

Biological Treatment of Heavy Metal in Aquatic Environment: A Review of Wetland Phytoremediation and Plant-Based Biosorption Methods

Oyewumi Tolulope O.¹, Ajayi Omoyemi O.¹

¹Federal University of Technology, Akure. Correspondence E-mail Id: editor@eurekajournals.com

Abstract

Aquatic bodies such as the lagoons, rivers and seas are known to be environmental sinks for heavy metal trapped within the soil matrix (from anthropogenic activities) as they are leached and wash-off via water percolation into the soil, erosion and floods. Thus designing treatment method under such condition (aquatic) becomes imperative. The use of chemical and physical method of treatments are established methods which are often times expensive to operate. The use of more sustainable method often referred to as biological method has put the use of techniques such as wetland phytoremediation and plant-based bioadsoptionas a more promising method of treatment.Both biological methods are cheaper, more sustainable and greener in approach compared to the physical and chemical method.

Wetland phytoremediation through the use of macrophyte are capable of metal uptake, precipitation, translocating and storage of metal toxins in thousands of ppm. These hyperaccumulators are highly vascularized plants and can be found in waterlogged areas or underground in water. Different wetland plants generally have dissimilar affinity for heavy metal absorption and thus specific macrophytes have been identified for a wide range of metal pollutant and used by water authorities around the world. On the other hand, plant-based biosorption function with the use of agricultural waste materials which are pretreated to improve their surface functionality and hence affinity for these pollutants. Unlike wetland phytoremediation, aqueous condition such as water pH, mineral solubility affects its effectiveness.

Keywords: Aquatic body, Macrophytes, plant-based bioadsorption, wetland Phytoremediation, Biological treatment.



Introduction

Considered to be one of man's greatest crime to nature [1]; environmental pollution continues to threaten life's sustainability and existence on the planet. The elevated concentrations of persistent organic pollutants (POPs), radionuclide, heavymetals etc., has accelerated since the dawn of the industrial age [2]. Their presences have greatly impaired the quality of the atmosphere, biosphere and the hydrosphere to sustain life [3].Anthropogenic activities such as chemical processes, mining, energy utilization etc., have been the main cause of these pollutants, which are not biodegradable and are stored up in living tissues.Among these pollutants are metals laden waste ceaselessly discharged as industrial effluence into the aquatic environment. Toxic metals ions, such as Pb(II), Cd(II), Hg(II), As(III), Cu(II), Ni(II), Zn(II), Cr(VI), Co(II) etc., are found at different concentration in aquatic bodies [26] and are well known to be carcinogenic, mutagenic toxic and hazardous to life.

However, economic needs for metals and minerals has had a profound effect on this increase. Needs stemmingfrom its value instructural reinforcement, machinery, metal frameworks, comes from its continuous demandin technological development and advancement. Thus, mining and metallurgical processes, has increasingly exposure man to toxins, through several sources such as water, food, air etc. Industrialization and urbanization are also culprits, as most of these metals accumulate in sediments and soil of water bodies [4,5]. Metal-laden waste are associated with industries such as tanneries, textile, pulp and paper, chlor-alkali, electroplating, fertilizers, dying and battery manufacturing [6,7]. In some cases erosions and surface run-off from such industrial site, polluted land and municipals, find their way into water bodies. With favourable geochemistry and redox conditions of the soil, heavy metal ions are transported into nearby lakes, rivers and groundwater oasis[8]. Hence, such conditions contribute to mass influx of heavy metal pollutant into fresh aquatic habitat.

Physico-chemical and biological factors also influence their speciation, sequestration and bioavailability in water as uptake of these heavy metals, depends on their ionic state. The term heavy metals generally refer to metals with high atomic weight and density, 5 times that of water[8]. With both assumption of heaviness and toxicity, these metals bioaccumulate in marine animals and are transported through the food chain to higher trophic levels[9, 10]. These processes of bioaccumulation and biomagnification continue over a long period of time until adverse health conditions crop-up. Although some heavy metals are said to be physiologically and nutritionally essential (Cu, Co, Zn, Fe etc.)Others like Hg, Cd, Pb, As and Cr are considered dangerous to organism even at trace quantity[5, 8]. And this has lead researchers to work on different heavy metal removal method with many published on the efficient of different methods of treatment.

Treatment of industrial effluence has majorly been based on physical method, chemical methods and the newly explored biological methods. Most commonare the physical and chemical methods of chemical precipitation, oxidation, ion-exchange, electrochemical



treatments and adsorption techniques. The high energy demand and cost of treatment required for these methods has increased the cost of production in mining industries, metallurgical industry, fertilizer and other chemical industries. Thus, the use of biological methods has been extensively researched. Biological treatment such as wetland phytoremediation and plant- based biosorptionare considered cheap, cost-effective, sustainable and ecofriendly.

Biological treatment involves the use of both living and dead biomass [11]. Living biomass (Wetland plants) such as water hyacinth, common reed, water lettuce, duckweed etc.,have high remediation potential for macronutrients due to their general fast growth and high biomass production. [12, 13]. However, theirability to accumulate heavy metals in the root, shoot and aboveground tissues is a determinate factor for metals:phytoextraction, rhizofiltration, phytovolatilization and phytostabilization[14]. On the other hand dead biomass in form of agricultural waste as equally attracted attention as potential plant-based bioadsorption. Biosorbent have a bonus of accessibility, potency and capability compared to the seasonality of living biomass. Unlike living biomass, it has the tendency of reaching a breakthrough (saturation), where no further pollutant can be adsorbed. In this method plant root, seed, shell, bark are pretreated to improve its surface functionality and cation exchange affinity.

This paper however seeks to review wetland phytoremediation and plant based biosorption as important biological treatment techniques, by understanding mechanism of each process; identifying potential biomass for each method; their constrains and future projections in treatment of heavy metals in polluted aquatic bodies. The reviewers have also endeavored to analyze the environmental impact of this pollution on man and also the ecosystem.

Anthropogenic Source of Heavy Metal Pollution

The ever increasing pace of globalization, industrialization and technological advancement, has increased man's exposure to heavy metals. Human propelled ventures such as mining and enrichment of nuclear fuels, burning of fossil fuels and smelting of metalliferous ores [15, 2] are the chief sources of these pollutants. They have single handedly account for the rising background concentrations of these metals in the soil, air and water. In tandem with the increasing energy demand; fossil fuel powered plants has actively contributed in two ways, the first being the burning of coal and gasoline, with contaminant plumes from coal-based thermal power plants prevalence in urban and industrial sites throughout the globe [2], increasing air contamination and as sediment on various surfaces. The second, is through its mining processes, which entails excavation of heavy metal laden impurities alongside mineral ores from the ground.

Mineral mining and smelting is also a potential source of heavy metals as ores of various economic minerals like Fe, Cu, Ag, Au, S, Pb etc. come with different degrees of impurities, which is a significant part of the admixtures of industrial waste and effluence. For instance,



the electroplating industry which is involved in metal purification and refining further contributes to these anthropogenic sources. Metal laden waste from them are however discharge into underground wells and river bodies as the treatment cost is relatively high compared to the cost of dumping.

Other industries such as the paper industry, chlor-alkali industries, tannery, dyes, paint industry, fertilizer industry also known to make use of chemicals such as additives, bleaching agents, pigment etc. which contains these heavy metals, which ultimately end-up as part of their effluence. Figure 1. Below however shows some anthropogenic sources for some specific metals

Heavy Metal	Anthropogenic source
Arsenic	Pesticides, smelting process, wood preservatives
Lead	Batteries, PVC plastics, Paint pigment
Mercury	Chloralkali plants, Paper industry, paints, fungicides
Cadmium	Smelting, cadmium batteries, paints
Chromium	Pant pigment, fertilizers, textiles, tannery
Copper	Fuel catalysts; batteries; smelting, alloys and solids
Zinc	Electroplating industry, paints
Nickel	Batteries, glass industries,

Table 1.Anthropogenic source for some selected Heavy metals

[†]Souce Abdi and kazemi, 2015;Naggar et al., 2018; Baby et al., 2010.

Heavy Metals in Aquatic Environment

Oceans, seas, rivers and stream are the receiving end of these pollutions as they act asnatural sink for all non-biodegradable environmental pollutant, most especially heavy metals[1]. The rate of input of thesegroups of pollutantshas however increased since the dawn of the 21st century[16]. And most disturbing arethe contaminations to ground water system from landfill leachates, deep well liquid disposal industrial waste etc. [17], as the quality of drinking water and wholesomeness of sea food are tampered with. These pollutants are transported from their different point-discharge sources into water bodies via surface run-offs, erosion, atmospheric depositions, underground water movements and floodsinto the marine ecosystem. These ends-up disrupting the ecological balance in such water bodies, as these metals remains non-biodegradable and accumulate in aquatic creatures-most especially fish and sea plants.

Although some trace heavy metal functions as nutrient foraquatic plants and animals, their elevated levels can adversely affect the safety of aquatic environment. However, many of these nutritive metals have toxic effects atelevated concentrations. Heavy metals like Hg, Cd, As, Pb and Cr, poses superior threat compared to Cu, Fe, Co, Ni, Zn etc. Because of their toxic, carcinogenic and mutagenic effects. Hg, Cd, As, Pb and Cr have been considered by



the United State Environmental Protection Agency (USEPA) and International Agency for Research on Cancer (IARC) as priority metal of severe public significance [8]. As their concentration varies from one water body to another due to the dilution factors which is a function of the volume of water present in such bodies.Smaller water bodies like lakes, rivers, streams and lagoons have shown elevated concentration due to discharge of untreated industrial effluent in them [1] and it consequence volume flow from the discharge source to other aquatic site.Depending on conditions within the aquatic habitat, factors such as, pH, cation exchange, temperature, organic matter, evaporation, living organism etc., would affect the metal speciation in the water [11].

Health Impact of Heavy Metals Pollution

Through history there has been incidence of specific heavy metal disease resulting from polluted aquatic system. The consumption of either water or fish from such polluted water body is evidence in some localized diseases. For instance, the Itai-Itai disease in Japan in 1912, is one of the well-known cases. In this situation cadmium was the culprit as significant quantity of waste from kamioka Mine increased the concentration of cadmium in the river [15]. Another incident of such pollution is the minimata bay disease which was caused by the release of methyl Mercury as an industrial waste from a chemical factory. Thus, Methyl mercury began to bioaccummulate in shellfish and fish, which when eating resulted into mercury poison for the locals around that area of Japan[15].

These two cases perfectly portrays the devastating effect of heavy metal pollution in aquatic habitats. As a major protein source, fishes and other marine creatures which forms an integral part of the food chain becomes a medium for the transportation of these pollutants to higher organism. However, bioaccummulation and biomagnification in fish and other aquatic animals helps in the transfer of such toxins from one trophic level to another [15]. In human, these heavy metals accumulate in soft tissues of the body as they cannot be metabolized and subsequently absorbed after ingestion into the body. Although many of these heavy metals at right concentration are essential micronutrient for man e.g. Iron, Copper, Manganesse, Cobalt, but the larger their amount the more danger they pose to the ecosystem and man. Thus the figure below (Table 2) shows the effect of specific metal toxin in man and their target tissue for bioaccumulation.



Table 2.Health effect and target human tissue for some selected Heavy metals				
Heavy Metal	Target human tissues	Chronic and Acute effects		
Arsenic	Blood, kidney, digestive system	Bone marrow, diabetes, hematological		
		disorder and liver tumors.		
Lead	Bones, blood, kidney thyroid	Nervous and renal systems, weakness,		
		anemia, brain damage, convulsion,		
		anorexia, constipation and cancer.		
Mercury	Brain and Kidney,	Nerve damage, death kidney and		
		neurological and renal disturbances.		
Cadmium	Liver, lungs, bone, kidney,	Cardiovascular diseases, hypertension,		
	brain	ltai-ltai disease, cancer, kidney damage,		
		bone lesions, weight loss.		
Chromium	Kidney, lungs	Epigastria pains, lung tumor, mutagenic,		
		cancer		
Copper	Nervous system,	Severe mucosal, irritation, cancer,		
	Gastrointestinal tract, blood	nuerotoxicity, dizziness, diarrhea.		
	cells			
Zinc	Kidney, gastrointestinal tract	Cancer, gastrointestinal distress, nausea		
		and diarrhea.		
Nickel	Lungs, skin, kidney	Lung cancer, respiratory problems,		
		chronic bronchitis, dermatitis, chronic		
		asthma.		

[†]Souce: Tchounwouet al.2014; Abdi and kazemi, 2015 Naggar et al., 2018; Baby et al., 2010.

Methods of Heavy Metal Treatment in Aquatic Environment

Poisons from heavy metal bioaccumulation have brought the need to effectively treat industrial waste for the purpose of removing these toxins before discharging them into water bodies. Although conventional, the expenses incurred in chemical precipitation, ionexchange, reverse osmosis, electro dialysis has led to intense research to improve the efficiency of treatment processes by using more sustainable methods such as phytoremediation and bioabsorption method. However in this review we shall look at;

- Wetland Phytoremediation (Living Biomass)
- Plant Based biosorption (Dead Biomass)

Wetland Phytoremediation

Phytoremediationexplore the use of natural biofilters (Macrophytes) in the treatment of heavy metals from aquatic systems [18]. Highly vascular plants with the unique ability to hyperaccumulate nutrients alongside heavy metals are used to ameliorate pollutants transported into aquatic environment (rivers or lakes). This form of bioremediation is



considered to be cost-effective, sustainable and environmentally friendly compared to other conventional methods such as chemical precipitation, ion-exchange and physical adsorption methods [2]. Characteristics of plant grown for this purpose includes dense root- to maintain and enhance adsorption efficiency-fast rate of growth, high affinity for nutrientand as a result they are described as Macrophytes or Hyperaccumulators.

Macrophytesare aquatic plants which grow on the surface or submerged under water.Most times these plants are seen in shallow and waterlogged areas. Common macrophyte recorded in literatures includes water hyacinth, common reed, duckweed etc.which are capable of heavy metal bioaccumulation, translocation and precipitation from soil, sediment and water [15, 19]. However seasonal fluctuation has limited the use of these plants in its natural settings.

In a more controlled system, they are hydroponically grown in constructed wetlands[20].Such constructed wetland facilitate allows a well-controlled system of regulating environmental infiltration into other water bodies, controlled waste water volume and effective biogeochemical processes. With more cleaning efficiency compared to the use of Natural wetlands [2,20]. This actual clean-up process is carried out via the combination of biogeochemical activities such as pollutants,

- Binding to soil, sediment and particulate matter
- Precipitation as insoluble salt
- > Uptake by bacteria, algae and macrophyte
- Harvest and removal of contaminated biomass (macrophytes)

According to [2, 13]. Also the different actions of plants and their associated rhizosphere bacteria on pollutantscan be responsible for bioaccumulation, root complexing and clean-up process [21]. The presence of the macrophytealso plays an essential role in the treatment of organic waste as they possess a well-developed root system and plant physiology(Hyper-accumulators) for storing heavy metals as well as degrading bio-organics [22, 12]. These mechanism include rhizofiltration, phytoextractionphytostabilization, and phytovolatilization [23].

Phytoremediation: Mechanism of Heavy Metal Removal in an Aquatic Environment

Absorption of nutrient from the environment in plantsis a well mastered bioactivities in which the plants induce pH changes, together with redox processesitprecipitates or solubilize and take up nutrient. In certain plant species, these processes are assisted by some microorganism or special chelating agents [19] produced by the plant. After uptake, thesenutrients are transported to the upper part of the plant and stored for use. In similar vein, heavy metal uptake translocation and storage is experienced in aquatic plants. However, some plant are more specialized in these than others. Certain group of plants known as hyper



accumulators are capable of storing metal toxins in thousands of ppm [19]. These metal accumulating species are useful for phytoremediation studies as metals like Cd, Pb, Hg, As, Co, Zn, Cu, Nietc can be extracted from waste water. The process of uptake, translocation and accumulation includes

- Phytoextraction: This involves the uptake/absorption of pollutant by the plant root and subsequent translocation to the upper part of the plant, which can be harvested and properly disposed.
- Phytostabilization: Through phytostabilization pollutants in the soil/ water environment (wetland) accumulate in the plant tissues or are adsorbed on the root system; precipitated (Chelating agent) around the root zone to prevent its migration in the sediments or water around the root. This basically takes the advantage of the ability of macrophyte to alter soil conditions [18].
- Rhizofiltration: Involves absorption, concentration and precipitation of metal toxins by plants through the root system[18]. Wetland plant follow this mechanism where root exudates precipitate heavy metal ions around its surface
- Phytovolatilization: In this process pollutants or modified form of pollutants is transpired (volatilized) through the leaves and then released into the atmosphere through the plants stomata.

Hyperaccumulators (macrophytes) generally exhibit fast growth and high biomass production, their above the root tissues are central points for metal phytoextraction[12, 13]. Although, the storage capacity in the plant's aerial parts varies during growing season and also influenced by variation in metal availability [24]. However this uptake process can is influenced and dependent on

- Species of plant (Hyperaccumulator /excluders) [24]
- > Wetland conditions like pH, temperature, moisture content [18, 19].
- Vegetative parameters like type of root system and type of enzyme(exudate)[19]. According to literature, macrophytes with large and numerous fine root systems tends to remove more metals than those with coarse root

List of Identified Wetland Plants (Phytoremediation)

Since the advantages of these plants were first explored in 1953 by Dr. Kaithe Seidel in Germany[20], different macrophytes have been researched by scientist. Common wetland plants seen in literature are listed in table 3.



Table 3.common macrophyte used in the study of specific target metals				
Wetland Plant	Scientific Name	Target Metals	Contributors	
Common reed	Phragmitesaustralis	Cu, Cd, Cr, Ni	Vymazalet al., 2007; Kumari,	
		and Fe	and Taripathi (2005)	
Water lettuce	Pistiastratiotes	PbandCd	Veselý et al.,2011; Qian <i>et al.</i> ,	
			1999;	
Water fern,	Azollacaroliniana,	Fe and Co	Bennicelliet al., 2004; Rai,	
Water velvet	Azollapinnata		2007a;	
Water hyacinth	Eichhorniacrassipes	As, Cd, Cr, and	Wang et al., 2002; Skinner,	
		Cu	Wright, and Goff, 2007; Rai and	
			Tripathi, 2009;	
Duckweed	Lemna minor	Zn, Pb and Ni	DeBusk et al., 1996; Isaksson	
			etal., 2007; Rai, 2007a	
Poplar trees	Populus deltoids	Ni, Pb	Southickaket al., 2006; Pajevic et	
			al.,2009	
Purple	Lythrumsalicaria	Ni	Bingol et al., 2017.	
loosestrife				
Yellow flag	Irish Pseudocorus	Cr and Zn	Skinner, Wright, and Rai 2009a	

Table	e 3.common macrophyte	used in the study of	of specific target metals
l Plant	Scientific Name	Target Metals	Contributors

Plan- Based Biosorbents

The removal of pollutant from waste stream via biosorption explores, adsorption mechanism, surface complexation and physical absorption with raw materials which are particularly regenerative, accessible and potent [25]. The use of plant based biosorption involves the use of treated plant biomass for the removal of metal ions from water and waste-water when they are present at lower concentration [26]. In reality, a plethora of biological (plant) biomass has affinity for metal species[27]. This method of treatment uses the metal binding properties of plant based adsorbent (supported by the functionalized cellulose and lignin within the biomass matrix). As plant-based biosorbent are sourced from agricultural waste, this method is said to be eco-friendly, clean, cost effective and sustainable compared to the use of physical, chemical and biological techniques in the treatment of wastewater.

Plant materials constitute of cellulose, lignin and hemicellulose which are effective ionexchange site. Oftentime plant materials are treated to modify the functionality of the exchange site so as to improve their affinity for metal cations. Studies on biosorption using plant material for heavy metal removal include common biosorbents sourced from bark, seed, leaf, root and peelof plants. And table 4 shows a different biomass investigated by researchers.



Table 4.Target metal, Absorptive capacity, Optimum pH for different plant biomass				
Target Metal	Biomass(plant part)	Absorptive capacity (mg/g)	pН	
Pb(II)	Oil palm root	150.00	7	
	Pine cone	27.53	5.2	
	Barley straw	23.20	6	
	Agave bagasee(raw)	36.00	5	
	Sunflower stalk	182.00	5	
Cd(II)	Polyalthialongifolia (Seeds of	20.74	6	
	IndianMast Tree)			
	Moringaoleifera (Camol)	171.37	5	
	Loquat leaves (<i>Eriobotrya japonica</i>)	29.24	6	
	Modified Orange peel (OPAA)	293.30	5.5	
	Coffee husk	6.90	4	
As(v)	Pine leaves	3.27	4	
As(III)	Hydrillaverticilata	11.65	6	
Hg(II)	Walnut shells (modified with ZnCl ₂)	151.50	5	
-	Coconut fiber (modified with NaOH	142.86	2-10	
Cr(III)	Bengal gram (Cicerarientinum)	91.64	2	
	Husk			
	Pecan nutshell	93.01	5.5	
Cr(VI)	Partheniumhysterophorus	24.50	1	
	Sugarcane	23.00	1.9	
	Trewianudiflora fruit peel	294.12	1-2	
Cu (II)	Moringaoleifera (CAMOL)	167.90	6	
	Oil palm root	200.00	7	
	Acacia leucocephalabark powder	147.10	6	
	Casava peel	8.00	8	

† Source: Jain et al., 2016

Although plant materials are none preferential in metal adsorption [27] their metal binding properties is enhanced by different pretreatment methods. Pretreatment of plant-based biomass involves functionalizing the cellulose-OH bonds within the plant material. Thus, different researches to discover potential plant material and its parameters for optimum absorption are continuously under way. Parameter such as the optimum pH condition; temperature of adsorption; adsorption dosage; contact time [28] have help provide us with catalogues of information for successful application and use of plant biomass.

Factor Influencing Absorption

1. Effect of **pH-** The aqueous chemistry of metal ion in solutions is strongly influenced by the pH. It governs the speciation or cation exchange between metal ions and the active



functional site on the adsorbent [28]. At low pH absorbent surface are protonated, hence the surfaces remains positively charged , thus minimal absorption occurs for more electropositive metal ions, but as the pH increases absorbent surface become deprotonated and thus attract the metal ions to it surface [29].

- **2. Contact Time-** Contact time is an important factor for an economic adsorption [28]. Adsorption processes are usually faster at the beginning but slowly decrease as the number of active surface decreases with continuous adsorptions of metalion.
- **3. Temperature-** Temperature increases the kinetic energy of the absorbate ions in an aqueous solution as well as activities of the functional sites.
- **4. Biomass Dosage-** As absorption uptake is govern by increase in cation exchange (functional) site: high biomass dosage implies higher surface area containing functional sites. However interference from increased functional site also makes the possibility of absorbate uptake low [16, 30].

Constraints/ Challenges in the Use of these Biotechnologies

Phytoremediation

Wetland plants general grow fast, but seasonal growth of macrophyte limits their all year available [18]. This seasonal fluctuation in growth patterns, population, and length of plant root, soil chemistry, and climatic conditions would affect the efficiency of treatment of metals. Thus assessing the efficiency of wetland is complex with conditions of hydrology, soil/sediment types, plant-species diversity, the growing season, and the process of ecological succession in wetlands factored in [24]. Also, this method can be time consuming when compared to other chemical and physical method which takes shorter time. As considerable amount of time is needed for the biogeochemical activities in the pond.

Most threatening is it disposal and high cost of selectively harvesting contaminated vegetation. There is need to give separate attention as contaminated macrophyte can decompose, forming sludge at the bed of the ponds. Hence the disadvantages of incomplete metal removal and fast decomposition of macrophytes and cost of maintenance of pond. For proper treatment, literature advise the use ofmetal recovery rather than disposal in landfill or deep ground disposal.

Biorsorption (Plant Based)

From this biotechnological method tremendous results has been obtained from laboratory experimentation [29,27], which are yet to be translated for possible commercialization and for use in macro-systems. Although plant biomass are sourced for clean-up of contaminated effluence, the cost of biomass pretreatment, generation of toxic sludges makes it less desireable [27] for a stationary water system. As the difficulty in removing heavy metal laden sludge, undermines the effectiveness of waste water treatment. There are also possibility for the effectiveness of the bioadsobent to plateau, when the pollutant level is extremely high,



sometimes leading to desorption, depending on aquatic conditions [25]. Further study is therefore required to drop the overall cost for pretreatments or to develop new methods (pretreatments) that are both cheap and effective [16].

Future Prospect and Projections

As one of the most pressing issues in recent timeenvironmental pollution, would need continuous monitory and strict waste management policies. However, unsolved is the questions on how best to ameliorate pollution involving heavy metals, especially in water bodies where these metals are continually released as a result of the increased industrial activity [29]. Thus, controlling and ameliorating the concentration of metal pollutants through the use of bio-environmental restoration/ remediation processes is constantly been researched as traditional physical and chemical methods demands large investments of economic and technological resources [31.Environmental pollution is envisaged to reduce as the combination of green chemists and sustainable technologists continuously advocate the use of eco-friendly industrial process and technology. These campaigns therefore puts biosorption and wetland phytoremediation at advantage as both methods are economical, viable and originates from biological materials [32].

Genetically engineered wetland plants arealso promising way to improving the efficiency of phytoremediation, by enhancing the metal tolerance and supporting the accumulation properties of macrophytes[33]. Although genetic engineering in macrophytes for enhanced heavy metal accumulation is still in its initial stage, there is still need for further research in this direction[18]. Also biosorptionis quoted as a low cost treatment procedure with advantages of low operating cost, minimal volume of chemical reagent in literature. It is futuristically hoped that more plant based biomass will be researched for increased accessibility and its effective usage in the treatment of metal-laden sewage and polluted lagoons

Acknowledgement

We the author would like to thank Dr. W.B Tomori as well as the member of staff of the Department of Chemistry, Federal University of Technology, Akure, Ondo.

References

- 1. Naggar Y, Khalil M.S.and Ghorab M.A. (2018),Environmental Pollution by Heavy Metals in the Aquatic Ecosystems of Egypt, Journal of Toxicology Vol. 3(1).
- 2. Rai, P.K. (2008a), Heavy-metal pollution in Aquatic Ecosystems and Its Phytoremediation Using Wetland Plants: An Eco-sustainable Approach. International Journal of Phytoremediation, Vol. 10(2), pp 133-160.
- 3. Hosam El-Din M. S and Refaat F. A (2015), Environmental Contamination by Heavy Metals, Heavy Metals, IntechOpen.



- 4. Musilova J, Arvay J, Vollmannova A, Toth T, Tomas J.(2016), Environmental Contamination by Heavy Metals in Region with Previous Mining Activity. Bulletin of Environmental Contamination and Toxicology. Vol.97: pp569-575.
- 5. Adegola B.O and Oyewumi T.O (2019), Comparative Study of the Nutritional Benefit and Potential Health Risk Assessment of selected heavy metals in Cat fish cultured in Earthen and Plastic pond, International Journal of Scientific and Engineering research Vol. 10 (9).
- 6. Stasinakis A.S, Thomadis N.S (2010), Fate and biotransformation of metal and metalloid species in biological wastewater treatment processes. Critical Review on Environmental Science Technoogyl Vol. 40, pp 307-364.
- 7. Manzoor Q, Nadeem R, Iqbal M, Saeed R and Ansari T. M (2013), Organic acids pretreatment effect on Rosa bourboniaphyto-biomass for removal of Pb(II) and Cu(II) from aqueous media. Bioresource Technology Vol. 132, pp 446-452.
- 8. Tchounwou P.B., Yedjou C.G.,Patlolla A.K., and Sutton D.J (2014), Heavy Metals Toxicity and the Environment, NIH Public access Vol.101, pp 133-164.
- 9. Arruti A, Fernandez-Olmo I, Irabien A. (2010), Evaluation of the contribution of local sources to trace metals levels in urban PM2.5 and PM10 in the Cantabria region (Northern Spain). Journal of Environmental Monitoring.Vol. 12(7), pp 1451-1458.
- 10. Lee G, Bigham J.M. and Faure G. (2002), Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. Applied Geochemistry. Vol. 17(5): pp 569-581.
- Selvi A, Rajasekar A, Theerthagiri J, Ananthaselvam A, Sathishkumar K, Madhavan J and Rahman P (2019), Integrated Remediation Processes Towards Heavy Metal Removal/ Recovery From Various Environments-A Review: frontier in Environmental science.
- 12. Stoltz, E. and Greger, M. (2002), Accumulation properties of As, Cd, Cu, Pb and Zn by four wetland plant species growing on submerged mine tailings. Environ. Exp. Bot.Vol.47, pp 271-280.
- Weis, J and Weis P. (2004). Metal Uptake, Transport and Release by Wetland Plants: Implications of Phytoremediation and Restoration. Environmental International. Vol. 30, pp 685-700.
- Salt, D.E. and Kramer, U. (2000) Mechanisms of metal hyperaccumulation in plants. In: Phytoremediation of Toxic Metals, Using Plants to Clean Up the Environment, pp. 231-246. (Raskin, I.and Ensley, B.D., Eds.). New York Wiley and Sons.
- Baby J., Raj J, Biby E., Sankarganesh P., Jeevitha M, Ajisha S and Sheeja R. (2011), Toxic Effect of Heavy Metals on Aquatic Environment, International Journal of Biological and Chemical Science. Vol. 4(10).
- 16. Abdi, O and Kazemi M (2015), A Review Study of biosorption of Heavy Metals and Comparison between Different Biosorbents. Journal of Materials and Environmental Science, Vol.6, pp 1386-1399.



- Oyeku, O. T., and Eludoyin, A. O. (2010), Heavy metal contamination of groundwater resources in a Nigerian urban settlement. African Journal Environment Science. Technology.Vol. 4, pp 201-214.
- 18. Rai P.K (2009a), Heavy Metal Phytoremediation from Aquatic Ecosystems with Special Reference to Macrophytes, Critical Reviews in Environmental Science and Technology, Vol.39, pp 697-753.
- 19. Tangahu B.V., Abdullah S.R.S., Basri H., Idris M., Anuar N. and Mukhlisin M.A. (2011.), Review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. International Journal of Chemical Engineering, Vol. 1.
- 20. Vymazal, J (2008), Constructed Wetlands For Wastewater Treatment: A Review Proceedings of Taal 2007. The 12th World Lake Conferences: pp 965-980
- 21. Cronk, J.K. and Fennessy, M.S. (2001). *Wetlands Plants. Biology and Ecology*. Boca Raton, FL,Lewis.
- 22. Baldantoni D., AlfaniA., Di Tommasi P., Bartoli G., and Virzo De Santo, A. (2004), Assessment of macro and microelement accumulation capability of two aquatic plants. Environmenta Pollution Vol. 130, 149-156.
- 23. US EPA (2001), *A Citizen's Guide to Phytoremediation*. US Environmental Protection Agency, Office of Solid Waste and Emergency Response. EPA-542-F-01-002.
- 24. Angier, J.T., McCarty, G.W., Rice, C.P., and Bialek,K. (2002), Influence of a riparianwetl and on nitrate and herbicides exported from an agricultural field. Journal of Agricultural Food Chemistry. Vol. 50(15), pp 4424-4429.
- 25. Silvas F.P., Buzzi D. C., Espinosa D.C., Tenório J.A. (2011), Biosorption of AMD metals using *Rhodococcusopacus*. Revista Escola de Minas. Vol. 64: pp 487-492
- 26. Jain C.K., Malik D.S. and Yadav A.K (2016), Applicability of plant based biosorbents in the removal of heavy metals: a review, Environ. Process, Springer International Publishing Switzerland 2016.
- 27. Gadd G (2009), Biorsorption: Critical Review OF Scientific Rationale, Environmental Importance and Significance for Pollution Treatment, Journal of Chemical Technology and Biotechnology. Vol. 84, pp 13-28.
- 28. Mishra D.A and Singha S. (2014), Application of dried plant biomass as novel low-cost adsorbent for removal of cadmium from aqueous solution International Journal of Environmental Science and Technology. Vol. 11, pp 1043-1050.
- 29. Gonzalez A. G., Pokrovsky, O., Santana-Casiano, J and Gonzalez-D.M. (2017), Bioadsorption of Heavy Metals, Prospects and challenges in Algal Biotechnology.
- Bennicelli, R., Stezpniewska, Z., Banach, A., Szajnocha, K., and Ostrowski, J. (2004), The ability of *Azollacaroliniana*to remove heavy metals (Hg(II), Cr(III), Cr(VI)) from municipal waste water. *Chemosphere* Vol.55, 141-146.
- Pajević S, Borišev M, Nikolić N, Krstić B, Pilipović A., and orlović S. (2009), Phytoremediation Capacity of Poplar (*Populus spp.*) and Willow (*Salix spp.*) Clones in relation to photosynthesis, Arch. Biol. Sci., Belgrade, Vol.61 (2), 239-247.



- 32. Bingöl N.A., Özmal F and Akın B (2017), Phytoremediation and Biosorption Potential of *Lythrumsalicaria*L. for Nickel Removal from Aqueous Solutions, Pol. J. Environ. Stud. Vol. 26(6), pp 2479-2485.
- 33. Moffat, A.S. (1999), Engineering plants to cope up with metals. *Science*, Vol.285, pp 369-370.
- 34. Kumari, M and Taripathi, B (2005), Efficiency of phragmitesaustralis and Typhalatifolia for heavy metal removal from wastewater, Journal of Ecotoxicology and Environmental Safety, Vol. 112.
- Veselý, T, Tlustoš, P and Száková, J (2011), The Use of Water Lettuce (PistiaStratiotes L.) for Rhizofiltration of a Highly Polluted Solution by Cadmium and Lead, International Journal of Phytoremediation, Taylor & Francis publishers, Vol. 13, pp 859 -872.
- 36. Bennicelli, R., Stezpniewska, Z., Banach, A., Szajnocha, K., and Ostrowski, J. (2004), The ability of *Azollacaroliniana*to remove heavy metals (Hg(II), Cr(III), Cr(VI))from municipal waste water. *Chemosphere*, Vol. 55, pp 141-146.
- 37. Rai, P.K. (2007a), Phytoremediation of Pb and Ni from industrial effluents using *Lemna minor:* An eco-sustainable approach. *Bull.* Biosci., Vol.5(1), 67-73.
- 38. Wang, Q., Cui, Y., and Dong, Y. (2002), Phytoremediation of polluted waters: Potentials and prospects of wetland plants. ActaBiotechnol. Vol22, pp 199-208.
- 39. Skinner, K., Wright, N., and Goff, E.P. (2007), Mercury uptake and accumulation by four species of aquatic plants. Environmental Pollution Vol.145, pp 234-237.
- 40. Rai, P.K. and Tripathi, B.D., (2009), Comparative assessment of Azollapinnata and Vallisneriaspiralis in Hg removal from G.B. Pant Sagar of Singrauli Industrial region, India, Environmental Monitoring and Assessment.
- DeBusk, T.A., and Reddy, K.R. (1987), Wastewater treatment using floating aquatic macrophytes: Contaminant removal processes and management strategies. In Reddy, K.R., and Smith, W.H. (eds.). Aquatic plants for water treatment andresource recovery. Orlando, Fla.: Magnolia Publishing, Inc., pp. 643-656.
- 42. Isaksson, R., Balogh, S.J., and Farris, M.A. (2007). Accumulation of mercury by the aquatic plant Lemna minor. Int. J. Environ. Studies, Vol.64(2), 189-194.
- McCormac, B.M. (1991), Mercury in the Swedish environment. Water, Air Soil Pollut. 55, 1-126.
- 44. Nriagu, J.O. and Pacyna, J.M. (1988), Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature Vol. 333, pp 134-139.
- 45. Purves, D. (1990), Toxic sludge. Nature Vol. 346, 617-618.
- 46. Kalff, J. (2002), *Limnology*. Upper Saddle River, NJ, Prentice Hall.
- 47. Vymazal, C., Jaroslav, S., and Lenka, K. (2007), Trace metals in *Phragmitesaustralis* and *Phalarisarundinacea* growing in constructed and natural wetlands. Ecol. Eng. Vol. 30(4), pp. 320-325.



- 48. Aslam, M.M., Malik, M., Baig, M.A., Qazi, I.A., and Iqbal, J. (2007), Treatment performances of compost-based and gravel-based vertical flow wetlands operated identically for refinerywastewater treatment in Pakistan. Ecol. Eng. Vol. 30, pp 34-42.
- 49. Quian, J.H., Zayed, A., Zhu, Y.L., Yu, M., and Terry, N. (1999), Phytoaccumulation of tace elements by wetland plants: III. Uptake and accumulation of ten trace elements by twelve plant species. Journal of Environmental Quality Vol. 28, pp 1448-1455.
- 50. Southichak, B., Nakano, K., Nomura, M., Chilba, N., and Nishimura, O.(2006), Phragmitesaustralis: a novel biosorbent for the removal of heavy metals from aqueous solution. Water Res. Vol.40, pp 2295-2302.