 Search

The first step for establishing a search plan was to appraise the main ideas being investigated in the review paper. This was commonly regarded as PICO: Problem, Intervention, Comparison, and Outcomes (Lefebvre, et al., 2021). Several search techniques were used throughout the literature search to figure out impartial research. In this review, phytoremediation was the main topic, while organic and inorganic pollutants, as well as aquatic macrophytes, were the context (Chen, et al., 2020). Therefore, keywords must be particularized from three concepts: 1) phytoremediation technique and mechanisms, 2) floating aquatic macrophytes, 3) organic and inorganic water contaminants. In particular, “heavy metals and metalloids” were the most frequently employed keywords by researchers in water pollution research. Also, four floating macrophytes, namely “duckweed/*Lemna minor*”, “water lettuce/*Pistia stratiotes*”, “water hyacinth/*Eichhornia crassipes*”, and “*Salvinia*” were widely used in other researchers’ studies. The descriptions for “rhizofiltration”, “phytoextraction”, “phytostabilization”, “phytovolatilization”, and “phytodegradation” were considered.

To have a better search result, the use of synonyms and alternative terms, Boolean operators, phrase searching, parentheses, truncation, wildcards, field codes were employed. The synonyms and similar words for the substitution of keywords were searched through the online thesaurus. Moreover, the Boolean operators like “and” and “or” were used to narrow down or focus on the search results and to broaden the search results, respectively (Comer, 2021). For example, “heavy metals uptake” and “floating aquatic plant”. Besides, the phrase search could be used by enclosing the keywords in the quotation marks. For instance, “phytoremediation of heavy metals” and “floating aquatic macrophytes” to have a more acute search result. Finally, the search statements were developed.

Furthermore, there were several ways of data searching. First and foremost, the background information was browsed via Wikipedia, encyclopedia, references books to know more about the big picture for the research scopes of interest. In this review paper, online databases and web resources were the two main data searching platforms. The online databases included the library resources, Science Direct, Research Gate, Springer, Google Scholar, ACS Publications, and others. The library resources were browsed using One Search and Online Catalogue Search through the insertion of either title, author, keyword, or subject search. The Science Direct alternative search was done by inserting keywords, author name, journal/book title, volume, issue, or pages. Additionally, Science Direct offered few searches alternatives like quick search, advanced search, and browsing (Ortiz-Martínez, et al., 2019).

3.6 Study Selection

According to the Preferred Reporting Items for Systematic Review methodology (Ortiz-Martínez, et al., 2019), various measured were implemented to reduce the bias and errors throughout the review stages. Study selection was one of the crucial aspects of systematic reviews. During the study selection process, the library with all the search results was initiated. Secondly, determined and eliminated the repeated references through continual checking using the Mendeley citation manager tool. Subsequently, the title abstract and the full-text review were screened for possible inclusion referring to the eligibility search criteria developed previously to eliminate the unrelated works (Lefebvre, et al., 2021).The 150 articles acquired from the three major comprehensive databases were checked to identify the duplicated works. Only relevant studies to the subject matter were chosen after reading the titles and abstracts of the papers. In the end, a total of 110 works fulfilled the eligibility criteria for the current systematic review.

3.7 Data Collection

Data extraction encompassed at least the study characteristics with specific details, outcomes measures, and results that were applied in the data synthesis. The elements for data extraction would consider the research questions and objectives, study eligibility criteria, and study characteristics. Generally, there were two types of research methods: qualitative and quantitative research. The data collection was performed qualitatively by surveying various literature reviews published by other authors (Streefkerk, 2021). Qualitative research was important for the understanding of concepts, experiences, and thoughts. Besides, it mainly focused on ideas exploration and hypothesis formulation. Analysis for qualitative research was done through classifying, interpreting, and summarizing. In another way, quantitative research was targeted at testing hypotheses and theories, which were commonly presented in graphs, numbers, and tables.

3.8 Reporting

The remaining qualified articles were scrutinized and compared among one and other, and subsequently sorted and arranged referred to the significant process parameter involved. The contents were eventually presented in a coherent structure. In general, 110 research works were studied and examined in-depth and summarized with regards to the abstract, contents, and other informative data.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Process Parameter Studies

The phytoremediation of heavy metals by floating aquatic plants was influenced by several factors, such as solution pH, solution temperature, exposure duration, water salinity, initial metal concentration, presence of other metals concentration in the culture medium, and the addition of chelating agent. Each parameter was studied in detail in the following subsections.

4.1.1 Effect of Solution pH

The uptake of metal ions by aquatic macrophytes is reliant on the solution pH. According to Obinnaa and Ebere (2019), the metal uptake was usually higher at lower solution pH of about 4, thus reducing the metal concentrations in the external culture medium. Notably, the pH of the medium would alter the metal speciation and metal bioavailability (Greger, 1999). In low pH or acidic environments, most heavy metal ions existed as free positively charged species because of the higher H^+ concentrations in the water, implying that more metals were soluble and bioavailable to biota. Therefore, plants could absorb the heavy metal ions easily, resulting in higher metal uptake. According to Soltan and Rashed (2003), the pH of water medium was dropped 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 (2012), the author suggested that plants showed 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 (2009), 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, as demonstrated in Figure 4.1.

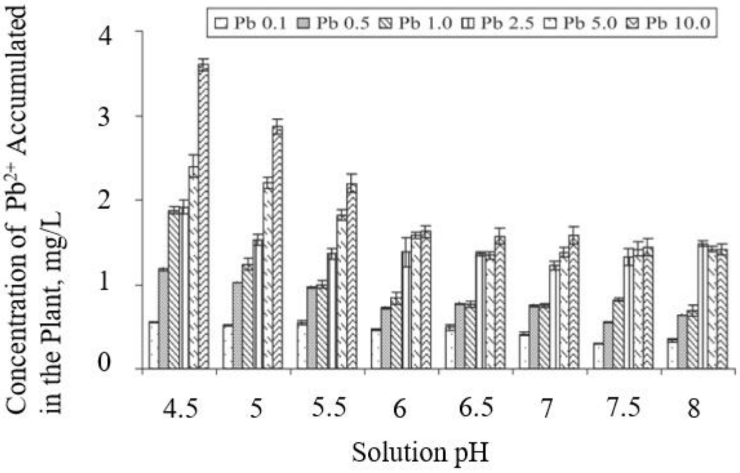

Figure 4.1: Effect of Solution pH on the Pb^{2+} Accumulation in Duckweed (Uysal and Taner, 2009).

Apart from that, the pH level would affect the growth of plants. Generally, the plant cytoplasm environment was best maintained at pH 7 to ensure optimal plant growth and survival. Besides, Keeffe, Hardy and Rao (1984) found that the Cd^{2+} uptake by plants increased within the pH ranges between 2 to 4. At pH 2, the acidic growth environment caused blenching of plant roots and death of plants, inhibiting the metal uptake. In other words, the heavy metals uptake by plants reduced significantly when the pH was brought down from 4 to 2 due to lesser anionic sites available for the ion exchange and more competitive metal binding between the protons and the metal ions to the plant cell wall (Rakhshaee, Khosravi and Ganji, 2006). However, it was noteworthy that the presence of other contaminants in the medium could affect the metal uptake efficiency (Dijoo, Ali and Hameed, 2020). For example, a solution with pH ranges between 6 to 9 might only be feasible for the remediation of wastewater without heavy metal contamination.

4.1.2 Effect of Solution Temperature

The solution temperature is another crucial ecological factor affecting the performance of metal uptake by aquatic macrophytes. The uptake of most metal ions by plants relied upon the medium temperature. This was because the change in temperature might influence the solubility and kinetic energy of the metal ions (Kumar and Deswal, 2020). Based on the findings presented by

Singh, Gupta and Tiwari (2012), the removal percentage of Pb^{2+} by plants increased by 22 % when raising the temperatures from 20 ℃ to 28 ℃. This finding was in agreement with Rai (2009), illustrating an increasing metal uptake trend by plants with escalating temperature. Uysal and Taner (2009) also revealed that the Pb^{2+} accumulation by plants was the highest at 30 ℃ and the lowest at 15 ℃. Yet, at the temperature beyond 30 ℃, the metal uptake reduced again. The increasing and decreasing metal uptake trends by plants are illustrated in Figure 4.2. The sudden decreased in the metal accumulation by plants might be due to the stress effects imposed on plants at the higher temperature of 35 ℃, thus lowering the metal uptake efficiency.

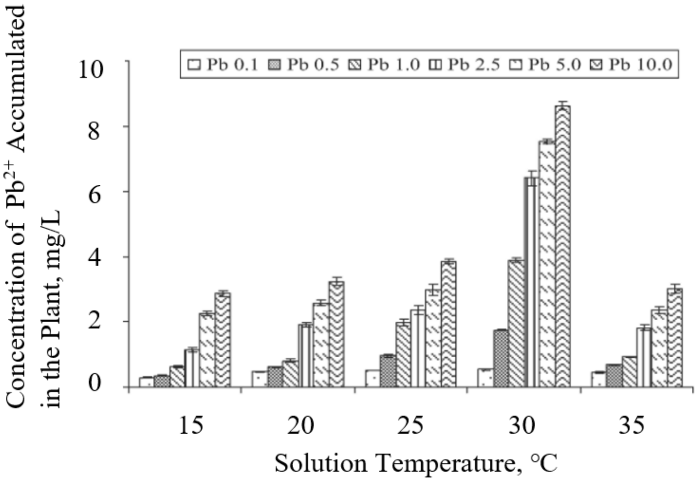

Figure 4.2: Effect of Solution Temperature on Pb^{2+} Accumulation in Duckweed (Uysal and Taner, 2009).

Similarly, Giri (2012) reported that the As and Cr metal ions removal by plants decreased gradually when increasing the temperature from 25 ℃ to 45 ℃. The author suggested that the fast absorption rate and maximum metal removal by plants had taken place at 25 ℃, which might be owing to the wide availability for metal binding sites on the plant root at the initial ion exchange process. Hence, it induced that the metal absorption process by plants were regulated by an exothermic process. Additionally, Rakhshaee, Khosravi and Ganji (2006) revealed that the metals uptake by plants increased with increasing temperatures from 10 to 25 ℃.

Apart from affecting the metal uptake efficiency, the solution temperature would influence the growth of plants. The behavior of aquatic accumulators varied depending on the temperature. The temperatures between 20 ℃ to 30 ℃ could result in the optimal cultivation of most aquatic plants. Conversely, the temperature equivalent to or lower than 10 ℃ could hinder the metabolic activities of most aquatic plants (Dijoo, Ali and Hameed, 2020). Additionally, it would hinder the growth of plants and inactivate the microbial activity, leading to a low metal removal efficiency by plants (Kumar and Deswal, 2020). Instead, a minimum temperature of 15 ℃ should be maintained to ensure an optimal pollutant removal by microbes. The study also suggested that the optimal water temperature for the growth of water hyacinth was between 28 to 30 ℃, while the optimum air temperature was within 21 to 30 ℃. Nevertheless, at greater than 33 ℃, it would suppress the successive growth of the plant (Huynh, Chen and Tran, 2021). Unfavorable culture medium temperature restricted the growth of plants and caused plants to cease. As a result, the plants showed incapability to accumulate the metals (Shah, et al., 2014). However, in some cases, plants could grow at colder temperatures.

4.1.3 Effect of Exposure Duration

Various exposure duration of aquatic plants to the metal concentrations in the culture medium would result in various metal uptake performances. Lu, et al. (2004) reported that total metal accumulation in roots and shoots of the plant generally increased with increasing exposure duration. Besides, Soltan and Rashed (2003) discovered that the plants cultivated in 100 mg/L of metal solution portrayed a declining metal uptake trend at increasing exposure duration due to wilting of plants resulting from the high toxicity of metal accumulated in the plant tissue. Consequently, the metal uptake by plants via diffusion and osmosis reduced significantly with increasing exposure time.

Furthermore, Keeffe, Hardy and Rao (1984) found that the Cd^{2+} uptake rate by plants was fast at the first 4 hours but decreased linearly for the subsequent 72 hours, implying that the percentage of metal uptake declined with increasing exposure duration. The trend of Cd^{2+} and Zn^{2+} absorption by the plants as the function of exposure time at various concentrations had been studied by Hasan, Talat and Rai (2007). The uptake of Cd^{2+} by the plants took place in two stages at higher metal concentrations of 4.0 and 6.0 ppm, as illustrated in Figure 4.3 (a). A greater uptake efficiency was observed during the second stage, from the 6th to 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 concentrations, as shown in Figure 4.3 (b).

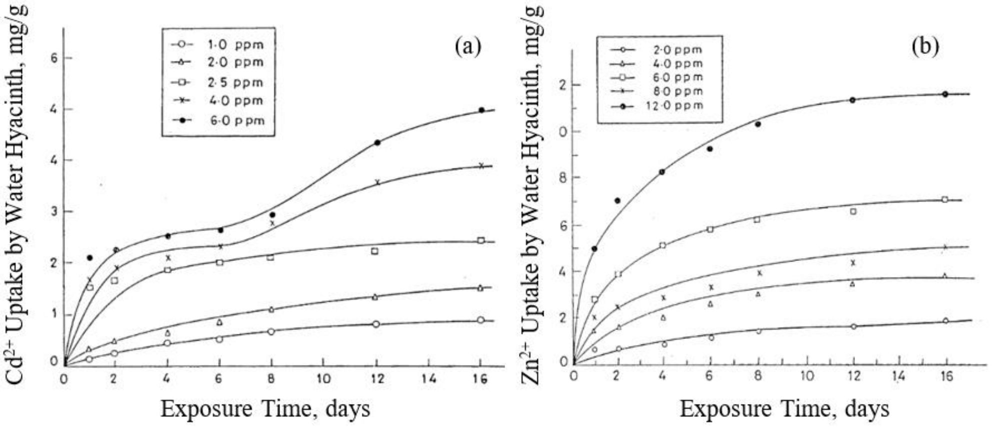

Figure 4.3: Effect of Exposure Time on (a) Cd^{2+} and (b) Zn^{2+} Uptake by Water Hyacinth at Different Initial Metal Concentrations (Hasan, Talat and Rai, 2007).

4.1.4 Effect of Water Salinity

Another crucial parameter manipulating the metal uptake by plants is water salinity. The salt concentrations in water would affect the growth and reproductive potential of aquatic plants. Different plants had varying degrees of salinity tolerance, which regulated the pollutants removal capability by plants from the water environment. It revealed that the floating macrophytes like water hyacinth and water lettuce were likely to be influenced by the low water salinity at about 2.50 % (Haller, 2016). In the case of high salt concentration in the water, it slowed down the transpiration rates and reduced the total dry weight of plants (Dijoo, Ali and Hameed, 2020). 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 (Greger, 1999). 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.

4.1.5 Effect of Initial Metal Concentration

The initial concentration of metal in the culture medium would also manipulate the metal uptake efficiency by plants' roots and leaves. The heavy metal uptake by plants usually increased with elevating initial metal concentrations (Soltan and Rashed, 2003). A similar observation was reported by Lu, et al. (2011), suggesting that the removal capacity of metal was higher when the aquatic plants were cultivated in the wastewater with higher metal contamination levels. For instance, Pb^{2+} accumulated in the roots and leaves of plants increased with the escalating Pb^{2+} concentrations in the growth medium (Vesely, et al., 2012).

Moreover, Uysal and Taner (2009) found that amount of metal accumulated in plants increased with escalating initial metal concentrations ranging between 0 to 50 mg/L. However, it decreased when increasing the metal concentrations from 50 to 100 mg/L, as illustrated in Figure 4.4. 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 metal ions in root to the surrounding solution, imposing adverse effects on the survival of plants. The common phytotoxicity effect on plants was truncated plant growth resulting from hindered photosynthesis (Soltan and Rashed, 2003). Furthermore, the higher concentrations of metal ions in the medium would impose inhibitory consequences on the plant metabolisms, alternately minimized plant growth, caused leaf necrosis, and destroyed plant physiology systems (Giri, 2012). 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.

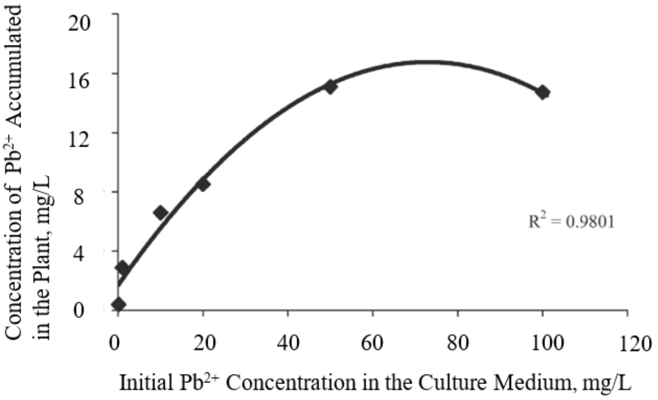

Figure 4.4: Effect of Initial Pb^{2+} Concentration on the Metal Accumulation in Duckweed (Uysal and Taner, 2009).

The metal concentrations in sediment and the metal accumulated in root of plant reflected positive linear correlation for most heavy metals like Co, Mn, Ni, and Sn with R^2 values of 0.3559, 0.4216, 0.7616, and 0.5158, respectively. This implied that the plant could accumulate and remove more heavy metals at higher contamination levels (Du, et al., 2020). However, the linear correlation between metal concentration in sediment and that accumulated in the plant root was weaker for the accumulation of Cu and Pb with R^2 values of 0.3338 and 0.3011, respectively. For instance, when plant was treated with escalating Pb concentrations, from 30 to 50 mg/L, it demonstrated a declining metal accumulation rate (Singh, Gupta, and Tiwari, 2012).

Nevertheless, the accumulation of Cd, Sb, and Zn in water hyacinth root 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 (Du, et al., 2020). A similar finding was reported by Greger (1999), where the metal uptake was not linearly correlated to the increasing initial metal concentrations. 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.

4.1.6 Effect of Other Metals Concentration

The presence of other metals in the culture medium would also affect the metal uptake by aquatic plants because of the metal binding competition at the plant cell wall (Greger, 1999). For example, the absorption of Cd^{2+} by plant roots declined when other cations of escalating ionic radii or valency were present. Specifically, the Cd^{2+} uptake by plants declined when increasing the concentration of Zn^{2+} in the medium (Keeffe, Hardy and Rao, 1984). Figure 4.5 reflects the effects of Zn^{2+} at different concentrations on the uptake of Cd^{2+} by plants. 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 (Hasan, Talat and Rai, 2007).

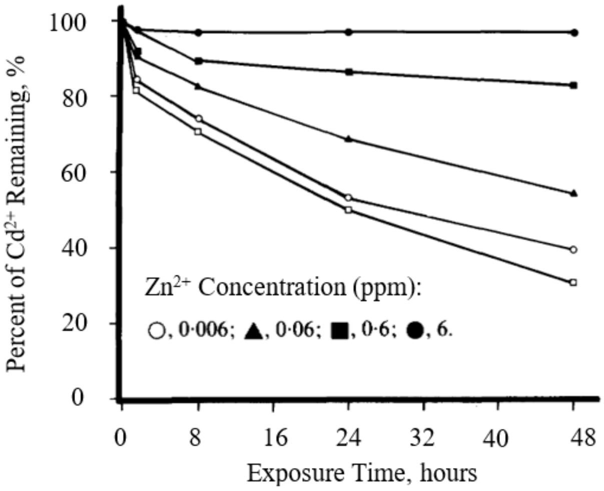

Figure 4.5: Effect of Increasing Zn^{2+} Concentrations on the Uptake of Cd^{2+} by Water Hyacinth (Keeffe, Hardy and Rao, 1984).

4.1.7 Effect of Chelating Agent Addition

Another crucial factor affecting the phytoremediation is the bioavailability of metals in the soil. Most metals were not readily bioavailable to the plant due to their high binding abilities to the soil (Liang, et al., 2017). According to Prasad (2003), heavy metals or metalloids like 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 soil and improve the metal uptake by plants. Upon introduction of chelating agent to the soil, it formed water-soluble metal-chelant complexes, which would further taken up by plants via the apoplastic route (Wuana and Okieimen, 2011). The formation of complexes, in turn, restricted the precipitation of the heavy metal, increased their mobility, enhanced the bioavailability of heavy metals, and promoted metal desorption (Oladoye, Olowe and Asemoloye, 2022).

Chelating agents could be generally classified into synthetic and organic types. Synthetic chelating agents included ethylenediamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid, and ethylene glycol tetra-acetic acid (Sarwar, et al., 2017). According to Dhaliwal, et al. (2022), the addition of chelating agent in soil improved the phytoextraction of Cd^{2+} uptake by plants. The results showed that the metal uptake was increased by about 15 % when increasing amounts of EDTA in 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 plant. Additionally, the dosage of EDTA at 2.7 mmol/kg enhanced the phytoextraction (Shinta, Zaman and Sumiyati, 2021).

EDTA was regarded as an efficient chelate, yet it had unfavourable toxic effects on plants, soils, and ecosystems, which might introduce risks to the environment (Lee and Sung, 2014). Accordingly, the natural, biodegradable, non-toxic, and environmental-friendly organic chelators like citric, acetic, oxalic, and malic acids had been proposed to overcome the toxic effects that resulted from the use of EDTA. Shinta, Zaman and Sumiyati (2021) suggested that the citric acid was more effective than EDTA as it acidified and lowered the pH level of soil, created the microbial community in the soil, and promoted the growth of plant root. As a result, plants showed higher metal absorption due to faster growth. On the other hand, Souza, et al. (2013) recommended that the organic chelating agents might be employed during the plant harvesting process to enhance the metal desorption and metal bioavailability in soil.

4.2 Kinetics of Phytoremediation

The kinetic model of phytoremediation is important to determine the efficiency, effectiveness, and natural behaviour of the aquatic plants during heavy metals removal from water or soil (Singh, et al., 2021). Besides, the kinetic model is useful in the investigation the mass transfer rate of metals from medium to plant tissues. On top of that, the kinetic study provides insightful information regarding the design and optimization of biological treatment technology at large scale. Based on the findings reported by Naaz (2013), 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 linearized first order kinetic equation proposed by Widianarko and Van Sraalean with minimal adjustments as presented in Equation (4.1). Moreover, Ingole and Bhole (2018) proposed linearized first order kinetics for the heavy metal removal by the plant, as shown in Equation (4.2). Notably, the uptake rate constant (k) for the plants was an important parameter to evaluate the metal uptake performance by plants (Ingole and Bhole, 2018). The linear relationship observed from the plot of log (C_t) versus time (t) confirmed the first order behaviour of heavy metals uptake by plants.

First order kinetic equation with slight adjustment:

$$\log(C_t) = -\frac{k}{2.303}t + \log(C_0) \tag{4.1}$$

First order kinetic equation:

$$\log(C_t) = -kt + \log(C_0) \tag{4.2}$$

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 removal by plants are summarized in Table 4.1. According to Singh, et al. (2021), 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 (2018) found that the heavy metal uptake by the plant fitted well to the first order behaviour. The plant demonstrated the highest uptake rate of 0.1027 day^{-1} during the removal of Pb compared to other metals like 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 (2006) revealed that the removal of heavy metals by living plants corresponded to the first order kinetic, following the descending sequence of 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 4.1: Kinetic Parameters of Heavy Metals Removal by Plants.

Heavy Metals	**k (day^{-1})**	**R^2**	**References**
Cd	0.0625	0.930	(Singh, et al., 2021)
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	(Ingole and Bhole, 2018)
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. (2017), 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 (4.3) and (4.4), respectively. By deriving Equation (4.4), the PSO kinetic equation generated a dumb-bell shape profile and eventually optimized the model, as displayed in Equation (4.5).

PFO kinetic model:

$$q = q_m - (q_m - q_0)e^{k_1(t_0 - t)} \tag{4.3}$$

PSO kinetic model:

$$q = \frac{q_0 - q_m(q_m - q_0)e^{k_2(t_0 - t)}}{1 - (q_m - q_0)e^{k_2(t_0 - t)}} \tag{4.4}$$

Derivation of PSO kinetic model:

$$D_q = \frac{{k_2}^2(q_m - q_0)^2 e^{k_2(t_0 - t)}}{1 - (q_m - q_0)e^{k_2(t_0 - t)}} \tag{4.5}$$

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 the high R^2 values ranging between 0.9979 to 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 (Kamalu, et al., 2017). Hence, it can be inferred that the natural phenomenal process of phytoremediation demonstrated a sigmoidal profile. Moreover, the concentration of metals uptake by 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 implied that the sigmoidal profile might set in at longer exposure times due to its natural behaviour.

4.3 Metal Recovery Pathways using Aquatic Plants

Phytoremediation using aquatic plants is a promising green technology that minimized the toxicity and health hazards induced by heavy metals in polluted water or soil. However, the application of phytoremediation could generate contaminated plant biomass after harvesting the plants. Since the toxic metals contained in the biomass had the potential to biomagnify and enter into the food chain, the development of effective and efficient biomass management approaches was crucial to dispose of the contaminated biomass safely. The existing phytoremediation biomass disposal approaches included composting, compaction, pyrolysis, direct disposal, leaching, incineration, and nanoparticle synthesis. The working mechanisms, advantages, and disadvantages of each disposal method were further discussed in the following subsections.

4.3.1 Composting

Composting is a microbial treatment technology that worked under aerobic conditions, in which oxygen was required. Aerobic microorganisms tended to degrade the organic matter of plants by transforming them into microbial cell substances and releasing them in the form of energy. Besides, the total metal content and water-soluble metal reduced after composting (Liu and Tran, 2021). According to Xu, et al. (2014), most of the metal lost from the phytoremediation biomass was due to the production of compost leachate rather than the lost through metal volatilization.

Composting is an acceptable biomass disposal method since it could lead to a significant reduction in biomass volume, weight, and water content, as well as minimization of transportation costs to the hazardous waste disposal sites (Oladoye, Olowe and Asemoloye, 2022). However, composting posed several limitations. For example, it required expensive technology and special equipment to treat the end product called leachate that contained harmful heavy metals prior to disposal, hence incurring additional treatment costs (Mohanty, 2016). Moreover, the disposal cycle was long, which required about two to three months, subsequently lowering the disposal efficiency (Shen, et al., 2022). Additionally, owing to its high toxic level, the compost product was unsuitable to be used in the agricultural field as manure or fertilizer. Furthermore, due to the water-soluble properties of metals such as Zn and As bioaccumulated in the plant biomass, the application of composting required strict monitoring to avoid leaching of hazardous metal ions to the environment and prevent recontamination of environmental (Xu, et al., 2014).

To overcome the issue of metal leachate, lime, fly ash, biochar, red mud, and other biodegradable uncontaminated biomass could be added into the existing contaminated biomass to form a mixed compost. As a result, it could lower the content of metal residual composition in the biomass, reduce the water solubility of metals, minimize leaching, preclude secondary pollution, and avoid extra treatment expenses (Oladoye, Olowe and Asemoloye, 2022). On the other hand, Zhu, et, al. (2019) suggested the application of heat treatment on the unstable compost to restrict the migration of heavy metals to the soil again.

4.3.2 Compaction

Compaction is another workable disposal technology. Compaction could be known as palletization, which compacted the contaminated plant biomass into the particulate product under pressure. The leachate after compaction was collected separately. The end products of this process comprised a high proportion of toxic heavy metals, thus requiring subsequent treatment in hazardous waste disposal facilities (Oladoye, Olowe and Asemoloye, 2022).

After compaction, the water was eliminated from the contaminated biomass, reducing the volume and weight of biomass. Accordingly, it could save the transportation cost while sending the compacted biomass to the hazardous waste sites (Mohanty, 2016). However, this method posed some disadvantages such as time-consuming, need for advanced technology, and generation of toxic end products (Shen, et al., 2022). From the economic point of view, this method incurred additional leachate usage costs, which were absent in the pyrolysis method. Compared to composting, the information and literature data available for compaction were limited. Hence, efforts could be made by the researchers to further explore the effects of biomass shaping, sizing, particle densities, and chemical compositions on compaction.

4.3.3 Direct Disposal

Direct disposal of post-harvested plant biomass is a time-effective method. However, this method was prohibited as it could lead to secondary environmental pollution. The risks associated with this method could be verified through leaching and solubility tests to monitor and regulate the possible threats (Vocciante, et al., 2019). Apart from causing environmental issues, this method imposed high expenses and required a longer time to reduce the contaminated biomass (Kovacs and Szemmelveisz, 2017).

4.3.4 Leaching

Leaching is a process of treating the compacted toxic biomass using various solvents. This disposal method was related to the percolation tendency of water-soluble metals into the transporting medium. Time and pH were the two important factors governing the recovery rate of heavy metals from biomass (Kovacs and Szemmelveisz, 2017). The residual biomass turned into non-hazardous material after the leaching process, followed by the extraction of metals from the leachate. Leaching offered several advantages like easy handling of biomass residual and the ability to recover metals. However, this method demanded further treatment for the biomass and percolate waste produced. Besides, the metal recovery process from the leachate was relatively expensive (Vocciante, et al., 2019).

4.3.5 Pyrolysis

Pyrolysis is another alternative option to dispose of the contaminated plant biomass. This method worked by decomposing the contaminated biomass under anaerobic conditions and at moderately high temperatures (Singh, Singh and Dhal, 2022). Hence, organic matter decomposition could occur without oxygen. The end products generated from this process comprise solids, liquids, and gaseous fractions. The highest metal contents existed in solid fractions, while the lowest metal content in liquid and gaseous fractions were favourable from the environmental safety perspective. Compared to the gasification or combustion method, pyrolysis required a lower operating temperature and generated fewer fractions of contaminated gaseous or vapour containing toxic heavy metals. In detail, the final products of pyrolysis were coke, biochar, bio-oil, and pyrolytic gas (Liu and Tran, 2021). Additional treatment of coke containing most toxic metals at the hazardous waste treatment facility was advisable to prevent environmental risks. Pyrolysis could be classified into four types referring to its rate, namely slow, intermediate, fast, and flash pyrolysis (Mohan, et al., 2014). The characteristics of slow and fast pyrolysis are tabulated in Table 4.2.

Table 4.2: Information of the Slow and Fast Pyrolysis (Mohan, et al., 2014).

Pyrolysis	Temperature (°C)	Pressure	Residence Duration	Main Product
Slow	350-800	Atmospheric	Seconds to hours	Biochar
Fast	400-600	Vacuum to atmospheric	Seconds	Bio-oil

The advantages of using pyrolysis in biomass disposal included its ability to minimize the biomass water content and volume, generate valuable end product of coke applicable in smelting plants, and operation at low to moderate temperatures, which avoided the evaporation of metal (Shen, et al., 2022). The main drawbacks of this method included the discharge of toxic coke breeze, high complexity of the operation, high operating and installation costs, and limited energy generation (Oladoye, Olowe and Asemoloye, 2022). Nevertheless, the high operating expenses could be compensated by transforming and producing the value-added products from the mixture end products. For instance, the bio-oil and pyrolysis gases could be utilized in the power generation or auxiliary chemicals synthesis. Lastly, the high costs associated with coke treatment could be avoided by processing the plant materials in the existing municipal waste facilities (Mohanty, 2016).

4.3.6 Incineration

Incineration is a thermal degradation process, which oxidized and combusted the contaminated phytoremediation biomass under high pressure using forced air. At the end of incineration, the plant biomass concentrated and turned into treatable ash (Shen, et al., 2022). This process resulted in a significant weight reduction of the heavy metal contaminated plant biomass. Besides, this method could reduce the biomass volume by 2 to 5 % under controlled conditions (Singh, Singh and Dhal, 2022). In addition, the heat generated during incineration could be used as an electrical and thermal energy supply. According to Liu and Tran (2021), the extent of weight reduction was dependent on the temperature of incineration. The process of biomass incineration could be divided into three stages operating from lower to higher temperatures. During the first stage, water contents in plant biomass started to evaporate at the temperature ranges between room temperature to 185 ℃. For the second stage, the temperature was in the range of 185 ℃ to 400 ℃. During this stage, the cellulose and hemicellulose of plant biomass degraded, resulting in significant weight loss. Lastly, the temperature was raised within 400 ℃ to 697 ℃ for continuous plant decomposition. Yet, the weight loss was slower at this stage. After the heat treatment, it formed a mixture product containing bottom ash, fly ash, flue gas, etcetera. Table 4.3 summarizes the operating temperatures and the changes on the incinerated plant biomass at each stage of incineration.

Table 4.3: Description of Incineration at Different Stages.

Stage	Temperature (°C)	Descriptions
1	20-185	- Evaporation of water from plant biomass. - Small weight reduction.
2	185-400	- Cellulose and hemicellulose degradation in plant biomass. - Significant weight reduction.
3	400-697	- Continual of plant biomass degradation. - Slow weight reduction.

Generally, the heavy metal vaporization rate increased with increasing temperatures. Besides, the higher concentration of metals was found in fly ash and flue gas, which related to the heavy metal volatilization behaviour (Zhong, et al., 2015). Since the metal concentration in the fly ash was well above the allowable legal limits, it was less acceptable to be reused in agricultural land and forestry as valuable fertilizer (Bonanno, et al., 2013). Similarly, the reutilization of bottom ash was limited as the metals that remained in it would leach easily and cause recontamination. The leaching capacity of metal was lower under higher incineration temperatures (Zhu, et al., 2019).

On the other hand, several additives such as kaolin, activated carbon, zeolite, and calcium oxide could limit the volatility of the heavy metals in the phytoremediation residues, preventing them from transforming into gaseous form. For instance, the addition of kaolin had successfully eliminated 91.20 % of Cd and 88.10 % of Zn from the flue gas (Wu, et al., 2013). The incineration technique is a feasible disposal option from an environmental and economic perspective. First, it achieved up to 99 % volume reduction of the phytoremediation biomass, hence saving the treatment expenses and transportation costs of the collected residue to the hazardous waste sites (Vocciante, et al., 2019). Secondly, it could decompose nearly all organic compounds in the biomass, making the end-product easy to handle in an environmental-friendly way. However, this method had a drawback which it required advanced technology to quantify and minimize the emissions of volatile and toxic metals in the flue gas.

4.3.7 Nanoparticle Synthesis

Nanoparticle usually had particle size ranges between 1 to 100 nm. Among various nanoparticles, metal oxide and metal nanoparticles offered the highest effectiveness as they provided a larger surface area to volume ratio (Liu and Tran, 2021). Biosynthesis of metal nanoparticles using phytoremediation plant biomass became the latest eco-friendly, straightforward, and one-step approach since it could achieve up to 100 % biomass reduction rate, offering greater effectiveness than other disposal techniques (Ahmed, et al., 2016). In this approach, the plants might transform the absorbed metals from the growth medium into nanoparticles. This could be done through the plants' metabolic activities and the accumulation of metals in their stems, leaves, and shoots (Singh, Singh and Dhal, 2022). Despite its high disposal efficiency, nanoparticle synthesis employing the heavy metal contaminated biomass was still not well established at the current time due to the limited research and study that had been done in this field. Therefore, more exploration and research could be done in preparing the nanomaterials from various plant species that absorbed multiple types of heavy metals were indeed important. Lastly, this method involved sophisticated operation and incurred high costs. The advantages and disadvantages of each disposal method are summarized in Table 4.4 for ease of comparison.

Table 4.4: Comparison between the Advantages and Disadvantages of Biomass Disposal Methods.

Disposal Methods	Advantages	Disadvantages	References
Composting	- Reduce water content, weight, and volume in the biomass. - Minimize transportation costs.	- Produce toxic compost products. - Need expensive technology and special equipment for leachate treatment. - Incur additional leachate treatment costs. - Long disposal cycle. - Require strict process monitoring.	(Oladoye, Olowe and Asemoloye, 2022; Mohanty, 2016; Shen, et al., 2022; Xu, et al., 2014)
Compaction	- Reduce water content, weight, and volume in the biomass. - Minimize transportation costs.	- Generate toxic end products. - Time-consuming. - Require advanced technology. - Need extra leachate usage costs. - Less well-established technology.	(Oladoye, Olowe and Asemoloye, 2022; Mohanty, 2016; Shen, et al., 2022)
Direct Disposal	- Time-effective.	- Cause secondary environmental pollution. - Require high costs. - Need longer time for the reduction of contaminated biomass.	(Kovacs and Szemmelveisz, 2017; Vocciante, et al., 2019)
Leaching	- Easy to handle the biomass residual. - Able to recover heavy metals.	- Require further treatment for biomass and percolate waste generated. - High expenses.	

Table 4.4 (Continued)

Disposal Methods	Advantages	Disadvantages	References
Pyrolysis	- Reduce water content, weight, and volume in the biomass. - Produce usable end product of coke in smelting plants. - Operation at moderate temperatures.	- Produce toxic coke products. - Need additional treatment. - Involve complex operation. - High operating and installation costs. - Generates minimal energy.	(Oladoye, Olowe and Asemoloye, 2022; Mohanty, 2016; Shen, et al., 2022)
Incineration	- Reduce water content, weight, and volume in the biomass significantly. - Save transportation costs. - Decompose nearly all organic matter in biomass. - Generate heat for electrical and thermal energy supply.	- Demand for advanced technology to quantify and lower the emissions of toxic metals from the flue gas.	(Shen, et al., 2022; Vocciante, et al., 2019; Zhong, et al., 2015)
Nanoparticle Synthesis	- Eco-friendly. - Simple process. - High biomass reduction rate.	- Not well-established technology. - Sophisticated operation. - Incur high costs.	(Ahmed, et al., 2016; Singh, Singh and Dhal, 2022)

4.4 Biosorption of Heavy Metals Using Dead Aquatic Plants

The metal absorption and accumulation by aquatic macrophytes in a batch or continuous flow system could be assessed through different kinds of biosorption kinetic and isotherm models. For examples, PFO, PSO, Langmuir, Freundlich, and Temkin. However, the prediction using PFO and PSO models posed some limitations since they only accounted for the biosorption of metals on the binding sites of the plants and envisaged the mechanism of internal diffusion. Meanwhile, it excluded the external diffusion of heavy metals into the plants. Apart from that, the assumption mentioning the presence of local equilibrium between the heavy metal concentrations and the contaminated medium during the use of Langmuir and Freundlich models could be ambiguous. Still, they had been applied in absorption and phytoremediation studies (Obinnaa and Ebere, 2019). In this case, the utilization of waste biomass from aquatic plants as a biosorbent was studied. The changes that happened in the surface morphology of the dead aquatic plants before and after heavy metals biosorption were evaluated using several methods like SEM, EDX, XPS, and FTIR analysis. Each analysis technique was studied and discussed together with explanations and findings from various reliable literature papers.

4.4.1 Scanning of Electron Microscopy (SEM)

SEM is widely employed to observe the surface morphology of biosorbent material. In this context, SEM images reflect the effect of metal biosorption on plant biomass. The variation in surface morphology of the water lettuce in the control sample and the treated samples with Zn^{2+} concentration of 105 mg/L and Cd^{2+} concentration of 10 mg/L for 72 hours were investigated (Rodrigues, et al., 2017). Figure 4.6 (a) to (c) shows the modifications to the surface morphology of the plant before and after treating with metal ions. The plant appeared in a wrinkled folded form instead of a smooth, linear surface in the uncontaminated control sample. Opposingly, the plant under Cd^{2+} treatment exhibited tiny protrusions, granules, and holes on its surface structure, which did not appear in the control sample. The creased surface of treated plant biomass might be due to the modification in its composition and the interaction of the functional groups on the plant surface with the metals of various atomic radii and the binding to the metals with different types of bonds. Eventually, it would cause metal ions immobilization on the plant root. In addition, the formation of granules might be due to the deposition of metal complexes. The functional groups were found randomly embedded in small voids, pores, or holes of the plant surface that trap the metals. Notably, metal biosorption by the plant occurred internally and externally with the formation of metals complexes.

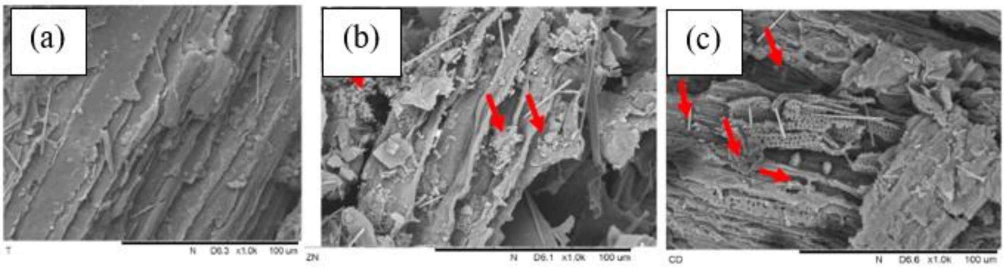

Figure 4.6: SEM Images of the Water Lettuce (a) Control Sample, (b) Treated with Zn^{2+} and (c) Treated with Cd^{2+} (Rodrigues, et al., 2017).

Moreover, Zheng, et al. (2016) also studied the surface morphology of water hyacinth. Based on the SEM images, the plant roots exhibited irregular and rough surfaces, which were preferable for metal biosorption. The accumulation of Cu^{2+} and Cd^{2+} in both single and binary metallic systems were also investigated, as shown in Figure 4.7 (a) to (d). As a result, both metals demonstrated a significant sorption amount on the biomass surfaces. This finding was agreed with the literature reported by Li, et al. (2014), in which the root of water hyacinth demonstrated an irregular shape despite a crystal clear appearance. The biosorption of Pb^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+} on the root of plants were portrayed from the SEM images, as shown in Figure 4.8 (a) to (e).

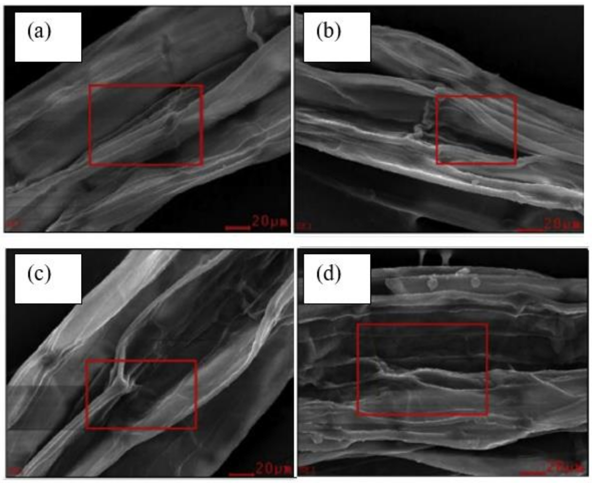

Figure 4.7: SEM Images of the Water Hyacinth Root Before Metal Sorption in the (a) Control Sample, and After the Metal Sorption of (b) Cu^{2+}, (c) Cd^{2+} and (d) Cu^{2+}/Cd^{2+} (Zheng, et al., 2016).

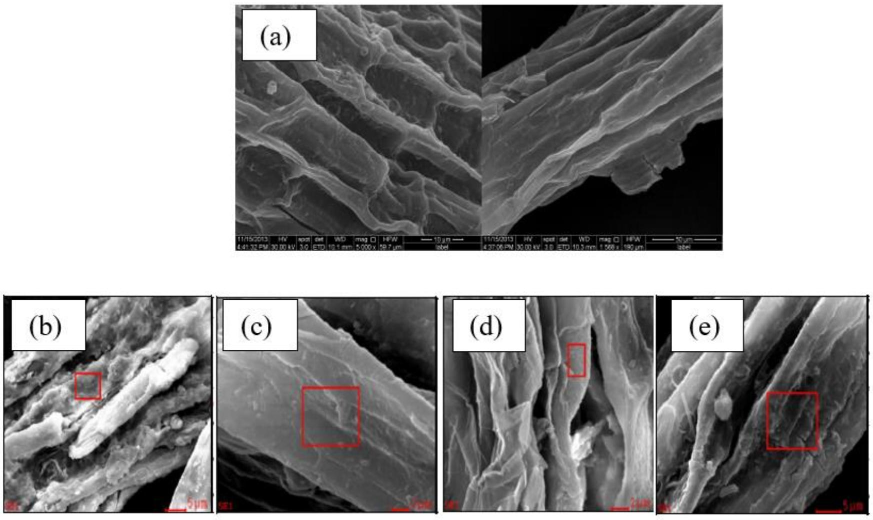

Figure 4.8: SEM Images of the Root of Water Hyacinth in the (a) Control Sample, and After Treated with (b) Pb^{2+}, (c) Zn^{2+}, (d) Cu^{2+} and (e) Cd^{2+} (Li, et al., 2014).

Moreover, Figure 4.9 (a) illustrates an obvious crinkled and indistinct texture of plant surface which could offer a larger surface area for metal biosorption. After the biosorption of Cr^{3+} and tetravalent chromium ions (Cr^{4+}), the surface of water hyacinth became rough and aggregated, whereas the microstructures turned irregular as demonstrated in Figure 4.9 (b) and (c). The variation spotted on the plant surface might be resulted from the accumulation and precipitation of Cr ions (Malar, et al., 2014; Parameswari, et al., 2021).

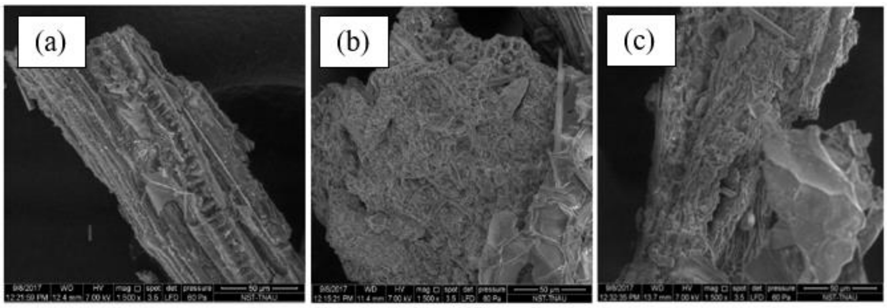

Figure 4.9: SEM Images of Water Hyacinth (a) Before Loaded, and After Loaded with (b) Cr^{3+} and (c) Cr^{4+} (Malar, et al., 2014; Parameswari, et al., 2021).

4.4.2 Energy-dispersive X-ray (EDX)

The SEM analysis is usually incorporated with the EDX analysis, which analyzes the elemental composition of the plant surface unloaded and loaded with metal ions. Parameswari, et al. (2021) found that the EDX spectra showed prominent peaks of Cr^{3+} coupled with a minor calcium (Ca) peak which was absent at the beginning. A declining trend was found in the magnesium (Mg), sodium (Na), potassium (K), and chlorine (Cl) composition. Specifically, Ca composition declined from 2.19 % to 0.96 %, while Na composition reduced from 0.49 % to 0 % after biosorption of Cr^{3+}. Moreover, the apparent peaks of Pb^{2+} observed in the EDX spectrum could be associated with the chelation effect of metals to organic compounds in the plant (Malar, et al., 2014).

Table 4.5 summarizes the elemental composition of the plant root without and with various metal biosorption. For example, Zheng, et al. (2016) suggested that the root of water hyacinth had stronger biosorption of Cu^{2+} than Cd^{2+}. Higher metal contents observed in the single metal system than the blank control sample confirmed the significant metal accumulation in plants. Nevertheless, the accumulated metal concentrations were reduced in the binary metal system. Furthermore, the results presented by Li, et al. (2014) demonstrated the highest biosorption of Pb^{2+}, followed by Cd^{2+}, Cu^{2+}, and Zn^{2+}. The elemental composition of the plants immersed in Cr^{3+} solution had been studied by Premalatha, et al. (2018). The results showed the existence of multiple functional groups like -COOH and hydroxyl (-OH) groups on the plant root due to the presence of Ca, carbon (C), and oxygen (O).

Table 4.5: Summary of Elemental Compositions of Water Hyacinth Plant Biomass Cultured in Various Metal Ions Solution.

Metal Ions	**Before/After Sorption**	**Elemental Compositions**	**References**
	Before	70.17 wt% carbon (C), 28.66 wt% oxygen (O), 0.33 wt% magnesium (Mg), 0.84 wt% calcium (Ca)	(Zheng, et al., 2016)
Cu^{2+}	After	61.54 wt% C, 3.92 wt% nitrogen (N), 30.19 wt% O, 4.21 wt% copper (Cu)	
Cd^{2+}	After	59.36 wt.% C, 4.02 wt% N, 31.19 wt% O, 5.43 wt% Cd	
Cu^{2+}/Cd^{2+}	After	58.61 wt% C, 5.16 wt% N, 31.94 wt% O, 3.66 wt% Cu, 0.62 wt% Cd	
Pb^{2+}	After	32.49 wt% C, 22.90 wt% O, 0.92 wt% silicon (Si), 1.88 wt% phosphorus (P), 4.80 wt% manganese (Mn), 2.09 wt% iron (Fe), 0.73 wt% Cu, 34.19 wt% lead (Pb)	(Li, et al., 2014)
Zn^{2+}	After	49.00 wt% C, 35.73 wt% O, 1.06 wt% Si, 1.95 wt% Mn, 2.26 wt% Fe, 9.98 wt% Zinc (Zn)	
Cu^{2+}	After	46.84 wt% C, 33.27 wt% O, 0.61 wt% aluminium (Al), 1.83 wt% Si, 2.74 wt% P, 0.26 wt% calcium (Ca), 1.03 wt% Mn, 2.56 wt% Fe, 10.85 wt% copper (Cu)	
Cd^{2+}	After	33.43 wt% C, 30.51 wt% O, 1.01 wt% Si, 3.69 wt% P, 1.08 wt% chlorine (Cl), 19.45 wt% Cd, 1.07 wt% Ca, 4.90 wt% Mn, 3.70 wt% Fe, 1.16 wt% Cu	
	Before	64.89 wt% C, 28.83 wt% O, 0.65 wt% sodium (Na), 0.58 wt% magnesium (Mg), 0.64 wt% Si, 1.51 wt% Cl, 1.50 potassium (K), 1.39 wt% Ca	(Premalatha, et al., 2018)
Cr^{3+}	After	37.60 C, 10.16 wt% O, 50.09 wt% Cr, 0.11 wt% Na, 0.08 wt% Mg, 0.54 wt% Si, 0.37 wt% Cl, 0.58 wt% K, 0.46 wt% Ca	

4.4.3 X-ray Photoelectron Spectroscopy (XPS)

XPS analysis is a method employed to provide insightful elemental surface analysis and chemical state analysis. This analysis is useful since the chemical environment surrounding the atom would influence the binding energy of the core electrons of an atom (Watts and Wolstenholme, 2019). The XPS spectra of plant roots before and after the metal biosorption study suggested that most nitrogen- and oxygen-consisting functional groups tended to bind with the metal ions, implying the active participation of metal biosorption on plant root (Zheng, et al., 2016). The water hyacinth root treated with Cd^{2+} demonstrated an insignificant shift of binding energy as compared to the control sample. This might be explained by the electron donation from the nitrogen atoms to the Cd^{2+} metal center, which indicated the metal chelation between the nitrogen-containing ligands and the metal ions.

Zheng, et al. (2016) found that biosorption of Cu^{2+} showed a greater binding ability to the amine groups, specifically with the protonated amine groups in the water hyacinth root as compared to the biosorption of Cd^{2+}. This was proven by the absence of the peak for protonated amine groups by liberating a significant amount of protons and cations. Based on the O1s deconvolution results, the ratio between C=O and C-O found in the plant root declined from 22% to 14% after the biosorption of Cd^{2+}, while it increased from 22% to 82% after the biosorption of Cu^{2+} (Zheng, et al., 2016). Such a shift indicated the change in electron density on different oxygen-comprising capabilities, which might be due to the complexation of the metal precipitates. To conclude, both metals could bind with the oxygen-containing groups on the plant root, yet water hyacinth demonstrated a stronger Cu^{2+} chelation potential than Cd^{2+}.

4.4.4 Fourier Transform Infrared (FTIR)

Apart from SEM-EDX and XPS study, the FTIR analysis had been performed to discover the functional groups participated in the metal biosorption by detecting the shifts in the vibration frequency of each functional group embedded on the plant surface before and after biosorption. Based on the finding reported by Li, et al. (2014), the FTIR result demonstrated obvious absorption peaks of water hyacinth root at nearly 3450, 2950, 2304, 1759, and

1500 cm^{-1}, respectively. These peaks represented different functional groups, such as hydroxyl, alkyl, carboxyl, phosphorus, and nitrogenous compounds, respectively. A broad range of absorption peak was observed between the range of 3200 to 3600 cm^{-1} on the root sample, which primarily indicated O-H and N-H stretching vibration of cell wall substances, proteins, and carbohydrates. The absorption bands situated at 2950, 2265-2455, 1650-1870, and 1335-1565 cm^{-1} represented C-H asymmetric stretching vibration in CH_3 and CH_2, P-H stretching vibration, C=O stretching vibration, and $-NO_2$ stretching vibration, respectively. The participating functional groups in the biosorption process with their associated wavelength are summarized in Table 4.6. In addition, Figure 4.10 illustrates the FTIR spectra of unloaded, Pb^{2+} loaded, Zn^{2+} loaded, Cu^{2+} loaded, and Cd^{2+} loaded plant root. A significant difference in the absorption peaks for several compounds, such as phosphorus, carboxyl, and nitrogenous, were observed after biosorption of heavy metals, implying that these functional groups had participated in the metal binding. Ester and ketone compounds that belong to the carboxyl groups were present in the cell wall pectin and membrane lipid, whereas phosphorus and nitrogenous compounds were essential materials to synthesize proteins.

Table 4.6: Functional Groups of Water Hyacinth Root with its Respective Wavelength (Li, et al., 2014).

Wavelength (cm^{-1})	**Functional Groups**
3200-3600	O-H and N-H stretching vibration of cell wall substance, proteins, and carbohydrate.
2950	C-H asymmetric stretching vibration in CH_3 and CH_2
2265-2455	P-H stretching vibration
1650-1870	C=O stretching vibration
1335-1565	NO_2 stretching vibration

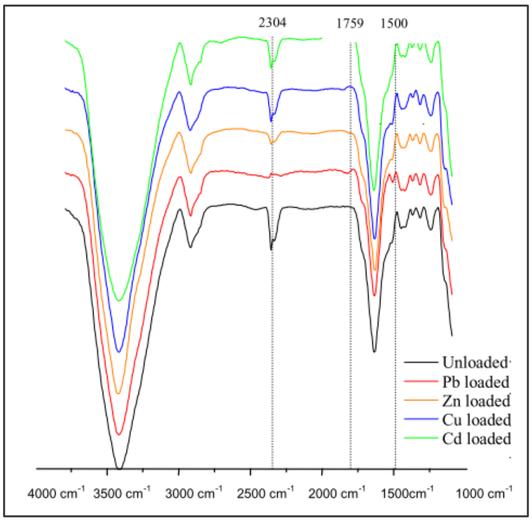

Figure 4.10: FTIR Spectra of Water Hyacinth Root (Li, et al.,2014).

The FTIR results discovered by different authors are tabulated in Table 4.7. Comparing the plant before or after biosorption of Cr^{3+}, Premalatha, et al. (2018) revealed a chemical shift in the peaks of O-H, N-H, and C-O groups. This finding was further supported by Parameswari, et al. (2021), who observed that the two extreme peaks between 2700 to 3500 cm^{-1} were represented the O-H groups stretching and N-H bonds, and indicated the presence of hydroxyl and amine groups. Moreover, intense spectral peak at 1024.98 cm^{-1} demonstrated the C-O group stretching. After Cr^{3+} biosorption, broad peaks were found at 1024.98 and 1019.19 cm^{-1}, exhibiting the existence of O-H, N-H, and C-O bonds stretching. Apart from that, the FTIR results of the Cr^{4+} loaded plant showed a broad peak at 3321.78 cm^{-1} and strong spectra at 1581.34 cm^{-1}, implying the O-H and N-H groups stretching and the NH_3 group antisymmetric deformation, respectively. Lastly, the peak at 1024.02 cm^{-1} was attributed to the C-O functional groups. Importantly, it was validated that C-H groups did not contribute towards biosorption of Cr because the peaks location and intensity at 2919.70 cm^{-1} remained similar after biosorption. Similarly, marked alterations were detected in the FTIR spectra of water hyacinth root before and after Cr^{3+} and Cr^{4+} loading, owing to the chemical shift in the positions of O-H, N-H, and C-O groups peaks. This confirmed the biosorption of Cr^{3+} and Cr^{4+} onto the plant.

Table 4.7: FTIR Results of Water Hyacinth Plant Biomass Before and After the Biosorption of Cr^{3+} and Cr^{4+}.

Heavy Metals	**Biosorption**	**Wavelength (cm^{-1})**	**Functional Groups**	**References**
Cr^{3+}/ Cr^{4+}	Before	3332.39	O-H group stretching	(Parameswari, et al., 2021; Premalatha, et al., 2018)
		2919.70	C-H groups stretching	
		2291.02	N-H groups stretching	
		2111.67	C≡C groups stretching	
		1615.09	C=O groups stretching	
		1024.98	C-O bonds stretching	
Cr^{3+}	After	3284.18	O-H and N-H groups stretching	
		2919.70	C-H groups stretching	
		1019.19	C-O bonds stretching	
Cr^{4+}	After	3321.78	O-H and N-H groups stretching	
		2919.70	C-H groups stretching	
		1581.34	NH_3 group antisymmetric deformation	
		1024.02	C-O bonds stretching	

4.4.5 Biosorption Kinetics

The biosorption kinetic is a method to determine and investigate the manipulating mechanism of biosorption, which can be chemisorption or mass transfer. Correspondingly, it aids in attaining the operating conditions for batch processes in the industry. The kinetic data with a good intercorrelation provides insightful information regarding the biosorption behaviour of the heavy metals on the plant surfaces (Anzeze, et al., 2014). Both the PFO model and PSO models were evaluated for the biosorption of Cd^{2+} onto the plant to identify the controlling mechanism. Equation (4.6) presents the PFO kinetic model equation, whereby the values of q_e and k_1 were obtained from the intercept and the slope of the graph of $\log(q_e - q_t)$ versus t. On the other hand, the PSO equation displayed in Equation (4.7) presumed that chemisorption was the limiting step in metal biosorption. Besides, it considered the binding of metal cations onto two active sites on the plant surface. The values of q_e and k_2 were obtained from the intercept and the slope of the graph of t/q_t versus t.

PFO model equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{4.6}$$

PSO model equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{4.7}$$

where

k_1 = PFO kinetic rate constant, min^{-1}

k_2 = PSO kinetic rate constant, g/mg·min

q_e = amount of metal sorbed at equilibrium, mg/g

q_t = amount of metal sorbed at time t, mg/g

t = contact time, min

Table 4.8 summarizes the experimental data for the important parameters of PFO and PSO kinetic models extracted from various sources. The PFO kinetic model showed infeasibility in describing the biosorption process of Cu^{2+}, Co^{2+}, and iron (III) ions (Fe^{3+}) onto the plant surface. This was because the plot of $\log{(q_e - q_t)}$ versus t reflected negative slopes and low correlation values (R^2). Opposingly, PSO kinetic model showed feasibility in demonstrating the metal biosorption process as the graph of t/q_t versus t fitted linearly with the calculated R^2 value greater than 0.999 (Sadeek, et al., 2015). Moreover, the testing of four kinetics models, such as PFO, PSO, elovich, and intraparticle diffusion model incorporated with the biosorption of Cr^{3+} and Cr^{4+} onto the water hyacinth biomass had been studied. As a result, relatively high R^2 values of 0.999 for both Cr ions were achieved by PSO kinetic model. Additionally, the q_e calculated for Cr^{3+} and Cr^{4+} were 10.2 mg/g and 9.01 mg/g, respectively. These computed values were highly consistent to the experimental q_e with the value of 9.99 and 8.99 mg/g (Parameswari, et al., 2021). To conclude, the PSO kinetics model demonstrated a well fit to the data than PFO, implying that the biosorption rate was manipulated by chemisorption.

Table 4.8: Kinetic Studies on the Heavy Metals Biosorption by Water Hyacinth Plant Biomass.

Plants	**Metal Ions**	**PFO Model**			**PSO Model**			**References**
		$q_{e,cal}$ **(mg/g)**	k_1 **(min^{-1})**	R^2	$q_{e,cal}$ **(mg/g)**	k_2 **(g/(mg·min))**	R^2	
Water hyacinth (*Eichhornia crassipes)*	Cr^{3+}	1.09	0.0701	0.9520	1.440	0.3307	1.0000	(Febrianto, et al., 2009)
	Cr^{4+}	1.27	0.0032	0.8730	1.910	0.0078	0.9550	
	Cr^{2+}	-	0.0310	0.9590	5.320	0.0284	0.9980	(Murithi, et al., 2014)
	Cu^{2+}	-	0.04145	0.9950	65.80	0.0280	1.0000	(Sadeek, et al., 2015)
	Co^{2+}	-	0.01612	0.9030	86.90	0.0160	0.9990	
	Fe^{3+}	-	0.00023	0.5640	181.8	0.0040	1.0000	
	Pb^{2+}	-	-	-	2.281	0.2831	0.9900	(Li, et al., 2014)
	Zn^{2+}	-	-	-	1.714	4.9386	0.9970	
	Cd^{2+}	-	-	-	1.658	2.7124	0.9910	

Furthermore, the intraparticle diffusion model was evaluated for the heavy metal biosorption behaviour. The kinetic model is presented in Equation (4.8).

Intraparticle diffusion model,

$$q_t = k_i t^{1/2} + C \tag{4.8}$$

where
k_i = interparticle diffusion rate constant, mg/(g·min$^{1/2}$)
C = degree of deviation from the interparticle diffusion kinetics, mg/g

The plot of biosorption capacity (q_t) versus square root of biosorption time ($t^{1/2}$) demonstrated curves with three trends. These trends were representing the three biosorption stages of metal ions by plant. The biosorption of heavy metals was first happening on the outer surface of the plant until reaching the saturation limit. Secondly, the sorbed metal ions started to diffuse into the pores of the plant biosorbent. During this stage, the rate of diffusion slowed down owing to the increasing resistance resulting from the crowded metal ions. In the last stage, the metal ions concentration remained in the solution and the metal ions concentration sorbed onto the biosorbent surface would reach the final equilibrium. The biosorption rate reduced greatly and took place at a longer duration at this stage. To further clarify, the continual decreasing trend of the biosorption capacity might be due to the desorption of metals from the plant surface to the solution (Sadeek, et al., 2015).

These findings were in agreement with the results reported by Parameswari, et al. (2021). The author suggested that the biosorption of Cr ions onto the plant surface might happen in two steps. The first step indicated the diffusion of metal ions at the boundary layer to the exterior surface of the plant, whereas the second step was due to the intraparticle diffusion. Moreover, Murithi, et al. (2014) revealed that the biosorption kinetics did not fit well to the intraparticle diffusion model since it gave a low R^2 value of 0.7347.

4.4.6 Biosorption Isotherms

The biosorption equilibrium between heavy metal ions and aquatic macrophytes is commonly determined by the biosorption isotherms. Among the four two-parameter biosorption isotherm models, namely Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models (Buasri, et al., 2012), Langmuir and Freundlich models were the commonly used models in biosorption since both isotherms are easy to understand, straightforward, and well-established (Rodrigues, et al., 2017).

For the Langmuir isotherm model, several assumptions had been made. First, it assumed that each biosorption site on the homogenous surface of plant could only sorb one metal ion. Secondly, the biosorption took place with identical activation energy (Premalatha, et al., 2018). Thirdly, it assumed monolayer biosorption and the maximum biosorption happened when the binding sites on the plant surface were saturated with metal ions (Sadeek, et al., 2015). Furthermore, the metal ions being sorbed will not interact with other ions (Rodrigues, et al., 2017). The Langmuir model is represented in the non-linearized and linearized forms, as shown in Equations (4.9) and (4.10). The maximum biosorption capacity and the Langmuir constant were acquired from the slope and intercept demonstrated in the graph of C_e/q_e versus C_e.

Non-linearized form of Langmuir model,

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{4.9}$$

Linearized form of Langmuir model,

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \tag{4.10}$$

where

K_L = Langmuir constant, L/mg

q_m = maximum monolayer biosorption capacity, mg/g

q_e = number of metal ions sorbed, mg/g

C_e = equilibrium constant of metal ions, mg/L

The further analysis of the Langmuir equation was performed employing the dimensionless constant known as separation factor (K_R) to indicate whether the biosorption of metal ion was unfavourable, favourable, linear, or irreversible (Premalatha, et al., 2018). The value of K_R between 0 and 1 indicated a favourable biosorption. However, if the value was greater than 1, it meant the biosorption was unfavourable. The K_R value of 1 and 0 indicated a linear and irreversible biosorption process, respectively. Equation (4.11) represents the definition of K_R.

$$K_R = \frac{1}{1+K_L C_o} \tag{4.11}$$

where

K_R = separation factor

C_o = initial metal concentration, mg/L

Opposingly, the Freundlich isotherm model is an equation describing the biosorption of metal ion onto the heterogeneous surface of plant biomass by considering multiple-layer biosorption (Buasri, et al., 2012). Apart from that, the biosorption capacity was correlated to the concentration of sorbed metal ions at equilibrium. This isotherm was more appropriate for indicating biosorption at high metal concentrations despite low concentrations (Sadeek, et al., 2015). The non-linear and linear forms of the Freundlich models are presented in Equations (4.12) and (4.13). The intensity of biosorbent (n) and the value of the Freundlich constant could be acquired from the gradient and intercept of the Freundlich graph of log q_e versus log C_e. The magnitude of the exponent n implied the intensity of biosorption process. The biosorption could be characterized as strong if the n value was between 2 to 10 while the n value of 1 to 2 was classified as moderately strong biosorption, and the n value smaller than 1 was considered as poor biosorption (Premalatha, et al., 2018).

Non-linearized form of Freundlich model,

$$q_e = K_F {C_e}^{1/n} \tag{4.12}$$

Linearized form of Freundlich model,

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \qquad (4.13)$$

where

K_F = Freundlich constant, mg/g

n = Freundlich biosorption intensity

Table 4.9 summarizes the biosorption isotherm constant and the R^2 values for Langmuir and Freundlich models. These data were acquired for the biosorption of different metal ions such as Cd^{2+}, Cr^{2+}, Cr^{3+}, Cr^{4+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+} onto various plant biomasses. The study conducted by Buasri, et al. (2012) suggested that the biosorption equilibrium data for Cu^{2+} fitted well to both Langmuir and Freundlich models. Nevertheless, the Langmuir model demonstrated a higher R^2 value of 0.9933 for Cu^{2+} biosorption, while the Freundlich model showed a greater R^2 value of 0.9948 for Zn^{2+} biosorption. The high R^2 values between 0.8397 to 0.9933 for Cu^{2+} biosorption and between 0.8041 to 0.9948 for Zn^{2+} biosorption were attained. Hence, the results confirmed that the equilibrium experimental biosorption data for both metal ions fitted well to the Langmuir and Freundlich isotherms.

Based on the experimental data presented by Miretzky, Saralegui and Fernández Cireslli (2006), the results showed that Cd^{2+} and Ni^{2+} only fitted well to the Langmuir model, indicating that the biosorption of these metal ions taken place in a monolayer form. The q_m results demonstrated a greater biosorption of Ni^{2+} than Cd^{2+} in *Lemna minor, Spirodela intermedia*, and *Pistia stratiotes* plant biomasses at higher metal concentrations. Opposingly, Cd^{2+} biosorption was higher than Ni^{2+} in these plant biomasses at lower metal concentrations. However, Freundlich isotherm was claimed as the better model for the coexistent biosorption of all heavy metals studied. The K_F values suggested that both *Lemna minor* and *Spirodela intermedia* showed a greater Pb^{2+} removal compared to *Pistia stratiotes*. Concretely, Freundlich isotherms could fully justify the high removal rate of Pb^{2+} by all plants.

Table 4.9: Summary of the Langmuir and Freundlich Isotherm Fittings for Various Plants.

Plants	**Metal Ions**	**Langmuir**			**Freundlich**			**References**
		q_m **(mg/g)**	K_L **(L/mg)**	**R^2**	n **(L/mg)**	K_F **(mg/g)**	**R^2**	
Water hyacinth (*Eichhornia crassipes*)	Cu^{2+}	181.80	0.0760	0.9933	2.7198	0.0760	0.9933	(Sadeek, et al., 2015)
		35.62	0.2300	0.9770	1.1905	1.0300	0.9930	(Li, et al., 2014)
	Zn^{2+}	70.23	0.2200	0.9840	1.4925	1.1600	0.9910	(Li, et al., 2014)
	Cr^{3+}	76.92	0.0844	0.9990	2.9142	12.0226	0.8640	(Parameswari, et al., 2021)
		6.61	0.0500	0.9570	2.3800	1.4400	0.9180	(Febrianto, et al., 2009)
	Cr^{4+}	55.56	0.0112	0.9890	2.0833	2.4434	0.8210	(Parameswari et al., 2021)
		0.34	0.9170	0.9950	6.2100	0.1500	0.9950	(Febrianto, et al., 2009)
	Co^{2+}	222.20	0.0380	0.9980	1.4000	1.3000	0.9990	(Sadeek, et al., 2015)
	Fe^{3+}	294.10	0.0210	0.9990	1.3000	0.2000	0.9990	
	Cr^{2+}	104.16	0.0178	0.9942	1.5420	2.7500	0.8940	(Murithi, et al., 2014)
	Pb^{2+}	87.61	0.3400	0.9640	2.6316	3.9200	0.9970	(Li, et al., 2014)
	Cd^{2+}	66.16	0.1800	0.9590	2.2727	1.2300	0.9910	(Li, et al., 2014)
		104.16	0.0178	0.9942	1.542	2.7479	0.8940	(Murithi, et al., 2014)

Table 4.9 (Continued)

Plants	**Metal Ions**	**Langmuir**			**Freundlich**			**References**
		q_m **(mg/g)**	K_L **(L/mg)**	**R^2**	n **(L/mg)**	K_F **(mg/g)**	**R^2**	
Duckweed (*Spirodela intermedia*)	Cd^{2+}	0.036	5.85	0.9990	0.69	0.43	0.9540	(Miretzky, Saralegui and Fernández Cirelli, 2006)
	Ni^{2+}	0.060	0.50	0.9050	0.79	0.16	0.9950	
	Pb^{2+}	-	-	-	1.41	166.49	0.9640	
	Cu^{2+}	-	-	-	1.09	1.01	0.9530	
	Zn^{2+}	-	-	-	1.19	1.03	0.9230	
Duckweed (*Lemna minor*)	Cd^{2+}	0.033	14.58	0.9990	0.58	0.34	0.9120	
	Ni^{2+}	0.057	1.40	0.9800	0.72	0.24	0.973	
	Pb^{2+}	-	-	-	1.48	447.92	0.96900	
	Cu^{2+}	-	-	-	0.90	0.74	0.9580	
	Zn^{2+}	-	-	-	1.12	1.06	0.8080	
Water lettuce (*Pistia stratiotes*)	Cd^{2+}	0.037	2.19	0.9960	0.77	0.77	0.9720	
	Ni^{2+}	0.082	0.12	0.6970	0.94	0.94	0.9970	
	Pb^{2+}	-	-	-	0.32	0.01	0.7170	
	Cu^{2+}	-	-	-	0.94	0.12	0.9870	
	Zn^{2+}	-	-	-	0.93	0.25	0.9870	

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Water plays an irreplaceable role in sustaining the life of living beings including humans, animals, and plants. The increasing water contamination with heavy metals became a serious concern nowadays due to fast 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 via an environmentally-friendly and cost-effective way. This research study investigated various process parameters affecting the phytoremediation behaviour 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. Besides, 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 kinetic of phytoremediation was studied to determine the effectiveness and natural behaviour 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 nanoparticles 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 the biomass volume, save transportation costs, and decompose almost all the organic matter in the contaminated plant biomass.

Characterization of plant biomass before and after biosorption of heavy metals was studied. From the SEM micrographs, the results suggested that the plant biomass had irregular, wrinkled, and folded surfaces before treating with metal ions, which was favourable for the metal biosorption attributable to the larger surface area. After biosorption of heavy metal, the plant surface became rough and aggregated along with tiny protrusions, granules, and holes, indicating the occurrence of heavy metal biosorption on the plant biomass. Based on the EDX analysis, the biosorption of heavy metal onto the plant biomass had been successfully proven through the presence of prominent peaks of sorbed metal ions such as Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, and Cr^{3+}, which were absent at the beginning. This followed by the reduction of other cations and anions like Mg^{2+}, Na^{+}, K^{+}, and Cl^{-} present initially in the plant biomass. Moreover, the XPS analysis result confirmed that the binding abilities of most nitrogen- and oxygen-consisting functional groups embedded in the plant surface with the metal ions through metal chelation and metal precipitation, which could be observed through the shift in binding energy at the individual peak that representing different functional groups. Additionally, the significant chemical shift in absorption peaks of O-H, N-H, and C-O groups had confirmed the participation of heavy metal ions in the biosorption process. In terms of kinetic and isotherm studies, most heavy metals biosorption onto the plant biomass were fitted well to the PSO kinetic model and Freundlich isotherm model with high R^2 values. The results implied that multilayer chemisorption of metal ions occurred on the heterogeneous surface of plant. Besides, monolayer biosorption of Cr^{3+} and Cr^{4+} onto the homogenous water hyacinth plant surface was suggested by the Langmuir isotherm model.

In a nutshell, all research objectives were attained. The aquatic plants, especially water hyacinth, demonstrated a great efficiency to absorb 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.

5.2 Recommendations for Future Work

In this study, it was found that the data reported by various researchers might be slightly different due to the different experimental setup and operating conditions. Apart from that, there was limited readily available information to demonstrate the efficiency, effectiveness, and feasibility of floating aquatic macrophytes in phytoremediation at large-scale implementation. Besides, the current research on the innovative post-harvested plant biomass disposal methods was scarce. Therefore, some recommendations were suggested to enhance the current phytoremediation technology.

Firstly, researchers could employ genetic engineering to cultivate transgenic plants and practice traditional breeding like crossbreeding to improve the performance of phytoremediation (Shen, et al., 2022). Specifically, transgenic plants could accumulate more metals, tolerate metal toxicity, and be highly adaptable to various climatic environments (Sarwar, et al., 2017), demonstrating favourable accumulator traits in phytoremediation. Additionally, the overexpression of the correlated genes could be manipulated to promote the uptake, translocation, and sequestration of metal ions by plants (Oladoye, Olowe and Asemoloye, 2022). Furthermore, the addition of plant hormones, organic acids, rhizobacteria, or fungi might be a novel approach to enhance phytoremediation. Efforts and further explorations of the known phytoremediation mechanisms, plant growth, and biomass disposal methods could be made. For example, the interaction between the specific microbes with the plants could be analysed at the biomolecular levels to offer in-depth knowledge of the metal uptake route within the plants (Kurniawan, et al., 2022). Lastly, the actual field remediation experiment could be optimized and tested to improve the phytoremediation performance in the future.

REFERENCES

Abbas, Z., Arooj, F., Ali, S., Zaheer, I.E., Rizwan, M. and Riaz, M.A., 2019. Phytoremediation of landfill leachate waste contaminants through floating bed technique using water hyacinth and water lettuce. *International Journal of Phytoremediation*, 21(13), pp.1356–1367.

Abdel-Shafy, H.I. and Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25(1), pp.107–123.

Adelagun, R.O.A., Kamba, E.A., Berezi, E.P., Airhole, E.F., Gnana, O.C. and Moonee, B.O., 2021. Phthalate esters in the environment: sources and quantification. *American Journal of Chemistry*, 11(2), pp.37–41.

Afroz, R., Masud, M.M., Akhtar, R. and Duasa, J.B., 2014. Water pollution: challenges and future direction for water resource management policies in Malaysia. *Environment and Urbanization ASIA*, 5(1), pp.63–81.

Ahmad, I., Imran, M., Hussain, M.B. and Hussain, S., 2017. Remediation of organic and inorganic pollutants from soil: the role of plant-bacteria partnership. *Chemical Pollution Control with Microorganisms*, pp.197–243.

Ahmed, S., Annu, Ikram, S. and Yudha, S., 2016. Biosynthesis of gold nanoparticles: a green approach. *Journal of Photochemistry and Photobiology Biology*, 161, pp.141–153.

Akpor, O.B., Otohinoyi, D.A., Olaolu, T.D., and Aderiye, B.I., 2014. Pollutants in wastewater: impacts and remediation process. *International Journal of Environment Research and Earth Science*, 3(3), pp.50–59.

Alhelou, H.H., Hamedani-Golshan, M.E., Njenda, T.C. and Siano, P., 2019. A survey on power system blackout and cascading events: research motivations and challenges. *Energies*, 12(4), pp.1–28.

Ali, S., Abbas, Z., Rizwan, M., Zaheer, I.E., Yavas, I., Ünay, A., Abdel-Daim, M.M., Bin-Jumah, M., Hasanuzzaman, M. and Kalderis, D., 2020. Application of floating aquatic plants in phytoremediation of heavy metals polluted water: a review. *Sustainability*, 12(5), pp.1–33.

Ali, Z., Waheed, H., Kazi, A.G., Hayat, A. and Ahmad, M., 2015. Duckweed: an efficient hyperaccumulator of heavy metals in water bodies. In: P. Ahmad, ed. *Plant Metal Interaction: Emerging Remediation Techniques*. Elsevier Inc. pp.411–429.

Ansari, A.A., Naeem, M., Gill, S.S. and AlZuaibr, F.M., 2020. Phytoremediation of contaminated waters: an eco-friendly technology based on aquatic macrophytes application. *Egyptian Journal of Aquatic Research*, 46, pp.371–376.

Anzeze, D.A., Onyari, J.M., Shiundu, P.M. and Gichuki, J.W., 2014. Equilibrium and kinetics studies for the biosorption of aqueous Cd (II) ions onto *Eichhornia crassipes* biomass. *IOSR Journal of Applied Chemistry*, 7(1), pp.29–37.

Aurangzeb, N., Nisa, S., Bibi, Y., Javed, F. and Hussain, F., 2014. Phytoremediation potential of aquatic herbs from steel foundry effluent. *Brazilian Journal of Chemical Engineering*, 31(4), pp.881–886.

Ayub, S., Ali, A., Khursheed, S., Zarei, A., Alam, I., Asgari, E. and Changani, F., 2020. Removal of heavy metals (Cr, Cu, and Zn) from electroplating wastewater by electrocoagulation and adsorption processes. *Desalination and water treatment*, 179, pp.263–271.

Bansode, R.R., 2002. *Treatment of organic and inorganic pollutants in municipal wastewater by agricultural by-product based granular activated carbons*. Master. Louisiana State University.

Bashir, A., Malik, L.A., Ahad, S., Manzoor, T., Bhat, M.A., Dar, G.N. and Pandith, A.H., 2019. Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods. *Environmental Chemistry Letters*, 17(2), pp.729–754.

Basile, A., Sorbo, S., Conte, B., Castaldo Cobianchi, R., Trinchella, F., Capasso, C. and Carginale, V., 2012. Toxicity, accumulation, and removal of heavy metals by three aquatic macrophytes. *International Journal of Phytoremediation*, 14(4), pp.374–387.

Bennicelli, R., Stępniewska, Z., Banach, A., Szajnocha, K. and Ostrowski, J., 2004. The ability of *Azolla caroliniana* to remove heavy metals (Hg(II), Cr(III), Cr(VI)) from municipal wastewater. *Chemosphere*, 55(1), pp.141–146.

Bonanno, G., Cirelli, G.L., Toscano, A., Giudice, R. L and Pavone, P., 2013. Heavy metal content in ash of energy crops growing in sewage-contaminated natural wetlands: potential applications in agriculture and forestry? *Science of the Total Environment*, 452, pp.349–354.

Buaisha, M., Balku, S. and Özalp-Yaman, S., 2020. Heavy metal removal investigation in conventional activated sludge systems. *Civil Engineering Journal*, 6(3), pp.470–477.

Buasri, A., Chaiyut, N., Tapang, K., Jaroensin, S. and Panphrom, S., 2012. Biosorption of heavy metals from aqueous solutions using water hyacinth as a low cost biosorbent. *Civil and Environmental Research*, 2(2), pp.17–25.

Burca, N. and Watson, R.R., 2014. Fish Oil Supplements, Contaminants, and Excessive Doses. In: R.R. Watson and F.D. Meester, eds. *Omega-3 Fatty Acids in Brain and Neurological Health*. Elsevier. pp.447–454.

Bushra, R., Naushad, M. and Ahmad, A., 2017. Removal of pollutants using organic/inorganic composite sorbents: a review. *Ion exchange letters*, 10, pp.6–16.

Buta, E., Paulette, L., Mihăiescu, T., Buta, M. and Cantor, M., 2011. The influence of heavy metals on growth and development of *Eichhornia crassipes* species, cultivated in contaminated water. *Notulae Botanicae Horti Agrobotanici Cluj-Napoca*, 39(2), pp.135–141.

Buta, E., Török, A., Csog, Á., Zongo, B., Cantor, M., Buta, M. and Majdik, C., 2014. Comparative studies of the phytoextraction capacity of five aquatic plants in heavy metal contaminated water. *Notulae Botanicae Horti Agrobotanici Cluj-Napoca*, 42(1), pp.173–179.

Chandra, S., 2020. Study of electrocoagulation process for removal of heavy metals from industrial wastewater: a review. *International Journal of Engineering Research & Technology*, 9(9), pp.993–999.

Chaudhary, K., Jan, S. and Khan, S., 2015. Heavy metal ATPase (HMA2, HMA3, and HMA4) genes in hyperaccumulation mechanism of heavy metals. *Plant Metal Interaction: Emerging Remediation Techniques*, pp.545–556.

Chen, D., Cheng, Y., Zhou, N., Chen, P., Wang, Y., Li, K., Huo, S., Cheng, P., Peng, P., Zhang, R., Wang, L., Liu, H., Liu, Y. and Ruan, R., 2020. Photocatalytic degradation of organic pollutants using TiO_2-based photocatalysts: a review. *Journal of Cleaner Production*, 268, pp.1–14.

Cobzaru, C. and Inglezakis, V., 2015. Ion exchange. Progress in Filtration and Separation. *Elsevier Ltd*., pp.425–498.

Comer, C., 2021. *Research guides: systematic reviews & meta-analyses: eligibility criteria*. [online] Available at: <https://guides.lib.vt.edu/SystematicReviews/EligibilityCriteria> [Accessed 17 August 2021].

Cunningham, S.D. and Ow, D.W., 1996. Promises and prospects of phytoremediation. *Plant Physiology*, 110(3), pp.715–719.

Das, S., Goswami, S. and Talukdar, A. Das, 2014. A study on cadmium phytoremediation potential of water lettuce, *Pistia stratiotes L. Bulletin of Environmental Contamination and Toxicology*, 92(2), pp.169–174.

Dhaliwal, S.S., Sharma, V., Taneja, P.K., Shukla, A.K., Kaur, L., Verma, G., Verma, V. and Singh, J., 2022. Effect of cadmium and ethylenediamine tetraacetic acid supplementation on cadmium accumulation by roots of *Brassica species* in Cd spiked soil. *Environmental Science and Pollution Research*, 29(4), pp.6000–6009.

Dhir, B., Sharmila, P. and Saradhi, P.P., 2008. Photosynthetic performance of *Salvinia natans* exposed to chromium and zinc rich wastewater. *Brazilian Journal of Plant Physiology*, 20(1), pp.61–70.

Dhir, B., Sharmila, P., Saradhi, P.P. and Nasim, S.A., 2009. Physiological and antioxidant responses of *Salvinia natans* exposed to chromium-rich wastewater. *Ecotoxicology and Environmental Safety*, 72(6), pp.1790–1797.

Dhir, B., Sharmila, P., Saradhi, P.P., Sharma, S., Kumar, R. and Mehta, D., 2011. Heavy metal induced physiological alterations in *Salvinia natans*. *Ecotoxicology and Environmental Safety*, 74(6), pp.1678–1684.

Dhokpande, S.R., and Kaware, J.P., 2013. Biological methods for heavy metal removal: a review. *International Journal of Engineering Science and Innovative Technology*, 2(5), pp.304–309.

Dijoo, Z.K., Ali, R. and Hameed, M., 2020. Role of free-floating aquatic macrophytes in abatement of the disturbed environs. *Bioremediation and Biotechnology*, 4, pp.259–274.

Dixit, A., Dixit, S. and Goswami, C., 2011. Process and plants for wastewater remediation: a review. *Scientific Reviews & Chemical Communication*, 1(1), pp.71–77.

Du, Y., Wu, Q., Kong, D., Shi, Y., Huang, X., Luo, D., Chen, Z., Xiao, T. and Leung, J.Y.S., 2020. Accumulation and translocation of heavy metals in water hyacinth: maximising the use of green resources to remediate sites impacted by e-waste recycling activities. *Ecological Indicators*, 115, pp.1–8.

Dyjak, A., 2021. *Health effects of heavy metal pollution in water*. [online] Available at: <https://www.hydroviv.com/blogs/water-smarts/heavy-metal-toxicity> [Accessed 28 June 2021].

Etim, E.E., 2012. Phytoremediation and its mechanisms: a review. *International Journal of Environment and Bioenergy*, 2(3), pp.120–136.

Emamverdian, A., Ding, Y., Mokhberdoran, F. and Xie, Y., 2015. Heavy metal stress and some mechanisms of plant defence response. *The Scientific World Journal*, pp.1–18.

Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y.H., Indraswati, N. and Ismadji, S., 2009. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *Journal of Hazardous Materials*, 162, pp.616–645.

Fletcher, J., Willby, N., Oliver, D.M. and Quilliam, R.S., 2020. Phytoremediation using aquatic plants. In: B.R. Shmaefsky, ed. *Phytoremediation. Concepts and Strategies in Plant Sciences*. Springer International Publishing, pp.205–260.

Fu, F. and Wang, Q., 2011. Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management*, 92(3), pp.407–418.

Gakwisiri, C., Raut, N., Al-Saadi, A., Al-Aisri, S. and Al-Ajmi, A., 2012. A critical review of removal of zinc from wastewater. *Lecture Notes in Engineering and Computer Science*, 2197, pp.627–630.

Giri, A.K., 2012. *Removal of arsenic (III) and chromium (VI) from the water using phytoremediation and bioremediation techniques*. PhD. Department of Chemistry National Institute of Technology.

GracePavithra, K., Jaikumar, V., Kumar, P.S. and SundarRajan, P.S., 2019. A review on cleaner strategies for chromium industrial wastewater: present research and future perspective. *Journal of Cleaner Production*, 228, pp.580–593.

Greger, M., 1999. *Metal availability and bioconcentration in plants*. Sweden: Stockholm University.

Gupta, P., Roy, S. and B. Mahindrakar, A., 2012. Treatment of water using water hyacinth, water lettuce and vetiver grass: a review. *Resources and Environment*, 2(5), pp.202–215.

Haller, W.T., 2016. Effects of salinity on growth of several aquatic macrophytes. *Ecology Society of America*, 55(4), pp.891–894.

Hasan, S.H., Talat, M. and Rai, S., 2007. Sorption of cadmium and zinc from aqueous solutions by water hyacinth (*Eichhornia crassipes*). *Bioresource Technology*, 98(4), pp.918–928.

Hegazy, A.K., Kabiel, H.F. and Fawzy, M., 2009. Duckweed as heavy metal accumulator and pollution indicator in industrial wastewater ponds. *Desalination and Water Treatment*, 12(1–3), pp.400–406.

Hua, J., Zhang, C., Yin, Y., Chen, R. and Wang, X., 2012. Phytoremediation potential of three aquatic macrophytes in manganese-contaminated water. *Water and Environment Journal*, 26(3), pp.335–342.

Huang, C.H., Shen, S.Y., Dong, C.D., Kumar, M. and Chang, J.H., 2020. Removal mechanism and effective current of electrocoagulation for treating wastewater. *Water*, 12(2614), pp.1–14.

Huynh, A.T., Chen, Y.C. and Tran, B.N.T., 2021. A small-scale study on removal of heavy metals from contaminated water using water hyacinth. *Processes*, 9(10), pp.1–9.

Ingole, N.W. and Bhole, A.G., 2018. Removal of heavy metals from aqueous solution by water hyacinth (*Eichhornia crassipes*). *Journal of Water Supply*, 8, pp.119–128.

Jeevanantham, S., Saravanan, A., Hemavathy, R. V., Kumar, P.S., Yaashikaa, P.R. and Yuvaraj, D., 2019. Removal of toxic pollutants from water environment by phytoremediation: a survey on application and future prospects. *Environmental Technology and Innovation*, 13, pp.264–276.

Jing, R., Fusi, S. and Kjellerup, B.V., 2018. Remediation of polychlorinated biphenyls in contaminated soils and sediment: state of knowledge and perspectives. *Frontiers in Environmental Science*, 6(7), pp.79.

Kamalu, C.I.O, Okere, P.C., Egbufor, U.C., Nwandikom, G.I., Obijiaku, J.C. and Asomugha, C.C., 2017. Modelling and optimization of phytoremediation kinetics of metals in soil by a plant hyperaccumulator. *American Journal of Engineering Research*, 6, pp.196–207.

Keeffe, D.H., Hardy, J.K. and Rao, R.A., 1984. Zinc uptake by the water hyacinth: effects of solution factors. *Environmental Pollution*, 34, pp.133–147.

Kovacs, H. and Szemmelveisz, K., 2017. Disposal options for polluted plants grown on heavy metal contaminated brownfield lands: a review. *Chemosphere*, 166, pp.8–20.

Kumar, S. and Deswal, S., 2020. Phytoremediation capabilities of *Salvinia molesta*, water hyacinth, water lettuce, and duckweed to reduce phosphorus in rice mill wastewater. *International Journal of Phytoremediation*, 22(11), pp.1097–1109.

Kumar, V., Singh, J., Pathak, V.V., Ahmad, S. and Kothari, R., 2017. Experimental and kinetics study for phytoremediation of sugar mill effluent using water lettuce (*Pistia stratiotes*) and its end use for biogas production. *3 Biotech*, 7(5), pp.1–10.

Kurade, M.B., Ha, Y.H., Xiong, J.Q., Govindwar, S.P., Jang, M. and Jeon, B.H., 2021. Phytoremediation as a green biotechnology tool for emerging environmental pollution: a step forward towards sustainable rehabilitation of the environment. *Chemical Engineering Journal*, 415, pp.129040.

Kurniawan, S.B., Ramli, N.N., Said, N.S.M., Alias, J., Imron, M.F., Abdullah, S.R.S., Othman, A.R., Purwanti, I.F. and Hasan, H.A., 2022. Practical limitations of bioaugmentation in treating heavy metal contaminated soil and role of plant growth promoting bacteria in phytoremediation as a promising alternative approach. *Heliyon*, 8(4), pp.1-14.

Laghlimi, M., Baghdad, B., Hadi, H.E. and Bouabdli, A., 2015. Phytoremediation mechanisms of heavy metal contaminated soils: a review. *Open Journal of Ecology*, 5(8), pp.375–388.

Lakshmi, K.S., Sailaja, V.H. and Reddy, M.A., 2017. Phytoremediation: a promising technique in wastewater treatment. *International Journal of Scientific Research and Management*, 5(6), pp.5480–5489.

Lasat, M.M., 2002. Phytoextraction of toxic metals. *Journal of Environmental Quality*, 31(1), pp.109–120.

Lasserson, T.J., Thomas, J., and Higgins, J.P., 2021. *Chapter 1: starting a review*. [online] Available at: <https://training.cochrane.org/handbook/ current/ chapter-01> [Accessed 27 August 2021].

Lee, J. and Sung, K., 2014. Effects of chelates on soil microbial properties, plant growth and heavy metal accumulation in plants. *Ecological Engineering*, 73, pp.386–394.

Lefebvre, C., Glanville, J., Briscoe, S., Littlewood, A., Marshall C., Metzendorf, M-I., Noel-Storr, A., Rader, T., Shokraneh, F., Thomas, J., Wieland, L.S., 2021. *Chapter 4: searching for and selecting studies*. [online] Available at: <https://training.cochrane.org/handbook/current/chapter-04# section-4-4> [Accessed 27 August 2021].

Li, Q., Chen, B., Lin, P., Zhou, J., Zhan, J., Shen, Q. and Pan, X., 2014. Adsorption of heavy metal from aqueous solution by dehydrated root powder of long-root *Eichhornia crassipes*. *International Journal of Phytoremediation*, 18(2), pp.103–109.

Liang, L., Liu, W., Sun, Y., Huo, X., Li, S. and Zhou, Q., 2017. Phytoremediation of heavy metal contaminated saline soils using halophytes: current progress and future perspectives. *Environmental Reviews*, 25(3), pp.269–281.

Lissy, P.N.M. and Madhu, G, 2011. Removal of heavy metals from wastewater using water hyacinth. *ACEEE International Journal on Transportation and Urban Development*, 1(1), pp.48–52.

Liu, J.L. and Wong, M.H., 2013. Pharmaceuticals and personal care products: a review on environmental contamination in China. *Environment International*, 59, pp.208–224.

Liu, Z. and Tran, K.Q., 2021. A review on disposal and utilization of phytoremediation plants containing heavy metals. *Ecotoxicology and Environmental Safety*, 226, pp.1–13.

Logisticon Water Treatment, 2022. *Membrane filtration*. [online] Available at: <https://www.logisticon.com/en/technologies/membrane-filtration> [Accessed 18 February 2022].

Lu, Q., He, Z.L., Graetz, D.A., Stoffella, P.J. and Yang, X., 2011. Uptake and distribution of metals by water lettuce (*Pistia stratiotes*). *Environmental Science and Pollution Research*, 18(6), pp.978–986.

Lu, X., Kruatrachue, M., Pokethitiyook, P. and Homyok, K., 2004. Removal of cadmium and zinc by water hyacinth. *Science Asia*, 30, pp.93–103.

Malar, S., Shivendra Vikram, S., JC Favas, P. and Perumal, V., 2014. Lead heavy metal toxicity induced changes on growth and antioxidative enzymes level in water hyacinths. *Botanical Studies*, 55(1), pp.1–11.

Miranda, A.F., Muradov, N., Gujar, A., Stevenson, T., Nugegoda, D., Ball, A.S. and Mouradov, A., 2014. Application of aquatic plants for the treatment of selenium-rich mining wastewater and production of renewable fuels and petrochemicals. *Journal of Sustainable Bioenergy Systems*, 4(1), pp.97–112.

Miretzky, P., Saralegui, A. and Cirelli, A.F., 2004. Aquatic macrophytes potential for the simultaneous removal of heavy metals (Buenos Aires, Argentina). *Chemosphere*, 57(8), pp.997–1005.

Miretzky, P., Saralegui, A. and Fernández Cirelli, A., 2006. Simultaneous heavy metal removal mechanism by dead macrophytes. *Chemosphere*, 62(2), pp.247–254.

Mishra, V.K. and Tripathi, B.D., 2009. Accumulation of chromium and zinc from aqueous solutions using water hyacinth (*Eichhornia crassipes*). *Journal of Hazardous Materials*, 164, pp.1059–1063.

Mohammed, A.K., Ali, S.A., Najem, A.M. and Ghaima, K.K., 2013. Effect of some factors on biosorption of lead by dried leaves of water hyacinth (*Eichhornia Crassipes*). *International Journal of Pure and Applied Sciences and Technology*, 17(2), pp.72–78.

Mohan, D., Sarswat, A., Ok, Y.S. and Pittman, C.U., 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent: a critical review. *Bioresource Technology*, 160, pp.191–202.

Mohanty, M., 2016. Post-harvest management of phytoremediation technology. *Journal of Environmental & Analytical Toxicology*, 6(5), pp.1-8.

Murithi, G., Onindo, C.O., Wambu, E.W. and Muthakia, G.K., 2014. Removal of cadmium(II) ions from water by adsorption using water hyacinth (*Eichhornia crassipes*) biomass. *BioResources*, 9(2), pp.3613–3631.

Naaz, M., Dutta, A., Kumari, S. and Farooqui, S., 2013. Bioaccumulation, phytoremediation, and kinetics of uptake of heavy metals (copper and zinc) by *Eichhornia crassipes*. *Journal of Ecology*, 2(1), pp.1-7.

Obinnaa, I.B. and Ebere, E.C., 2019. A review: water pollution by heavy metal and organic pollutants: brief review of sources, effects and progress on remediation with aquatic plants. *Analytical Methods in Environmental Chemistry Journal*, 2(3), pp.5–38.

Ogbozige, F.J. and Nwobu, H., 2021. Biosorption of Ni^{2+} and Cr^{3+} in synthetic sewage: adsorption capacities of water hyacinth (*Eichhornia crassipes*). *Environmental Research and Technology*, 4(4), pp.342–351.

Oladoye, P.O., Olowe, O.M. and Asemoloye, M.D., 2022. Phytoremediation technology and food security impacts of heavy metal contaminated soils: a review of literature. *Chemosphere*, 288, pp.1-14.

Ortiz-Martínez, V.M., Andreo-Martínez, P., García-Martínez, N., Pérez de los Ríos, A., Hernández-Fernández, F.J. and Quesada-Medina, J., 2019. Approach to biodiesel production from microalgae under supercritical conditions by the PRISMA method. *Fuel Processing Technology*, 191, pp.211–222.

Özkara, A., Akyil, D. and Konuk, M., 2016. Pesticides, environmental pollution, and health. In: M.L. Larramendy and S. Soloneski, eds. *InTech*, pp.3-15.

Parameswari, E., Premalatha, R.P., Davamani, V., Kalaiselvi, P., Paul Sebastian, S. and Suganya, K., 2021. Biosorption of chromium ions through modified *Eichhornia crassipes* biomass form the aqueous medium. *Journal of Environmental Biology*, 42(1), pp.62–73.

Phearkeo, O., 2015. *A study on removal of heavy metals from wastewater by floating plants*. Master. Sirindhorn International Institute of Technology Thammasat University.

Prasad, M.N.V., 2003. Phytoremediation of metal-polluted ecosystems: hype for commercialization. *Russian Journal of Plant Physiology*, 50(5), pp.686–701.

Prasad, M.N.V., 2018. Prospects for manipulation of molecular mechanisms and transgenic approaches in aquatic macrophytes for remediation of toxic metals and metalloids in wastewaters. *Transgenic Plant Technology for Remediation of Toxic Metals and Metalloids*. Elsevier Inc. pp.395-428.

Premalatha, R.P., Parameswari, E., Davamani, V., Malarvizhi, P. and Avudainayagam, S., 2018. Biosorption of chromium (III) from aqueous solution by water hyacinth biomass. *Madras Agricultural Journal*, 106(1–3), pp.12–21.

Qasem, N.A.A. and Mohammed, R.H. and Lawal, D.U., 2021. Removal of heavy metal ions from wastewater: a comprehensive and critical review. *npj Clean Water* 4, 36, pp.1-15.

Rai, P.K., 2009. Heavy metal phytoremediation from aquatic ecosystems with special reference to macrophytes. *Critical Reviews in Environmental Science and Technology*, 39(9), pp.697-753.

Rakhshaee, R., Khosravi, M. and Ganji, M.T., 2006. Kinetic modelling and thermodynamic study to remove Pb(II), Cd(II), Ni(II) and Zn(II) from aqueous solution using dead and living *Azolla filiculoides*. *Journal of Hazardous Materials*, 134(1–3), pp.120–129.

Ramachandra, T.V and Ahalya, N., 2014. Phytoremediation: processes and mechanisms. *Journal Ecobiol*, 18(1), pp.33–38.

Reinsel, M., 2016. *Industrial water treatment for inorganic contaminants physical treatment processes*. [online] Available at: <https://www.wateronline.com/doc/industrial-water-treatment-for-inorganic-contaminants-physical-treatment-processes-0001> [Accessed 9 August 2021].

Rezania, S., Din, M.F.M., Taib, S.M., Dahalan, F.A., Songip, A.R., Singh, L. and Kamyab, H., 2016a. The efficient role of aquatic plant (water hyacinth) in treating domestic wastewater in continuous system. *International Journal of Phytoremediation*, 18(7), pp.679–685.

Rezania, S., Ponraj, M., Talaiekhozani, A., Mohamad, S.E., Md Din, M.F., Taib, S.M., Sabbagh, F. and Sairan, F.M., 2015. Perspectives of phytoremediation using water hyacinth for removal of heavy metals, organic and inorganic pollutants in wastewater. *Journal of Environmental Management*, 163, pp.125–133.

Rezania, S., Taib, S.M., Md Din, M.F., Dahalan, F.A. and Kamyab, H., 2016b. Comprehensive review on phytotechnology: heavy metals removal by diverse aquatic plants species from wastewater. *Journal of Hazardous Materials*, 318, pp.587–599.

Rodrigues, A.C.D., do Amaral Sobrinho, N.M.B., dos Santos, F.S., dos Santos, A.M., Pereira, A.C.C. and Lima, E.S.A., 2017. Biosorption of toxic metals by water lettuce (*Pistia stratiotes*) biomass. *Water, Air, and Soil Pollution*, 228, pp.1-11.

Sadeek, S.A., Negm, N.A., Hefni, H.H.H. and Abdel Wahab, M.M., 2015. Metal adsorption by agricultural biosorbents: adsorption isotherm, kinetic and biosorbents chemical structures. *International Journal of Biological Macromolecules*, 81, pp.400–409.

Saha, P., Shinde, O. and Sarkar, S., 2017. Phytoremediation of industrial mines wastewater using water hyacinth. *International Journal of Phytoremediation*, 19(1), pp.87–96.

Sarwar, N., Imran, M., Shaheen, M.R., Ishaque, W., Kamran, M.A., Matloob, A., Rehim, A. and Hussain, S., 2017. Phytoremediation strategies for soils contaminated with heavy metals: modifications and future perspectives. *Chemosphere*, 171, pp.710–721.

Schell, L.M., Knutson, K.L. and Bailey, S., 2012. Environmental Effects on Growth. In: N. Cameron and B. Bogin, eds. *Human Growth and Development*. Elsevier Inc. pp.245–286.

Shaari, N.E.M., Tajudin, M.T.F.M., Khandaker, M.M., Majrashi, A., Alenazi, M.M., Abdullahi, U.A. and Mohd, K.S., 2021. Cadmium toxicity symptoms and uptake mechanism in plants: a review. *Brazilian Journal of Biology*, 84, pp.1–17.

Shah, M., Hashmi, H.N., Ali, A. and Ghumman, A.R., 2014. Performance assessment of aquatic macrophytes for treatment of municipal wastewater. *Journal of Environmental Health Science and Engineering*, 12(1), pp.1–12.

Shanthi, T. and Selvarajan, V.M., 2012. Removal of Cu (II) ions from aqueous solution by carbon prepared from henna leaves, pungam bark and CAC. *Journal of Chemical and Pharmaceutical Research*, 4(9), pp.4296–4306.

Sharma, R.K., 2014. Biological effects of heavy metals : an overview. *Journal of Environmental Biology*, 26, pp.301–313.

Sharma, S., Tiwari, S., Hasan, A., Saxena, V. and Pandey, L.M., 2018. Recent advances in conventional and contemporary methods for remediation of heavy metal-contaminated soils. *3 Biotech*, 8(216), pp.1–18.

Shen, X., Dai, M., Yang, J., Sun, L., Tan, X., Peng, C., Ali, I. and Naz, I., 2022. A critical review on the phytoremediation of heavy metals from environment: performance and challenges. *Chemosphere*, 291, pp.1–11.

Shinta, Y.C., Zaman, B. and Sumiyati, S., 2021. Citric Acid and EDTA as chelating agents in phytoremediation of heavy metal in polluted soil: a review. *IOP Conference Series: Earth and Environmental Science*, 896(1), pp.1-9.

Singh, B.S.M., Singh, D. and Dhal, N.K., 2022. Enhanced phytoremediation strategy for sustainable management of heavy metals and radionuclides. *Case Studies in Chemical and Environmental Engineering*, 5, pp.1–8.

Singh, D., Gupta, R. and Tiwari, A., 2012. Potential of duckweed (*Lemna minor*) for removal of lead from wastewater by phytoremediation. *Journal of Pharmacy Research*, 5(3), pp.1578–1582.

Singh, J., Kumar, V., Kumar, P. and Kumar, P., 2021. Kinetics and prediction modelling of heavy metal phytoremediation from glass industry effluent by water hyacinth (*Eichhornia crassipes*). *International Journal of Environmental Science and Technology*, pp.1–12.

Singh, K. and Pandey, S.N., 2011. Effect of nickel-stresses on uptake, pigments and antioxidative responses of water lettuce, *Pistia stratiotes L.* *Journal of Environmental Biology*, 32(3), pp.391–394.

Singh, R.M. and Gupta, A., 2017. Water pollution: sources, effects and control water pollution-sources, effects, and control. *Research gate*, 5(3), pp.1–17.

Soltan, M.E. and Rashed, M.N., 2003. Laboratory study on the survival of water hyacinth under several conditions of heavy metal concentrations. *Advances in Environmental Research*, 7(2), pp.321–334.

Souza, L.A., Piotto, F.A., Nogueirol, R.C. and Azevedo, R.A., 2013. Use of non-hyperaccumulator plant species for the phytoextraction of heavy metals using chelating agents. *Scientia Agricola*, 70(4), pp.290–295.

Streefkerk, R., 2021. *Qualitative versus quantitative research: differences and methods*. [online] Available at: <https://www.scribbr.com/methodology/qualitative-quantitative-research/> [Accessed 16 August 2021].

Tangahu, B.V., Sheikh Abdullah, S.R., Basri, H., Idris, M., Anuar, N. and Mukhlisin, M., 2011. A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. *International Journal of Chemical Engineering*, 2011, pp.1–31.

Thaçi, B.S. and Gashi, S.T., 2019. Reverse osmosis removal of heavy metals from wastewater effluents using biowaste materials pre-treatment. *Polish Journal of Environmental Studies*, 28(1), pp.337–341.

Tufaner, F., 2018. Post-treatment of effluents from UASB reactor treating industrial wastewater sediment by constructed wetland. *Environmental Technology*, 41(7), pp.912–920.

Ubuza, L.J.A., Padero, P.C.S., Nacalaban, C.M.N., Tolentino, J.T., Alcoran, D.C., Tolentino, J.C., Ido, A.L., Mabayo, V.I.F. and Arazo, R.O., 2020. Assessment of the potential of duckweed (*Lemna minor*) in treating lead-contaminated water through phytoremediation in stationary and recirculated set-ups. *Environmental Engineering Research*, 25(6), pp.977–982.

Unadkat, K. and Parikh, P., 2017. A review on heavy metal absorption capacity of aquatic plants : sources, impact and remediation technique. *IJAPRR International Peer Reviewed Refereed Journal*, 4(12), pp.23–30.

Uysal, Y. and Taner, F., 2009. Effect of pH, temperature, and lead concentration on the bioremoval of lead from water using *Lemna minor*. *International Journal of Phytoremediation*, 11(7), pp.591–608.

Verma, R.K., Sankhla, M.S., Jadhav, E.B., Parihar, K. and Awasthi, K.K., 2022. Phytoremediation of heavy metals extracted from soil and aquatic environments: current advances as well as emerging trends. *Biointerface Research in Applied Chemistry*, 12(4), pp.5486–5509.

Vesely, T., Neuberg, M., Trakal, L., Szakova, J. and Tlustoa, P., 2012. Water lettuce *Pistia stratiotes L.* response to lead toxicity. *Water, Air, and Soil Pollution*, 223(4), pp.1847–1859.

Vocciante, M., Caretta, A., Bua, L., Bagatin, R., Franchi, E., Petruzzelli, G. and Ferro, S., 2019. Enhancements in phytoremediation technology: environmental assessment including different options of biomass disposal and comparison with a consolidated approach. *Journal of Environmental Management*, 237, pp.560–568.

Wang, L.K., Vaccari, D.A., Li, Y. and Shammas, N.K., 2005. Chemical precipitation. *Physicochemical Treatment Processes*, pp.141–197.

Watts, J.F. and Wolstenholme, J., 2019. *An introduction to surface analysis by XPS and AES*. [online] Available at: <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781119417651.ch1> [Accessed 21 January 2022].

Wentz, D.A., Brigham, M.E., Chasar, L.C., Lutz, M.A. and Krabbenhoft, D.P., 2014. The quality of our nation's waters mercury in the nation's streams-levels, trends, and implications. *Geological Survey Circular,* pp.1–90.

Witters, N., Mendelsohn, R., Passel, S.V., Slycken, S.V., Weyens, N., Schreurs, E., Meers, E., Tack, F., Vanheusden, B. and Vangronsveld, J., 2012. Phytoremediation, a sustainable remediation technology? II: economic assessment of CO_2 abatement through the use of phytoremediation crops for renewable energy production. *Biomass and Bioenergy,* 39, pp.470–477.

World Health Organization and UNICEF, 2019. *Water and sanitation the urban and rural challenge of the decade target*. [online] Available at: <https://www.who.int/water_sanitation_health/monitoring/jmpfinal.pdf> [Accessed 28 June 2021].

World Health Organization, 2005. *Nickel in Drinking-water Background document for development of WHO Guidelines for Drinking-water Quality*. [online] Available at: <https://www.who.int/water_sanitation_health/gdwqrevision/nickel2005.pdf> [Accessed 28 June 2021].

World Health Organization, 2011. *Lead in Drinking-water Background document for development of WHO Guidelines for Drinking-water Quality*. [online] Available at: <https://www.who.int/water_sanitation_health/dwq/chemicals/lead.pdf> [Accessed 28 June 2021].

Wu, L., Zhong, D., Du, Y., Lu, S., Fu, D., Li, Z., Li, X., Chi, Y., Luo, Y. and Yan, J., 2013. Emission and control characteristics for incineration of sedum plumbizincicola biomass in a laboratory-scale entrained flow tube furnace. *International Journal of Phytoremediation*, 15(3), pp.219–231.

Wuana, R.A. and Okieimen, F.E., 2011. Heavy Metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *International Scholarly Research Network ISRN Ecology,* 2011, pp.1–20.

Xu, Y., Wang, X.F., Zhou, T., You, L.J., Wang, N. and Guo, H., 2014. Research progress of disposal technology for hyperaccumulator. *Advanced Materials Research*, 955–959, pp.2851–2858.

Zhang, C., Feng, Y., Liu, Y.W., Chang, H.Q., Li, Z.J. and Xue, J.M., 2017. Uptake and translocation of organic pollutants in plants: a review. *Journal of Integrative Agriculture*, 16(8), pp.1659–1668.

Zheng, J.C., Liu, H.Q., Feng, H.M., Li, W.W., Lam, M.H.W., Lam, P.K.S. and Yu, H.Q., 2016. Competitive sorption of heavy metals by water hyacinth roots. *Environmental Pollution*, 219, pp.837–845.

Zhong, D.X., Zhong, Z.P., Wu, L.H., Xue, H., Song, Z.W. and Luo, Y.M., 2015. Thermal characteristics and fate of heavy metals during thermal treatment of sedum plumbizincicola, a zinc and cadmium hyperaccumulator. *Fuel Processing Technology*, 131, pp.125–132.

Zhu, Z., Huang, Y., Zha, J., Yu, M., Liu, X., Li, H. and Zhu, X., 2019. Emission and retention of cadmium during the combustion of contaminated biomass with mineral additives. *Energy and Fuels*, 33(12), pp.12508–12517.