

BIOSORPTIVE REMOVAL OF HEAVY METALS FROM WASTEWATER USING DUCKWEED

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Abstract

Water pollution has been recognized as a problem for decades. The use of heavy metals in industries and their regular mining increases their concentration in water bodies. Unlike organic compounds, metals cannot degrade, and therefore effective cleanup requires their immobilization to reduce or remove toxicity. A few conventional methods employed to remove heavy metals from wastewater are expensive, require skilled labors and maintenance. Therefore, the use of aquatic plants has come up since the last few decades. Duckweed is one such plant employed as a biosorbent and has been considered a better alternative than any other aquatic plant because of high tolerance to cold than water hyacinth, more easily harvested than algae, capable of rapid growth (0.1 to $0.5 \text{ g g}^{-1} \text{ day}^{-1}$) and small size of plant. This study aims to determine the suitability of this plant for biosorbing toxic heavy metals commonly found in industrial wastewater, domestic wastewater, and seepage water.

Keywords: Aquatic plants, Biosorption, Duckweed, Heavy metals, Water pollution

1. Introduction

We all depend on earth's ecological and atmospheric balance for survival. But the increasing industrialization and urbanization has affected this balance by the introduction of pollutants. These hazardous pollutants consist of a variety of organic compounds and heavy metals, which pose serious risks to human health. Heavy metals are primarily a concern because they cannot be destroyed by degradation¹. The most common heavy metals at hazardous waste sites are Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni) and Zinc (Zn). Of these, lead and mercury are two of the most significant contaminants, posing serious and sometimes life threatening health hazards².

The potential use of plants to remediate contaminated soil and groundwater has recently received a great deal of interest. Up to this point the most widely used wastewater treatments such as trickling filters have been mechanical³. Such plants have proven to be too complex, costly, and energy-intensive. Wastewater treatment systems which are simple and require little or no maintenance must be developed to fulfill these needs. It is becoming evident that aquatic plants have great potential for wastewater treatment and reclamation. These plants can absorb nitrate, phosphate, heavy metals such as manganese, and other chemical compounds. They are generally used to provide secondary treatment of effluents, in small lagoons filled with cattails or totora^{4, 5}. There are now more than fifteen aquatic plant wastewater

treatment systems currently in operation such as Duckweed, Water lettuce, Cat-tails, Water spinach, Water ferns, Aquatic mosses and liver worts⁶. Duckweed appears to be a better alternative and have been recommended for wastewater treatment as they are more tolerant to cold, easily harvested, has rapid growth rate and small size. This plant floats on or just beneath the surface of still or slow-moving water. It has properties such as adsorbing toxins, heavy metals, nitrates and phosphates, controlling mosquito breeding, reducing water evaporation and removes carbon dioxide from the atmosphere, filtering out bacteria and reducing light-generated growth of photoautotrophic algae⁶.

2. Conventional methods for treatment: The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. The process description of each method is presented below^{7,8}.

2.1. Reverse Osmosis: It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive.

2.2. Electro dialysis: In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of

concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

2.3. Ultra filtration: They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge.

2.4. Ion-exchange: In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include: high cost and partial removal of certain ions.

2.5. Chemical Precipitation: Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

Hence the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents⁷.

3. Aquatic plants

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to Aquatic plants. They have also proven useful in removing organic wastes from water. Some examples are cattails, calla lilies, arrowhead, ginger lilies, pickerelweed, water hyacinths, water lettuce, water spinach, aquatic mosses and liver worts. Their roles are presented in Table 2. These systems can

be used for schools, motels, hospitals, office complexes, mobile home parks, and so forth. The vegetation resulting from wetland systems can be utilized as compost or as animal feed supplements, or digested to produce methane. Skill requirements for the operation and maintenance of wetland treatment systems are low⁴.

The aquatic plants usually work on the principle of biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and /or biological sludge, No additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery.

4. Using duckweed as a biosorbent

Nutrient removal from wastewater prevents eutrophication from occurring downstream where the wastewater is discharged into water bodies such as rivers and reservoirs. One nutrient removal system that has been researched extensively over the past 40 years utilizes duckweed plants (Lemnaceae). Duckweed (botanically known as Lemnaceae) is a stem less, aquatic flowering plant. Duckweed is a small and free floating and grows on the surface of still or slow moving water in carpet-like groups. Common Duckweed has 1 to 3 leaves measuring 1/16 to 1/8

inches in length. 1 to 6 roots may grow from each plant. Duckweeds are Stemless and seed bearing plant. There are several varieties of Duckweed that grow together in dense colonies¹⁰. Duckweed systems rely on three basic principles: nutrient uptake, harvesting, and solids management⁹. Duckweed grows naturally in almost every region with a growing season of at least five months. Duckweed is a monocot; it floats on water, and has one of the fastest growth rates of any of the macrophytes. Duckweed is the common name for the Lemnaceae family of plants, with species like *Lemna minor*, *Lemna Gibba*, *Spirodela Polyrhizza*, and *Wolffia* (genus name)⁹. Generally reproduction rate of duckweed is marvelous as they grow twenty times faster than a corn and are able to cover 1 acre in just 45 days if unrestrained¹¹.

Fresh duckweed fronds contain 92 to 94 percent water. Fiber and ash content is higher and protein content lower in duckweed colonies with slow growth. The solid fraction of a wild colony of duckweed growing on nutrient-poor water typically ranges from 15 to 25 % protein and from 15 to 30 % fiber. Duckweed grown under ideal conditions and harvested regularly will have a fiber content of 5 to 15 % and a protein content of 35 to 45 %, depending on the species involved. Data were obtained from duckweed colonies growing on a wastewater treatment lagoon and from a duckweed culture enriched with fertilizer. Duckweed protein has higher concentrations of the essential amino acids, lysine and methionine, than most plant proteins and more closely resembles animal protein in that respect¹². Duckweed can be used as a

water purifier. The profitable characteristics of duckweed are high productivity, high protein content, wide geographic distribution and control of negative impacts from conventional wastewater treatment ponds¹³.

5. The mechanism

The plants are grown hydroponically (in the absence of soil). Their roots, which are home to large numbers of bacteria and other microorganisms, extend into the wastewater. These microorganisms feed off the minerals and organic chemicals that pollute the wastewater. While digesting the pollutants, the microorganisms produce by-products such as sugars and amino acids, which are absorbed by the plant roots as food^{9, 14}. The plants in turn supply oxygen and low levels of nutrients to the microorganisms for their rapid growth. This mutually beneficial, or symbiotic, relationship allows wastewater to be purified by the plant roots, and the plants' abundant new leaves help restore oxygen to the air and regulate the level of carbon dioxide and other atmospheric gases. Using aquatic plants is thus an excellent solution for wastewater and for nonindustrial sewage in particular¹⁴.

6. Metals being removed by duckweed

The discharge of heavy metals and other pollutants into aquatic ecosystems has become a matter of concern in India over the last few decades. These pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. The pollutants of concern include Copper, Lead, Zinc, Cadmium, Total suspended solids, Nitrates and Phosphates. These toxic materials may be derived from

mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives. Over the few decades, several researchers have tried to find the efficiency of duckweed in removing these pollutants.

6.1. Copper: Various studies have been done on the role of Duckweed in copper removal from wastewater. In Egypt, its 100% removal was seen in a study testing Duckweed as an alternative cost effective natural biological tool in wastewater treatment by Wafaa Abou El-Kheir et al. (2007)¹⁸. In a different study in Algeria by N. Khellaf and M. Zerdaoui, (2010) showing growth response of duckweed to Copper and Nickel phytoaccumulation, copper was tolerated by Duckweed at a concentration of ≤ 0.3 mg/L¹⁵. Similarly, in Iraq, by Jameel M. Dhabab, (2010) a study for the removal of metal ions from wastewater was done. Here, The mixed metal ions solution from cations (Fe²⁺, Cu²⁺, Zn²⁺ and Pb²⁺) was prepared of concentration 1000 ppm. 65% of Copper ions were successfully removed¹⁶. So, because copper is present in very less amounts in wastewater it is easily removed.

6.2. Lead: Lead is a poisonous metal that can damage nervous connections cause blood and brain disorders¹⁸. In the Assessment of the Efficiency of Duckweed in Wastewater Treatment, conducted at Egypt, 100% removal was seen in primary treated sewage water systems by Wafaa Abou El-Kheir et al (2007)¹⁸. But in a similar study was

conducted in Mexico by Miranda, M. G. Ouiroz, A. and M. Salazar (2000) at concentrations ranging from 50 to 300 mg/L in a greenhouse with controlled photoperiod and temperature. There was no correlation between the Pb content in plants and in the nutrient solution, this is indicative of the fast attainment of plants saturation state and the result of combination of absorption and adsorption phenomena¹⁹. In another study with Bioremoval of lead from water using Duckweed, North Dakota, USA, exposed to a single dose of lead (from $\text{Pb}(\text{NO}_3)_2$) at a concentration of 5.0 mg/l for a time period of 21 days. Viable biomass removed 85–90% of the lead, viable duckweed previously exposed to lead removed 70–80% of the lead, non-viable biomass (control group) removed 60–75% of the lead, and there was no removal in the 'no-biomass' control group. Based on these results it was concluded by Gazi Nazmul Haq Rahmani and Steven P. K. Sternberg (1999) that the viable biomass is effective in removing lead present at sub-lethal levels²⁰.

6.3. Zinc: Excessive absorption of zinc suppresses copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish³⁵. In Algeria, The ability of the duckweed *Lemna gibba* to remove zinc from water was investigated in a quarter coic solution containing 18 mg/L of Zn^{2+} supplied such as zinc sulphate (ZnSO_4). The Duckweeds reduced Zn concentration to 0.3 mg/L which is below the safety limit set by the US Environmental Protection Agency (EPA) as shown by N. Khellaf and M. Zerdaoui (2010)²². Similarly, the uptake of zinc (Zn) by the duckweed

Lemna gibba L., native to the north-east region of Algeria, was investigated in quarter Co c solutions enriched with 6.0, 10.0, 14.0 and 18.0 mg l⁻¹ of Zn supplied as zinc sulphate (ZnSO_4). The metal removed percentages were 61–71%²². The results showed that this aquatic plant can be successfully used for Zn removal.

6.4. Cadmium: It causes chemical pneumonitis, pulmonary edema, and death. Cadmium accumulated in the rice crops growing along the riverbanks downstream of the mines and people consuming the contaminated rice usually develop itai-itai disease and renal abnormalities, including proteinuria and glucosuria²³. In a study conducted in Egypt, Assessment of the Efficiency of Duckweed (*Lemna gibba*) in Wastewater Treatment was done. There was 66.7% decrease in Cadmium concentration as concluded by Wafaa Abou El-Kheir et al. (2007)¹⁸. In Mexico, Duckweed was exposed during 7 days to Cadmium, and lead, at concentrations ranging from 50 to 300 mg/L in a greenhouse with controlled photoperiod and temperature. According to Miranda, M. G. Ouiroz, A. and M. Salazar (2000), there was more than 50% decrease in chlorophyll content in all tests in relation with control¹⁹. Turkey was not far behind as Cadmium tolerance was investigated under hydroponics conditions. Within a span of 4 days, the plant was capable of removing about 75–85% Cd from 100 mL of both kinds of wastewaters as seen by Yeşim Kara and Izzet Kara (2005)²⁴. As the potential dangers of heavy metal pollution in aquatic environments is well known, it is very important the treatment of wastewater. Effluents

containing these metals may be treated by continuously passing them through a bed of these plants growing in ponds.

6.5. Total suspended solids: As levels of TSS increase, a water body begins to lose its ability to support a diversity of aquatic life. Suspended solids absorb heat from sunlight, which increases water temperature and subsequently decreases levels of dissolved oxygen²⁵. A decrease from 200 to 300 mg/L in influent to less than 10mg/L in effluent was seen in The LemnaŽ System which treats municipal and industrial wastewater using an aquaculture (aqua farming) method that relies on the growth of duckweed to reduce concentrations of BOD, TSS, and inorganic contaminants²⁶.

6.6. Nitrates and Phosphates: When Nitrates and Phosphates are added to an aquatic system through fertilizers or sewage, Eutrophication takes place due to which hypoxia occurs. This induces reductions in specific fish and other animal populations²⁸. In a study for Nitrogen removal in recirculated duckweed ponds system in France (2007), two pilot scales recirculated Duckweed-based Ponds were employed to treat municipal wastewater. The average removal efficiencies for TN, TKN and NH₄-N were 75%, 89% and 92%, respectively at TN loading of 1.3 g/m².d and were 73%, 74% and 76%, respectively at TN loading of 3.3g/m².d²⁹. Another work in Israel showed Nitrogen removal and conversion by duckweed grown on waste-water. Dry yield of the duckweed approached 15 g m⁻² day⁻¹ with a protein content of about 30% in the short retention-time treatments as seen by Gideon Oron et al. (2003)³⁰. Phosphate is a limiting factor

and must be removed from the effluent before being discharged. In Turkey, The capacity of duckweed in phosphate removal from secondary effluents was studied in laboratory to understand the mechanism of biological phosphate uptake. Orthophosphate can be efficiently removed if duckweed is frequently harvested. According to E. Öbek and H. Hasar, (2002) the initial phosphate concentration decreased from 15 mg L⁻¹ to 0.5 mg L⁻¹ at the end of an 8 days period³¹. Duckweed plants typically contain more phosphorus in its tissue than other floating plants, which makes them suitable for phosphorus removal. According to the Wellsville (UT) Municipal Sewage Lagoons studies (2010), while 1%-P is very common in oven dried duckweed, values have been reported from 0.3 up to 2.6%-P. Percent dry matter ranges from 5.4-8% with 69-86% being the organic (volatile) fraction. The N: P ratio is typically 5:1³².

It shows that duckweed is active to clean the environment from the wastewater. Also, duckweed is found to be a promising adsorbent for the removal of metal cations from mixed metal ions solution, representing an effective and environmentally clean waste matter.

Harvesting is an essential component of duckweed nutrient removal systems because it physically removes nutrients from the system via the biomass. Without harvesting, the plant tissue would die, settle to the bottom of the lagoon, decompose and then release the nutrients back into the water column. This harvested biomass can be used as compost, fodder rich in protein, or to generate fuel like methane⁹. Table 1 summarizes the average percentage of

heavy metals being removed by duckweed in different experiments conducted.

Conclusion

The use of aquatic plants in wastewater treatment is a promising technology for the future. We now have a promising and economical means of recycling domestic and industrial waste through a natural biological process that does not pollute the environment or consume vast amounts valuable energy resources. In addition, it promises to provide an inexhaustible supply of raw materials for future generations while maintaining a clean, ecologically stable environment. Use of Duckweeds today has reached new horizons such as poultry and other animal feed due to its high nutritional value, as a mineral sink because waterlogged, salinized soils, which are an important constraint on irrigated agriculture worldwide, may be a favorable environment for duckweed cropping. Little has yet been done to assess and harness genetic variance both within and among duckweed species. Studies are needed to develop strains that are more tolerant of variations in pH and temperature. Recent advances in recombinant technology point to the possibility of developing optimized strains in the near future. By virtue of their structural simplicity and their ability to clone, the duckweed family is one of the most amenable of the higher plants to genetic engineering¹².

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Table I: Percentage of heavy metals being removed by duckweed^{8, 33, 25, 34}

HEAVY METALS AND OTHER COMPOUNDS	PERCENTAGE REMOVED
Total suspended solids	96.3%
Biological oxygen demand	90.6%
Chemical oxygen demand	89%
Nitrate	100%
Ammonia	82%
Ortho- phosphate	64.4%
Copper	100%
Lead	100%
Zinc	93.6%
Cadmium	66.7%

Table II: Different roles of aquatic plants^{9, 35, 36}

AQUATIC PLANTS	USE IN TREATMENT
Typha or Cattail or Bullrush	Arsenic and dirt
Duckweed ²⁸	Nitrates, Phosphates, toxins, Pb, Cu, U, Ni, Fe, K, removes algae as well, mosquito breeding, odour control, prevents evaporation of water ^{19, 16, 12}
Water hyacinth	Removes Cd, Cr, Co, Ni, Pb, Hg, Cyanide, enhances nitrates
Drumsticks	Extract from the seeds is used as a flocculant in a low-cost form of water treatment, bacterial reduction
Hydrilla	Resistant to high salinity in water... not much effective in treating waste water
Jatropha	Land reclamation and bio fuel production
Bamboo	Bamboo filter for water desalination
Calla lily	Nitrate, ammonium, total Kjeldahl nitrogen (TKN), dissolved oxygen (DO), redox potential (Eh), hydrogen potential (pH), and COD, (research being done on surfactant removal)