

## Phytoremediation of Polluted Waterbodies with Aquatic Plants: Recent Progress on Heavy Metal and Organic Pollutants

Isiuku Beniah Obinna and Enyoh Christian Ebere

Department of Chemistry, Imo State University, Imo State, Nigeria

Corresponding Author: [cenyoh@gmail.com](mailto:cenyoh@gmail.com)

### Abstract

Heavy metals and organic pollutants are ubiquitous environmental pollutants affecting the quality of soil, water and air. Over the past 5 decades, many strategies have been developed for the remediation of polluted water. Strategies involving aquatic plant use are preferable to conventional methods. In this study, an attempt was made to provide a brief review on recent progresses in research and practical applications of phytoremediation for water resources with the following objectives: (1) to discuss the toxicity of toxic chemicals pollution in water to plant, animals and human health (2) to summarise the physicochemical factors affecting removal of toxic chemicals such as heavy metals and organic contaminants in aqueous solutions by aquatic plants; (3) to summarise and compare the removal rates of heavy metals and organic contaminants in aqueous solutions by diverse aquatic plants; and (4) to summarise chemometric models for testing aquatic plant performance. More than 20 aquatic plants species have been used extensively while duckweed (*L. minor*), water hyacinth (*Eichhornia crassipes*), water lettuce (*P. stratiotes*) are the most common. Overall, chemometrics for performance assessment reported include: Growth rate (GR), Growth rate inhibition (% Inhibition), Metal uptake (MU), translocation/transfer factor (TF), bioconcentration factor (BCF), Percent metal uptake (% MU), Removal capacity (RC) and Tolerance index (TI) while absorption rate have been studied using the sorption kinetics and isotherms models such as pseudo-first-order (PFO), pseudo-second-order (PSO), Freundlich, Langmuir and Temkin. Using modeling and interpretation of adsorption isotherms for performance assessment is particularly good and increases level of accuracy obtained from adsorption processes of contaminant on plant. Conclusion was drawn by highlighting the gap in knowledge and suggesting key future areas of research for scientists and policymakers.

**Keywords:** Chemical pollutants, Chemometrics, Constructed wetlands, Hydroponics, Macrophytes, Models, Toxicity, Water pollution

### 1. Introduction

One precious natural resource is water, which is relied on for agricultural sustainability and mankind civilization. Water covers over 70 % of the earth crust and majority of the water have been subjected to maximum exploitation and severely degraded or polluted due to anthropogenic activities. Surface water and groundwater have often been studied and managed as separate resources even though they are interrelated [1]. Surface water seeps through the soil and becomes groundwater. Conversely, groundwater can also feed surface water sources. Sources of surface water pollution are generally grouped into two categories based on their origin. The pollution origin of water include point (from a single, identifiable source) and non-point (does not originate from a single discrete source) sources. Irrespective of the contamination source, damaging effects are still made to the ecosystem. However, contaminations that add heavy metals or organic pollutants to waters are of serious concern due to their persistence in the environment and carcinogenicity to human beings. These pollutants cannot be easily destroyed biologically but are often transformed from one oxidation state or organic complex to another [2,3], thus remaining in the environment for a very longtime. Therefore, toxic chemical pollution of water poses a great threat to the environment and human health.

Many technologies that are easy to use have been developed as part of the continuous efforts to make water free from contamination, be of good quality of waters, sustainable and economically feasible. Physicochemical

approaches (involving isolation and containment, chemical extraction, chemical redox process, thermal method, electrokinetics) have been widely used for remedying polluted water, especially at a small scale while difficult to use at large scale due to high costs and side effects [4]. Therefore, the search for an alternative clean and cheap technique for water cleaning became important.

The use of plant species for cleaning polluted waters named as phytoremediation has gained great interest and adopted by scientist, governmental and non-governmental organizations. However, the concept of using plants to clean up contaminated environments is not new. About 300 years ago, plants were proposed for use in the treatment of wastewater and have gained increasing attention since last two decade, as an emerging cheaper technology [5]. Many studies have been conducted in this field in the last two decades with majority focusing on contaminated soils while regarding water medium have been less studied. Numerous aquatic plant species have been identified and tested for their traits in the uptake and accumulation of different heavy metals and organic pollutants in water [4]. Mechanisms of metal and organic pollutant uptake by whole plant as well as remediation performance using chemometrics have been investigated. Progresses have been made in the practical application aspects of phytoremediation of water using hydroponics or field experiment. They were reviewed and reported in this paper.

## 2. Methodology

This research was carried out through a collection of data and information from scientific articles regarding the potential of some aquatic plants for phytoremediation of toxic chemicals such as heavy metals (specifically: As, Cu, Cr, Hg, Cd, Ni, Pb and Zn) and organic pollutants. The scientific articles were sought majorly from Google scholar and back searches through references. For an article to be included, it must be published in year 2000 and above, in order to ensure that current information was provided. However, few selected articles prior to 2000 included were due to their importance in the initial set of empirical studies.

## 3. Water pollution

All life forms on earth depend on water for their presence in the ecosystem. According to [6], water is the second most important element required by human for survival after the air we breathe. The quality of water globally has been affected negatively because of the overgrowth of the population, human activities, fast industrialization, unskilled utilization of natural water resources and unplanned urbanization. Even though, the United Nations recognizes the availability of good drinking water for humans as a human right, considerable numbers of people worldwide are still suffering with the absence of new and clean drinking water. Currently 7.7 billion people are in the world of which over 900 million people don't have accessed to enhanced drinking water. A value which present a significance decrease from around 2.6 billion peoples in 1990 and approximately 600 billion people expected in 2015 if the United Nations' Millennium Development Goal was achieved having access to enhanced drinking water [7,8]. Furthermore, World Water Council estimated that around 3.9 billion people by 2030 will be living in water scarce areas [9]. In Nigeria, irrespective of the total replenishable water resource estimated at 319 billion cubic meters, only 58% and 39% of the inhabitants in urban and rural areas have access to potable water supply respectively [10].

Whilst there is an increase in urbanization, industrialization and population explosion, the demand for water assets is expanding daily and thereby leading to serious contamination of surface and ground water. The chief sources of water pollution are sewage and other waste, industrial effluents, agricultural discharges and industrial wastes from chemical industries, fossils fuel plants and nuclear power plants. Surface water pollution can be grouped into marine pollution and nutrient pollution. The later refers to contamination by excessive inputs of nutrients, which is primarily responsible for eutrophication of surface waters. It is remarkable that 70–80% of all problems in developing countries are identified with water pollution, especially for children. The toxic pollutants released in wastewaters can be harmful to aquatic organisms which also cause the regular waters to be unfit as consumable water sources [11-13]. A substantial number of poisonous substances, for example, toxic metals, pharmaceuticals,

pesticides, dyes, surfactants, and others have polluted the water resources and are ecologically dangerous to individuals and creatures [14]. It has been suggested that water pollution is the leading worldwide cause of death and diseases [15, 16], accounting for the deaths of 1.8 million people in 2015 [17]. Water pollution is a major global problem, therefore requiring ongoing evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells).

### 3.1 Heavy metals

Heavy metals are referred to as those metals which possess a specific density of more than 5 g/cm<sup>3</sup> and adversely affect the environment and living organisms [18]. Generally, metals are of high electrical conductivity, malleability, and luster, which voluntarily lose their electrons to form cations. Heavy metals are ubiquitous in nature and found naturally in the earth's crust. Heavy metal compositions vary among different localities, resulting in spatial variations of surrounding concentrations [19-21]. The metal distribution in the atmosphere is monitored by the properties of the given metal and by various environmental factors [22].

Water (surface and ground) pollution by heavy metals is a global issue. Many surface and ground water in many countries (if not all) of the world have been affected by heavy metal pollution, but the severity of pollution vary enormously and controlled mainly by local activities. Many areas in Europe have been reported to be greatly affected by heavy metals [23] while in the USA, government statistics revealed that more than 19000 km of US streams and rivers have been contaminated by heavy metals from coal mine and acid mine drainage [24,25]. In Asia, some countries such as India, Pakistan and Bangladesh are experiencing severe pollution of surface water due to untreated effluents being poured in surface drains by small industrial units and from the use of raw sewage in producing vegetables near big cities, which ends in surface water by runoff and groundwater by leaching processes [25]. Generally, heavy metals identified in the polluted rivers in Asia include As, Cu, Cd, Pb, Cr, Ni, Hg and Zn.

In different parts of Africa including North, East, South and West Africa, there are reports on heavy metal (notably Pb, Cd, Hg, Cu, Co, Zn, Cr, Ni, Mn, Fe, As and V) concentrations in surface water exceeding recommended limits, thereby polluting the surface waters in the region [26]. In Nigeria alone out of inland freshwater system estimated to be about 283,293.47 hectares, only about 84,988.041 is still useful due to pollution [21]. Petroleum extraction, corrosion of oil pipelines, discharges from oil industries and frequent acts of sabotage to oil facilities are the major causes of pollution in West Africa [21,26]. In Northern Africa, the contribution of agricultural activities (use of phosphate fertilizers and pesticides), East Africa include indiscriminate dumping of waste while in Southern Africa, mining activities are the major sources of environmental pollution [26].

Numerous studies show that continuous influx of metal contaminants in the environment can be classified into two broad sources, namely natural rock weathering or geogenic sources and anthropogenic sources [27, 28]. Anthropogenic sources are the more common sources majorly from emission or effluent from the use of products containing heavy metals or capable of absorbing metals [20,29]. The summary of sources of various heavy metals is listed in Table 1 while the consumption related emissions are presented in Table 2. The presence of any metal may vary from site to site, depending upon the source of individual pollutant as well as the intensity of anthropogenic activities. Generally urban waterbodies have higher concentrations of heavy metals compared to less urbanized areas. However, in Europe the emission of some metals is decreasing perhaps due to increase in use of clean(er) technologies, improvements in emission controls and phasing out of leaded petrol, following the 1998 Heavy Metals Protocol enforced by 29 December 2003. The trend of emission of selected heavy metals between the years 1990 to 2016 is presented in Figure 1. The emissions of Cd, Hg and Pb have declined by approximately 35 %, 30 % and 10 % respectively since 1990 [30]. Furthermore, other priority heavy metals emissions such as As, Cu, Ni and Zn are simultaneously reduced by 57%, 53%, 65% and 29%, respectively [31].

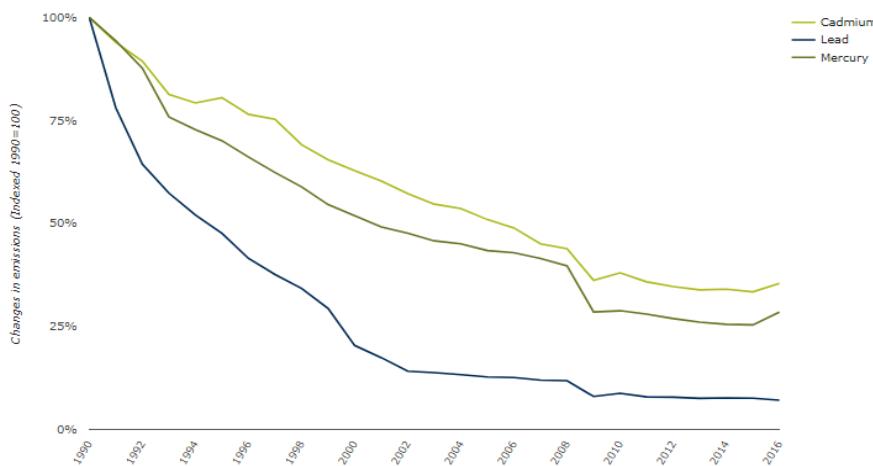


Figure 1. Trends in emissions of heavy metals from 1990 to 2016 (Source: [30])

**Table 1: Different sources of some heavy metals**

Heavy metals (HM)	Sources
As	Semiconductors, petroleum refining, wood preservatives, animal feed additives, coal power plants, herbicides, volcanoes, mining and smelting
Cd	Geogenic sources, anthropogenic activities such as metal smelting and refining, fossil fuel burning, application of phosphate fertilizers, sewage sludge
Cr	Electroplating industry, sludge, solid waste, tanneries
Cu	Electroplating industry, smelting and refining, mining, biosolids
Hg	Volcanic eruptions, forest fire, emissions from industries producing caustic soda, coal, peat and wood burning
Ni	Volcanic eruptions, land fill, forest fire, bubble bursting and gas exchange in ocean, weathering of soils and geological materials
Pb	Mining and smelting of metalliferous ores, burning of leaded gasoline, municipal sewage, industrial wastes enriched in Pb, paints
Zn	Electroplating industry, smelting and refining, mining, biosolids

Source: [25].

**Table 2: Consumption-related emissions factors (ppm) of heavy metals**

HM	Metallic use <sup>a</sup>	Plating and coating <sup>b</sup>	Paint pigments <sup>c</sup>	Electron tubes and batteries <sup>d</sup>	Other electrical equipment <sup>e</sup>	Chemical uses, not embodied <sup>f</sup>	Chemical uses, embodied <sup>g</sup>	Agricultural uses <sup>h</sup>	Non-agricultural uses <sup>i</sup>	Medical and dental <sup>j</sup>	Misc. NEC
As	0.001	0	0.5	0.01	NA	NA	0.05	0.50	0.8	0.8	0.15
Cd	0.001	0.15	0.5	0.02	NA	1	0.15	NA	NA	NA	0.15
Cr	0.001	0.02	0.5	NA	NA	1	0.05	NA	1	0.8	0.15
Cu	0.005	0	1.0	NA	0.10	1	0.05	0.05	1	NA	0.15
Hg	0.050	0.05	0.8	0.20	NA	1	NA	0.80	0.9	0.2	0.50
Pb	0.005	0	0.5	0.01	NA	1	0.75	0.05	0.1	NA	0.15
Zn	0.001	0.02	0.5	0.01	NA	1	0.15	0.05	0.1	0.8	0.15

NA- Not available

a. As alloys or amalgams (in the case of Hg) not used in plating, electrical equipment, catalysts or dental work. Losses can be assumed to be due primarily to wear and corrosion, except for mercury which volatilizes.

b. Protective surfaces deposited by dip coating (e.g. galvanizing, electroplating vacuum deposition, or chemical bath (e.g. chromic acid). Losses in use are mainly due to wear and abrasion (e.g. silverplate), or flaking (decorative chrome trim). In the case of mercury-tin "silver" for mirrors, losses were largely due to volatilization.

c. Paints and pigments are lost primarily by weathering (e.g. for metal-protecting paints), by wear, or by disposal of painted dyes or pigmented objects, such as

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magazines. Copper- and mercury-based paints slowly volatilize over time. A factor of 0.5 is rather arbitrarily assumed for all other paints and pigments.

d. Includes all metals and chemicals (e.g. phosphorus) in tubes and primary and secondary batteries, but excludes copper wire. Losses in manufacturing may be significant. Mercury in mercury vapour lamps can escape to the air when tubes are broken. In all other cases it is assumed that discarded equipment goes mainly to landfills. Minor amounts are volatilized in fires or incinerators or lost by corrosion; lead-acid batteries are recycled.

e. Includes solders, contacts, semiconductors and other special materials (but not copper wire) used in electrical equipment control devices and instruments, etc. Losses to the environment are primarily via discard of obsolete equipment to landfills. Mercury used in instruments is lost via breakage and volatilization or spillage.

f. Chemical uses not embodied in final products include catalysts, solvents, reagents, bleaches, etc. In some cases a chemical is basically embodied but there are some losses in processing. Losses in chemical manufacturing per se are included here. Major examples include copper and mercury catalysts (especially in chloride mfg); copper, zinc and chromium as mordants for dyes; mercury losses in felt manufacturing; chromium losses in tanning; lead in desulphurization of gasoline; zinc in rayon spinning, etc. In some cases virtually all of the material is actually dissipated. We include detonators such as mercury fulminate and lead azide (and explosives) in this category.

g. Chemical uses embodied in final products other than paints or batteries include fuel additives (e.g. TEL), anti-corrosion agents (e.g. zinc dithiophosphate), initiators and plasticizers for plastics (e.g. zinc oxide), etc. Also included are wood preservatives and chromium salts embodied in leather. Losses to the environment occur when the embodying productivity is utilized, for example gasoline containing TEL is burned and largely dispersed into the atmosphere. However, copper, chromium, and arsenic are used as wood preservatives and dispersed only if the wood is later burned or incinerated.

h. Agricultural pesticides, herbicides, and fungicides. Uses are dissipative but heavy metals are largely immobilized by soil. Arsenic and mercury are exceptions because of their volatility.

i. Non-agricultural biocides are the same compounds, used in industrial, commercial, or residential applications. Loss rates are high in some cases.

j. Medical/dental uses are primarily pharmaceutical (including cosmetics) germicides, also dental filling material. Most are dissipated to the environment via waste water. Silver and mercury dental fillings are likely to be buried with the dead body

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Source: [32]

### 3.1.1 Effects of heavy metals pollution of water

Many previous studies have extensively reviewed the adverse effects of heavy metals to human and ecological system [14, 18, 33-36]. Increased levels of heavy metal contaminants in water affect negatively the ecological function of water. Functions including recycling and primary production of nutrients. Also affected is the health of wildlife and humans through bioaccumulation in the food chain with the lasting impact of metal tolerance development among certain organisms. Furthermore, harmful ecological impacts of metals may include info-disruption, that impact intra and interspecies interaction among freshwater organisms and microbes [21]. However, the effects of heavy metal pollution in water shall be discussed under the following; plants, aquatic animals and humans. The toxicity of heavy metals to aquatic plant, animal and human is depended on the solubility and bioavailability of the metals, organism tolerance, pH, and presence of other ions that interfere with bioavailability, among other issues that may interfere with the result of contact with the element [37].

#### 3.1.1.1 Plant

Aquatic plants require certain heavy metals for their growth and upkeep; excessive amounts of these metals can become toxic to plants. The ability of plants to accumulate essential metals equally enables them to acquire other nonessential metals. As metals cannot be broken down, when concentrations within the plant exceed optimal levels, they adversely affect the plant both directly and indirectly. High concentrations of heavy metals in plant may interfere with metabolic functions, including physiological and biochemical processes such as oxidative stress from production of reactive oxygen species (ROS), inhibition of photosynthesis, and respiration and degeneration of main cell organelles, even leading to death of plants [2, 38, 39]. Other specific response of plants to contact with heavy metals depends on the concentration and exposure to them, presenting some phytotoxicity traits as reduced growth (especially the root system is more affected), chlorosis and leaf necrosis followed by traces of senescence and abscission, which changes lead to lower nutrient uptake and interfere with the biomass acquired [40]. A visual symptom of metal toxicity to plant is presented in Figure 2.

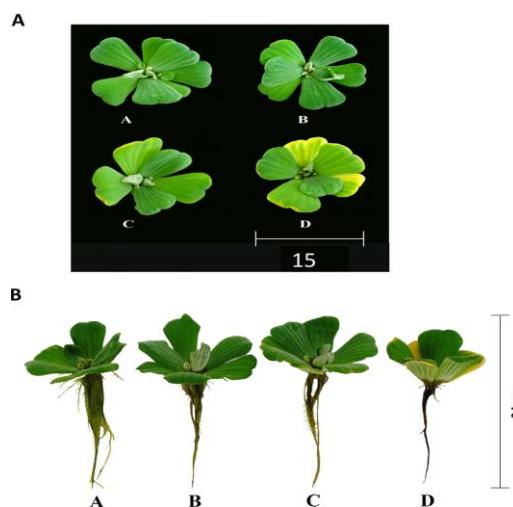


Figure 2. Visual symptoms of arsenic toxicity in leaves (A) and roots (B) of *Pistia stratiotes* exposed to three As<sup>III</sup> concentrations after four days (reprinted from [41]).

The effect of heavy metal toxicity on the aquatic plants varies according to the particular heavy metal involved in the process, multi-metal interaction in the water and the plant itself. In terms of particular heavy metal, exposure of Water hyacinth (*Eichhornia crassipes*) to excess arsenic (As) concentration of 6 mg/L over  $\geq 8$  days lead to the death of the plant while the plant became unhealthy after 3 days of exposure [42]. At the same concentration of 6 mg/L and a different concentration of 2.5 mg/L, *Eichhornia crassipes* was able to withstand zinc (II) and cadmium (II) sorption respectively in water [43]. Furthermore, in terms of plant, Brake fern (*Pteris vita*) accumulated As up to concentration of 7500 mg/kg without showing symptom of toxicity [44] while Water hyacinth (*Eichhornia crassipes*) survives at that concentration. Generally, for metals such as Pb, Cd, Hg, and As which do not play any beneficial role in plant growth, adverse effects have been recorded at very low concentrations of these metals in the growth medium. Also, effects maybe enhanced or reduced by the combination or presence of many metals in the media. Wiafe [45] observed that the level of uptake of metals (As, Hg, Cd and Pb) by *Typha capensis* was inhibited when either two of the heavy metals existed in the solution.

Some plants counteract the damages of heavy metals while some at certain concentration increase in nutrient. For example, when *E. camaldulensis* species was exposed to 45  $\mu$ mol/L cadmium there was an increase of carotenoids (related to the tolerance to oxidative stress), and there is also an increase in the thickness of the epidermis and root endoderm according to the increased doses of the metal and the decrease in the thickness of the mesophyll and leaf limb related to the decrease of the photosynthetic capacity [37, 51]. The tolerance could be due to some phyto-compounds such as anthocyanins, thiols, and antioxidant scavenging enzymes [52]. Furthermore, at 50 mg/kg of Co, there was an increase in nutrient content of tomato plants [53] and increase in plant growth, nutrient content, biochemical content, and antioxidant enzyme activities (catalase) in radish and mung bean [54, 55]. Chen et. al., [50] observed that *Ipomoea aquatica* (water spinach) increased in root size becoming fatter rather than longer when exposed to high Cr<sup>3+</sup> concentration of 10 mg/L in contaminated water for 14 days in an hydroponic experiment. Table 3 shows a summary of the toxic effects of specific metals on growth, biochemistry, and physiology of some aquatic plants. Some aquatic plants have the tendency to recover within days after exposure to high concentration of heavy metals. For instance, Drost et al., [56] observed that after high exposure to copper, nickel and cadmium toxicity, Duckweed recovered within days. It is safe to say, that where plant survives a high level of exposure to a toxicant or stress, there is a potential for full recovery [57].

**Table 3: Effect of heavy metal toxicity on some aquatic plants**

Me tal	Aquatic Plant	Toxic effect	Reference
Al	Duckweed ( <i>Lemna minor</i> L.)	Decline in enzymatic activity, reduced efficiency of photosynthetic energy conversion	[46]
As	Water hyacinth ( <i>Eichhornia crassipes</i> )	Stunted growth, chlorosis, wilting, death	[42]
	Water lettuce ( <i>Pistia stratiotes</i> L.)	Sharp reduction in the root volume, chlorosis, organ also became darker, cell membrane damage, reduction in relative growth rate; reduced photosynthetic O <sub>2</sub> evolution activity, high enzyme activity such as superoxide dismutase (SOD), catalase (CAT), peroxidase (POX) and ascorbate peroxidase (APX)	[41]
	Brake fern ( <i>Pteris</i> vita)	Decline in enzymatic activity, reduced efficiency of photosynthetic energy conversion	[44]
Cd	Duckweed ( <i>Lemna minor</i> L.)	Reduced shoot growth; inhibition of root growth	[47]
	Iridaceae ( <i>Gladiolus</i> ), Isoetaceae ( <i>Isoetes taiwaneneses</i> D.) and Amazon sword plant or burhead ( <i>Echinodorus Amazonicus</i> )	Reduced shoot growth; inhibition of root growth	[48]
	Water hyacinth ( <i>Eichhornia crassipes</i> )	Stunted growth, plant height and root length decreased, chlorosis	[49]
	Water lettuce ( <i>Pistia stratiotes</i> L.)	Stunted growth, plant height and root length decreased, chlorosis	[49]
Cr	Water spinach ( <i>Ipomoea aquatica</i> )	Increased in root size, root length decreased	[50]
Zn	Duckweed ( <i>Lemna minor</i> L.)	Decline in enzymatic activity, reduced efficiency of photosynthetic energy conversion, decrease in chlorophyll	[46]
	Water hyacinth ( <i>Eichhornia crassipes</i> )	Stunted growth, plant height and root length decreased, chlorosis	[49]
	Water lettuce ( <i>Pistia stratiotes</i> L.)	Stunted growth, plant height and root length decreased, chlorosis	[49]

### 3.1.1.2 Aquatic animals

One major biomarker of heavy metal toxicity in aquatic environment is fish. Fish are of great economic importance, but are affected immensely by various chemicals including heavy metals directly from contaminated water or indirectly in different ways via the food chain. Several reports indicate high mortality of juvenile fish and reduced breeding potential of adults after long term exposure to heavy metals [58-61]. The toxicity may cause structural changes in the organs at microscopic cellular, DNA, chronic stress and organ level leads to alterations of the function systems and eventual growth inhibition [62]. In fish system, highest concentration of heavy metals was reported to be in the kidney and liver [63]. Creatures in benthic environment, such as worms, crustaceans and insects are greatly by contaminated sediment by heavy metals, affecting their feeding habit and eventual death and reducing the food availability for larger animals such as fish [64].

### 3.1.1.3 Human health

In water, metals are present as complex mixtures of discrete mineral phases. However, bioavailability of metals determines the impacts on human health. Bioavailable forms of metals are determined through metal speciations or partitioning and easily absorbed in the body and easily convey toxicity. Several studies have explored routes of

exposure from water which include dermal contact and the most direct exposure pathway including oral ingestion [6,10,13,27-28,65-66]. Adverse health impacts to people are controlled by amounts of contaminated water ingested, high absorptive rate of metals from digestive tracts and higher haemoglobin-metal affinity [28,66]. Generally, assessment of health risk of potentially toxic metals involves the quantitative assessment of the possibility of the deleterious impacts occurring in a given set of conditions [66]. Summary of selected heavy metal impacts on human health and major biomarkers of importance is presented in Table 4.

**Table 4: Human health effects of some heavy metals**

Metal	Effects	Most common Biomarkers of Exposure	References
<b>Cd</b>	Increased risk of osteoporosis, renal tubular, glomerular and lung damage, by affecting cardiovascular, developmental, digestive, nervous, urinary, reproductive, and respiratory (From the nose to the lungs) systems.	Blood, urine, feces, liver, Kidney and Bone.	[67]
<b>Cr</b>	Causes allergic dermatitis, low birth weight and also affecting immune, urinary, respiratory and cardiovascular systems.	Blood or urine	[68]
<b>Co</b>	Nausea and vomiting Dermatitis.	Urine and Blood.	[69]
<b>Cu</b>	Liver and kidney damage, immunotoxic, and death.	Blood, urine, hair, and nails.	[70]
<b>Ni</b>	Dermatitis, allergic reaction and chronic bronchitis.	Blood, bone, and urine.	[71]
<b>Pb</b>	Affects the central nervous system, impair neurodevelopment in children, metabolic processes, renal, gastrointestinal, ocular and musculoskeletal systems, thereby causing nausea, anorexia, severe abdominal cramps, colic, weight loss, renal tubular dysfunction, abortion, muscle and joint pains and strong biochemical effect behavioral disorders, low intelligence, strokes.	Blood, bone, and urine.	[72]
<b>Zn</b>	Attacks digestive, haematological, and respiratory system and causing anemia, pancreas damage, and decrease high density lipoprotein (HDL) cholesterol.	Serum zinc level. High levels of zinc in feces or urine are indicative of recent exposure	[73]

### 3.2 Organic pollutants

Organic pollutants are pollutants that are organic in nature i.e basically containing carbon covalently bonded with other compounds. They are known to be toxic or carcinogenic in nature. Their presence in water in large quantity of organic compounds caused considerable and widespread concern since two decades ago. Rivers, particularly those in lowland regions, which may act as receptors for treated sewage effluents, industrial effluents and urban and rural run-off [74], serves as hotspot for organic pollutant loading.

Organic water pollutants generally include: detergents, disinfection by-products (found in chemically disinfected drinking water, such as chloroform), food processing waste (which can include oxygen-demanding substances, fats and grease), insecticides and herbicides (a huge range of organohalides and other chemical compounds), petroleum hydrocarbons (including fuels such as gasoline, diesel fuel, jet fuels, and fuel oil) and lubricants (motor oil), and fuel combustion byproducts (from storm water runoff) [75], volatile organic compounds (such as industrial solvents, from improper storage), chlorinated solvents (which are dense non-aqueous phase liquids, may fall to the bottom of reservoirs, since they don't mix well with water and are denser), perchlorate (various chemical compounds found in personal hygiene and cosmetic products), drug pollution (involving pharmaceutical drugs and their metabolites, this can include antidepressant drugs or hormonal medicines such as contraceptive pills). These organic water pollutants

contain compounds that are persistent in nature and elicited most concern from the international community regarded as persistent organic pollutants (POPs). POPs are heterogeneous set of man-made compounds that are easily transported from their source and easily reconcentrated in the new environment to potential toxic or hazardous levels. Concern regarding the toxicities of these pollutants brought about a global treaty, known as the Stockholm Convention, launched in 2001 to reduce drastically or eliminate POP release to the environment [76].

There are many evidences of organic pollutants in surface and ground water sources. The total concentration of organic substances in drinking water rarely exceeds 20 mg/L [74], but this small fraction comprises an exceedingly complex and varied mixture of compounds, both in terms of chemical nature and molecular weight. Certain of these compounds are naturally present, whilst others are of synthetic origin. Some organic pollutants, such as hormones and persistent organic pollutants (POPs), including polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and antibiotics, herbicides and bisphenol A (BPA), have drawn significant attention in environmental science research [77]. However, other organic pollutants considered low priority pollutants may be in form of nutrient or dissolved materials including phosphates, nitrate, sulphate, ammonium nitrate, nitrite etc. Major sources of specific classes of pollutant in water are summarized in Table 5.

Table 5: Major sources of organic pollutants in water

Chemical class	Sources
Aliphatic and aromatic hydrocarbons (including benzenes, phenols and petroleum hydrocarbons)	Petrochemical industry wastes, Heavy/fine chemicals industry wastes, Industrial solvent wastes, Plastics, resins, synthetic fibres, rubbers and paints production, Coke oven and coal gasification plant effluents, Urban run-off, Disposal of oil and lubricating wastes
Polynuclear aromatic hydrocarbons (PAHs)	Urban run-off, Petrochemical industry wastes, Various high temperature pyrolytic processes, Bitumen production, Electrolytic aluminium smelting, Coal-tar coated distribution pipes
Halogenated aliphatic and aromatic hydrocarbons	Disinfection of water and waste water, Heavy/fine chemicals industry wastes, Industrial solvent wastes and dry cleaning wastes, Plastics, resins, synthetic fibres, rubbers and paints production, Heat-transfer agents, Aerosol propellants, Fumigants
Organochlorine pesticides	Agricultural run-off, Domestic usage, Pesticide production, Carpet mothproofing, Timber treatment
Polychlorinated biphenyls	Capacitor and transformer manufacture, Disposal of hydraulic fluids and lubricants, Waste carbonless copy paper recycling, Heat transfer fluids, Investment casting industries PCB production
Phthalate esters	Plastics, resins, synthetic fibres, rubbers and paints production, Heavy/fine chemicals industry wastes, Synthetic polymer distribution pipes

Source: [74]

### 3.2.1 Adverse effects of Organic pollutants in water

Although organic polluting load in water can be eliminated gradually by the activities of micro organisms. This self-purification process involves the use of oxygen (in sufficient concentration), dilution, sedimentation and sunlight processes to breakdown of complex organic molecules into simple organic molecules. The adverse effect of organic pollutants in water sources shall be discussed briefly under the following headings; plant, aquatic animal and human.

#### 3.2.1.1 Plant

Exposure of aquatic plants to organic pollutants is generally through uptake from roots influenced by their low volatility and through plant leaves by contact from air, often a consequence of agricultural spraying with organochemicals. After uptake by plants, organic pollutants are translocated to different parts of the plants, where

toxicity may occur. Generally, two kinds of organic pollutant transport pathways in higher plants have been reported: (i) intracellular and intercellular transport (short distance transport) and (ii) conducting tissue transport (long distance transport) [78]. Transport of the hydrophobic organic pollutants is limited in phloem by the nature of the chemical. Phloem and membrane transport is often not compatible because hydrophobic compounds that easily cross the membrane are not readily transported in the phloem. Anthropogenic chemicals can also be rapidly degraded by active enzymes [79].

The tolerance of aquatic plant to organic pollutants uptake seems to correlate with the ability to deposit large quantities of pollutant metabolites in the 'bound' residue fraction of plant cell walls compared to the vacuole, where enzymatic and metabolic activities may occur [80]. However, toxicity of organic pollutants may be based on plant part viz root and leave. To the leave cell, toxic effects may include cell ultrastructure, biosynthesis, membrane stability and DNA while to the root cell, toxic effects include inordinate mitotic division [81]. Other effects may be on plant physiological and biochemical responses. Studies by [82], [83], [84] and [85] respectively studied the effect of an organic pollutant (Linear Alkylbenzene Sulphonate, (LAS)) on the defense system and growth of aquatic plants; *Chara vulgaris L.*, *Lemna minor L.*, *H. dubia* (Bl.) Backer and *Potamogeton perfoliatus L* respectively. Their results indicated that the physiological and biochemical responses of aquatic plants are affected by the LAS stress but effects varied among different plant species. Similarly, [86] reported that at concentration of 840 mg/L of ammonium nitrate in water, the growth rate, carbon contents, carbon-nitrogen ratio, photochemical cells and induced reactive oxygen stress (ROS) of *Lemna minor L* (Duckweed) was reduced, resulting in cell mortality of the aquatic plant. Increased ROS in aquatic plant is an indication of environmental stress, compromising the ability or potentials of such plants to carry out its regular ecological function of regulating nutrients in aquatic environment [57]. Information regarding the toxic effects of organic pollutants especially POPs on aquatic plant species or macrophyte is very scarce. Therefore, more studies are required to fill this knowledge gap.

### **3.2.1.2 Aquatic animals**

Organic pollution affects the organisms living in a stream by lowering the available oxygen in the water. This causes reduced fitness, or, when severe, asphyxiation. The increased turbidity of the water reduces the light available to photosynthetic organisms. Organic wastes also settle out on the bottom of the stream, altering the characteristics of the substratum. Organic pollutants have been detected in marine organisms, including the green mussel, *Perna viridis* [87-90], barnacles [91], odontocete species [92] and fish species [58-61, 93].

### **3.2.1.3 Human health**

Environmental xenobiotic compounds that are both persistent and bioaccumulative have the potential to induce adverse effects on human health [94]. A common example is hydrophobic contaminant like POPs are known to be a potential endocrine disruptor compounds. The threat of organic pollutant to human life have not been yet fully examined [95-99]. But, mounting evidence exists suggesting that long-term exposure to low concentrations of certain organic chemicals can be an important factor in the development and manifestation of some chronic diseases. Between 80 and 90% of cancer cases are associated with its exposure [74]. Other toxic effects could be on ovarian function in women [100], reproductive disorders in both male and female [101] and female breast cancer [102]. In addition, exogenous organic pollutant such as LAS can results to blood poisoning in humans and irritate human eyes and skins [103].

## **4. Decontamination strategy: Phytoremediation**

According to United Nations Environment Programme [104], phytoremediation can be defined as "the efficient use of plants to remove, detoxify or immobilise environmental contaminants in a growth matrix (soil, water or sediments) through the natural biological, chemical or physical activities and processes of the plants". Phytoremediation is environmentally friendly, inexpensive method basically by using plant to clean up a

contaminated medium. The process involves plant collecting pollutants by roots and either decomposed to less harmful forms or accumulates in tissues. The concept of phytoremediation of contaminated medium has been extensively discussed in many scientific, governmental and non-governmental studies [41, 104-114]. The overall objective of any remediation approach is to create a final solution that is protective of human health and the environment [29]. Whilst there are many studies on remediation of contaminated soil by plant, aquatic medium by aquatic plants have generally been less studied and reviewed.

Aquatic phytoremediation involves the use of plants for the removal of contaminants from aqueous solutions. Generally, members of Cyperaceae, Potamogetonaceae, Ranunculaceae, Typhaceae, Haloragaceae, Hydrocharitaceae, Najadaceae, Juncaceae, Pontederiaceae, Zosterophyllaceae, Lemnaceae, mainly represent aquatic plants [4]. These plants are either emergent (i.e. their roots are attached to the substrate at the bottom of water bodies while the leaves grow to or above the surface of the water), submerged (their root system is attached to the substrate but their leaves do not reach the surface of the water), or free floating (i.e. exclusively found on the surface of water bodies, usually found in standing or slow moving waters) [115]. Aquatic plants are extremely important components of an aquatic ecosystem for primary productivity and nutrient cycling [116-118]. Furthermore, it assists varieties of several organisms by providing refuge, habitat and food for them. The aquatic plants have been reported for long to detoxify environmental pollutants [4]. The notable environmental contaminants are inorganic and organic pollutants which can be phytoremediated in various ways.

The overview of phytoremediation techniques or mechanism for the different pollutants is presented in Figure 3. For heavy metals removal mechanism include phytoextraction, phytostabilization, phytoaccumulation, phytofiltration (rhizofiltration/ blastofiltration) while for organic pollutants mechanism include phytodegradation, phytostimulation, phytotransformation, phytovolatilization, phytodetoxication, phytoassimilation, phytoevaporation. Phytoextraction and phytoaccumulation technique is based on hyper-accumulation, contaminant extraction and capture by plant; phytofiltration is based on the use of plant roots (rhizofiltration) or seedlings (blastofiltration) to accumulate, extract and capture contaminants; phytostabilization is based on complexation and/or contaminant destruction; phytodegradation is based on contaminant destruction; phytovolatilization is based on volatilisation by leaves, contaminants extraction from media and release into air; phytoassimilation is based on contaminant transport and metabolism in plant chloroplast [119-120].

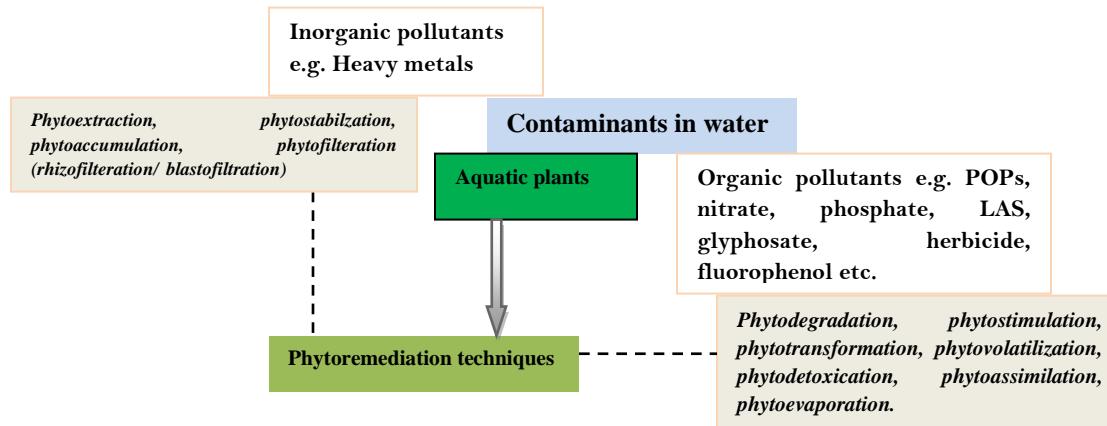


Figure 3: Overview of phytoremediation techniques by aquatic plant for both organic and inorganic contaminants removal in water

Research status of aforementioned phytoremediation techniques is either at laboratory (involving use of hydroponics), pilot or field applications stages (involving use of constructed wetlands) [106, 107, 121] (see Figure 4). Phytoextraction and phytoaccumulation is at laboratory, pilot and field applications stages, phytofiltration is at

laboratory and pilot scale stages, phytostabilization, phytodegradation (including rhizodegradation) is at field demonstration and application stage, phytovolatilization is at laboratory and field application stages while phytoassimilation, phytoevaporation, phytodetoxication, phytostimulation and phytotransformation is at laboratory or field demonstration stages. In any approach, plant biomass is harvested, dried and ashed for disposal. Metal accumulators, but not root-shoot translocators, are preferable in aquatic phytoremediation, as efficient translocators produce polluted above ground biomass, which increases the cost of processing, as well as the risk of exposing wildlife to the contaminated plants [4].

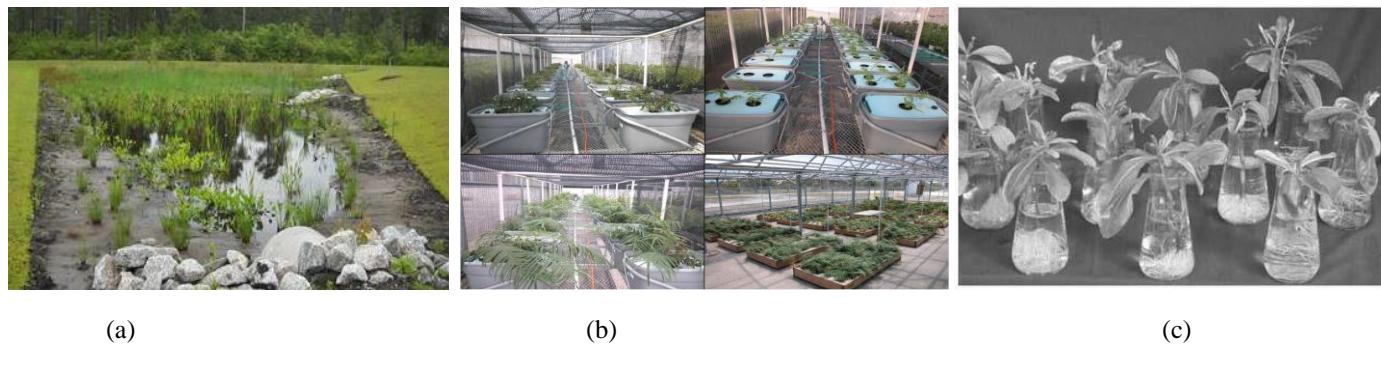


Figure 4: Experimental system for aquatic phytoremediation. (a) Field experiment showing a constructed wetland [122], (b) Pilot scale setup using *Pteris vittata* for removal of As from contaminated water [80] (c) Hydroponic system developed for rhizofiltration of environmental contaminants by *Talinum cuneifolium* (Portulacaceae) [4].

#### 4.1 Physicochemical factors affecting phytoremediation

Cellular mechanism for detoxification and tolerance has been discussed recently (see ref [112]). In general, the efficacy of the detoxification or remediation function of aquatic plants depends on water and contaminant physico-chemistry, plant physiology and genotype [4, 123, 124]. However, in this study emphasis was placed on the physicochemistry summarized in Table 6. These parameters can be manipulated or modified in water to enhance phytoremediation.

Table 6. Physical and chemical factors known to affect the pollutants uptake, accumulation, and toxicity

Parameter	Effects
	<b>Heavy metal</b>
Temperature	More uptake/toxicity at higher temperatures
Light	Uptake is light dependent in some cases
pH	Lower pH generally increases the uptake/capacity
Salinity Monovalent Cations (K, Na)	Lower salinity increases the content/toxicity
Divalent Cations Ca, Mg, Mn, Fe	Increasing monovalent cations reduces the uptake
Anions	Increasing divalent cations reduces the uptake
Organic Acids	Reduces uptake and toxicity
Sediment Fraction	Binds metals, reduces uptake/toxicity
Heavy Metals	Reduces uptake/toxicity by binding metals Complex metals, reduces uptake/toxicity Zn/Cd, Ni, Cu combinations are antagonistic. Fe can stimulate Cu accumulation
Suspended solids	Complex metals, reduces uptake/toxicity
Sulphate	Insignificant but reduces uptake slightly
Nitrate(N)	Significantly reduces toxicity
Polypeptides	Reduces uptake/toxicity by complexation
Polysachharides	Chelate metals, reduces uptake/toxicity
Sulphur (amino acids)	Reduces uptake and toxicity indirectly
Extracellular Products	Reduces toxicity

Source: [125]

**Organic pollutants**

Solubility and concentration of organic pollutants	Increases uptake
pH	Lower pH generally increases the uptake
Light intensity	Uptake is light dependent in some cases
Nitrates	Significantly reduces removal
co-occurring ions	Increasing dissolved ions reduces the uptake
Partition coefficients	High partition coefficient between octanol and water ( $K_{ow}$ ), and low partition coefficient between octanol and air ( $K_{OA}$ ) increases uptake/absorption from water and air respectively
Molecular mass of pollutants	Generally, mass $< 1000$ increases uptake
Lipid content	High lipid contents increases uptake/toxicity
Temperature	Higher temperature coefficient for diffusion processes of organic pollutants can accelerate passive absorption by the plant. On the other hand, temperature rise stimulated transpiration stream rate and enzyme activity of plants
Transpiration stream concentration factor (TSCF)	The TSCF can show the capacity of organic pollutant translocation from roots to aboveground parts.

Sources: [80], [81], [113], [126-132].

Currently, studies modifying water physicochemistry for phytoremediation of toxic chemicals is at infancy. There is therefore, need for more efforts for their effective use in the future. The solubility of heavy metals in the polluted water can be increased by reducing organic acids, thus enhancing the phytoextraction capabilities of many plant species. Plant roots can increase metal bioavailability by exuding protons that acidify the water and mobilize the metals. The lowering of water pH increases the adsorption of heavy metals and reduces their concentrations in the aqueous solution [133,134]. Also, the salt contents in terms of salinity, when in high concentrations reduces uptake of metals in water.

For organic pollutant uptake and translocation by plants, the physical and chemical properties of organic pollutants influencing plant uptake include molecular mass and hydrophobicity with partition coefficient between octanol and water ( $K_{ow}$ ), and the partition coefficient between octanol and air ( $K_{OA}$ ). Positive correlation has been found between high  $K_{ow}$  and low  $K_{OA}$  values for easy uptake of organic pollutants in plants in water and absorption from air. Succinctly, organic contaminants with a  $\log K_{ow} < 1$  are considered to be very watersoluble, and plant roots do not generally accumulate them at a rate surpassing passive influx into the transpiration stream (measured as TSCF) while contaminants with a  $\log K_{ow} > 3.5$  show high sorption to the roots but slow or no translocation to the stems and leaves. However, plants readily take up organic contaminants with a  $\log K_{ow}$  between 0.5 and 3.5, as well as weak electrolytes (weak acids and bases or amphoteres as herbicides) [80]. Log  $K_{ow}$  (octanol–water partition coefficient) values of some frequently found organic contaminants have been reviewed (see ref [80]).

Lipid content has the strongest influence on the uptake of organic pollutants, since most of the organic pollutants are hydrophobic organic contaminants (HOCs). Other factors which impact uptake of by influencing the adsorption of organic pollutants on sediments or chelates formation; include metal type in the solution, dissolved organic carbon (DOC) concentration, pH, organic matter content, light intensity and presence of nitrate. High intensity of light and presence of nitrate was reported to negatively affect perchlorate removal by *Pistia sp.* [131] and willow trees grown in hydroponic solution [135]. These results suggest that for successful phytoremediation of metal/organic polluted water, a strategy should be developed to combine a rapid screening of aquatic plant species possessing hyperaccumulating tendency with practices focusing on physicochemical factors listed in Table 6.

#### 4.2 Phytoremediation of heavy metal polluted water

Several aquatic species have been identified and tested for the phytoremediation of heavy metals from the polluted water. These include sharp dock (*Polygonum amphibium* L.), duck weed (*Lemna minor* L.), water hyacinth (*Eichhornia crassipes*), water lettuce (*P. stratiotes*), water dropwort (*Oenanthe javanica* (BL) DC), calamus (*Lepironia articulata*), pennywort (*Hydrocotyle umbellata* L.), Water fern (*Azolla filiculoides*), Poaceae (*Phragmites communis* Trin), spiny water nymph, spiny naiad and holly-leaved naiad (*Najas marina*), Water lilies (*Nymphaea spontanea*), Poaceae (*Phragmites australis* Cav.), Se a clubrush, cosmopolitan bulrush, alkali bulrush, saltmarsh bulrush, and bayonet grass (*Bolboschoenus maritimus* L.), water-starwort (*Callitricha cophocarpa* Sendtn), umbrella palm (*Cyperus alternifolius*), Salviniaceae (*Salvinia herzogii*), Water Mint (*Mentha aquatica* L.), Water Mint (*Mentha sylvestris* L.), Canna (*Canna × generalis*), Cannaceae (*Canna indica* L.), giant baby tears (*Micranthemum umbrosum*), aquatic moss (*Warnstorffia fluitans*), hippo grass (*Vossia cuspidata*), blue moon (*Iris sibirica*), marigold (*Tagetes erecta*), yellow bur head (*Limnocharis flava*), willow (*Salix matsudana*), Alpine penny-cress (*Noccaea caerulescens*), Mint (*Elsholtzia argyi*) and Mint (*Elsholtzia splendens*) (Table 7). The summary of concentrations, period, experimental framework, removable rate of different aquatic plants reported in literature for heavy metals phytoremediation is presented in Table 7.

Table 7. Summary of selected heavy metals in aqueous medium associated with aquatic plants remediation

Metal	Concentration	Exposure duration	Experimental framework	Plant specie	Removal rate (%)	References
As	0.5	21d	Field	Duckweed ( <i>L. minor</i> )	5	[136]
	96 µg/L	3 d	Field	Duckweed ( <i>L. minor</i> )	7070	[137]
	0-100 µM	192 h	Hydroponic	<i>Warnstorffia fluitans</i>	82	[138]
	16.31 ppb	25 d		Duckweed ( <i>L. minor</i> )	90.95	[139]
	20	24 h	Field	Water lettuce ( <i>Pistia stratiotes</i> )	77	[41]
Cd	1-8	12 d	Hydroponics	Duckweed ( <i>Wolffia globosa</i> )	50-90	[140]
	17.20-26.25 µg/L	Inconsistent	Field	Poaceae ( <i>Phragmites communis</i> Trin)	45.6-80	[141]
	17.20-26.25 µg/L	Inconsistent	Field	spiny water nymph, spiny naiad and holly-leaved naiad ( <i>Najas marina</i> )	45.6-80	[141]
	0.5-4	12 d	Hydroponic	Water hyacinth ( <i>Eichhornia crassipes</i> )	50-90	[142]
	0.003-10 <sup>-7</sup> M	28	Field	Duckweed ( <i>L. minor</i> )	95	[143]
	0.5-3.0	22	Field	Duckweed ( <i>L. minor</i> )	42-78	[144]
			Hydroponic	<i>Veronica anagallis</i>	50-90	[145]
			Hydroponic	<i>Epilobium laxum</i>	50-90	[145]
	0.018	7 d	Field	Duckweed ( <i>L. minor</i> )	78	[146]
	0.01-10	48 h	Field	Duckweed ( <i>L. minor</i> )	97.32	[147]
	0-12.39	28 d	Field	Duckweed ( <i>L. minor</i> )	72-91	[148]
	10 µM	7 d	Field	Duckweed ( <i>L. minor</i> )	38	[149]
	0-12.39	28	Field	Water fern ( <i>Azolla filiculoides</i> )	72-91	[148]
	1.47 ppb	25 d	Hydroponic	Duckweed ( <i>L. minor</i> )	97.79	[139]
	Variable concentrations	10 d	Field	umbrella palm ( <i>Cyperus alternifolius</i> )	3	[150]
	Variable concentrations	10 d	Field	Water hyacinth ( <i>Eichhornia crassipes</i> )	20	[150]
Cr	1-8	12 d	Hydroponics	Duckweed ( <i>Wolffia globosa</i> )	50-90	[140]
	<0-2.20 µg/L	Inconsistent	Field	Poaceae ( <i>Phragmites communis</i> Trin)	45.6-80	[141]
	<0-2.20 µg/L	Inconsistent	Field	spiny water nymph, spiny naiad and holly-leaved	45.6-80	[141]

				naiad ( <i>Najas marina</i> )		
1.0-2.0	24 h	Field	Salviniaceae ( <i>Salvinia herzogii</i> )	( <i>Salvinia herzogii</i> )	70-83	[151]
0.1-1.0	12 d	Hydroponic	Water fern ( <i>Azolla caroliniana</i> )	( <i>Azolla caroliniana</i> )	100	[152] <sup>a</sup>
0.1-1.0	12 d	Hydroponic	Water fern ( <i>Azolla caroliniana</i> )	( <i>Azolla caroliniana</i> )	74	[152] <sup>b</sup>
1	15 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	96.94	[153]
1.0-2.0	24 h	Hydroponic	Water lettuce ( <i>Pistia stratiotes</i> )	( <i>Pistia stratiotes</i> )	58-80	[151]
1-10	9 w	Hydroponic	Water lilies ( <i>Nymphaea spontanea</i> )	( <i>Nymphaea spontanea</i> )	31.6	[154]
< 0 – 0.51	Inconsistent	Field	Poaceae ( <i>Phragmites australis</i> Cav.)	( <i>Phragmites australis</i> Cav.)	50-80	[155]
< 0 – 0.51	Inconsistent	Field	Sea clubrush, cosmopolitan bulrush, alkali bulrush, saltmarsh bulrush, and bayonet grass ( <i>Bolboschoenus maritimus</i> L.)	( <i>Bolboschoenus maritimus</i> L.)	50-80	[155]
0.04-98	60 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	25-77.42	[156]
10	3 w	Hydroponic	water-starwort ( <i>Callitrichia cophocarpa</i> Sendtn)	( <i>Callitrichia cophocarpa</i> Sendtn)	50-80	[157] <sup>a</sup>
0.25-5.0	14 d	Pilot with continuous flow	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	76.4-20.0	[134] <sup>a</sup>
10.946	7 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	99.97	[158]
10.4	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	75	[159]
0.776	7 d	Field	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	63	[146]
0-0.20 mM	16 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	27.6	[160]
2	15 d	Field	<i>Phalaris arundinacea</i> Water hyacinth ( <i>Eichhornia crassipes</i> )	( <i>Eichhornia crassipes</i> )	99.9	[161] [162] <sup>a</sup>
67.33 ppb	25 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	90.25	[139]
0-12.39	28 d	Field	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	72-91	[148]
0-12.39	28 d	Field	Water fern ( <i>Azolla filiculoides</i> )	( <i>Azolla filiculoides</i> )	90	[148]
<b>Cu</b>	1.95-4.20 µg/L	Inconsistent	Field	Poaceae ( <i>Phragmites communis</i> Trin)	45.6-80	[141]
	1.95-4.20 µg/L	Inconsistent	Field	spiny water nymph, spiny naiad and holly-leaved naiad ( <i>Najas marina</i> )	45.6-80	[141]
1-7	4 d	Hydroponic	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	77.78	[163]
1	15 d	Hydroponic	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	96.94	[153]
1-7	15 d	Hydroponic	Mint ( <i>Elsholtzia argyi</i> )	( <i>Elsholtzia argyi</i> )	50-90	[164]
1-7	15 d	Hydroponic	Mint ( <i>Elsholtzia splendens</i> )	( <i>Elsholtzia splendens</i> )	45-80	[164]
1.23 – 1.75	Inconsistent	Field	Poaceae ( <i>Phragmites australis</i> Cav.)	( <i>Phragmites australis</i> Cav.)	50-80	[155]
1.23 – 1.75	Inconsistent	Field	Sea clubrush, cosmopolitan bulrush, alkali bulrush, saltmarsh bulrush, and bayonet grass ( <i>Bolboschoenus maritimus</i> L.)	( <i>Bolboschoenus maritimus</i> L.)	50-80	[155]
0.003-10 <sup>-7</sup> M	7 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	86.5	[143]
0.46	20 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	71.4	[165]
4.359	7 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	99.97	[158]
3	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	40	[159]
1.432	7 d	Field	Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	86	[146]
67 µg/L	3 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	87	[137]
0.5 and 0.25	7 d		Duckweed ( <i>L. minor</i> )	( <i>L. minor</i> )	0	[166]

			Duckweed ( <i>L. minor</i> )	90	[167]	
1-5 200 $\mu$ M	4 w 3 d		Duckweed ( <i>L. minor</i> )	20.2	[168]	
			<i>Vossia cuspidata</i>		[169][170]	
2	2 w		Duckweed ( <i>L. minor</i> )	54.2	[171]	
0.05-1.2	5 d		Duckweed ( <i>L. minor</i> )	83.3	[172]	
0-12.39	28 d	Field	Duckweed ( <i>L. minor</i> )	72-91	[148]	
23.84 ppb	25 d		Duckweed ( <i>L. minor</i> )	98.46	[139]	
0-12.39	28 d	Field	Water fern ( <i>Azolla filiculoides</i> )	80	[148]	
0.09-0.73	15 d	Field	Water hyacinth ( <i>Eichhornia crassipes</i> )	36.98-87.09	[173]	
0.08-0.46	15 d	Field	Water lettuce ( <i>Pistia stratiotes</i> )	39.72-72.58	[173]	
<b>Hg</b>	0.1-1.0	12 d	Hydroponic	Water fern ( <i>Azolla caroliniana</i> )	75-93	[152]
0.04-98	60 d	Field	Duckweed ( <i>L. minor</i> )	25-77.42	[156]	
0.23	20 d	Hydroponic	Duckweed ( <i>L. minor</i> )	66.5	[165]	
0.5 and 0.25	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	0	[166]	
		Hydroponic	<i>Salix matsudana</i>		[160]	
200 $\mu$ M	3 d	Hydroponic	Duckweed ( <i>L. minor</i> )	20.2	[168]	
0-30 $\mu$ M	6 d	Hydroponic	Duckweed ( <i>L. minor</i> )	58.3	[81]	
		Field	<i>Limnocharis flava</i>		[174]	
0.36 ppb	25 d	Hydroponic	Duckweed ( <i>L. minor</i> )	82.84	[139]	
<b>Ni</b>	1-8	14 d	Hydroponic	Water Mint ( <i>Mentha aquatica</i> L.)	22.3	[175]
1-8	14 d	Hydroponic	Water Mint ( <i>Mentha sylvestris</i> L.)	17.9	[175]	
0.0-10.0	24 h	Batch	Duckweed ( <i>L. minor</i> )	82	[176]	
1.90-17.30 $\mu$ g/L	Inconsistent	Field	Poaceae ( <i>Phragmites communis</i> Trin)	45.6-80	[141]	
1.90-17.30 $\mu$ g/L	Inconsistent	Field	spiny water nymph, spiny naiad and holly-leaved naiad ( <i>Najas marina</i> )	45.6-80	[141]	
1.98 – 4.51	Inconsistent	Field	Poaceae ( <i>Phragmites australis</i> Cav.)	50-80	[155]	
1.98 – 4.51	Inconsistent	Field	Sea clubrush, cosmopolitan bulrush, alkali bulrush, saltmarsh bulrush, and bayonet grass ( <i>Bolboschoenus maritimus</i> L.)	50-80	[155]	
0.04-98	60 d	Field	Duckweed ( <i>L. minor</i> )	25-77.42	[156]	
15	10 d	Hydroponic	Water hyacinth ( <i>Eichhornia crassipes</i> )	19.54	[177]	
		Hydroponic	<i>Tagetes erecta</i>		[178]	
0-12.39	28	Field	Duckweed ( <i>L. minor</i> )	72-91	[148]	
0-12.39	28	Field	Water fern ( <i>Azolla filiculoides</i> )	72-91	[148]	
346.81 ppb Variable concentrations	25 d 10 d	Field	Duckweed ( <i>L. minor</i> )	98.08	[139]	
Variable concentrations	10 d	Field	Umbrella palm ( <i>Cyperus alternifolius</i> ),	66	[150]	
Variable concentrations	10 d	Field	Canna (Canna $\times$ generalis)	31	[150]	
0.07-1.83	15 d	Field	Water hyacinth ( <i>Eichhornia crassipes</i> )	25.68-81.56	[173]	
0.03-1.36	15 d	Field	Water lettuce ( <i>Pistia stratiotes</i> )	28.96-68.79	[173]	
Variable concentrations	10 d	Field	Water hyacinth ( <i>Eichhornia crassipes</i> )	68	[150]	
<b>Pb</b>	0.0-10.0	24 h	Batch	Duckweed ( <i>L. minor</i> )	76	[176]
1	15 d		Duckweed ( <i>L. minor</i> )	98.55	[153]	

0.70-4.45 µg/L	Inconsistent	Field	Poaceae ( <i>Phragmites communis Trin</i> )	45.6-80	[141]	
0.70-4.45 µg/L	Inconsistent	Field	spiny water nymph, spiny naiad and holly-leaved naiad ( <i>Najas marina</i> )	45.6-80	[141]	
0.1-10.0	24 h	Hydroponic	Duckweed ( <i>L. minor</i> )	58-79	[133]	
0.04-98	60 d	Field	Duckweed ( <i>L. minor</i> )	25-77.42	[156]	
0.003-10 <sup>-7</sup> M	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	93	[143]	
0.875	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	99.97	[158]	
0.2	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	85	[159]	
0.655	7 d	Field	Duckweed ( <i>L. minor</i> )	84	[146]	
7.5 µg/L	3 d	Field	Duckweed ( <i>L. minor</i> )	1259	[137]	
10-41	21d	Field/peat	Cannaceae ( <i>Canna indica L.</i> )	81.16	[179]	
0.5 and 0.25	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	0	[166]	
200 µM	3 d	Hydroponic	Duckweed ( <i>L. minor</i> )	20.2	[168]	
23.37 ppb	25 d	Hydroponic	Duckweed ( <i>L. minor</i> )	99.61	[139]	
0.09-0.86	15 d	Field	Water hyacinth ( <i>Eichhornia crassipes</i> )	36.09-84.41	[173]	
ND-0.55	15 d	Field	Water lettuce ( <i>Pistia stratiotes</i> )	43.02-76.66	[173]	
<b>Zn</b>	5- 40	12 d	Hydroponic	Water hyacinth ( <i>Eichhornia crassipes</i> )	50-90	[142]
1	15 d	Field	Duckweed ( <i>L. minor</i> )	95.20	[153]	
< 0 µg/L	Inconsistent	Field	Poaceae ( <i>Phragmites communis Trin</i> )	45.6-80	[141]	
< 0 µg/L	Inconsistent	Field	spiny water nymph, spiny naiad and holly-leaved naiad ( <i>Najas marina</i> )	45.6-80	[141]	
< 0– 63.5	Inconsistent	Field	Poaceae ( <i>Phragmites australis Cav.</i> )	50–80	[155]	
	Inconsistent	Field	Sea clubrush, cosmopolitan bulrush, alkali bulrush, saltmarsh bulrush, and bayonet grass ( <i>Bolboschoenus maritimus L.</i> )	50–80	[155]	
0.04-98	60 d	Field	Duckweed ( <i>L. minor</i> )	25-77.42	[156]	
0.003-10 <sup>-7</sup> M	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	63.5	[143]	
0.2-30	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	75	[180]	
0.816	7 d	Field	Duckweed ( <i>L. minor</i> )	62	[146]	
1-5	4 w	Field	Duckweed ( <i>L. minor</i> )	90	[167]	
730 µg/L	3 d	Field	Duckweed ( <i>L. minor</i> )	628	[137]	
0.5 and 0.25	7 d	Hydroponic	Duckweed ( <i>L. minor</i> )	0	[166]	
200 µM	3 d	Hydroponic	Duckweed ( <i>L. minor</i> )	20.2	[168]	
0-12.39	28 d	Field	<i>Cyperus alternifolius</i>		[181] [182]	
0-12.39	28 d	Field	Duckweed ( <i>L. minor</i> )	72-91	[148]	
		Field	Water fern ( <i>Azolla filiculoides</i> )		[148]	
		Hydroponic	Alpine penny-cress ( <i>Noccaea caerulescens</i> )		[183]	
49.59 ppb	25 d	Hydroponic	Duckweed ( <i>L. minor</i> )	98.00	[139]	
0.91-1.67	15 d	Field	Water hyacinth ( <i>Eichhornia crassipes</i> )	21.55-90.18	[173]	
0.26-1.31	15 d	Field	Water lettuce ( <i>Pistia stratiotes</i> )	26.99-79.57	[173]	

<sup>a</sup> used Cr<sup>6+</sup>, <sup>b</sup> used Cr<sup>3+</sup>; Concentrations are in (mg/L) unless otherwise noted; d-days, h-hour(s), w-week(s); field: water samples treated or plant used was collected from aquatic environment, outdoor experiment or involves a constructed wetland, Hydroponics: growing plants in water cultures, or nutrient solution, without soil as a rooting medium; Pilot with continuous flow: wastewater in a continuous flow pond system used to simulate a wastewater treatment pond and a natural wetland as habitat for the plants

It was found that the roots of Indian mustard to be effective in the removal of Cd, Cr, Cu, Ni, Pb from hydroponic solutions [25]. Water hyacinth (*Eichhornia crassipes*) possesses a well-developed fibrous root system and large biomass and has been successfully used in wastewater treatment systems to improve water quality. Removal rates by the plant in hydroponic solution for Cd, and Zn was 50-90 % for both metals [142] while for Ni removal was 68 % in field experiment ([150]) and 19.84 % in hydroponics after 10 d exposure to 15 mg/L of Ni [177]. Strong removal was also observed for Cd removal by water hyacinth conducted in a pot by Wang et. al., (2002) cited by ref [25]. Li and colleagues [48] conducted a laboratory study in hydroponics to test different levels of Cd uptake by three hydrophytes: *Gladiolous*, *Isoetes taiwaneneses* Dwvol and *Echinodorus amazonicus*. The data show that the biomass of all the plants decreased with an increase in Cd concentration from 5 to 20 mg/L with highest accumulation in *Gladiolous* than the other two plants. Zhang et al. [164] investigated the efficiency of Cu removal from the contaminated water by *Elsholtzia argyi* and *Elsholtzia splendens* in hydroponics. The results show that *Elsholtzia argyi* showed better Cu phytofiltration (removal rate of 50-90 %) than *Elsholtzia splendens* (removal rate of 45-80 %), which was associated with better ability to higher Cu concentrations and translocation to shoots. Boonyapookana et. al., [140] examined the phytoaccumulation of cadmium (Cd), and chromium (Cr) on a common duckweed, *Wolffia globosa*. *W. globosa* were cultured in 3% Hoagland's nutrient medium, which was supplemented with 1, 2, 4, and 8 mg/L of Cd and Cr and were separately harvested after 3, 6, 9, and 12 days. The accumulation of Cd and Cr in *W. globosa* showed significant increases when the exposure time and metal concentration were increased with removal rates up to 90 % for both metals. Axtell et. al., [176] examined the ability of *Lemna minor* to remove soluble Pb and Ni under various laboratory conditions. *L. minor* was tested in a batch process with lead and nickel to examine the potential competition between metals for adsorption. Initial lead concentrations were 0.0, 5.0, and 10.0 mg/l, and nickel concentrations were 0.0, 2.5, and 5.0 mg/l in the experiment. Overall, *L. minor* removed 76% of the lead, and 82% of the nickel. No synergistic/antagonistic effect was noted for the multiple metal experiments, in terms of metal removal. Lu et. al., [142] demonstrated the phytoremediation potential of *Eichhornia crassipes*, for the removal of cadmium (Cd) and zinc (Zn). Water hyacinths were cultured in tap water, which was supplemented with 0.5, 1, 2 and 4 mg/L of Cd and 5, 10, 20, and 40 mg/L of Zn, and were separately harvested after 0, 4, 8 and 12 days. The experiment showed that removal of metals from solution was fast especially in the first four days with overall removal rates of 50-90 %. The accumulation of Cd and Zn in shoots and roots increased with the initial concentration and also with the passage of time. Plants treated with 4 mg/L of Cd accumulated the highest concentration of metal in roots (2044 mg/kg) and shoots (113.2 mg/kg) after 8 days; while those treated with 40 mg/L of Zn accumulated the highest concentration of metal in roots (9652.1 mg/kg) and shoots (1926.7 mg/kg) after 4 days. The maximum values of bioconcentration factor (BCF) for Cd and Zn were 622.3 and 788.9, respectively, suggesting that water hyacinth was a moderate accumulator of Cd and Zn and could be used to treat water contaminated with low Cd and Zn concentrations. Baldantoni, et. al. [141], measured the concentrations of eight trace metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in the leaves and roots of the emergent plant, *Phragmites communis* Trin., and submersed *Najas marina* L., taken from Lake Averno (Naples, Italy). The two plant roots exhibited significantly higher concentrations of trace metals than leaves. However, *Phragmites communis* roots had higher values of Cr, Cu, Fe, Mn and Ni than *Najas marina* roots, while Cd, Cr, Fe, Ni, Pb and Zn concentrations were higher in *Najas marina* shoots than in *Phragmites communis* leaves. Overall, the author concluded that *Phragmites communis* showed high capability to accumulate trace metals in the roots and appears a good monitor of lake contamination, better than *Najas marina*. Bennicelli et. al., [152] investigated the capacity of a small water fern, *Azolla caroliniana* Willd. (Azollaceae), in purifying waters polluted by Hg and Cr in hydroponic solution. During 12 days of the experiment the fern was grown in solution containing concentration 0.1, 0.5 and 1.0 mg/L for both metals. After day 12 of the experiment, metal contents in the solution decreased to 0–0.25 mg/L, which comprised between 74 – 100 % removal rates. Maine et. al., [151] examined the capacity of *Salvinia herzogii* and *Pistia stratiotes* to remove Cr (III) from water in outdoor experiments. Results showed that both macrophytes efficiently removed Cr from water at concentrations of 1, 2, 4 and 6 mg Cr L<sup>-1</sup>. *S. herzogii* was the best adapted species. At a greater initial concentration, greater bioaccumulation rates were observed. Root Cr uptake was a rapid process that was completed within the first 24 h up-to 80 % removal rates. The author pointed that Cr uptake through direct contact between the leaves and the solution is the main cause of the increase of Cr in the aerial parts, Cr being poorly translocated from the roots to the

aerial parts. Both mechanisms were fast processes. Bragato et. al., [155] used a constructed wetland, located in the Venice lagoon watershed, to investigate shoot accumulation of heavy metals (Cr, Ni, Cu and Zn) by two dominating macrophytes: *Phragmites australis* and *Bolboschoenus maritimus*. Investigations were conducted over a vegetative season at three locations with different distance to the inlet point to assess effects on vegetation. Results showed that overall heavy metal concentrations were higher in shoots of *P. australis* than in *B. maritimus*. Joanna et. al., [157] found that *Callitricha cophocarpa* (water-starwort) to be an excellent chromium accumulator in a hydroponic culture up to 3 weeks. The authors also reported that *Callitricha cophocarpa* is a good candidate for wastewaters remediation purpose. Uysal [134] examined the ability of *Lemna minor* to remove Cr (VI) ions from wastewater in a continuous flow pond system. The authors used the system to simulate a wastewater treatment pond and a natural wetland as habitat for the plants. Results showed that the removal rates varied between 20 – 76.4 % suggesting the potentiality of the plants for Cr removal in wastewater. Nevena et. al., [179] tested an ornamental plant *C. indica* for phytoremediation of Pb in wastewater. The results from this research showed removal rates of 81.16 % and support the idea that terrestrial plants are more suitable for rhizofiltration than aquatic plants and that *C. indica* can be used in rhizofiltration systems or floating islands for treatment of water polluted with lead. Priyanka et. al., [162] used water hyacinth species *Eichhornia crassipes* to remediate wastewater at Sukinda chromite mines (SCM) area of Orissa (India) containing high levels of toxic hexavalent chromium (CrVI). Results showed that the plant was able to remove 99.5% Cr (VI) of the processed water of SCM in 15 days. Furthermore, the authors performed a large-scale experiment using 100 L of water from SCM and the same removal efficiency (99.5 %) was achieved. More recently, [150] studied the uptake of Cd, Cr, Pb, and Zn by four aquatic plants including umbrella palm (*Cyperus alternifolius*), duckweed (*Lemna minor*), water hyacinth (*Eichhornia crassipes*), and canna (*Canna × generalis*) in different environments i.e., Gohar Rood river, Zarjoob river, Eynak lagoon, Anzali lagoon, and control solution. Results showed that the highest uptake rates of cadmium, chromium, zinc, nickel, and lead were observed for duckweed fronds. The highest bioconcentration factor (BCF) of nickel was related to duckweed stem and water hyacinth root, and the highest BCF of cadmium belonged to duckweed fronds and canna root. The highest rate of uptake of cadmium, chromium, zinc, and lead was related to control. Generally, based on the results of their study, it can be stated that duckweed is suitable for the uptake of most heavy metals [150]. Abbas et. al., [173] evaluated the effectiveness of water hyacinth and water lettuce for the phytoremediation of landfill leachate for the period of 15 days. The authors used fifteen plastic containers in experimental setup and the aquatic plants was fitted as a floating bed with the help of thermopole sheet. Results from their study showed that the removal rates of heavy metals like Zn, Pb, Cu and Ni from landfill leachate gradually increased from day 3 to day 15 of the experiment. The maximum removal rate for heavy metals such as for Zn (80–90%), Pb (76–84%), Cu (72–87%) and Ni (68–81%) was attained by the plants. Low values (< 1) of BCF and translocation factor, indicating low transport of heavy metals from roots to the above-ground parts of the plants. Therefore, from their results, they suggested that these aquatic plants are suitable candidate for the removal of pollution load from landfill leachate.

#### 4.3 Phytoremediation of organic pollutant in water

The desire to treat wastewater effluents from municipal and industry spurred the development and advancement in aquatic phytoremediation of aquatic pollutant. The removal of organic load, odour and colour in order to improve water quality before release into stream, rivers or groundwater spur the diverse research from wastewater treatment plant to natural and man-made or engineered wetlands [57].

Aquatic organic pollutants to have been remediated from aqueous solution by aquatic plants using either field and/or hydroponic experiment include the following: chemical and biological oxygen demand (COD and BOD), nitrate, phosphate, sulphate; from agricultural chemicals including atrazine, dimethomorph, pyrimethanil, Isoproturon, glyphosate, metazachlor, chloroacetamide, flazasulfuron, terbutylazine, 4-chloro-2-fluorophenol (4-Cl-2-FP), lactofen, herbicide norflurazon; from pharmaceuticals and personal care products (PPCPs) including sucralose, fluoxetine, tyramine, putrescine, cadaverine, spermidine, spermine, cefadroxil, metronidazole, trimethoprim, sulfamethoxazole, triclosan, diclofenac, naproxen, caffeine, ibuprofen, clofibric acid, sulfachloropyridazine,

oxitetracycline, chlorpyrifos, venlafaxine, 3-fluorophenol, 3-trifluoromethylphenol, phenol, ibuprofen, fluoxetine, cisplatin, linear alkylbenzene sulfonate; from dyes and toxin including textile dyes (AB113, RB198, BR46), blue dye, triacontanol, cyanotoxin microcystin-LR., perchlorate, toluidine Blue; and from petroleum hydrocarbons including 1H-benzotriazole, 4-methyl-1Hbenzotriazole, 5-methyl-1Hbenzotriazole, xylotriazole, 5-chlorobenzotriazole, 3-trifluoromethylphenol, phenanthrene.

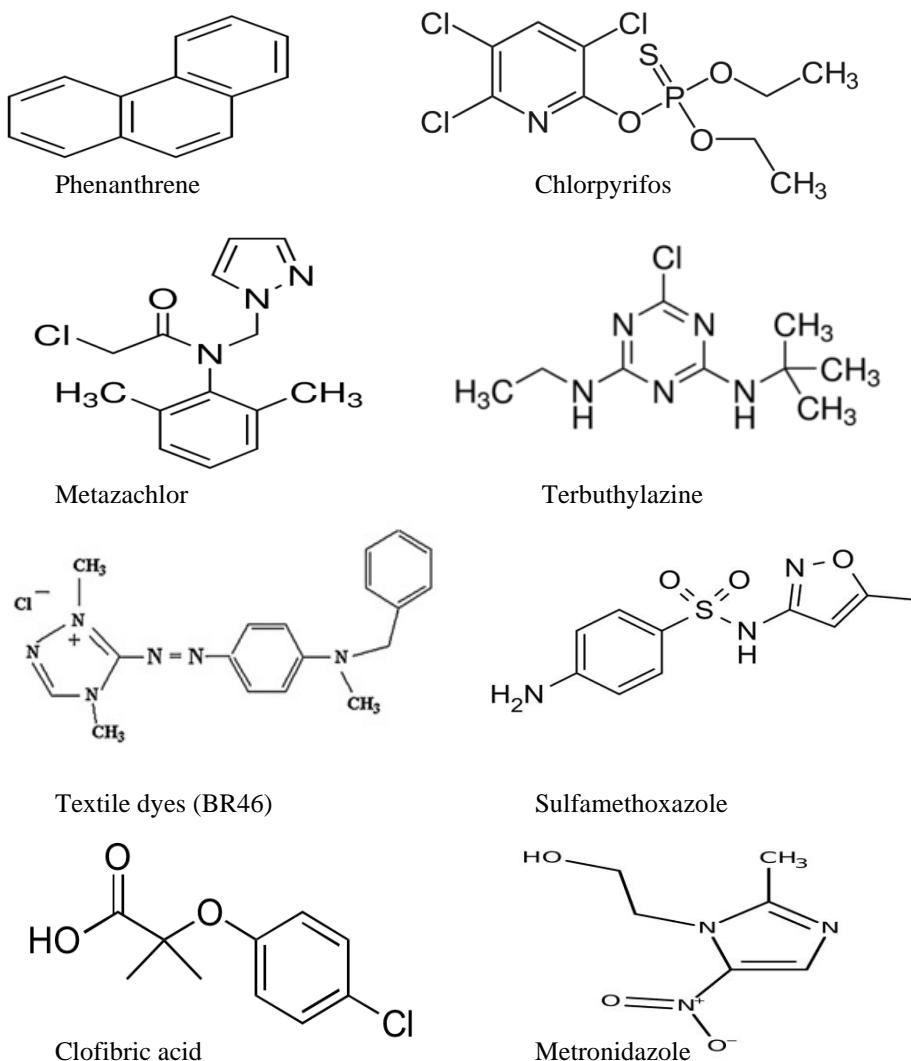


Figure 5: Structures of some priority and emerging pollutants to have been treated from aqueous solution with aquatic plants. Emerging pollutants are mainly from pharmaceutical and personal care products (PPCPs). PPCPs maintain chemical properties that can vary widely, usually containing a non-polar core with a polar functional moiety [184-186].

Few aquatic plants to have generally been tested recently for phytoremediation of aquatic organic pollutant include *M. spicatum* [103, 148, 187]; *Azolla filiculoides* [148], *Canna generalis* [188], *Pistia stratiotes* L [131, 173, 189]; *Eichornia* sp. [131, 173, 190, 191]; *Lemna* sp. [51, 131, 192]; *Salvinia* sp. [131], *Chara vulgaris* L. [82], *H. dubia* (Bl.) Backer [84], *Potamogeton perfoliatus* L. [85], *Hydrilla verticillata* (L.f.) Royle and *Vallisneria natans* (Lour.) Hara [193]; giant reed (*Arundo donax*) [194], and Poaceae (*Phragmites australis*) [194] and *Ipomoea aquatica* [195] while *Myriophyllum aquaticum* (watermilfoil) [196] and bulrush (*Scirpus lacustris*) [197] have also been used earlier. Some of these plants in some cases have been reported to better treat wastewater than normal wastewater

treatment plant for remediation of municipal effluents [198] and combination of two or more plant increased the effectiveness of removal [199-201].

Domestic as well as industrial activities introduced over 70 % organic pollutants into the aquatic environment. Bhaskara and coworkers [131] evaluated the phytoremediation potential of free floating macrophytes (*Eichornia*, *Pistia*, *Salvinia* and *Lemna*) in removing perchlorate from water. Among the plants tested, Pistia showed  $63.8 \pm 4\%$  (w/v) removal of 5 mg/L level perchlorate in 7 days, while other plants showed low removal (< 1 %). The mechanism involved in removal identified was phytoaccumulation (18.2 %) and rhizodegradation (45.68 %). Phenol from wastewater removal by water hyacinth was demonstrated [190]. *Myriophyllum spicatum* L., a submerged aquatic plant was tested for the accumulation of exogenous organic pollutant linear alkylbenzene sulfonate (LAS) [103]. Results showed that plant can accumulate LAS concentration of 50-100 mg/L without showing physiological changes. Previous studies conducted by [82], [84] and [85] respectively on the uptake LAS by *Chara vulgaris* L., *Lemna minor* L., *H. dubia* (Bl.) Backer and *Potamogeton perfoliatus* L. showed the potentiality of these plant in removing LAS (anionic surfactant) at moderate concentrations from water. Idris et. al., [194] evaluated and compared the removal ability of two emergent macrophytes, giant reed (*Arundo donax*) and Poaceae (*Phragmites australis*), in experimental subsurface flow, gravel-based constructed wetlands (CWs). Results showed that the BOD, total suspended solids (TSS), total phosphorus (TP), total nitrogen (TN), total ammoniacal nitrogen (TAN) and nitrate nitrogen ( $\text{NO}_3^-$ ) removal in the *A. donax* and *P. australis* beds was 94%, 67%, 96%, 97%, 99.6%, and effectively 100% and 95%, 87%, 95%, 98%, 99.7%, and effectively 100%, respectively, with no significant difference in performance between the two aquatic plants. Tran et. al., [188] using *Canna generalis* (a common reed and easy to grow plant both in water and wet land conditions) to organic pollutants such as BOD<sub>5</sub>, TSS, NH<sub>4</sub>-N and PO<sub>4</sub>-P from wastewater in two kinds of hybrid constructed wetlands viz Facultative pond combined with free water sub-surface constructed wetlands system and horizontal subsurface flow combined with Aerobic pond system. Results showed that the ponds played an important role in the hybrid system performance and enhanced the performance of constructed wetlands. The pollutant removal efficiencies of the hybrid systems were all higher than the single constructed wetlands. The BOD<sub>5</sub>, TSS, NH<sub>4</sub>-N and PO<sub>4</sub>-P removal efficiencies averaged 81%, 85%, 93% and 77%, respectively for the hybrid horizontal subsurface flow constructed wetlands system operated at a hydraulic loading rate of 0.075 m/day, while they were 89%, 97%, 97%, and 68%, respectively for the hybrid free water sub-surface constructed wetlands system operated at a hydraulic loading rate of 0.1 m/day. Yilmaz and Akbulut [199] reported a removal rate of 79 to 83% of BOD in effluent by *Lemna gibba*. Also, a removal rate of 94, 72, 63, 82, 82 and 82 % respectively for biochemical oxygen demand, ammonia, total suspended solids, total nitrogen, ammonium nitrate, and phosphate by duckweed in effluent was reported [57]. Blue dye and textile dyes were removed at a rate of 59.6% and 10-96 % respectively by *L. minor*, indicating the plant can be very useful in textile industries to remediate effluents [203, 204], supported in further study by Neag et al. [205] using Toluidine Blue dye. The usefulness of duckweed for phytoremediation of wide range of organic pollutants has been extensively reviewed recently (see ref [57]). The review covers the state of duckweed application for the remediation of diverse aquatic pollutants including organic pollutants. The removal of diverse organic pollutants from aqueous solutions has been well demonstrated in many studies reviewed. Unfortunately, to the best of our knowledge, studies concerning the removal of POPs such as PCB and OCPs from aqueous solution are lacking.

## 5. Chemometrics for aquatic phytoremediation

Chemometric is simply the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods/models [6]. It captures relationships between system variables and widely used in environmental analytical research [6, 207]. Information from models is viewed as simplified concepts of environmental issues. Thereby making for easy understanding by policy makers, this way decisions on environmental issues are quickly arrived at [19, 21, 207-209].

Overall, in phytoremediation studies, chemometric models are used to evaluate plant performance after the experimental period. Commonly used models includes; Growth rate (GR), Growth rate inhibition (% Inhibition),

Metal uptake (MU), translocation/transfer factor (TF), bioconcentration factor (BCF), Percent metal uptake (% MU), Removal capacity (RC) and Toxicity index (TI). These models are repeatedly used in aquatic phytoremediation studies of metals in aqueous medium [48, 156, 177, 175, 176, 141, 155, 44, 143, 165, 158, 146, 137, 166, 167, 168, 171, 172, 148, 139, 150, 173, 210, 211] and can also be used in organic pollutant remediation studies.

Growth rate (GR) value is an important index for estimating growth trends of plants used for remediation. GR is also referred to as relative growth rate (RGR). It was proposed by Fisher [212] and calculated using either equation (1) or (2), where  $DB_{AH}$  (g) and  $DB_{BP}$  (g) are the dry biomass after and before harvest, respectively, while TAH (days) and TBP (days) are the planting periods after and before harvest, measured over the study period. RGR: represents the relative growth rate (mg/g/d);  $\ln(m_1)$ : logarithm of the final dry mass (g);  $\ln(m_0)$ : logarithm of the initial dry mass (g);  $t_0$ : initial time (d);  $t_1$ : final time (d).

$$GR = \frac{DB_{AH} - DB_{BP}}{T_{AH} - T_{BP}} \quad (1)$$

$$RGR = \left( \frac{\ln(m_1) - \ln(m_0)}{t_1 - t_0} \right) * 1000 \quad (2)$$

The tolerance index (TI) was proposed by Wilkins [213]. It provides information regarding the tolerance of the plant to metal contamination in the solution; calculated using equation (3) as the ratio of growth rate of the plant in the solution contaminated to growth rate of the plant in the uncontaminated control solution. In the equation, RGR is the growth rate of the plant in the solution contaminated while  $RGR_c$  is the growth rate of the plant in the control solution, without contamination.

$$TI = \left( \frac{RGR}{RGR_c} \right) * 100 \quad (3)$$

Metal uptake (MU) indicates the metal content in whole plant tissue or in a selected plant part and can be calculated using equation (4): where  $C_{metal}$  (mg /kg or mg/L or any acceptable units) is the metal concentration in the plant tissue and DB (g) is the dry biomass of the plant.

$$MU(g/plant) = C_{metal} * DB \quad (4)$$

The TF indicates the efficiency of the plant to transport an element from the root to the shoot; and the BCF allows for evaluating the efficiency of the plant in accumulating the chemical element, taking into account its concentration in the medium or simply the ratio of metal concentrations in the roots to those in the water. Both the TF and BCF can be estimated according to equations (5) and (6), respectively [44, 211].

$$TF = \frac{C_{metal} \text{ in roots}}{C_{metal} \text{ in shoots}} \quad (5)$$

$$BCF = \frac{C_{metal} \text{ in plants}}{C_{metal} \text{ in solution or medium}} \quad (6)$$

Percent metal uptake (% MU) indicates the potential for metal uptake in plant tissue; uptake also corresponds with reduced metal concentration in solution. It can be calculated using equation (7), where  $C_i$  and  $C_f$  are the initial and final metal concentrations in solution, respectively.

$$\% MU = \left[ \frac{(C_i - C_f)}{C_i} \right] * 100 \quad (7)$$

Removal capacity (RC) indicates the potential of plants to remove metal from solution over an entire study period and can be calculated using equation (8); where RC is the removal capacity (mg/d/g),  $C_i$  and  $C_f$  remains as in equation (6), V is the liquid volume (L), D (days) is the days, and B (g) is the mean dry biomass [49].

$$RC = (C_i - C_f) - VDB \quad (8)$$

Growth rate inhibition (% Inhibition) indicates the extent of inhibition to growth of plant caused by the contaminant. % Inhibition can be calculated according equation (9), where variables remain the same as in equation (3)

$$\% \text{ Inhibition} = 1 - \left( \frac{RGR}{RGR_c} \right) \quad (9)$$

Rhizofiltration potential (RP) is based on adsorbed heavy metals by the aqueous system and inform on the performance of the plant to accumulate or remediate contaminants using roots. RP is calculated as equation (10), where, C is concentration of heavy metal;  $C_{leaves}$  is concentration of heavy metal in leaves;  $C_{roots}$  is concentration of heavy metal in roots; M is dry biomass yield,  $M_{total}$  is leaves and root biomass yield (g DW/m<sup>2</sup>/yr),  $M_{plant}$  is the mean of plant yield (g DW/m<sup>2</sup>/yr),  $M_{root}$  is the mean of root biomass yield (g DW/m<sup>2</sup>/yr),  $M_{leaves}$  is the mean of leaves biomass yield (g DW/m<sup>2</sup>/yr) (Rezania et al., 2016).

$$RP \text{ (mg/m}^2/\text{year}) = \left[ \frac{(C_{leaves} * M_{leaves}) + (C_{root} * M_{root})}{M_{total}} \right] * M_{plant} \quad (10)$$

However, in a batch or continuous flow system, the accumulation or absorption may be studied by using different sorption kinetics and isotherms models such as pseudo-first-order (PFO), pseudo-second-order (PSO), Freundlich, Langmuir and Temkin. Some of the models have significant limitations e.g PFO and PSO models, which only considers adsorption step on the active sites and predicts the internal diffusion while ignoring the external diffusion. In the use of Freundlich and Langmuir isotherms models, assumption is made that there is a local equilibrium between the contaminated aqueous medium and contaminant, an assumption that may be misleading. However, they have been widely used in absorption studies [215-217] and recently used in phytoremediation studies [188, 205, 218, 219].

The pseudo-first order kinetic equation and pseudo second order kinetic equation simply indicates if the reaction is more inclined towards physisorption or chemisorptions depending on the closeness of regression coefficient value ( $r^2$ ) to unity (1). Furthermore, they represent the degradation rate of pollutants in the biological treatment system [188]. The kinetic equation for the pseudo-first order and pseudo second order can be calculated respectively following equation (11) and (12): where  $C_e$  is the outflow concentration of metal at t day (d);  $C_i$  is the initial concentration of metal; and k is the first-order removal rate constant.

$$C_e = C_i * e^{-k.d} \quad (11)$$

$$\frac{d}{C_e} = \frac{1}{k * C_e^2} + \frac{1}{C_e * d} \quad (12)$$

Langmuir adsorption equation is the very common linear model for monolayer adsorption and it used for utilized to assess the adsorption process. Langmuir model for adsorption on a homogeneous surface with a finite number of identical sorption can be calculated using equation (13): where  $qL$  is the quantity of metal adsorbed per unit weight of sorbent (in this case, plant) and  $C_e$  is unadsorbed or outflow metal concentration remaining in water. Q corresponds to the maximum quantity of metal adsorbed per unit dry weight of the plant to form a complete monolayer on the surface and k is a constant associated with affinity of the binding site.

$$qL = \frac{Q * k * C_e}{1 + k * C_e} \quad (13)$$

Freundlich model is described adsorption onto a heterogeneous surface [219] as in equation (14): where  $C_e$  refers to solution equilibrium concentration (mg/L), q is the adsorption capacity (metal concentration on adsorbing substrate, mg/kg), and k and (1/n) are constants linked to adsorption capacity.

$$q = k * C_e^{(1/n)} \quad (14)$$

Temkin isotherm model corresponds to a factor associated with explicitly taking into the account of sorbent-adsorbate interactions. Temkin model is given in equation (15): where q is the metal concentrations in the plant biomass (mg/kg), Ce corresponds to metal concentration (mg/L) remaining in outflow, B and kt are the constant related to adsorption process [219].

$$q = B \ln(kt) + B \ln(C_e) \quad (15)$$

## 6. Conclusion, Knowledge gap and Future Areas of Research

Water resources management and protection from toxic chemicals pollution due to anthropogenic activities is of critical concern to scientist, governmental and non-governmental organizations and the general public. Phytoremediation is largely accepted and desirable to several conventional methods for the treatments of water pollution. Many aquatic plants (emergent, submerged or free flowing) have been applied extensively recently and mostly conducted using hydroponics or field experiment by constructed wetlands. Results from literature reviewed have generally established the effectiveness in remediating organic pollutants and heavy metals by aquatic plants, although heavy metals have been extensively studied than organic pollutants. Most commonly used plant include; duckweed (*L. minor*), water hyacinth (*Eichhornia crassipes*) and water lettuce (*P. stratiotes*), due to their ubiquitous nature, invasive mechanism, sporadic reproductive capacity, bioaccumulation potentials and resilience in polluted environment [57]. However, the removal rates are varied and mainly controlled by the physicochemical properties of the water, contaminants, plant and the experimental framework. Using modeling and interpretation of adsorption isotherms for performance assessment is particularly good and increases level of accuracy obtained from adsorption processes of contaminant on plant. Despite the promising efforts so far, there are still limitations in certain areas to demonstrate the effectiveness of the aquatic plant in phytoremediation of chemical pollutants.

### Knowledge gap and Future Areas of Research

(1) There is need for extensive study of the plant in the face of emerging chemicals (e.g polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) etc) that defy conventional remediation methods in order to establish acceptable remediation strategies and ecological benchmark for improvement of constructed wetlands for wastewater effluents treatment [57].

(2) Some other priority organic pollutants such as 1,2,3-trichlorobenzene, pyrene, 1,3-Dinitrobenzene, lindane and 2,4-Dinitrotoluene have been removed in terrestrial environment by terrestrial plant [220] while studies are lacking for their removal in aquatic environment. Therefore, there is need for an extensive study of aquatic plant for removal of these types of organic pollutants.

(3) There should be more studies undertaken to determine precise transfer pathways and their temporal pattern, and to pinpoint genotoxicity more precisely in plants cells. An improved understanding of these factors will allow improved control of cumulative toxic effects on plants and reduce harmful impacts of pollutants as well as enhancing the role of aquatic plants as a vital ecological based bioremediation agent for water pollution.

### Conflicts of interest

The researchers declares no conflicts of interest regarding the publication of this manuscript

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