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Review

An Overview of the Valorization of Aquatic Plants in Effluent Depuration through Phytoremediation Processes

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Abstract: Environmental biotechnologies are a popular choice for using efficient, low-cost, low-waste, and environmentally friendly methods to clean up and restore polluted sites. In these technologies, plants (terrestrial and aquatic) and their associated micro-organisms are used to eliminate pollutants that threaten the health of humans and animals. They have emerged as alternative methods to conventional techniques that have become increasingly aggressive to the environment. Currently, all actors of the environment, whether governors, industrialists, or citizen associations are more interested in the application and development of these technologies. The present overview provides available information about recent developments in phytoremediation processes using specifically aquatic plants. The main goal is to highlight the key role of this technology in combating the drastic organic and inorganic pollution that threatens our planet daily. Furthermore, this study presents the valorization of aquatic plant after phytoremediation process in energy. In particular, this article tries to identify gaps that are necessary to propose future developments and prospects that could guarantee sustainable development aspired by all generations.

Keywords: aquatic plant; heavy metal; organic pollutant; phytoremediation; sustainable development

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1. Introduction

During the last decades, biotechnological techniques have gained public recognition as a multidisciplinary research field. In addition to their use in the production of valuable products (pharmaceutical, food, and cosmetic products), they have been used in the protection of the environment with the development of depuration processes with micro-organisms, such as biofilters, activated sludge tanks, biological oxidation, etc. These traditional techniques, called environmental biotechnologies, have been very efficient in pollution treatment, due to the production of less waste and use of less energy than the physicochemical treatments. Nowadays, the knowledge of biological techniques explaining previously unknown phenomena has greatly increased, which has led to other biological purification processes based on the use of plants and their associated micro-organisms. Thus, phytotechnology, which is commonly referred to as phytoremediation, is an increasingly popular choice for using efficient, low-cost, low-waste, and environmentally friendly methods to clean up and restore polluted sites. Phytoremediation is a relatively recent technology that uses the natural ability of plants to extract, reduce, degrade, or immobilize toxic and/or undesirable organic and inorganic compounds present in contaminated media. It is used to reduce metals, pesticides, solvents, explosives, oil, radionuclides, nanomaterials, and other unwanted contaminants initially present in air, water, soils, and sediments [1–3]. The advantage of this green technology is to treat large areas or large volumes at a low cost without generating major disturbances of the environment. In addition, this process ensures a pleasant cover, which reduces visual pollution. The aesthetically pleasant aspect of phytoremediation renders it more economical and ecological than conventional treatment methods [4–6].

During the 1990s, it was noted that soils contaminated with toxic metals and surface water charged with organic substances and nutrients were accompanied by an excessive multiplication of terrestrial or aquatic plants. Without intervention, urban and industrial wastelands were quickly colonized by vegetation [7]. Phytoremediation emerged as a scientific field from the study of vegetation at polluted sites and was the purpose of several studies. This was how the first works and studies on phytoremediation processes emerged in research and scientific circles.

The presence of hazardous pollutants in the environment and the severity of their effects on human health and the environment have forced governments to adopt standard values to protect human, fauna, and flora from potential exposure to these contaminants. This is highlighted by the large number of limit values existing for the atmosphere, water, aquatic environments, sewage sludge, sediments, and soils. These limit values are usually set by international environmental agencies (Environmental Protection Agency, World Health Organization, Climate Action Network, etc.).

2. Mechanisms of Phytoremediation and its Application in the Field

Phytoremediation technologies can be applied to organic and inorganic pollutants in soils, water, and atmosphere [8]. Globally, the purification processes and their selection are based on the type of pollutant, biological factors, and nature and environment of plant. These interrelated groups of factors (Table 1) play a role in the interaction between contaminants and biological barriers. Pollutant phytoremediation depends upon numerous biotic and abiotic factors.

Table 1. Factors involved in the interactions between contaminants and biological barriers.

Factors	Characteristic Properties
Type of pollutant	Organic or inorganic, nature (gas, liquid, solid), concentration, chemical form, bioavailability.
Biological factors	Exchange surface, accessibility of fixation sites, transport process, absorption capacity, growth, reproduction, nutrition, excretion.
Nature of plant environment	Temperature, pH, light, concentration of suspended matter, salinity, ionic strength, organic and inorganic ligands.

Temperature and pH are the most important environmental characteristics affecting chemical uptake and distribution within living plants [2,9]. Particularly, temperature governs the physiological processes of plants maintaining a relationship with growth rate and other functions; alternatively, pH affects the ionization state of some functional groups of the cell wall [10]. Several researchers reported that an acidic media had direct detrimental effects on the physiology of plants following a decrease in the electrochemical gradient across the plasma membrane [11,12].

During the physiological process of exchange with the surrounding environment, exogenous molecules penetrate through the biological barriers, namely from the external environment into the internal environment of the organism. When contamination occurs, these barriers show biological properties linked to their structure and to the physicochemical conditions of the environment. The biological factors of the organism, which are involved in the different interactions are: exchange surface and accessibility of binding sites, transport process and absorption capacity; in addition, the different physiological processes, such as growth, reproduction, nutrition, excretion, etc. can intervene on a larger scale [13].

Phytoremediation can be increased through using chelating agents, namely EDTA and specific acids; this specifically concerns metal pollutants that need to be absorbed by plants as complex compounds. In parallel, the addition of plant growth regulators (PGRs) can improve plant phytoremediation efficiency by increasing plant biomass and decreasing the negative effects of the presence of contaminants in the plant [14].

All these factors (Table 1) are important to the design and implement effectively a sustainable phytoremediation technology.

2.1. Mechanisms of Phytoremediation

The interaction between chemicals and plants led to distinguishing different mechanisms, as summarized in Figure 1. Although not exhaustive, the figure gives some pollutants (in italic) that have been studied at the laboratory and field scale. The majority of scientific and popular articles researching this topic has summarized well the different techniques and explained the mechanisms involved. They have also identified key factors (nature of pollutant, concentration, and toxicity level) that are needed in order to design and effectively implement a sustainable phytoremediation technology [15].

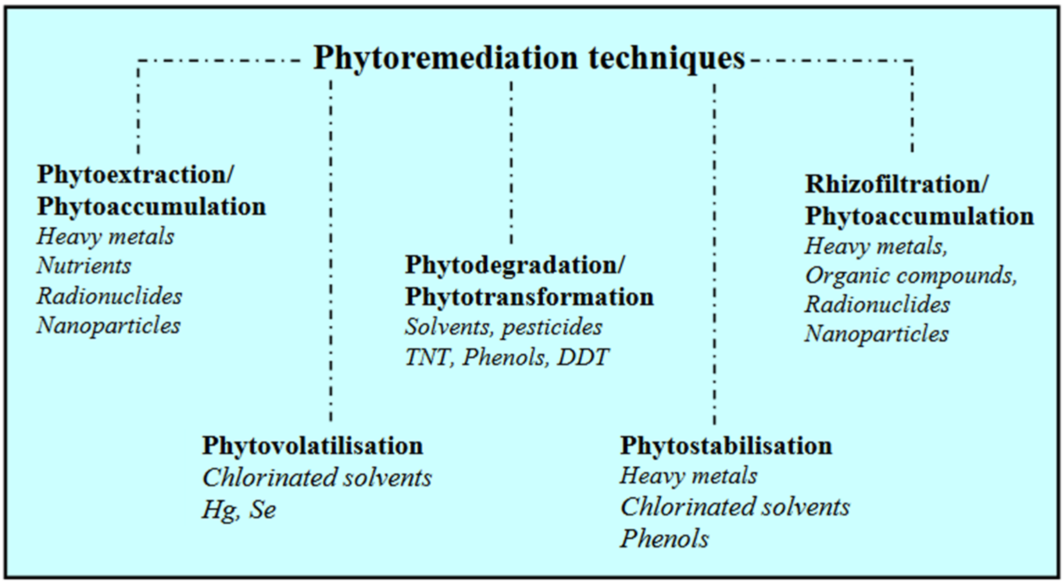

Figure 1. Different techniques of phytoremediation.

It is important to understand how pollutants are accumulated, how they are being translocated to the plant cells, and how they are being detoxified [16]. In water, divalent metals are present in hydrated form, complexed by organic (fulvic and humic acids) or inorganic ligands, or are adsorbed on particles. The physicochemical characteristics of water (pH, light, temperature, ionic strength, content of organic, and inorganic ligands) affect the degree of dissociation between the complexed and ionic forms. In ionic form, metals can attach very quickly to the membrane surface of plants (their introduction into the cell is facilitated by diffusion). Depending on its nature, the metal element is integrated into the membrane or fixed on the sites reserved for nutrients (phosphates, for example). However, the exact mechanisms of absorption are still poorly understood, especially for some elements, such as metals considered as very toxic for plants (Cd, Pb, As, etc.). Nowadays, some metals are considered to be passively absorbed by certain proteins, while others are actively taken up by a selective, energy-requiring transport protein [17].

2.2. Field Application

Phytoremediation has been applied on a large scale in USA, Canada, and some European countries. In some African countries (Kenya, Zambia, South Africa, Nigeria, and Tanzania), some phytoremediation projects have been considered to remediate polluted sites with heavy metals [18]. Some field applications of extracting heavy metals using various terrestrial plants have been implemented in China [19], Portugal, and Russia [20].

Generally, the content of extractable metals decreased in soil after the field experiments. Specifically, Table 2 gives some in-situ decontamination operations of polluted sites.

Table 2. Some in-situ phytoremediation of polluted sites.

Site Name	Treatment Process
Chernobyl, Ukraine	Decontamination of soil contaminated by radioelements (uranium)
INCO Sudbury, Canada	Treatment of mine waste (nickel, copper)
	Depollution of metal industry waste storage site
Jales, Portugal	Treatment of sites contaminated with non-ferrous metals
Bordeaux, France	Treatment of sites contaminated by sludge inputs
San Joaquin Valley, California	Decontamination of soil and water contaminated with selenium

3. Selection of Plant Species

In their review study, Akhtar et al. [21] asserted that more than 400 plant species have been tested and proved to have the ability to remediate soil and water pollution. For a good phytoremediation process, an appropriate selection of plant species is an important tool to ensure optimal performance of remediation. The selection is based on the type of pollutant element, the geographical location, the environmental conditions, and the knowledge of the element's ability to accumulate in plants. Generally, terrestrial plants possess greater biomass and a faster-growing root system than aquatic plants. Sunflowers and Indian mustard are considered as the first terrestrial plants tested at laboratory and field-scale [22]. Several research works reported the treatment of pollutants removal from soil using consortia of soil microbial flora and terrestrial plants. An in-situ phytoremediation of soil accumulated dyes from textile wastewaters was conducted successfully by Chandanshive et al. [23] using terrestrial plants on ridge beds of a constructed wetland. Their results revealed that the use of plants could be a wise strategy for soil clean-up affected by textile industry effluents. Additionally, during the process, plants absorbed contaminants from the soil and thus prevented horizontal contamination of groundwater [18].

Buscaroli [24] established in its review article a list of factors and indexes to evaluate the performance of terrestrial plants in phytoremediation processes. This interesting terminology avoided confusion in the interpretation of experimental data.

4. Aquatic Plants

Aquatic plants are plant species visible to the naked eye growing in wetlands, such as lakes, ponds, streams, etc. They are also found in wastewater streams considered as eutrophic media. Various species have been inventoried around the world in various aquatic environments. Their abundance and their distribution depend strongly on the hydraulic regime, nutrients and water quality [25].

Numerous studies have been published on the use of various aquatic plants for phytoremediation of both organic and inorganic contaminants. Macrophytes, with fixed or free culture (floating, submerged, and peri-aquatic) are excellent candidates for cleaning up contaminated sites with toxic or undesirable substances. Several species have been tested in laboratory and some have been used on a large scale.

4.1. Phytoremediation of Heavy Metals Using Aquatic Plants

Biogeochemical cycles of metals considered as normal constituents of the biosphere have been modified by anthropogenic activities, resulting in their presence in the different compartments of the environment. There are various sources of metals: natural erosion and corrosion processes, mining activity, metallurgical industry, electroplating, surface treatment, power generation, and the leaching of contaminated areas. These anthropogenic activities can be considered as the main cause of contamination of soils, streams, rivers, and even groundwaters. This contamination is a real concern since metals do not decompose, unlike most organic compounds, and as such they can accumulate in most systems by adsorption or complexation. They can also be bioaccumulated by both fauna and flora causing an increase in the concentration of metal in the living organisms. If the excretion phase is slow, it may result in a biological accumulation phenomenon. It has been shown that most metals undergo biological magnification as they progress through the food chain [26].

Heavy metals when entering aquatic and terrestrial ecosystems become potentially hazardous and tend to accumulate in sediments and to concentrate in aquatic food chains. From the point of view of impact assessment and risk assessment, it is necessary to study the inputs and loads, the distribution and the fate of contaminants into the receptacle systems. In particular, there is a need to study quantitative and qualitative characteristics, as well as the routes they take when they disperse into the environment, and their effects on the environment. However, to rationally manage and control this pollution, it is necessary to think of depuration processes of effluent before their release into the environment in order to limit as much of their polluting load as possible. Phytoremediation of water and soil polluted by heavy metals can be a technology of choice to clean up contaminated sites. It can be effective by an appropriate selection of plant species used for this purpose.

Inorganic pollutants that can be treated by aquatic plants are numerous. Table 3 gives some elements and compounds that have already been tested either in the laboratory or on a large scale during the last ten years.

Table 3. Inorganic pollutants treated with aquatic plants as phytoremediators (2009–2020).

Aquatic Plant	Species	Pollutant	Application	Reference
Water hyacinth	*E. crassipes*	Cr, Zn	Laboratory	[27]
		Fe, Mn, Zn, Cu, Pb, Cr, Cd	Field	[28]
Water lettuce	*P. stratiotes*	Cu, Fe, Hg	Laboratory	[29]
		Cu, Zn	Laboratory	[30]
		Fe, Mn, Zn, Cu, Pb, Cr, Cd	Field	[28]
Duckweed	*L. minor*	Co, Cd, Zn, Cr, Ni, Cu, Fe	Field	[31]
		Mn, N, P		[32]
		U, Th	Laboratory	[33]
		B	Laboratory	[34]
	L. gibba	Zn	Laboratory	[9]
		B	Laboratory	[34]
		Cd, Cu, Zn	Laboratory	[35]
	S. intermedia			
	S. polyrrhiza			
Water fern	*W. velvet*			
	S. natants			
	S. auriculata	Pb		[36]
	S. molestela	Fe, Mn, Zn, Cu, Pb, Cr, Cd	Field	[28]
	A. filiculoides	Pb, Hg		[3]
		Co, Cd, Zn, Cr, Ni, Cu, Fe	Field	[31]
		Mn		
Submerged macrophyte	*Vallisneria natans*	As		[37]

4.2. Phytoremediation of Organic Pollutants using Aquatic Plants

Our environment suffers enormous physical and chemical challenges caused by human activities and by the ecological imbalance observed in recent decades. The most important anthropogenic activities that lead to the contamination of soils and waters by organic pollutants concern the supply of sewage sludge and mineral fertilizers, various phytosanitary products, urban composts, and agri-industrial wastewaters and atmospheric releases near industrial sites. This danger has led governments to think about solutions by setting directive laws and stringent regulating measures to treat industrial effluents and encouraging scientists to look for the best methods for preserving the environment.

There are fewer organic pollutants treated by aquatic plants than inorganic pollutants, but large-scale application has been greater during the last ten years (Table 4).

Table 4. Organic pollutants treated with aquatic plants as phytoremediators (2010–2020).

Aquatic plant	Species	Pollutant	Application	Reference
Water lettuce	*P. stratiotes*	Chlorpyrifos	Laboratory	[38]
		Perchlorate	Laboratory	[39]
Duckweed	*L. minor*	Terbuthylazine	Laboratory	[40]
		Chlorpyrifos	Laboratory	[38]
		Chloroacetamide	Laboratory	[41]
		Wastewater	Laboratory	[42]
Water fern				
	Azolla filiculoides	Dyes	Laboratory	[43]
	Salvinia molesta	Dyes	Field scale	[44]
Aquatic ipomea	*Ipomoea aquatica*	Dyes	Field scale	[45]
Reed	*Typha angustifolia*	Dyes	Field scale	[46]
	Juncus fontanesii			
Hydrilla	*Hydrilla verticillata*	Phenantrene, Pyrene	Laboratory	[47]
Potamot	*Potamogeton crispus*	Phenantrene, Pyrene	Laboratory	[48]
Aquatic plant	*Scirpus grossus*	Real sago mill effluent	Laboratory	[49]

5. Prospects and Future Developments

Phytoremediation provides effective methods for removing pollutants from water, soil, and air to provide a healthy and pleasant environment for humans. It had emerged around the 1980s in the United States and Canada and was developed in 1990s. The first patent (Phytotech Inc.) was filed in 1994 and was followed by research conducted at the laboratory-scale and tested at pilot and field-scale systems for remediation of uranium-contaminated water [22,50]. The large-scale application of this technology in the 2000s has allowed phytoremediation to move from the conceptual phase to the commercial phase. However, in Europe this technology is still slightly exploited despite certain projects supported by the European Commission (EU); these projects were mainly oriented towards basic research [51].

Due to its advantages (low cost, ease of operation, eco-friendly aspect), phytoremediation is supported by scientists, industrialists, ecological organizations, and citizens' communities. Other advantages of this technology include extraction of valuable metals (phytomining) and increased soil fertility/quality [18].

Firstly, future studies should focus on the potentials of aquatic plants for the removal of organic pollutants present in effluents, such as industrial wastewaters, acid mines, pulp and paper, and dairy effluents. According to the recent review of [8], only 11% of the pollutants treated by some aquatic species concern organic pollutants. *Lemna minor* is able to reduce chemical oxygen demand (COD) by 92% from wastewater blended from textile, distillery, and domestic sources [30].

Despite these strengths, phytoremediation possesses limitations and research studies must be conducted to expand their use. For this purpose, the exploitation of tolerance, uptake, and translocation of pollutants in plants should be considered. Additionally, an appropriate plant species can be considered as a phytoremediator if it displays some specific characteristics, namely (a) a high rate of accumulation of the pollutant, (b) an ability to accumulate large concentrations of contaminants, (c) an ability to accumulate various elements, (d) a rapid growth and high biomass production, and (e) a high resistance to diseases and harmful insects.

The selected plant species must display all these characteristics. Furthermore, the interaction plant–microbe for pollution bioremediation must be studied at all levels (laboratory, pilot, and large scale) to understand the symbiotic relationships of plants with rhizospheric organisms. In this context, the ramping up of the modern biotechnology in which manipulation of genes from different organisms led to modify genetically some plants to increase their capacity to tolerate and hyperaccumulate several pollutants can be considered as an opportunity. Indeed, the involvement of genetically modified micro-organisms can further increase the phytoremediation capacity leading to total purification of impacted ecosystems. However, genetic engineering has not yet gained public recognition as an ethical science.

Since traditional phytoremediation process poses some limitations regarding their applications at large scale, it is important to improve the efficiency removal by coupling with chemical or/and biological processes [6,52].

Another advantage of phytoremediation technology comes from the biomass value added, which presents economic opportunities in the form of biofuels and bioenergy [53]. Indeed, the production of energy and element recovery from biomass significantly increases the financial viability of this process and reduces the environmental impacts of disposal for contaminated biomass [54]. Aquatic weeds contain high amount of cellulose and hemicellulose and low lignin content, which give them a potential for biofuel and biomethane production [55]. It is economically possible to produce bioethanol using water hyacinth [56]. The anaerobic fermentation of the contaminated biomass is possible with biogas production containing 60% of methane [57]. Oil crops used for the phytoremediation of contaminated soils with heavy metals can be used for biodiesel production by the supercritical methanol method [58]. Mthethwa et al. investigated the valorization of an aquatic weed, *Pistia stratiotes* for biohydrogen production via a dark fermentation process [59]. The novel process, hydrothermal liquefaction (THL), is well adapted to the valorization of aquatic plant. Indeed, a study based on recycling of waste of the Zn accumulator *Sedum plumbizincicola* via the THL process showed the production of hydrochar, bio-oil, and carboxylic acids. Approximately 90% of Zn was released from biomass during THL at 200 °C. Consequently, hydrochar was poor in this metal and could be used as fertilizer [60].

Aquatic weeds are rich in nitrogen and phosphorus, so their potential to generate coproducts such as fertilizers and compost from their waste residues after biofuel production needs to be evaluated as it reduces the production cost and further improve the system efficiency [55]. In the same way, Shen et al. recognized the possibilities to valorize the contaminated biomass by pyrolysis, incineration, composting, and compaction, but alerted on the cost and security problems [61]. Moreover, it is important to improve the knowledge on the possible transfer of metals from contaminated aquatic plant to some by-products or residues during biofuel production [62].

Finally, after phytoremediation processes, various disposal and utilization methods, such as heat treatment (incineration, pyrolysis and gasification), extraction treatment (with liquid extractants), microbial treatment (compost and fermentation), compression landfill, and synthesis of nanomaterials (to use in electrochemistry, catalysis, medical industry, etc.) should be applied for the treatment of plant biomass containing organic and inorganic pollutants [63].

6. Conclusions

The use of natural and synthetic chemicals in human activities imposes the need to reduce their transfer and accumulation in aquatic and terrestrial ecosystems through the adoption of efficient and ecological processes of depuration. Furthermore, the cost-effective removal of pollutants from effluents remains a challenge in industrial and urban wastewater treatments. Phytoremediation emerged as an alternative method to conventional treatment processes and represents an interesting technology as it is considered a low-cost, low-waste, and environmentally friendly method for cleaning up polluted sites. The choice of plant species used as phytoremediator depends on several factors, including: its abundance, its growth rate, and its tolerance and capacity to accumulate and/or degrade the pollutant. Over a period of thirty years, a large number of research studies have been developed trying to find, with the contribution of genetic engineering, the most appropriate species for optimal use in phytoremediation. However, genetic engineering has not yet gained public recognition as an ethical science.

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