



A Review: Water pollution by heavy metal and organic pollutants: Brief review of sources, effects and progress on remediation with aquatic plants

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ABSTRACT

Heavy metals and organic pollutants are ubiquitous environmental pollutants affecting the quality of soil, water and air. Over the past 5 decades, a lot of strategies have been being developed for treatment of polluted water. Strategies involving aquatic plant use are preferable to conventional methods. In this study, an attempt was made to provide a profound and brief review on latest and newest progresses in research and practical applications of phytoremediation for water resources with the following objectives: (1) to discuss the toxicity of 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 specie 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 emphasizing the gap in knowledge and suggesting very important 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 because of anthropogenic activities. Often times, water resources (including surface water and groundwater) even though they are interrelated and connected, are sperately

managed and studied [1]. Surface water seeps through the soil and becomes groundwater and vice versa. Therefore, both surface and groundwater sources maybe containinated by similar pollution sources. Pollution sources may include point (from a single, identifiable source) and non-point (many sources) sources. Irrespective of the contamination source, damaging effects are still made to the ecosystem; especially those sources that add heavy metals or organic pollutants to waters because they are persistent in the environment and have been associated with mutagenic, teratogenic and carcinogenic effects. These pollutants cannot be easily destroyed biologically but are often

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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 ecosystem. 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, sustainable and economically feasible. Approaches involving chemical extraction, chemical isolation and containment, thermal method, chemical redox process, and electrokinetics have been widely used, 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. Plants use in treating contaminated water was proposed about 300 years ago, as an emerging cheaper technology [5]. Over the years, the concept has gained increasing attention and has been adopted by scientist, governmental and non-governmental organizations. Many studies regarding plant use for environment clean-up has focused on contaminated soils while regarding water medium have been less studied. Many aquatic plant species have been identified and tested for removing heavy metals and organic pollutants in water [4]. Mechanisms of uptake by whole plant as well as remediation performance studied using chemometrics have been done. There are progresses made over the years 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 due to man-made activities including unskilled utilization of natural water resources. 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 clean and new drinking water. Over 900 million people out of the 7.7 billion people currently in the world, lack access 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 scare 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, 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 presented in Table 1 and 5. Marine pollution and nutrient pollution are the two types of surface water pollution. The former involves introduction of toxic substances (such as toxic metals, pharmaceuticals, pesticides, dyes, and surfactants) while the later refers to contamination by excessive inputs of nutrients, which is primarily responsible for eutrophication of surface waters. It is considerable that 70–80% of all well-known problems in developing countries are identified

with water pollution, especially for children. The toxic pollutants released in wastewaters can be detrimental to aquatic organisms which also cause the regular waters to be unfit as consumable water sources [11-14]. Studies have implicated water pollution as the leading cause of death and diseases worldwide [15-16]. In 2015, water pollution caused the deaths of 1.8 million people [17]. Thereby, making water pollution a global concern, which requires continuous assessment and revision of water resource policy at all levels (international down to individual aquifers and wells).

3.1. Heavy metals

Metals with high density ($\geq 5 \text{ g/cm}^3$) are often regarded as heavy metals. They are ubiquitous in nature and adversely affect the environment and living organisms [18]. The levels and compositions of heavy metal are often determined and controlled/influenced by local activities [19-21] while those ones suspended in air is monitored by the metal properties and various environmental factors [22] such as precipitation, rainfall and wind etc. 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]. In West Africa, major pollution source is petroleum-related activities including frequent acts of sabotage to oil facilities [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]. Literatures reveal that natural rock weathering or geogenic sources and anthropogenic sources (man-made based from emission or effluent from the use of products containing heavy metals or capable of absorbing metals) are two broad sources for heavy metals introduction into the environment [20, 27-29]. The summary of sources of various heavy metals is listed in Table 1 while the consumption related emissions are presented in Table 2. The intensity of pollution is controlled by local activities; high anthropogenic activities may cause high heavy metal pollution. Generally urban waterbodies have higher heavy metals' concentrations in comparison with 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 is simultaneously reduced by 57%, 53%, 65% and 29%, respectively [31].

3.1.1. Effects of heavy metals pollution of water

Many previous studies have extensively reviewed the adverse effects of heavy metals to human

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, 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	Volcano 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 ^a	Plating and coating ^b	Paint pigments ^c	Electron tubes and batteries ^d	Other electrical equipment ^e	Chemical uses, not embodied ^f	Chemical uses, embodied ^g	Agricultural uses ^h	Non-agricultural uses ⁱ	Medical and dental ^j	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 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

Source: [32]

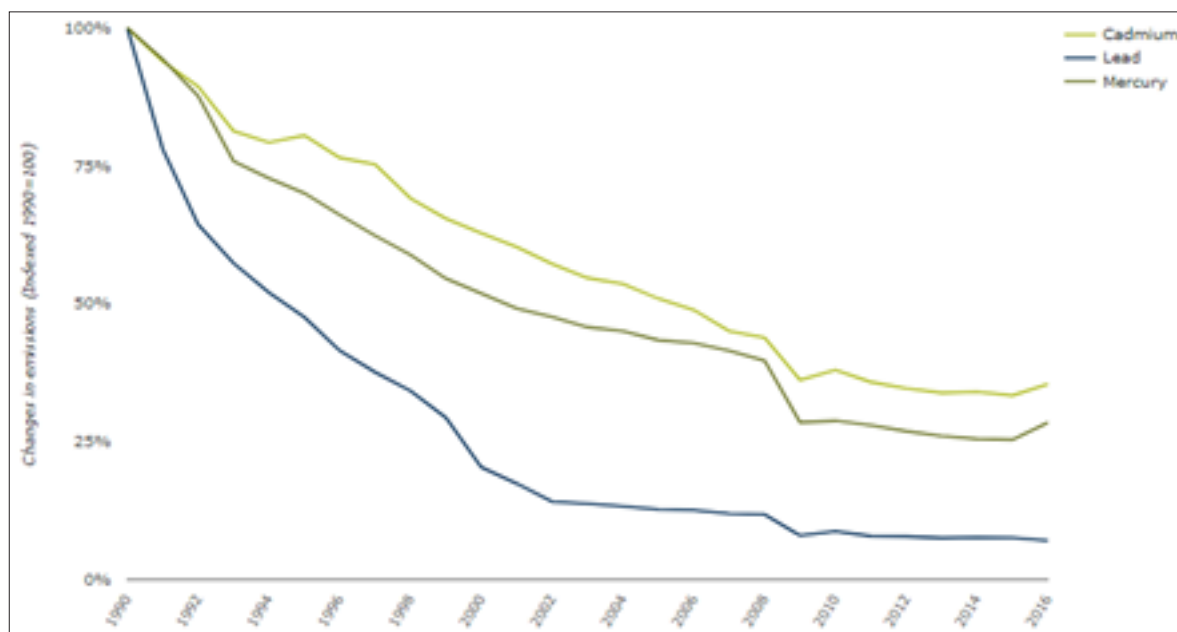


Fig. 1. Trends in emissions of heavy metals from 1990 to 2016 (Source: [30])

and ecological system [14, 18, 33-36]. Increased levels of heavy metal contaminants in water affect negatively the ecological function of water 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

Some heavy metals are needed for upkeep and growth by aquatic plants. However, when the concentrations become excessive, the plant may be at risks of heavy metal toxicity 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 effects include growth reduction (especially the origin and main part of 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.

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 ≥ 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

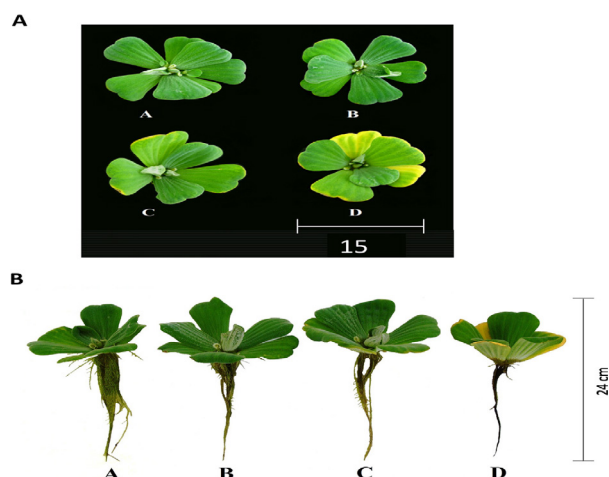


Fig. 2. Visual symptoms of arsenic toxicity in leaves (A) and roots (B) of *Pistia stratiotes* exposed to three As^{III} concentrations after four days (reprinted from [41]).

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. Literature reveals that adverse effects have been observed in aquatic plants for Pb, Cd, Hg, and As at very low concentration 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 tolerate or counteract the damages of heavy metals while some at certain concentration increase in nutrient and size. For example, when *E. camaldulensis* species was exposed to $45 \mu\text{mol/L}$ Cd, an increase of carotenoids (related to the tolerance to oxidative stress), epidermis and root endoderm thickness was observed [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]. Over 14 days exposure of *Ipomoea aquatica* (water spinach) to high Cr^{3+} (10 mg L^{-1}) in contaminated water (in hydroponic

system), the root of the plant increased in size (becoming fatter) rather than longer [50]. 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 state where plant survives a high level of exposure to a toxicant or stress, there is a potential for full recovery [57].

3.1.1.2. Aquatic animals

One major biomarker of heavy metal toxicity in aquatic environment is fish. Although, they are of great importance economically, they are greatly affected by heavy metals. Exposure of fish species to heavy metals may be from contact directly or from food web or chain indirectly. Long term exposure can cause death to juvenile fish and reduced breeding potential of adults fish as indicated in many reports [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 (determined through metal speciations) determines the impacts on human health. 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 human health are mainly controlled by concentrations (amount) ingested and individuals (with compromised metabolism and poor clearance

Table 3. Effect of heavy metal toxicity on some aquatic plants

Metal	Aquatic Plant	Toxic effect	References
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 ₂ evolution activity, high enzyme activities such as superoxide dismutase (SOD), catalase (CAT), peroxidase (POX) and ascorbate peroxidase (APX)	[41]
	Brake fern (<i>Pteris vita</i>)	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>Gladiolous</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>Ipomonea 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]

mechanisms) [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.

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 causes considerable and widespread concern. Rivers serve as hotspot for organic pollutant loading, particularly those in

lowland regions [74].

Organic water pollutants generally include: detergents, disinfection by-products (having “down-the-drain” applications [221]), food processing waste, insecticides and herbicides, petroleum hydrocarbons and lubricants, and fuel combustion byproducts (from storm water runoff) [75], volatile organic compounds, chlorinated solvents, perchlorate (from personal care products), drug pollution (involving pharmaceutical drugs and their metabolites). Some of 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

Table 4. Human health effects of some heavy metals

Metal	Effects	Most common Biomarkers of Exposure	References
Cd	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]
Cr	Causes allergic dermatitis, low birth weight and also affecting immune, urinary, respiratory and cardiovascular systems.	Blood or urine	[68]
Co	Nausea and vomiting Dermatitis.	Urine and Blood.	[69]
Cu	Liver and kidney damage, immunotoxic, and death.	Blood, urine, hair, and nails.	[70]
Ni	Dermatitis, allergicreaction and chronic bronchitis.	Blood, bone, and urine.	[71]
Pb	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]
Zn	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]

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 which is known as the Stockholm Convention, launched in 2001 to reduce drastically or eliminate POP release to the environment [76]. Many evidences exist regarding waterbodies pollution by organic pollutants. In drinking water, concentration rarely exceeds 20 mg/L⁻¹ [74]. Some organic pollutants including polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), antibiotics, herbicides and bisphenol A (BPA), have drawn significant attention by environmental researchers [77, 227]. However, other organic pollutants considered low priority pollutants may be inform 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.

3.2.1 Adverse effects of Organic pollutants in water

Although microorganisms can degrade organic

pollutant load in water through a self-purification process involving using of sufficient oxygen, dilution, sedimentation and sunlight. 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. Transport pathways in higher plants generally involves; short distance transport (intracellular and intercellular) and long distance transport (conducting tissue transport) [78]. However, some chemical based on their chemistry (e.g water-hating organic chemicals) are only limited in phloem [78-79]. Aquatic plant tolerance to uptake of organic pollutants seems to correlate with the ability to deposit large quantities of

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]

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. Some recent studies [82-85], found that the system of defense and growth of *Chara vulgaris* L., *Lemna minor* L., *H. dubia* (Bl.) Backer and *Potamogeton perfoliatus* L respectively are affected by Linear Alkylbenzene Sulphonate, (LAS). Furthermore, our re-interpretation of their data reveals that the effects are varied among the different aquatic 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. A simple indicator of aquatic plants exposure to organic pollutant is seen by the increased ROS production, leading to plants inability to do 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

Available oxygen in water is reduced organic pollutants. This affects water organisms by causing reduced fitness or death from asphyxiation. Effects also include increased turbidity (especially by petroleum-related wastes) of the water, which reduces the available light for photosynthetic organisms and potentially leading to its death. It can also settle on the benthic and alters the characteristics. 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 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. Although, impact of organic pollutants to human health is yet to be fully examined [95-99], evidences still exists which correlates development and manifestation of some chronic diseases to exposure of certain organic chemicals. Particular, cancer cases has been greatly linked [74]. Other toxic effects could be on ovarian function in women [100], reproductive disorders in both male and female [101], female breast cancer [102], blood poisoning, eyes and skin irritation (by exogenous pollutant e.g. LAS) [103].

4. Decontamination strategy: Phytoremediation

According to United Nations Environment Programme [104], the efficient use of plants for removing, detoxifying, or immobilising environmental contaminants is regarded as phytoremediation. The strategy is eco-friendly and cheap. The concept of phytoremediation of contaminated medium has been extensively discussed in many scientific, governmental and non-governmental studies [41, 104-115]. The overall objective of any treatment method 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 plants are extremely important components of an aquatic ecosystem for primary

productivity and nutrient cycling [116-118] and providing refuge, habitat and food for some aquatic organisms. 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]. 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

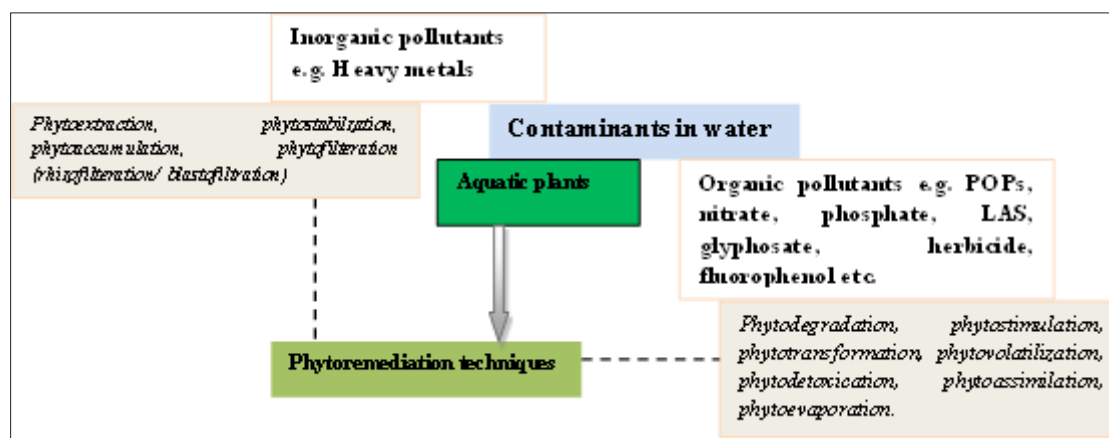


Fig. 3. Overview of phytoremediation techniques by aquatic plant for both organic and inorganic contaminants removal in water

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].

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, at the end of the exercise, plant biomass is often harvested, dried and ashed

for disposal or extracted using appropriate solvent before analysis. Aquatic plants which operate by rhizofiltration are preferable in aquatic phytoremediation than those plants that efficiently transfer the contaminants (translocators) from root to shoot. The reason is that translocators can potentially pollute above ground biomass, which increases the cost of processing, as well as the risk of exposing the ecosystem to the contaminated plants [4]. The analyses for heavy metals and organic pollutants concentrations in plant biomass are often done by spectroscopic and chromatographic techniques following extraction processes. Extraction technique for heavy metals is commonly by acid digestion while organic pollutants include liquid-liquid extraction (LLE), solid-phase extraction (SPE) and matrix solid-phase dispersion (MSPD). Common techniques for analysis after extraction include atomic absorption spectroscopy (for heavy metals) [6, 24], ultraviolet-visible spectroscopy (for dyes), high performance liquid chromatography (HPLC), liquid chromatography/tandem mass spectrometry (LC-MS/MS) or gas chromatography/mass spectrometry (GCMS) (for agricultural chemicals and

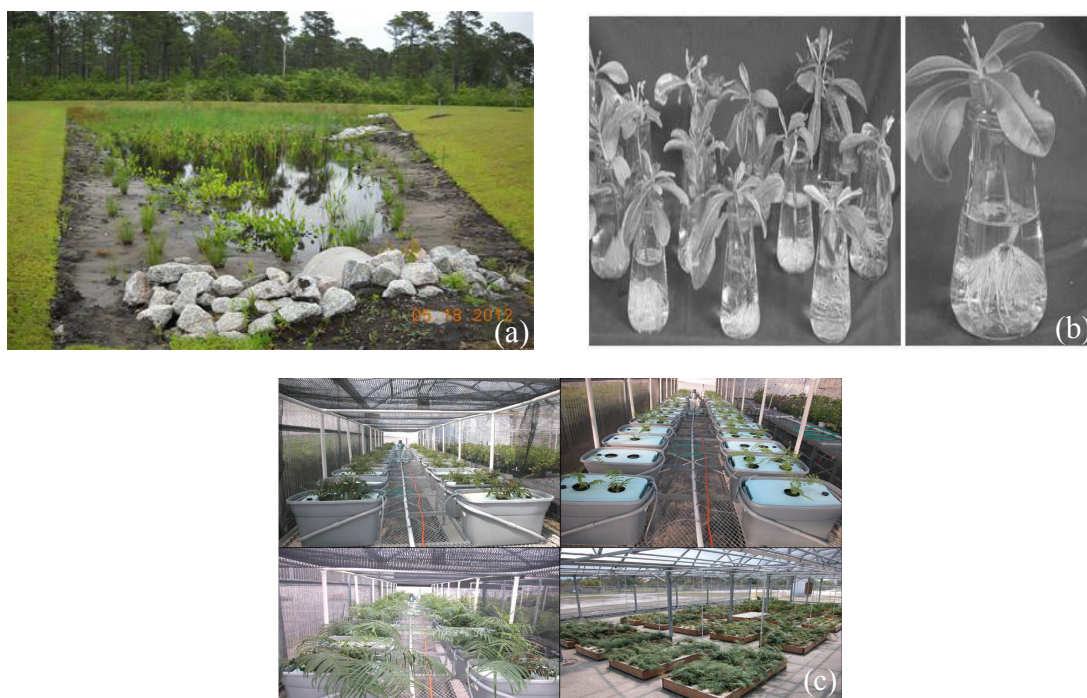


Fig. 4. Experimental system for aquatic phytoremediation. (a) Field experiment showing a constructed wetland [122], (b) Pilot scale setup using *Pteris vittata* for removal of As from contaminated water [80] (c) Hydroponic system developed for rhizofiltration of environmental contaminants by *Talinum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

petroleum hydrocarbons).

4.1. Physicochemical factors affecting phytoremediation

Cellular mechanism for detoxification and tolerance has been discussed recently [112]. In general, the efficiency of removal by aquatic plants depends on water and contaminant physico-chemistry as well as physiology and genotype of the plant [4, 123-

124]. However, in this study emphasis was placed on the physiochemistry summarized in Table 6. These parameters can be manipulated or modified in water to enhance phytoremediation.

Currently, studies modifying water physico-chemistry for phytoremediation of toxic chemicals is at infancy. There is therefore, need for more efforts for their effective use in the future. For metals,

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

Parameter	Effects
Heavy metal	
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].

phytoextraction capabilities of many plant species can be enhanced by reducing the concentration of organic acids in the water, since organic acids are known to form complexes with metals [6, 13, 65, 125]. Reducing organic acid will thereby increase the concentration of free metal ions readily available for uptake. In addition, the bioavailability of metals can also be enhanced by aquatic plant roots exuding acidifying protons in water. The lowering of water pH increases the adsorption of heavy metals and reduces their concentrations in the aqueous solution [6, 65, 125, 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, parameter such as molecular mass and hydrophobicity with partition coefficients (between octanol and water (K_{ow}) /air (K_{oa})) plays crucial roles. Many reports have shown that high K_{ow} and low K_{ao} values of organic pollutants correlated positively to easy (high) uptake of organic pollutants in water and absorption from air by aquatic plants [80, 127-130]. Succinctly, when $\log K_{ow}$ is less than 1, the organic pollutant becomes more soluble in water and mainly absorb on the plant roots at a rate surpassing passive influx into the transpiration stream (measured as TSCF) while at $\log K_{ow} > 3.5$, due to high sorption on the roots, aquatic plants may not or very slowly passed the contaminants into the transpiration stream and further to the stems and leaves [80, 127]. $\log K_{ow}$ values of some frequently found organic contaminants in the environment have been reviewed [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

Literature reviewed reveals that many aquatic species have been identified and tested for the phytoremediation of selected heavy metals (As, Cu, Cr, Hg, Cd, Ni, Pb and Zn) from the polluted water (Table 7). These include sharp dock (*Polygonum amphibium* L.), duck weed (*Lemna minor* L.), water hyacinth (*Eichhornia crassipes*), water lettuce (*P. stratiotes*), water dropwort (*Oenathe javanica* (BL) DC), calamus (*Lepironia articulate*), pennywort (*Hydrocotyle umbellate* 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 (*Callitriche 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 (*Warnstorfia fluitans*), hippo grass (*Vossia cuspidate*), blue moon (*Iris sibirica*), marigold (*Tagetes erecta*), yellow bur head (*Limnocharis flava*), willow (*Salix matsudana*), Alpine penny-cress (*Noccaea caerulea*), 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.

Some plants are considered hyper-accumulator due to their well-developed fibrous root system and large biomass e.g *Azolla* species, water hyacinth,

duckweed etc. Removal rates by the water hyacinth 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]. Furthermore, strong removal was also observed for Cd removal (> 90 %) conducted in a pot [25]. Also using water hyacinth, Lu et. al., [142] demonstrated the potential for the removal of Cd and Zn. In their study, the plant was exposed to concentrations of 0.5, 1, 2 and 4 mg/L of Cd and 5, 10, 20, and 40 mg/L of Zn, and harvested separately after days 0, 4, 8 and 12. They observed fast removal in the first 4 days with overall removal rates of 50-90 %. They concluded that the plant was a moderate accumulator of Cd and Zn at low concentrations. Abbas et al [173] assessed the effectiveness of

water hyacinth for the phytoremediation of landfill leachate for the period of 15 days. The authors used fifteen plastic containers in experimental setup and the plant 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 the plant is suitable for the removal of pollution load from landfill leachate. Priyanka et al [162] tested water

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>Warrnstorfia fluitans</i>	82	[138]
	16.31ppb	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 Trin</i>)	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 ⁻⁷ 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]

Table 7. (Continue)

Metal	Concentration	Exposure duration	Experimental framework	Plant specie	Removal rate (%)	References
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 Trin</i>)	45.6-80	[141]
	<0-2.20 µg/L	Inconsistent	Field	spiny water nymph, spiny naiad and holly-leaved naiad (<i>Najas marina</i>)	45.6-80	[141]
	1.0-2.0	24 h	Field	Salviniaceae (<i>Salvinia herzogii</i>)	70-83	[151]
	0.1-1.0	12 d	Hydroponic	Water fern (<i>Azolla caroliniana</i>)	100	[152] ^a
	0.1-1.0	12 d	Hydroponic	Water fern (<i>Azolla caroliniana</i>)	74	[152] ^b
	1	15 d		Duckweed (<i>L. minor</i>)	96.94	[153]
	1.0-2.0	24 h	Hydroponic	Water lettuce (<i>Pistia stratiotes</i>)	58-80	[151]
	1-10	9 w	Hydroponic	Water lilies (<i>Nymphaea spontanea</i>)	31.6	[154]
	< 0 – 0.51	Inconsistent	Field	Poaceae (<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.)	50-80	[155]
	0.04-98	60 d		Duckweed (<i>L. minor</i>)	25-77.42	[156]
	10	3 w	Hydroponic	water-starwort (<i>Callitriche cophocarpa</i> Sendtn)	50-80	[157] ^a
	0.25-5.0	14 d	Pilot with continuous flow	Duckweed (<i>L. minor</i>)	76.4-20.0	[134] ^a
	10.946	7 d		Duckweed (<i>L. minor</i>)	99.97	[158]
	10.4	7 d	Hydroponic	Duckweed (<i>L. minor</i>)	75	[159]
	0.776	7 d	Field	Duckweed (<i>L. minor</i>)	63	[146]
	0-0.20 mM	16 d		Duckweed (<i>L. minor</i>)	27.6	[160]
				<i>Phalari arundinacea</i>		[161]
	2	15 d	Field	Water hyacinth (<i>Eichhornia crassipes</i>)	99.9	[162] ^a
	67.33 ppb	25 d		Duckweed (<i>L. minor</i>)	90.25	[139]
	0-12.39	28 d	Field	Duckweed (<i>L. minor</i>)	72-91	[148]
	0-12.39	28 d	Field	Water fern (<i>Azolla filiculoides</i>)	90	[148]
Cu	1.95-4.20 µg/L	Inconsistent	Field	Poaceae (<i>Phragmites communis Trin</i>)	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>)	77.78	[163]
	1	15 d	Hydroponic	Duckweed (<i>L. minor</i>)	96.94	[153]
	1-7	15 d	Hydroponic	Mint (<i>Elsholtzia argyi</i>)	50-90	[164]
	1-7	15 d	Hydroponic	Mint (<i>Elsholtzia splendens</i>)	45-80	[164]
	1.23 – 1.75	Inconsistent	Field	Poaceae (<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.)	50-80	[155]

Table 7. (Continue)

Metal	Concentration	Exposure duration	Experimental framework	Plant specie	Removal rate (%)	References
Hg	0.003-10 ⁻⁷ M	7 d	Hydroponic Field	Duckweed (<i>L. minor</i>)	86.5	[143]
	0.46	20 d		Duckweed (<i>L. minor</i>)	71.4	[165]
	4.359	7 d		Duckweed (<i>L. minor</i>)	99.97	[158]
	3	7 d		Duckweed (<i>L. minor</i>)	40	[159]
	1.432	7 d		Duckweed (<i>L. minor</i>)	86	[146]
	67 µg/L	3 d		Duckweed (<i>L. minor</i>)	87	[137]
	0.5 and 0.25	7 d		Duckweed (<i>L. minor</i>)	0	[166]
	1-5	4 w		Duckweed (<i>L. minor</i>)	90	[167]
	200 µM	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		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		Water fern (<i>Azolla filiculoides</i>)	80	[148]
	0.09-0.73	15 d		Water hyacinth (<i>Eichhornia crassipes</i>)	36.98-87.09	[173]
	0.08-0.46	15 d		Water lettuce (<i>Pistia stratiotes</i>)	39.72-72.58	[173]
	0.1-1.0	12 d		Water fern (<i>Azolla caroliniana</i>)	75-93	[152]
	0.04-98	60 d		Duckweed (<i>L. minor</i>)	25-77.42	[156]
	0.23	20 d		Duckweed (<i>L. minor</i>)	66.5	[165]
	0.5 and 0.25	7 d		Duckweed (<i>L. minor</i>)	0	[166]
				<i>Salix matsudana</i>		[160]
	200 µM	3 d		Duckweed (<i>L. minor</i>)	20.2	[168]
	0-30 µM	6 d		Duckweed (<i>L. minor</i>)	58.3	[81]
Ni				Field <i>Limnocharis flava</i>		[174]
	0.36 ppb	25 d		Duckweed (<i>L. minor</i>)	82.84	[139]
	1-8	14 d		Water Mint (<i>Mentha aquatica</i> L.)	22.3	[175]
	1-8	14 d		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 µg/L	Inconsistent		Field Poaceae (<i>Phragmites communis Trin</i>)	45.6-80	[141]
	1.90-17.30 µg/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]

Table 7. (Continue)

Metal	Concentration	Exposure duration	Experimental framework	Plant specie	Removal rate (%)	References
Pb	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	25 d		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 (<i>Canna × generalis</i>)	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]
	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 ⁻⁷ 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]
Zn	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]

Table 7. (Continue)

Metal	Concentration	Exposure duration	Experimental framework	Plant specie	Removal rate (%)	References
	0.04-98	60 d	Field	Duckweed (<i>L. minor</i>)	25-77.42	[156]
	0.003-10 ⁻⁷ 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]
			Field	<i>Cyperus alternifolius</i>		[181] [182]
	0-12.39	28 d	Field	Duckweed (<i>L. minor</i>)	72-91	[148]
	0-12.39	28 d	Field	Water fern (<i>Azolla filiculoides</i>)		[148]
			Hydroponic	Alpine penny-cress (<i>Noccaea caerulea</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]

^a used Cr⁶⁺, ^b used Cr³⁺; 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

hyacinth in clean wastewater at Sukinda chromite mines (SCM) area of Orissa (India) containing high levels of toxic hexavalent chromium (CrVI). Results showed that the plant could remove 99.5% Cr (VI) of the processed water of SCM in 15 days. Using hydroponics, they [48] tested different levels of Cd (5 to 20 mg L⁻¹) rate by three hydrophytes: *Gladiolous*, *Isoetes taiwanenses* Dwvol and *Echinodorus amazonicus* and observed highest accumulation in *Gladiolous* than the other two plants. Also, high removal rates following phytofiltration were reported for *Elsholtzia argyi* (50-90 %) and *Elsholtzia splendens* (45-80 %) for Cu [164]. Boonyapookana et al [140] observed high phytoaccumulation rates (reaching 90 %) for Cd and Cr by *W. globosa*, which correlates positively with exposure time and metal concentration were increased. Small water fern (*Azolla caroliniana* Willd.), was investigated for water purification potential by [152]. The experiment was conducted

in 12 days using hydroponic solution polluted by Hg and Cr. Initial concentrations were 0.1, 0.5 and 1.0 mg/L for both metals and day 12, metal contents the solution decreased to 0–0.25 mg L⁻¹, corresponding between 74 – 100 % removal rates. Baldantoni et al [141] studied the leaves and roots *Phragmites communis* Trin. (an emergent plant), and *Najas marina* L. (submerged plant), taken from Lake Averno (Naples, Italy) for levels Cd, Cr, Cu, Fe, Ni, Pb, Zn and found higher accumulation in root than leaves. However, between the two plants, *Phragmites communis* showed high capability to accumulate trace metals in the roots better than *Najas marina* [141]. By constructing a wetland in the Venice lagoon watershed, they [155] investigated the removal efficiency of *Phragmites australis* and *Bolboschoenus maritimus* in removing Cr, Ni, Cu and Zn from water. Investigations were conducted over a vegetative season with various distances to the inlet point to assess effects on

vegetation. Results showed that overall heavy metal concentrations removed ranged from 50–80 % and *P. australis* was a better phytoaccumulator to in *B. maritimus* (accumulating more in roots). Using outdoor experiments, capacity examination of *Salvinia herzogii* (Salviniaceae) and *Pistia stratiotes* (water lettuce) to remove Cr (III) from water was conducted by [151]. Results from their study showed that both plants efficiently removed Cr (up 83 % for Salviniaceae and up 80 % for water lettuce, Table 7) from water. Furthermore, water lettuce was also found by [173] to be very effective with maximum removal rate over 15 days for Zn (80–90%), Pb (76–84%), Cu (72–87%) and Ni (68–81%) respectively from landfill leachates. The author reported that the plant exhibited low (< 1) bioconcentration factor (BCF) and translocation factor (TF), indicating low transport of heavy metals from roots to the upper parts of the plant. Another excellent Cr removal from polluted water was found in *Callitriche cophocarpa* (water-starwort) by [157]. The authors used a hydroponic culture for up to 3 weeks and reported removal rate up 80 % (Table 7). Nevena et. al., [179] tested an ornamental plant *C. indica* for phytoremediation of Pb in wastewater. Removal rates of 81.16 % was obtained and therefore concluded that *C. indica* can be used in rhizofiltration systems or floating islands for treatment of water polluted with lead [179]. Most recent studies have used duckweed more when compared to other plants. Axtell et al [176] examined the ability of *Lemna minor* using a batch process to remove Pb and Ni under different laboratory conditions. Initial concentrations were 0.0, 5.0, and 10.0 mg/l for Pb, and 0.0, 2.5, and 5.0 mg/l for Ni. Overall, *L. minor* removed 76% of Pb and 82% of Ni. They further observed that there was no synergistic/antagonistic effect for the multiple metal experiments, in terms of metal removal [176]. In a continuous flow pond system, Uysal [134] examined the ability of *Lemna minor* to remove Cr (VI) ions from wastewater. The authors used the system to simulate a wastewater treatment pond and a natural wetland as habitat for the plants and reported removal rates between 20

– 76.4 % suggesting the potentiality of the plants for Cr removal in wastewater. 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 were observed for duckweed fronds (> 70 %) while highest removal throughout the study for specific plants was water hyacinth 68 %, umbrella 66 % and canna 31 % respectively. Based on the results of their study, duckweed was suitable for the uptake of most heavy metals [150].

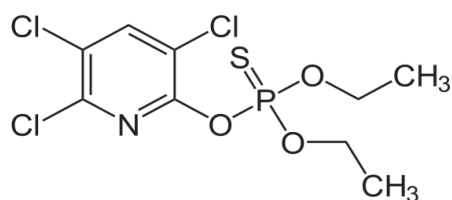
4.3. Phytoremediation of organic pollutant in water

Few aquatic plants have been generally been tested recently for removal of aquatic organic pollutant. It has been less studied compared to heavy metals mainly due to the complex properties (physical and chemical) of organic pollutants. 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, terbuthylazine, 4-chloro-2-fluorophenol (4-Cl-2-FP), lactofen, cyanophos, 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, sulfachlorpyridazine, 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

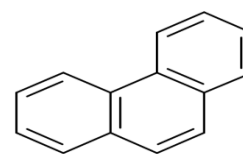
microcystin-LR., perchlorate, toluidine Blue; and from petroleum hydrocarbons including 1H-benzotriazole, 4-methyl-1Hbenzotriazole, 5-methyl-1Hbenzotriazole, xylotriazole, 5-chlorobenzotriazole, 3-trifluoromethylphenol, phenanthrene.

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*

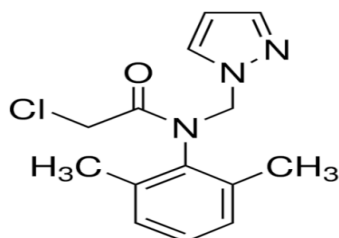
L. [85], *Hydrilla verticillata* (L.f.) Royle [193], *Vallisneria natans* (Lour.) Hara [193], giant reed (*Arundo donax*) [194], Poaceae (*Phragmites australis*) [194], broadleaf plantain (*Plantago major* L.) [222] and *Ipomoea aquatica* [195] while *Myriophyllum aquaticum* (watermilfoil) [196] and bulrush (*Scirpus lacustris*) [197] have also been used earlier. For remediation of municipal effluents, some of these plants in some cases have been reported to better treat wastewater than normal wastewater treatment plant [198] and combination of two or more plant increased the effectiveness of removal [199-201]. Domestic as well as industrial



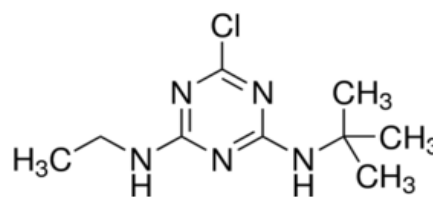
Phenanthrene



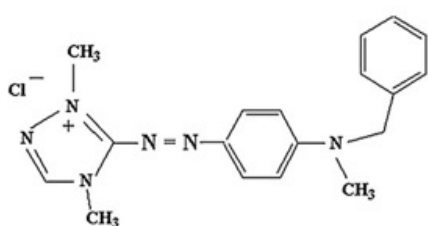
Chlorpyrifos



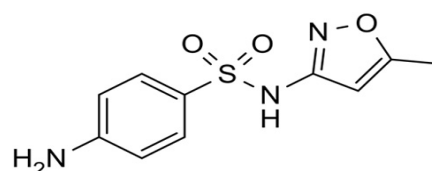
Metazachlor



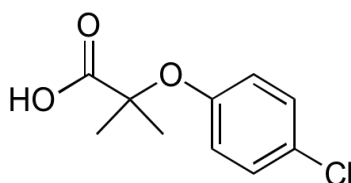
Terbutylazine



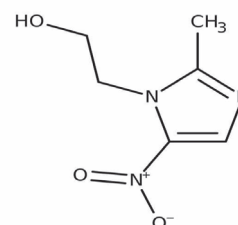
Textile dyes (BR46)



Sulfamethoxazole



Clofibric acid



Metronidazole

Fig. 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].

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^{-1} 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 alkylbenzenesulfonate (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 (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 remove organic pollutants such as BOD_5 , TSS, $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ from wastewater in two kinds of hybrid constructed wetlands viz Facultative pond combined with free watersub-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_5 , TSS, $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ 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

The science of relating chemical data from chemical processes to state of system by applying mathematical or statistical methods/models is considered chemometrics [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 assess 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 [44, 48, 137, 139, 141, 146, 155-158, 165-168, 171-173, 175-177, 210-211] and can also be used in organic pollutant remediation studies. Growth rate (GR) value is an important index for predicting 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 stands for 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).

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

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

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) shows the metal content in whole plant tissue or in a selected plant part; moreover, MU can be calculated by 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 shows 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 concentrations of each metal 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].

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

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

The potential for metal uptake in plant tissue is shown by percent metal uptake (% MU); the uptake also corresponds with reduced metal concentration in solution. In addition, 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 for removing 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) shows 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/m²/yr), M_{plant} is the mean of plant yield (g DW/m²/yr), M_{root} is the mean of root biomass yield (g DW/m²/yr), M_{leaves} is the mean of leaves biomass yield (g DW/m²/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 [221]. 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 Equations 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.

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

$$d/C_e = 1/k * C_e^2 + 1/C_e * d \quad (12)$$

Langmuir adsorption equation is the very ubiquitous linear model for monolayer adsorption, and it is used to assess the adsorption process. Langmuir model 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 explained adsorption onto a heterogeneous surface [219] as in Equation 14: where, C_e refers to solution equilibrium concentration (mg L⁻¹), q is the adsorption capacity (concentration of metal on adsorbing substrate, mg/kg), and k and (1/n) are constants connected to adsorption capacity.

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

Temkin isotherm model corresponds to a factor which is 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), C_e corresponds to metal concentration (mg/L) remaining in outflow, B and kt are the constant

related to adsorption process [219].

$$q = \text{Bln}(kt) + \text{Bln}(C_e) \quad (15)$$

The removal efficiency (RE %) of dye from aqueous solution in a batch study can be studied by equation (16) while the amount of dye in the plant phase can be calculated using equation (17); where q_e is the amount of dye adsorbed per gram of adsorbent at equilibrium (mg/g), C_0 and C_e are the initial and equilibrium concentrations of the dye in solution (mg/L); V is the volume of solution (mL); m is the weight of the adsorbent (plant) (g) [205].

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 (emerging, 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]. Heavy metals consider as water pulltant and must be removal from waters and reviers [223-226]. 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.

7. Knowledge gap and Future Areas of Research

(1) A need is there for studying the plant in the face of emerging chemicals (e.g polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) etc) which defy conventional remediation approaches for establishing acceptable remediation strategies and ecological benchmark for improvement of constructed wetlands for wastewater effluents treatment [57]. 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) More studies are required to understand better the precise transfer pathways of pollutants and their temporal pattern, in order to pinpoint toxicity more precisely in aquatic plants. Such studies will generate an improved understanding which will help in controlling cumulative toxic effects of pollutants on plants and enhancing the role of aquatic plants as a vital ecological based bioremediation agent for water pollution.

8. Conflicts of interest

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

9. References

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