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Review Article

# Phytoremediation Method for Removal of Selected Heavy Metals from Pharmaceutical Effluent

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## ABSTRACT

Pharmaceutical effluents are wastes generated by pharmaceutical industries during the process of drugs manufacturing. Their risk to human health and environmental species cannot be overemphasized. Phytoremediation technologies are becoming recognized as cost- effective methods for remediating sites contaminated with toxic metals. The phytoremediation of lead, Cadmium, Nickel, Cr(VI) and Copper from pharmaceutical waste water by the *Aloe vera plant* cultivated in the soil can be consider as a suitable hyper-accumulator by its relatively large ratio of biomass concentration of the contaminant to soil concentrations. The algae have many features that make them ideal candidates for the selective removal and concentration of heavy metals, which include high tolerance to heavy metals, ability to grow both autotrophically and heterotrophically, large surface area/volume ratios, phototaxy, phytochelatin expression and potential for genetic manipulation. Our current critical review of algal species removal of Lead, Cadmium, Nickel, Cr(VI) and Copper from pharmaceutical waste water indicated that Given their abundance in various environmental systems, their adaptability to different environmental conditions, and their ability to accumulate large amounts of heavy metals, algae appear to be the most appropriate microorganism for monitoring pollution of water resources by heavy metals.

**Keywords:** Heavy metals; Pharmaceutical effluent; Phytoremediation technologies

## INTRODUCTION

Global estimates suggest that over half of all medicines are prescribed, dispensed or sold inappropriately, and that half of all patients fail to take them as directed [1,2]. Pharmaceutical effluents are wastes generated by pharmaceutical industries during the process of drugs manufacturing. Their risk to human health and environmental species cannot be overemphasized. As well as impacting negatively on individual health, and resulting in costly resource waste, it is increasingly recognized that this rise in pharmaceutical use – and "misuse" – can have significant adverse repercussions on wildlife and ecosystems, particularly when unused medicines are disposed of inappropriately [3,4].

The pharmaceutical industry is a major player in our world. They are concerned with research, testing, development, and distribution of pharmaceutical products to treat various diseases. The advancement in pharmaceuticals is what has led to lower morbidity and mortality rates all around the world. They are an important factor when it comes to treating diseases, providing us therapeutics with higher potency and a better safety profile. However, like any major industry in the world, the pharmaceutical industry is also a widespread cause of pollution and its negative impact on the environment is well-known. The industry produces a lot of waste that is concerned with the development and manufacturing of medicines that can eventually lead to various types of pollution like land, air, and water pollution [3].

Pharmaceuticals are a large and diverse group of compounds designed to prevent, cure, and treat disease, and improve health [5,6]. Significant fractions of the parent compound are excreted in un-metabolized form or as metabolites (active or inactive) into raw sewage and wastewater treatment systems. Municipal sewage treatment plant effluents are discharged to water bodies or reused for irrigation, and bio-solids produced are reused in agriculture as soil amendment or disposed to landfill. Pharmaceuticals enter the environment from a myriad of scattered points [7].

Particular types of medicines have seen especially large increases in use in recent years, reflecting wider demographic and lifestyle changes. Medicine use for preventive purposes is also now commonplace in some countries, with biomarkers used to assess

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risks often resulting in medicine use, even when health risks are relatively low [2]. In England, for example, prescriptions for just one type of statin used to reduce cholesterol rose from 12.8 million items to 18.2 million items over one year alone. Similarly, data show that the use of antidepressants across 29 countries in the European Region increased on average by almost 20% per year from 1995 to 2010 / large increases in the dispensing of antibiotics, antiepileptics, antidepressants, drugs for treating diabetes and some analgesics have also been reported across many parts of the Region [1]

The main sources of contamination include pharmaceutical production plants, WWTPs (waste water treatment plants), hospitals, landfills and even graveyards [8,9]. The most investigated route of entry of pharmaceuticals into the environment is that from municipal WWTPs. Human excretion of unchanged or slightly transformed Active pharmaceutical ingredients (APIs) conjugated to polar molecules such as glucoronide enters the WWTP where these conjugates may then be cleaved, releasing the original API into the environment[10]. Activated sludge WWTPs has received particular attention [11,12]. A limited number of studies also found pharmaceuticals in drinking water [13] and hospital wastewater [14].

Pharmaceutical wastewater streams containing heavy metals are produced from different laboratories such as Toxicology and Food Toxicology Labs. Some examinations and chemical test and processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, silver and titanium) from a variety of analyses tests. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells [15].

The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition.

Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. Lime and limestone are the most commonly employed precipitant agents due to their availability and low-cost in most countries [16,17]. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge.

Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [17]. Recently, adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. The efficacy of various plants in eliminating different heavy metal contaminants, particularly Lead and Cadmium is a major concern nowadays due to the vast soil pollution in many countries around the world [18-22]. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/ or chemical interactions [23].

Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle. Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent.

Phytoremediation is environmental-friendly, cost-effective and natural green biotechnology for the removing xenobiotic, including toxic metals, from the environment using some species of the plants. Phytoremediation is comprised of two components, one by the root colonizing microbes and the other by plants themselves, which degrade the toxic compounds to further non-toxic metabolites. Various compounds, viz. organic compounds, xenobiotics, pesticides and heavy metals, are among the contaminants that can be effectively remediated by plants.

The plant used in the phytoremediation technique must have a considerable capacity of metal absorption, its accumulation and reducing the time of decontamination of an ecosystem [12]. Plants are known to be able to accumulate many heavy metals. Heavy metal tolerance in plants may be conferred by their immobilization in the cell wall, or by their compartmentalization in vacuoles [23].

Majority of plant requires very fertile land, providing favorable conditions spatially for various medicinal plants to grow. Since ancient times, local people in almost every part of the world have grown different plant that in their home gardens for differ purposes including using the leaves these plants for medicinal values spatially in healing wounds.

Some algae show a high capacity for accumulation of heavy metals as results of tolerance mechanisms and many algae synthesize phytochelatins and metallothioneins that can form complexes with heavy metals and translocate them into vacuoles. Another advantage of the use of the algae in phytoremediation is the high biomass production by these species leading to high absorption and accumulation of heavy metals [24].

The purposes of this review article were to review some of the work done by researchers in the area of Pharmaceutical Effluent treatments by the potential ability of different plants including A. Vera and some Algal species), and hence decrease the heavy metal toxic levels from waste water of pharmaceutical research and educational laboratories and also and the probable capability of this plant and algal species to phytoextract different metals (Chrome, Nickel, Copper, Lead and Cadmium).

## CONCEPTS OF PHYTOREMEDIATION'S

Phytoremediation is a cost-efficient plant-based approach that takes advantage of the ability of plants to concentrate elements and compounds from the environment and metabolize various molecules in their tissues. It refers to the natural ability of certain plants to bio accumulate, degrade, or render harmless contaminants in soil, water, or air. Toxic heavy metals and organic pollutants are the targets for phytoremediation [19] (Figure 1).

- **Phytoremediation** is a bioremediation process that employs

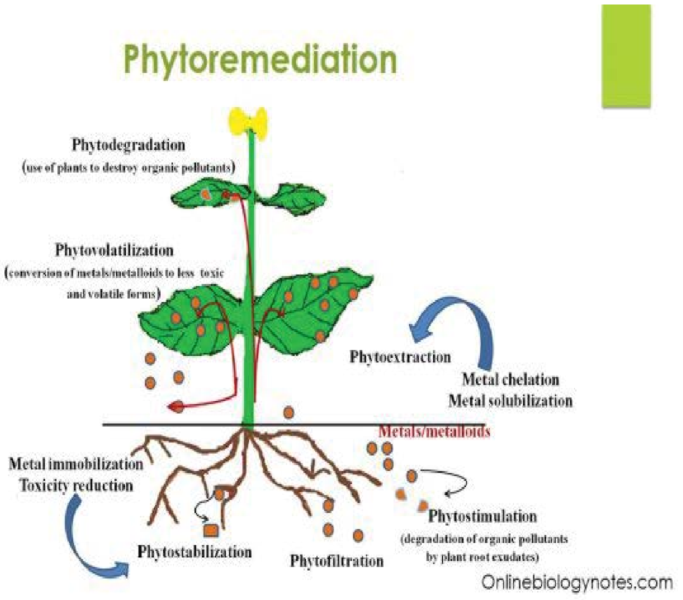


**Figure 1:** Different types of phytoremediation.

varieties of plants to eliminate, transfer, maintain, extract or degrade contaminants in the soil and groundwater.

## Classification of Phytoremediation on the Basis of Mechanisms

There are different types of phytoremediation mechanisms that are used to eliminate or degrade contaminants from soil and water discussed as follows:

### Rhizosphere Biodegradation:

- In this process, the plant secrets natural substances from its roots and these are nutrients needed for growth of micro-organisms in the soil.
- The micro- organisms grow speedily and stimulate biological degradation of contaminants present in soil.

**Phytostabilisation:** The process in which certain plant species are used to immobilize the contaminants in the soil and groundwater is termed as phytostabilisation.

- In this process, chemical compounds secreted by the plant immobilize contaminants, rather than degrade them.
- This takes place through absorption and accumulation in plant tissues, adsorption onto roots, or precipitation within the root zone prohibiting their migration in soil, as well as their transportation by erosion and deforestation.

### Phytoaccumulation (Phytoextraction):

- The process of uptake/absorption and translocation of contaminants by plant roots into the plant shoots, that can be harvested and metabolized to gain energy and also for recycling the metal from the ash is termed as phytoextraction.
- In this process, rhizosphere part of the plant roots function to absorb the contaminants along with other nutrients and water.
- The contaminant is not detoxified but stored in the part of plant such as shoots and leaves. This method is mostly employed for wastes consisting of metals.
- Plant species selected for their ability to take up large quantities of lead (Pb) are seen to uptake water-soluble metals.
- The plants aerial shoots store the metals, which are harvested and either smelted for potential metal recovery or are disposed of as a hazardous waste.
- Generally bioavailable metals for plant uptake include cadmium, nickel, zinc, arsenic, selenium, and copper.
- Moderately bioavailable metals are cobalt, manganese, and iron. Lead, chromium, and uranium are not very bioavailable.
- Chelating agent can play a vital role to get metal bioavailable, for instance, lead can be made much more bioavailable by the addition of chelating agents to soils.
- Likewise, the availability of uranium and radio-cesium 137 can be improved by use of citric acid and ammonium nitrate, as chelating agents.

**Rhizofiltration (Hydroponic systems for treating water streams):**

- The process in which adsorption or precipitation of contaminants occurs onto plant roots or absorption and sequestration in the roots is known as rhizofiltration.
- Contaminants that are found in solution form encloses the root zone by formation of wetland for cleaning up contaminated wastewater.
- Rhizofiltration is almost identical to phyto-accumulation, but the plants used for this purpose are grown in greenhouses with their roots in water not in soil.
- This system can be implied for *ex situ* groundwater treatment.
- Groundwater is drawed to the surface to irrigate these plants and at that time period these plants arrest contaminants in different part of plants.
- Typically hydroponic systems utilise an artificial soil medium, such as sand mixed with perlite or vermiculite.
- As the roots become soaked with contaminants, they are harvested and disposed of.

**Phytovolatilization:**

- In this process plants uptake water containing organic contaminants and free the contaminants into the air through their leaves as volatile components.
- The uptake and elimination of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant during transpiration is termed as phytovolatilization.
- It takes place when growing trees and other plants uptake water along with the contaminants present in water.
- These contaminants pass through the plants to the leaves and vapour out into the atmosphere at comparatively low concentrations.
- Plants also play a major role in physically stabilizing the soil with the help of their root system.
- This also aids for preventing erosion, protecting the soil surface, and decreasing the impact of rain.
- At the same time, plant roots delivers nutrients that help

to enhance the growth of microbes to convert it to a rich microbial community in the rhizosphere.

- The complex interactions between soil type, plant species, and root zone location affects the presence of bacterial community and its composition in the rhizosphere region.
- Due to availability of nutrients nearby this rhizosphere part of soil and also due to a symbiotic relationship between soil micro-organisms and plants, the population of micro-organisms is generally higher in the rhizosphere compare to the root-free soil.
- Due to this symbiotic relationship, bioremediation processes can be accelerated.
- Plant roots also plays role as surfaces provider for absorption or precipitation of metal contaminants. In this remediation process the root zone acts as focus of interest.
- The root absorbs the contaminants to be eventually stored or metabolized by the plant.
- The plant enzymes released from the roots degrade contaminants in the soil which is also an important phytoremediation mechanism.
- Many contaminants prefer route in which passive uptake takes place, via., microspores in the root cell wall and finally into the root, where degradation occurs.

**Phytodegradation:**

- In this process, specific plant species is used for a particular contaminant on the basis of the degradation capability of plant species.
- In this process, plants actually metabolize and deteriorate contaminants within plant tissues.

The contamination of the environment with toxic metals has become a worldwide problem. Metal toxicity affects crop yields, soil biomass and fertility. Soils polluted with heavy metals pose a serious health hazard to humans as well as plants and animals, and often requires soil remediation practices. Phyto extraction refers to the uptake of contaminants from soil or water by plant roots and their translocation to any harvestable plant part. Phyto extraction has the potential to remove contaminants and promote long-term cleanup of soil or wastewater.

The success of phyto extraction as a potential environmental cleanup technology depends on factors like metal availability for uptake, as well as plants ability to absorb and accumulate metals in aerial parts. Efforts are ongoing to understand the genetics and biochemistry of metal uptake, transport and storage in hyperaccumulator plants so as to be able to develop transgenic plants with improved phytoremediation capability.

Many plant species are being investigated to determine their usefulness for phyto extraction, especially high biomass crops. The present review aims to give an updated version of information available with respect to metal tolerance and accumulation mechanisms in plants, as well as on the environmental and genetic factors affecting heavy metal uptake. The genetic tools of classical breeding and genetic engineering have opened the door to creation of 'remediation' cultivars. An overview is presented on the possible strategies for developing novel genotypes with increased metal accumulation and tolerance to toxicity.

## PHARMACEUTICAL EFFLUENT IMPACT

Pharmaceuticals are synthetic or natural chemicals that can be found in prescription medicines, over-the-counter therapeutic drugs and veterinary drugs which contain active ingredients that have been designed to have pharmacological effects and confer significant benefits to society. They include painkillers, birth control pills, tranquilizers and anti-depressants among many others. Waste from pharmaceuticals fall in the category of emerging toxicants and pollutants. These pollutants are currently undergoing a regularization process although the directives and legal frameworks are not set-up yet [8].

The overwhelming population growth in recent decades and water crisis along with limited and uneven geographical distribution of fresh water resources is a growing challenge for the economic and human development. Wastewater reclamation and use could be an alternative for intact water sources and a promising solution to water scarcity and unequal distribution. However, wastewater is a double-edged resource both as an accessible water source for food production and human usage and concurrently may carry uncharacterized content with unknown toxicological profile causing acute or long-term health risks [9].

Pharmaceuticals, cosmeceuticals, nanomaterials and their chemical decomposition derivatives found in wastewater are not well known in many cases. Their unknown toxicity, teratogenicity and carcinogenicity profile associated with lack of monitoring and control measures impose a significant hazard risk on the public health [11]. Pharmaceutical industries involved in the manufacturing of finished dosage forms and drug development use water for different purposes. Pharmaceutical water could be categorized based on its use into general use water, manufacturing process water, and research and development water. The wastewater from the first category could be treated as municipal while the second one contains mostly the known product being manufactured. The third type contains different and unknown compounds, but in lower concentrations [25]. Moreover, active pharmaceutical ingredients (API) manufacturing plants that conduct large scale chemical synthesis processes to produce APIs may also release both the final API and the intermediates from the preliminary synthesis steps during the manufacturing process as the second type. However, the first and third categories remain the same for the API manufacturers [25].

Wastewater carries three major chemical hazards classes with toxicological implications that include acute and chronic toxicity, carcinogenicity, and reproductive, developmental, and neurotoxicity. It is postulated that carcinogenic and neurotoxic effects are not bound to thresholds. However, certain chemicals can produce different types of toxicities. Nevertheless, more than one toxic effect can be exerted by the same chemical substance [26].

Arsenic, 1,4-dioxane and vinyl chloride are sample carcinogens found in wastewater. However, the potential effects of low dose, but chronic exposure to pharmaceuticals and personal care products through wastewater are an evolving concern, especially because there exist no reliable long term toxicological studies for these compounds [27]. In addition, recent use of nanomaterials as nano-pharmaceuticals requires close attention when it comes to mind that our current knowledge of nano-toxicology is pretty limited and the regulatory authorities experience a lag phase in enforcing control measures. Lack of objective and convenient measurement capabilities intensifies this concern in comparison to enteric infections [28,29].

This paper reviews the evidence on the health risks associated with the wastewater use for irrigated food production and the imposed risk on the end consumers mainly from pharmaceutical industry and related research facilities. Then, we suggest an applied framework for planning and policy-making to mitigate the health risks and optimally employ reclaimed wastewater for human purposes.

### Impacts of Heavy Metals

Wastewater is released from various industries such as plastic, petroleum, rubber, fertilizer, coal, pharmaceutical, steel and mining industries [13].Pharmaceutical compounds are generally man-made chemicals and are defined as "red category" because of its higher biological oxygen demand(BOD), chemical oxygen demand (COD), solids content, dissolved solids and suspended solids. It also contains chlorides, phenols, sulphides, oil and heavy metals such as aluminium, copper, lead, zinc, nickel, arsenic, manganese, chromium, cadmium, iron and mercury. Once it is released into the environment it harms the ecosystem and aquatic life [30].

Pharmaceutical wastewater contains a wide variety of heavy metals. These have densities higher than 5 g/cm3 and are found to be toxic [31]. The prominent among them are zinc, nickel, lead, cadmium, cobalt, copper, iron, chromium, arsenic, manganese and mercury [25]. These metals are very much toxic to the ecosystem, living organisms even at very low concentration. The pollutants are released from the wastewater of different industries into the environment [32].

Heavy metals toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals. Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. They are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer [32].

## METHODS OF TREATMENTS OF PHARMACEUTICAL EFFLUENT

In recent years, the main emphasis of the scientific research and engineering application has shifted to advanced treatment of pharmaceutical wastewater, which main method is physicochemical technology. It means that wastewater is treated by physical or chemical methods, like coagulation and sedimentation, flotation, activated carbon adsorpt-ion, advanced oxidation processes, membrane separation [11].

### Coagulation and Sedimentation

Coagulation is adding chemical agents to wastewater, dispersing by rapid mixing, then making stable pollutants into unstable and precipitable matters. The mechanism of coagulating is complex. For advanced treatment of pharmaceutical wastewater, the key is how to squeeze and remove bound water round hydrophilic colloid [12]. So the character of flocculent is important, which related to the effect of coagulation. Inorganic metal salts and polymers are frequently used as flocculent. This method can remove SS, chromaticity and toxic organic matter. Meanwhile, it can improve the biodegradability of pharmaceutical wastewater [12].

Sedimentation is the most common method after coagulation. Under the gravity, pollutants can be separated, which has greater density than wastewater. Coagulation and sedimentation have some advantages, such as easy operation and mature technology, but it is hard to remove dissolved organic matter.

#### Flotation

Except for sedimentation, flotation can also remove suspended solids of secondary effluent. The technology characteristic is producing a large number of tiny bubbles by injecting air into wastewater, forming floating floc with smaller density than wastewater. And it can float to the surface of wastewater to separate.

### Activated Carbon Adsorption

Activated carbon, as a kind of adsorbent, has many advantages. It has large specific surface area, multilevel pore structure, high adsorption capacity and stable chemical property. Therefore, it is widely used as adsorbent or catalyst carrier to remove pollutants [13,14]. In industrial effluents treatment, activated carbon is used for effluent, which is toxic and hard to achieve discharge standard. It is an important method of advanced treatment of pharmaceutical wastewater as well.

Activated carbon adsorption can be classified as physical adsorption and chemical adsor-ption. Physical adsorption is reversible, and no selectivity to adsorbate. When activated carbon saturated by adsorbates, it is easy to desorb. To the contrary, chemical adsorption adsorbs only one or several specific adsorbates, which is irreversible and hard to desorption. For cyclic utilization, saturation of activated carbon restores its adsorption property by regeneration. This method is widely used for advanced treatment, because it can be recycled, its better treatment effect and wide suitability. But there are some disadvantages, such as high costs relatively, low efficiency of regeneration and complex operation, which limit application.

### Advanced Oxidation Processes

Advanced oxidation processes (AOPs), which can oxidize pollutants by forming free radicals. Those kinds of pollutants cannot be degraded by common oxidizing agent. There are many kinds of AOPs, such as wet air oxidation supercritical water oxidation, Fenton reagent, photocatalytic oxidation, ultrasound oxidation, electrochemical oxidation and ozonations.

**Wet air oxidation (WAO):** WAO has been put forward by F. J. Zimmer Mann in 1958, which was used for papermaking black liquid treatment. By using of air or oxygen as the oxidant, this method decomposes organic matter into inorganic or small molecules at high temperature (150-350 °C) and high pressure (0.5-20 Mpa). WAO is generally used in pretreatment of wastewater advanced treatment. This method has wide range of applications, high efficiency of COD removal, which can even reaches more than 90 % under appropriate conditions, low energy consumption, less secondary pollution, and it is easy management [14].

**Supercritical water oxidation (SCWO):** SCWO is chemical reaction between dissolved oxygen and organic pollutants in supercritical water. Organic matter, air, and supercritical water were complete mixed at 24 Mpa pressure and 400 °C temperature, becoming homogeneous phase. Under these conditions, organic compounds spontaneously initiate the oxidation reaction. With the increase of the reaction temperature, 99.9 % or more of the organic matter is rapidly oxidized into simple non-toxic small molecules in a period of time, achieving the purpose of removing pollutants [23]. SCWO has high oxidation efficiency, will not cause secondary pollution, organic can be oxidized completely. However, this method has some shortcomings, such as it requires high operating conditions and high cost [23].

**Electrochemical oxidation:** The use of electrochemical reaction to remove toxic and harmful pollutants in the water is known as the electrochemical method. Electrochemistry is a new method in water treatment field. The principle of the method is as follow: in the electrochemical reaction process, the reactant will lost electrons and be oxidized in the anode. Conversely, the reactant in the cathode will lose electrons and be reduced.

In general, the removal of refractory organic matter, mainly due to the oxidation of the anode. Conventional electrochemical wastewater treatment processes includes: electrolytic recovery, electrochemical oxidation, electrolytic air flotation, electrodialysis and micro-electrolysis. Electrochemical method is also known as "Environmentally Friendly" process, has a great advantage compared with other methods. For example, the electrochemical method is generally carried out under normal temperature and pressure and has high efficiency, can be used alone or in combination with other processes, and it covers a small area and no secondary pollution, has relatively high degree of automation. The main research direction of the electrochemical reaction in the future is the research of the anode and electrochemical reactor [17].

Due to the complexity of pharmaceutical processes, pharmaceutical wastewater has some characteristics, such as poor biodegradability and high concentration. From these characteristics, treatment of pharmaceutical wastewater is very necessary. There are many kinds of advanced treatment; each method has its own features. Through rational utilization of various methods, can effectively improve the quality of pharmaceutical wastewater effluent.

Phytoremediation is potentially applicable to a variety of contaminants, including some of the most significant ones, such as petroleum hydrocarbons, chlorinated solvents, metals, radionuclides, nutrients, pentachlorophenol (PCP), and polycyclic aromatic hydrocarbons (PAHs). Phytoremediation technologies are becoming recognized as cost- effective methods for remediating sites contaminated with toxic metals at a fraction of the cost of conventional technologies, such as soil replacement, solidification and washing strategies [24].

## SELECTED HEAVY METAL REMOVALS FROM PHARMACEUTICAL EFFLUENT

### Heavy metal Removal by Aloe vera L.

According to the investigation conducted by [5], in which Chemical extraction of the soil profile before and after planting *A.Vera* samples during 60 days were studied in pH= 5.6-7.1. The phytoremediation of these heavy metals from pharmaceutical effluent showed significant differences in cadmium, Cr (III), Cr (VI) and lead up taking by roots and leaves of plant. The best results were obtained for uptake of Nickel and copper was in the soil with pH=6.2 among different samples while for lead up taking was in 6.4 and for copper up taking was in pH=5.9[5].

The phytoremediation of lead, Cadmium, Nickel, Cr(VI) and Copper from pharmaceutical waste water by the *Aloe vera plant* cultivated in the soil can be consider as a suitable hyper-accumulator by its relatively large ratio of biomass concentration of the contaminant to soil concentration [5] (Table 1).

### Heavy metal Removal by Some Algal Species

The algae have many features that make them ideal candidates for the selective removal and concentration of heavy metals, which include high tolerance to heavy metals, ability to grow both autotrophically and heterotrophically, large surface area/ volume ratios, phototaxy, phytochelatin expression and potential for genetic manipulation [34]. several species of the green algae Enteromorpha and/or Cladophora have been utilized to measure heavy metal levels in many parts of the world [35] (Table 2).

Given their abundance in various environmental systems, their adaptability to different environmental conditions [36], and their ability to accumulate large amounts of heavy metals such as cadmium, lead, zinc, copper, chromium, and manganese [37], algae appear to be the most appropriate microorganism for monitoring pollution of water resources by heavy metals [38].

As a result Sargassum filipendula and Sargassum fluitans are hyper-absorbents and hyper-accumulators for Copper [39], absorbing and accumulating these elements from their environment into their bodies. These algae can be hyper-phytoremediators and their presence in waste water reduces water Copper pollutant [39,40] (Figure 2). Suggests that Sargassum natans and Sargassum vulgare a marine green microalgae (Figure 3), had a very excellent Lead uptake capacity.

The obtained result by [40] show that biosorption of lead by the marine algal biomass is considerable, particularly considering that there was no pretreatment of the biomass. This study also showed that Sargassum fluitans have considerable Nickel uptake with tremendous hyper-accumulating capacity. Cross linking of S. Jluitans and F. vesiculosus with formaldehyde improved their nickel uptake [40].

**Table 1:** Heavy Metal concentration in effluent before treating (taken from [1].

| Heavy Metal Content | Concentration (mg/kg DW ± SE*) |
|---|---|
| Lead | 30.731± 0.106 |
| Cadmium | 9.879 ± 0.011 |
| Nickel | 30.98 ± 0.318 |
| Chrome | 19.043± 1.204 |
| Copper | 101.650± 10.006 |

SE* = Standard Error

**Table 2:** Uptake and accumulation of metals by some algal species.

| Species | Heavy Metal | References |
|---|---|---|
| Sargassum natans | Lead (Pb) | Holan and Volesky [42] |
| Sargassum vulgare | Lead (Pb) | Holan and Volesky [42] |
| Micrasterias denticulata | Cadmium (Cd) | Volland et al. [43] |
| Sargassum fluitans | Nickel (Ni) | Holan and Volesky [42] |
| Phormedium bohner, | Cromium (Cr) | Dwivedi et al. [44] |
| Sargassum filipendula | Copper (Cu) | Davis et al. [45] |
| Sargassum fluitans | Copper (Cu) | Davis et al. [45] |

**Figure 2:** Sargassum Filipendula.

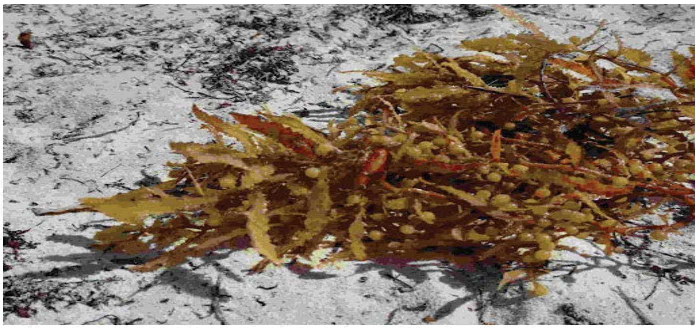

**Figure 3:** Sargassum Natans.

Investigating the capacity of the capacity of diffent aquatic macrophytes, in removing Cadmium, [41] found that *Micrasterias denticulata* showed better potential for removing Cd. Cadmium induces phytochelatins $PC_2$, $PC_3$, $PC_4$ in the conjugating alga *Micrasterias*. Glutathione levels remained constant upon treatment with cadmium, chromium and copper [41].

According to the study by [42], the maximum accumulation of Cr was shown by Phormedium bohneri followed by Oscillatoria tenuis, Chlamydomonas angulosa, Ulothrix tenuissima, and Oscillatoria nigra; all of which demonstrated a transfer factor of >10% for Cr. The study also indicates that the phytoplankton diversity was modified by Cr pollution.

The main extraordinary mechanism of metalliccation sequestration involves the formation of complexes between a metal ion and functional groups on the surface or inside the porous structure of the biological material. The carboxyl groups of alginate play a major role in the complexation. Different species of algae and the algae of the same species may have different adsorption capacity [39] (Figure 4a and 4b).

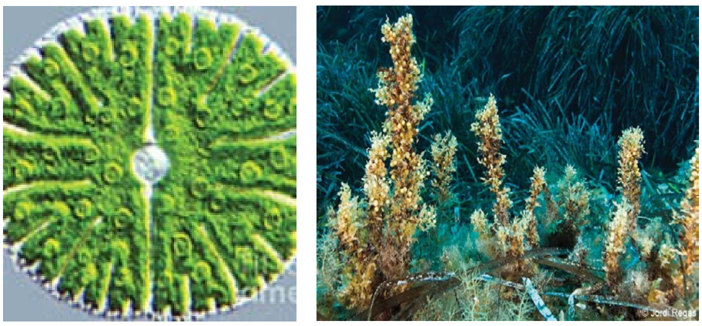

**Figure 4:** **(a)** Micrasterias denticul **(b)** Sargassum vulgare.

## SUMMARY

Phytoremediation technologies are becoming recognized as cost-effective methods for remediating sites contaminated with toxic metals at a fraction of the cost of conventional technologies, such as soil replacement, solidification and washing strategies.

The phytoremediation of lead, Cadmium, Nickel, Cr(VI) and Copper from pharmaceutical waste water by the *Aloe vera plant* cultivated in the soil can be consider as a suitable hyper-accumulator by its relatively large ratio of biomass concentration of the contaminant to soil concentrations.

The algae have many features that make them ideal candidates for the selective removal and concentration of heavy metals, which include high tolerance to heavy metals, ability to grow both autotrophically and heterotrophically, large surface area/volume ratios, phototaxy, phytochelatin expression and potential for genetic manipulation.

Our current critical review of algal species removal of Lead, Cadmium, Nickel, Cr(VI) and Copper from pharmaceutical waste water indicated that Given their abundance in various environmental systems, their adaptability to different environmental conditions, and their ability to accumulate large amounts of heavy metals, algae appear to be the most appropriate microorganism for monitoring pollution of water resources by heavy metals.

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