

Review

# Aquatic Macrophytes in Constructed Wetlands: A Fight against Water Pollution

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Abstract: There is growing concern among health institutions worldwide to supply clean water to their populations, especially to more vulnerable communities. Although sewage treatment systems can remove most contaminants, they are not efficient at removing certain substances that can be detected in significant quantities even after standard treatments. Considering the necessity of perfecting techniques that can remove waterborne contaminants, constructed wetland systems have emerged as an effective bioremediation solution for degrading and removing contaminants. In spite of their environmentally friendly appearance and efficiency in treating residual waters, one of the limiting factors to structure efficient artificial wetlands is the choice of plant species that can both tolerate and remove contaminants. For sometimes, the chosen plants composing a system were not shown to increase wetland performance and became a problem since the biomass produced must have appropriated destination. We provide here an overview of the use and role of aquatic macrophytes in constructed wetland systems. The ability of plants to remove metals, pharmaceutical products, pesticides, cyanotoxins and nanoparticles in constructed wetlands were compared with the removal efficiency of non-planted systems, aiming to evaluate the capacity of plants to increase the removal efficiency of the systems. Moreover, this review also focuses on the management and destination of the biomass produced through natural processes of water filtration. The use of macrophytes in constructed wetlands represents a promising technology, mainly due to their efficiency of removal and the cost advantages of their implantation. However, the choice of plant species composing constructed wetlands should not be only based on the plant removal capacity since the introduction of invasive species can become an ecological problem.

Keywords: emerging contaminant; metals; cyanotoxins; antibiotics; phytoremediation

# 1. Introduction

Providing a clean source of drinkable water is a major concern for health institutions around the world. According to a report published by the World Health Organization, 2.1 billion people do not have access to clean water, and 844 million do not have access to basic sanitation [1]. As a response to that scenario, the United Nations established universal and equitable access to clean water by 2030 as one of its Sustainable Development Goals [2].



Although wastewater treatment operations remove many contaminants, they are much less efficient at removing the so called emerging contaminants [3,4]. Those compounds can have synthetic or natural origins and have not previously been monitored in waters — often due to the absence of analytical capacity or appropriate legislation for their detection and control [3,4]. Those emergent contaminants come from industrial, agricultural, laboratory, hospital, or domestic sewage residues, and include pharmaceutical (PhACs) and personal care (PCPs) products, endocrine-disrupting chemical (EDCs) and their degradation products [5], and it is now known that many of those compounds are potentially dangerous to ecosystems and to human health [6]. Due to their toxicological concerns, cyanotoxins, produced during cyanobacterial blooms caused by factors such as water eutrophication and global warming, have also been classified as emerging contaminants [7]. From 2015, recommendations for public water systems to manage cyanotoxins in drinking water have been published [8] and cyanotoxins entered in the list of emerging contaminants of the Environmental Protection Agency (EPA, USA) and Society of Environmental Toxicology and Chemistry, being one of the 20-priority research questions by the Global Horizon Scanning Project [9]. The occurrence of trace levels of emerging contaminants in already treated residual waters is of significant concern to human and environmental health [5]. Additionally, trace metals, although they do not belong to the group of emerging contaminants, are also responsible for significant contaminations of aquatic environments. Those metallic elements can bio-accumulate, persist, and be concentrated in tropic chains, and are toxic to many organisms [10,11]. Although they are eliminated in large part through standard water treatment processes, the presence of trace amounts of metals in ecosystems can result in additive or synergetic interactions with emergent contaminants [12].

Emergent contaminants in aquatic environments (including sewage, subterranean, surface, and drinking water) can occur at concentrations varying from  $ng \cdot L^{-1}$  to  $mg \cdot L^{-1}$  [13,14]. Many of those contaminants have been liberated now for long periods of time, although their identifications have only been possible with the development of new detection techniques [15], and while ecotoxicological studies have identified their negative effects [12,16–18], many countries still do not have any regulations concerning their occurrence in treated waters [15,19]. With increasing knowledge of the presence of emergent contaminants in waters consumed by human populations and their toxic effects on health, new directives have been established, and those chemicals have become priority targets for control and prevention through the establishment of the Water Framework Directive 2000/60/EC emitted by the European Union [20].

As standard sewage treatment systems have only limited capacities to remove micro- contaminants, additional techniques (such as coagulation-flocculation, activated carbon adsorption, ozonation, micro-membrane processing, and bioreactors) have been used [5]. None of them alone, however, are capable of completely removing all contaminant residues due to their individual particularities, making the development of new or combined systems increasingly important [5]. Additionally, traditional sewage treatment systems have high maintenance costs, and their construction and operation become more difficult in distant or rural regions [21]. Within that context, wetland systems appear to be a useful option due to their low installation costs, easy maintenance, and high-efficiencies in treating residual waters from domestic sewage, industrial and agricultural sources, and mining wastes. They are also ecologically sound, as they provide green areas that can be used for recreation, serve as habitats for many animals, and add aesthetic value [22,23].

Wetlands occur naturally or can be constructed. On top of their filtering role to process degrade and remove contaminants, they represent transition zones between terrestrial and aquatic environments, can act in controlling flooding, provide water for irrigation systems, and may be used as sites for the commercial production of fish and crustaceans [24]. The water in those systems will drain through substrates holding plants with microbiological communities that can remove and degrade noxious compounds extracted from the waters through phytoremediation processes [24]. One of the criteria for structuring artificial wetlands is the choice of plant species capable of both tolerating and removing contaminants. Within that context, significant attention must be given to the use of aquatic

macrophytes due to their high tolerance to contaminants, significant capacities for phytoremediation, easy management and control and demonstrated high biomass production levels [5,12,20]—Desirable characteristics for constructed wetland systems. Moreover, macrophytes exhibit some morphological changes in response to contaminants, which can be easily measured on-site (i.e., aerial elongation and leaf senescence) and used to monitor the ecological state of waters [25]. Although aquatic macrophytes can improve the capacity of constructed wetlands to reclaim contaminants from water, the choose of plant species to be used in systems constitutes a constraint. Some studies have shown that the contaminant removal efficiency of non-planted wetlands did not differ from planted ones [26,27], and in those cases, plants can become a problem: in addition to the possible introduction of non-indigenous species, appropriated destination of plant biomass is needed. Here, we provided an overview of the role and use of aquatic macrophytes in constructed wetlands. We aimed to summarize whether the use of these plant species is effective in promoting wetland performance to remove contaminants. Moreover, we discuss possible management and destination of the plant biomass produced in the systems.

## 2. Wetland Systems

## 2.1. Natural and Constructed Wetlands

Wetlands include swamps, bogs, lakes, and the floodplains of rivers, and can be permanently wet or flooded only during certain periods [28]. Those wetland systems have enormous ecological importance, as they act as filters to prevent erosion, fix enormous quantities of carbon, and provide habitat and food resources for an enormous variety of organisms [29]. Natural wetlands are not recommended for removing water contaminants derived from anthropic activities, since those contaminants will interfere with ecosystem functioning. The solution, therefore, resides in the construction of new wetland systems [29]. Based on the observation of these natural systems the constructed wetlands were designed.

Wetland system technologies were originally developed in Germany in the 1970s, although many other countries have now demonstrated interest in them [30]. Wetland systems basically use plants to remove contaminants and treat residual waters [30], and they can also be used to control flooding, produce foods and fibers through aquiculture, and create habitats to compensate for natural areas converted for agricultural purposes and urbanization [24]. Different from natural wetlands, constructed wetlands have predetermined sizes, locations, types of substrate, hydraulic conditions, and controlled retention times [24]. Among the advantages of constructed wetlands are their low maintenance costs compared to other water treatment facilities, their use of renewable energy resources (solar and kinetic) and natural elements (microorganisms and plants) that do not depend on high technology, and their capacity to process large volumes of water containing different types of contaminants [24]. Additionally, those systems can serve as public visitation sites and for environmental education and research purposes [24]. The limitations of wetland systems include their sensitivity to high levels of ammonia, the necessity of occupying large land areas (their main disadvantage in relation to conventional systems) [31], uncertainties concerning their treatment efficiencies due to the interactions of various factors, and their potential for creating insect (mosquito) pests [32]. Moreover, constructed wetlands demand higher retention time than technical systems [31]. Research during the last 25 years, however, has demonstrated positive results in terms of wetland construction for treating domestic and municipal sewage, although their use for treating industrial residues is still challenging (due to their greater contaminant contents) [29].

The removal of contaminants in constructed wetland systems occurs mainly due to sedimentation and biodegradation processes [33]. Aquatic macrophytes provide structure for enhancing flocculation and sedimentation, and essential conditions for microbial activities to stabilization and degradation of contaminants [34]. Microbial biofilms are a group of microorganisms surrounded by a matrix of extracellular polysaccharides which remain adhered to any surface, for example, the contaminant and root surfaces (the rhizosphere) [35]. Thus, the efficiency of wetland constructed systems depends mainly

on two factors: the tolerance of aquatic macrophytes to contaminants present in the environment [36] and the favoring of microorganism's growth present in the rhizosphere [37].

In addition to aquatic macrophytes, microorganisms present in the rhizosphere of plants used in planted systems play important roles in the treatment, removal and degradation of contaminants [38]. For this reason, the study of microorganisms present in biofilm is fundamental for understanding the processes of treatment and stabilization of contaminants [39,40]. It is important to highlight, however, that different plant species may differently favor the growth and development of microorganisms due to differences on root exudates released, which determine the activity of the microorganisms [35,41]. In this context, in addition to their role in the uptake of contaminants, the chosen of correct plant species to constitute wetlands may increase the system efficiency due to their direct determination of biofilm development.

There are currently a number of different types of constructed wetland systems developed for specific purposes, as described below.

#### 2.2. Types of Constructed Wetlands

Wetland systems can be characterized according to their hydrological processes, types of vegetation utilized, and flow directions [21], with two principal types: superficial flow and sub-surface flow (Figure 1).

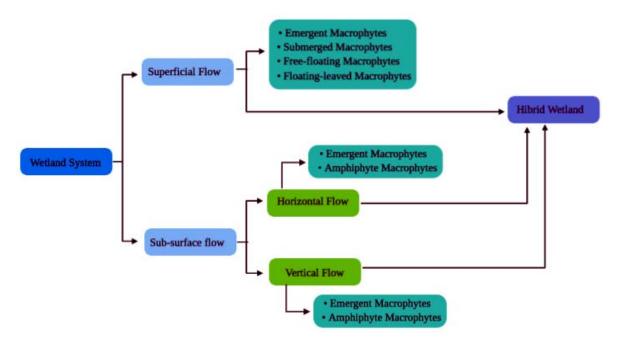


Figure 1. Types of wetland systems (modified from Sehar and Nasser [16]).

Superficial Flow Systems (Figure 2A) are characterized by the use of floating, emergent, or submerged aquatic macrophytes to remove industrial, agricultural, or domestic contaminants; they are also indicated for treating lixiviates, residues in subterranean waters, and flow from mining operations [21,42]. Depending on the type of macrophyte chosen, a shallow layer of substrate (0.30–0.40 m deep) is necessary to fix the plants in a shallow basin system insulated below with appropriate material to prevent infiltration into the ground [29]. Water flow will then facilitate the processes of sedimentation, filtration, oxidation, reduction, adsorption, and precipitation, which allow residue treatment [42].

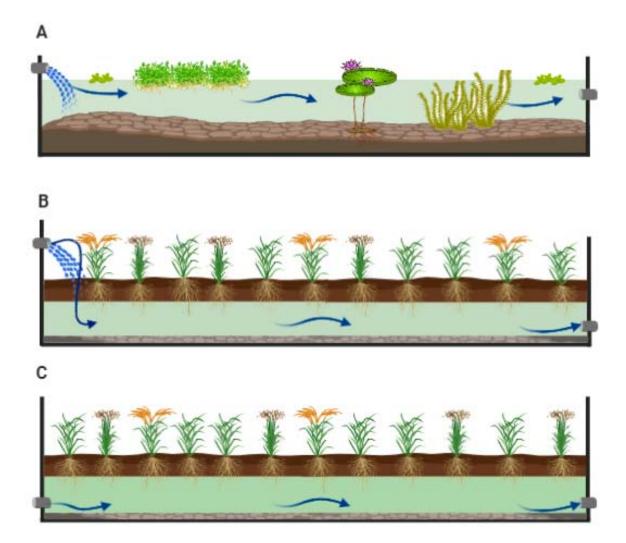
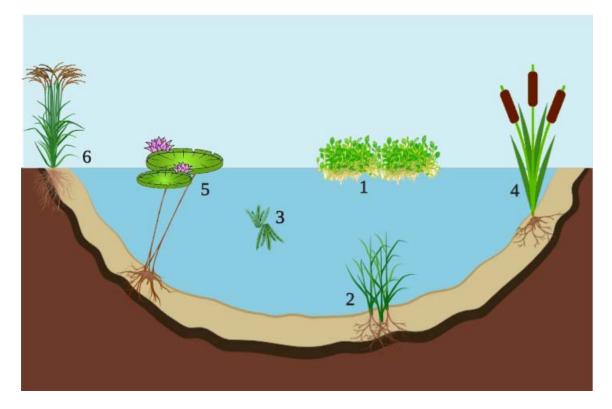


Figure 2. Illustrations of Wetland systems. Arrows indicate the direction of wastewater input and output flow. (A): Superficial wetland. (B): Vertical flow subsurface wetland. (C): Horizontal flow subsurface wetland.

Subsurface Flow Systems use emergent macrophytes fixed on permeable substrates (soil, rocks, or gravel) that allow water percolation; the substrate thickness is generally 0.6 m, with an impermeable insulating layer below [24]. According to Sehar and Nasser [21], the substrate layer of this system is efficient in filtering and removing contaminants, can function as a biofilm, and the substrate will accumulate trace elements, phosphorus, and other persistent substances. Subsurface systems can demonstrate both vertical and horizontal flow (Figure 2B and Figure 2C, respectively). Vertical flow systems require a smaller area for installation and have high purification performance from the beginning [31]. Moreover, this system provides good oxygen supply and nitrification and is of simple hydraulics. In contrast, vertical flow systems allow short flow distance but require higher technical skills [31]. Moreover, vertical flow systems do not favor the growth of denitrifying bacteria, thus limiting denitrification process [43]. In comparison to the horizontal flow systems, horizontal ones have longer life cycle, allow long flowing distance and both nitrification and denitrification are possible [31]. However, disadvantages of these systems are the complication of having equal waste water supply and the demand for careful calculation of hydraulics to optimize O<sub>2</sub> supply [31]. The latter hybrid wetland type represents a combination of the systems described above to optimize contaminant removal [21]. In hybrid systems, the combination of vertical or horizontal flow systems, diminishes their individual disadvantages [44]. With all of the types described, experimental systems can be constructed at microcosmic of mesocosmic scales.

### 3. Macrophytes and Wetlands

Macrophytes, hydrophytes, helophytes and aquatic plants, are terms used to designate vascular (angiosperms and pteridophytes) or avascular (mosses) plants that grow in aquatic or boggy environments [45]. Macrophytes are classified according to their biotypes, reflecting their interactions with the aquatic environment as immersed, emergent, floating, submerged free, submerged rooted, submerged with floating leaves or amphiphytes (Figure 3) [46].



**Figure 3.** Classification of aquatic macrophytes according to their biotypes. (1) Free floating. (2) Rooted submerged. (3) Submerged free. (4) Emergent. (5) Submerged with floating leaves. (6) Amphiphytes.

Brix [45] reported that while pteridophytes (such as *Salvinia* sp. and *Azolla* sp.) and algae (such as *Cladophora* sp.) are useful, angiosperms dominate constructed wetland systems. Machado et al. [47] listed the macrophytes most widely used in wetland constructions, and noted that species of the Poaceae family are most popular, with species of the *Cynodon* genus predominating, followed by the species *Typha domingensis* and *T. latifolia* (family Typhaceae). Some authors, however, indicate the use of terrestrial plants of commercial interest, such as *Agapanthus africanus* (African Lily), *Anturium andreanum* (Painter's-palette), *Zantedeschia aethiopica* (Arum-lily), and *Strelitzia reginae* (Bird of paradise flower), which can aggregate commercial value to the wetlands and are efficient at removing waterborne contaminants [48].

The vegetative organs of the macrophytes have key roles in wetland systems, avoiding particle resuspension, absorbing nutrients and removing contaminants, producing oxygen, and reducing the impacts of solar radiation; they are also aesthetically pleasing (Figure 4) [45]. Although not all wetland systems incorporate plants into their structures, they can play important roles in removing contaminants, providing oxygenation, increasing substrate porosity and infiltration rates, and producing an environment favorable to microorganism fixation [23]. In studies comparing the removal of contaminants from planted and non-planted wetlands, most of the former demonstrated greater decontamination efficiencies [49–52]. In some studies, however, aquatic plants do not significantly contribute to the removal of contaminated substances [53–55]. Machado et al. [47] proposed that wetland designs and operations affect the requirements for plants in those systems,

which impedes a single conclusion with respect to their use (or not). Additionally, as most studies have focused on testing a variety of plants (and therefore did not include replicates), there is very little solid data available on which to base firm conclusions [47].

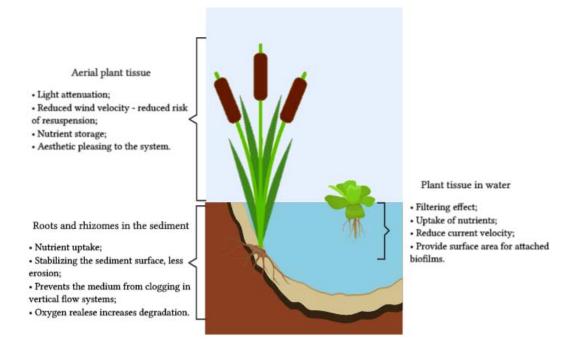


Figure 4. Illustration of the main functions of macrophytes in wetland systems (Modified from Brix [45]).

Environmental differences can also affect the efficiencies of plants in such studies. Wang et al. [56] observed that planted and non-planted wetlands did not demonstrate significant differences in terms of their oxygen demands or the removal of ammonia during the summer season; during the winter, however, planted wetlands were more efficient in relation to those measures. Those differences were related to the actions of microbiological communities, which are more sensitive to environmental temperatures when not associated with plants [56]. Finally, macrophytes differ in their capacities for bio-accumulating contaminants, and co-occurrences and interactions between different types of chemicals can apparently maximize or minimize their decontamination and removal efficiencies. As such, systems using macrophyte polycultures tend to be more efficient at removing contaminants than monoculture systems. The use of various plant species therefore allows greater phytoremediation when exposed to different contaminants, and provides diverse habitats for biofilm establishment [57].

Table 1 presents some recent studies concerning the utilization of plants in wetland areas (including macrophytes and terrestrial species) to remove different types of aquatic contaminants, their removal efficiencies, and destinations for the biomasses produced. The bibliographic search for the present work was carried out in the databases of Science Direct, Scielo, Google Scholar and Tandfonline published in the period from 2012 to 2020, through the search system with the combination of the descriptors "Constructed Wetlands", "Macrophytes", "Phytoremediation", "Removal", "Plants", "Contaminants", "Trace Elements", "Pesticides", "Sewage", "Nanoparticles", "Cyanotoxins", "Drugs", "Antibiotics". A total of 14 articles written in English and published in international journals were selected.

**Table 1.** Experiments using macrophytes and land plants in wetland systems. Abbreviations: VF: Vertical Flow. HF: Horizontal Flow. SF: Superficial Flow. Zn: Zinc.Cu: Copper. Hg: Mercury. Cr: Chromium. Pb: Lead. Ag: Silver TS: Total Solids. ARG: Antibiotic Resistance Genes. BOD: Biochemical Oxygen Demand. COD:Chemical Oxygen Demand. TP: Total Phosphate. TC: Total Coliforms. EF: Fecal Streptococci.

| Contaminant(s)                         | Species Used   | Wetland System<br>Type | Planted System<br>Removal Efficiency   | Non-Planted System<br>Removal Efficiency | Plant Removal<br>Efficiency  | Study                         |
|--|--|------------------------|--|--|--|-------------------------------|
| Trace Element                          |  |                        |  |  |  |                               |
| Hg                                     | Limnocharis flava  | HF                     | 90%  | 21%                                      | 69%  | Marrugo-Negrete et al. [49]   |
| Zn, Cu and Pb                          | Phragmites australis<br>Typha latifolia  | SF                     | Cu: 60%<br>Zn: 86%<br>Pb: 31%  | -  | -  | Gill et al. [58]              |
| Cr                                     | Phragmites karka<br>Cyperus alternifolius<br>Typha domingensis<br>Borassus aethiopum | HF                     | P. karka: 97.7%<br>C. alternifolius: 98%<br>T. domingensis: 99%<br>B. aethiopium: 99.3%                  | 97.4%                                    | There were no<br>significant differences<br>between planted and<br>non-planted systems | Tadesse and Seyoum [53]       |
| Drugs                                  |  |                        |  |  |  |                               |
| Ibuprofen and                          | Heliconia rostrata   | VF                     | Ibuprofen: 95.5%   | -  | -  | De Oliveira                   |
| Caffeine                               | Eichornia crassipes  | SF                     | Caffeine: 89%  |  |  | et al. [59]                   |
| Antibiotics and ARG                    | Thalia dealbata<br>Iris tectorum   | VF<br>HF<br>SF         | Antibiotics:<br>75.7–98.6%<br>ARG: 63.9–84.0%  | Antibiotics: 85%<br>ARG: 85.8%           | Antibiotics: -9.3 to<br>13.6%<br>ARG: 1.8 to 21.9%                                     | Chen et al. [60]              |
| Pesticides                             |  |                        |  |  |  |                               |
| Imidacloprid<br>Cyhalothrin            | Nymphaea amazonum<br>Eleocharis mutata   | SF                     | Imidacloprid:<br>N. amazonum: 75%<br>E. mutata: 15%<br>Cyhalothrin:<br>N. amazonum and<br>E. mutata: <1% | -  | -  | Mahabali and<br>Spanoghe [61] |
| Chlorpyrifos<br>(Organophos-<br>phate) | Polygonum punctatum,<br>Cynodon spp.<br>Mentha aquatica                              | HF                     | Overall average:<br>98.6%  | 99%                                      | There were no<br>significant differences<br>planted and<br>non-planted systems         | Souza et al. [55]             |

| Contaminant(s)  | Species Used  | Wetland System<br>Type               | Planted System<br>Removal Efficiency   | Non-Planted System<br>Removal Efficiency                           | Plant Removal<br>Efficiency  | Study                   |
|---|---|--------------------------------------|--|--|--|-------------------------|
| Sewage  |   |                                      |  |  |  |                         |
| BOD, COD, TS, TP,<br>TC and EF.   | Juncus effusus<br>Lolium perenne<br>Washingtonia robusta<br>Nerium oleander<br>Typha latifolia<br>Cyperus papyrus<br>Canna indica | HF                                   | TS: 91–96%<br>TM: 60%<br>BOD: 80–95%<br>COD: 80%<br>Pathogenic bacteria<br>(TC and EF): 99%  | -  | -  | Saggaï et al. [62]      |
| TS, TP, fluorides,<br>chloride and<br>ammonia.                                      | Canna hibrid<br>Alpinia purpurata<br>Hedychium coronarium   | HF<br>Polyculture and<br>Monoculture | There were no<br>differences in removal<br>between monoculture<br>and polyculture<br>systems | -  | -  | Marín-Muniz et al. [26] |
| Cyanotoxins   |   |                                      |  |  |  |                         |
| Microcystin-LR and algal blooms   | Iris pseudacorus L.   | VF                                   | ≥90%   | ≥90%   | There were no<br>significant differences<br>between planted and<br>non-planted systems | Wang et al. [27]        |
| Nanoparticles   |   |                                      |  |  |  |                         |
| Ag  | Phragmites australis  | VF                                   | 78.53%   | 40.96%   | 37.57%   | Bao et al. [63]         |
| Cerium  | Phragmites australis  | VF                                   | 17.9%  | -  | -  | Hu et al. [64]          |
| Ag  | Iris pseudacorus  | VF                                   | 96%  | -  | -  | Huang et al. [65]       |
|   | als & Pesticides  |                                      | A set such a sub-  | A  |  |                         |
| Acetaminophen,<br>Carbamazepine<br>(pharmaceuticals)<br>and Atrazine<br>(herbicide) | Canna flaccida  | SF                                   | Acetaminophen:<br>100%<br>Atrazine: 100%<br>Carbamazepine:<br>73–81.8%                       | Acetaminophen:<br>100%<br>Atrazine: 21%<br>Carbamazepine:<br>51.8% | Acetaminophen: 0%<br>Atrazine: 89%<br>Carbamazepine:<br>21–30%                         | Hwang et al. [66]       |

Table 1. Cont.

Plant removal efficiency = removal efficiency of planted system—removal efficiency of non-planted system.

## 4. Wetland Removal of Water Contaminants

#### 4.1. Trace Metal Elements

Trace metals are largely liberated by industrial and agricultural activities, poorly-treated sewage, and mining activities, and must be closely monitored in bodies of water due to their environmental persistence and their tendencies for bio-accumulation and bio-amplification. When consumed in drinking water, or through the ingestion of contaminated foods, trace elements can present significant threat to human health [67].

Marrugo-negrete et al. [49] tested a horizontal flow wetland system for the ability to remove mercury (Hg), a common mining residue. While systems without plants demonstrated removals of only up to 21% of that metal after 30 days, a system incorporating *Limnocharis flava* was able to remove 90% of the mercury for the same period of time (Table 1). The great ability of plants to uptake the metal resulted in the greatest efficacy of Hg removal of the planted in relation to the non-planted system (Table 1). However, different studies examining Hg removal have demonstrated different results, according to the type of system employed and the plant species used—with efficiencies varying from 25 to 99% [68–71]. Gill et al. [58] studied a wetland system for nine years that had been planted with *T. latifolia* and *P. australis* and designed to remove cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb) derived from highway surface runoff, and observed greater efficiencies in removing Cu (60%) and Zn (95%) than Pb (31%) or Cd (5%). Those same authors reported a diminishing efficiency of metal removal over time, with the system capable of removing 95% of the Cd, 88% of Cu, 86% of Pb, and 95% of Zn in the first year. Although the authors did not compare the removal efficiency of planted and non-planted systems, plants are known to absorb large concentrations of these metals [72] which may, therefore, increase the metal removal ability of planted systems.

Wetlands planted with the macrophytes *B. aethiopium*, *T. domingensis*, *C. alternifolius*, and *P. karka* were efficient for removing more than 97% of chrome (Cr) [53], although no significant differences were observed in relation to non-planted wetland systems, which removed 97.4% of that metal. The removal of Cr by the non-planted system occurred because of its partitioning in the clay and gravel sediment (which was also observed in the macrophyte system). The mean retention of chrome in plant tissues was 35.43%, with *T. domingensis* showing the greatest retention percentage (48.68%), mainly in its roots. Tadesse and Seyoum [53] reported a high tolerance of *P. karka* to that metal.

Yang et al. [73] studied a wetland system for 16 years that was planted with *T. latifolia*, *P. australis*, *C. dactylon*, and *Cyperus malaccensis* to treat mining effluents, and observed an efficiency rate > 90% for the removal of Cd, Pb, Zn and suspended solids. They also noted a positive relationship between system maturity and water quality, with a gradual increase in the presence of various organisms over time, including plants, birds and protozoans.

### 4.2. Pharmaceuticals

Water contamination by antibiotics is a current worldwide concern. The persistence of sublethal concentrations of those compounds can result in induced tolerance in microorganisms, including pathogenic bacteria, thus creating public health problems [74]. Additionally, antibiotic toxicity in ecosystems and productivity losses have been observed due to the use of contaminated irrigation water [12,75–77]. The development of wetland systems efficient at antibiotic removal from residual waters is therefore quite urgent.

Planted wetland systems of the superficial and vertical types with *Heliconia rostrata* and *Eichornia crassipes* have been found to be efficient in removing more than 80% of dissolved ibuprofen and caffeine, as well as organic, nitrogen containing, and phosphorylated compounds [59]. Those authors observed differences in the decontamination efficiencies of different systems, with the vertical flow system demonstrating greater efficiency at retaining contaminants in the substrate. The efficiency of non-planted systems to remove pharmaceutical products was not presented. However, macrophytes

have been used for phytoremediation of ibuprofen [78] and, therefore, plants could help to improve the reclaim capacity of the system.

An evaluation on a mesocosm scale by Hwang et al. [66] demonstrated the efficiency of superficial wetland systems planted with Canna flaccida for removing carbamazepine (73 to 81.8%) and acetaminophen (100%) contaminants. Although the efficiency of removal of acetaminophen between planted and non-planted systems did not differ (Table 1), plants increased the carbamazepine removal capacity of the system by 21–30% (Table 1). In addition, the system planted with C. flaccida was aesthetically agreeable due to that plant's exuberant flowering, elevated tolerance to adverse factors, and the fact that it is only a low-level invasive species [66] that does not threaten local communities through elevated reproduction. Chen et al. [60] analyzed the efficiency of wetlands in removing the antibiotics azithromycin, monensin, clarithromycin, leucomycin, sulfamethoxazole, trimethoprim, sulfamethazine, and sulfapyridine, as well as antibiotic resistance genes (ARG). Reductions in antibiotic concentrations and ARG in 75.8–98.6% and 63.9–84%, respectively, were observed in systems planted with Thalia dealbata and Iris tectorum. Plants increased by 9.3% and 21.9% the capacity of the systems to reclaim antibiotics and ARG, respectively (Table 1), demonstrating their importance to minimize the widespread of antibiotic resistance in the environment. Likewise, Pei et al. [79] observed that most constructed wetlands can remove ARGs, and demonstrate greater efficiencies than traditional sewage treatment systems. According to those authors, the fate of ARGs will depend on the structures and operating conditions of the treatment systems, as well as factors such as temperature, type of substrate, and water flow velocity—all of which influence the bioavailability of antibiotic contaminants. In that context, wetlands coupled to traditional sewage treatment systems can guarantee greater removal of emergent organic contaminants, ARGs and antibiotic resistant bacteria [80]. De Oliveira et al. [59] observed that a subsurface system proved more efficient than a superficial system, and the biodegradation observed in the former played an important role in removing antibiotics. The adsorption of antibiotics into substrates, as well as their absorption by plants or their biodegradation [60] result in their lower bio-availability, and consequently, lower occurrence of ARG.

## 4.3. Pesticides

Agricultural activities represent a major source of water contamination. The uncontrolled use of agricultural defensive chemicals has resulted in surface runoff and the contamination of water courses [12]. In addition to their environmental toxicity, the presence of pesticides in water has been associated with productivity losses [12] and the induction of resistance in pathogenic bacteria [81]. The removal of those substances in treatment stations, while highly necessary, has not been effective. Some macrophytes such as *Lemna minor, Myriophyllum aquaticum, Spirodela oligorrhiza, Elodea canadensis, P. australis, Nymphaea lotus* and *T. latifolia*, however, have been shown to have significant potential for removing agro-chemicals (such as chlorhydrates, organophosphates, pyrethroids, and carbamates), principally through bioaccumulation or metabolism [16,82,83], and their use in wetland systems is promising.

In experiments with superficial flow type wetland systems, *Nymphaea amazonum* plants demonstrated the ability to decrease imidacloprid pesticide concentrations by 79%, while only 0.5% of the applied amount of imidacloprid was detected in *Eleocharis mutata* plant material [61]; both species, on the other hand, removed less than 1% of the applied pesticide Cyhalothrin [61]. The removal of pesticides from water by macrophytes depends on the chemical properties, such as solubility in water, as well as the physiological mechanism used by plants for their uptake. For example, the presence of high amounts of phosphorous in water can disrupt glyphosate uptake by aquatic plants, since this herbicide uses phosphorous channels in plant membranes for its absorption [84]. However, it varies between plant species and some species can show high uptake capacity of glyphosate when great phosphorous concentrations are available [85]. Frequently, hydrophilic pesticides are easily removed from water by plants, which may increase the capacity of planted systems to remove those contaminants. For instance, Hwang et al. [66] evaluated superficial flow wetland systems planted with

different proportions of *C. flaccida* to determine their ability to remove atrazine, and observed significant great efficiency of planted systems in removing that pesticide, independent of the proportions of those plants used (as long as they covered more than 50% of the wetland surface) (Table 1). Vymazal and Březinová [86] reported that the superficial flow system is widely used to remove pesticides, although its effectiveness is quite variable. That variability is principally due to the different species employed, but may also be related to the diversity of contaminants and local environmental conditions. According to those authors, the principal pesticide classes that those systems remove are organophosphates, pyrethroids, organochlorines and estrobin, while lower rates of removal are observed with triazinone and aryloxyalkanoic acid.

Souza et al. [55] tested *Polygonum punctatum, Cynodon* spp. and *Mentha aquatica* for their capacity to remove chlorpyrifos pesticides in a horizontal flow system under different water retention times, and reported the removal of 98.6% of those chemicals, principally through adsorption and bacterial degradation processes. They noted, however, that there were no significant differences between planted and non-planted wetlands, and that a water retention time of 24 h was sufficient for contaminant removal, independently of the plant absorption. Liu et al. [87] reported that while water soluble pesticides can be removed through biodegradation, most hydrophobic pesticides, such as chlorpyrifos, undergo sorption by the substrate in wetland systems. Those authors also noted that the most efficient wetland systems for removing organophosphate pesticides are of the subsurface horizontal and vertical flow types, due to their greater interactions with system components, including plants (which have important roles in pesticide removal through absorption, rhizodegradation, and partitioning).

#### 4.4. Sewage

Residual waters, or sewage, are produced by anthropic activities such as industries, residences, and office buildings. Their appropriate treatment is fundamental to avoiding contamination in surface, subterranean, marine waters and the soil. Wetland systems are commonly used to treat those types of residues, and generally produce favorable and economically efficient results [88]. Hybrid wetlands have also been shown to be efficient at removing total solids, total nitrogen, ammonia, and reducing the chemical oxygen demands (COD) of effluents, as compared to other systems [88].

Evaluations made during the first three to seven days in wetland systems planted with P. karka and *E. crassipes* and used to treat residual water from coffee processing demonstrated their efficiency at removing total solids [50]. That efficiency diminished over 20 days due to the deaths of E. crassipes plants, however, which contributed to increases in total solids; as a result, the COD was lower and the water remained clearer than the control [50]. At the end of the experiment, the planted system had reduced total solids by 94%, the COD by 95% and water color by 79%. Kasak et al. [89] evaluated the efficiency of a hybrid wetland system with a vertical flow filter followed by a horizontal flow filter to remove nitrogen and phosphorus. Vertical flow systems are known to have high capacities for removing carbon, which would otherwise be used in the denitrification processes of FH systems [89]. That limitation was overcome by the use of biochar in the FH substrate. Biochar is rich in carbon, and can also sequester carbon from the atmosphere and transfer it to the soil. Systems containing plants (*T. latifolia*) and incorporated biochar were found to be more efficient at removing N and P than systems with just plants or just biochar. Although the biochar itself does not absorb any contaminants, the organic carbon it contains actually diminishes because it provides C to form biofilms and promote plant growth, as could be confirmed by increases in plant mass seen in systems incorporating biochar (and therefore demonstrating high levels of nutrient removal) [89]. Although biochar contributed to overall water treatment efficiency, those authors reported a low efficiency of P removal in relation to other studies [89], which could be related to the decreased pH of the medium with incorporated biochar [89]. Alkaline environments are known to promote P removal [89], so that the use of a substrate capable of furnishing carbon and at the same time promoting the alkalinization of the system will contribute to P removal.

#### 4.5. Cyanotoxins

Cyanotoxins are secondary metabolic products produced by cyanobacteria growing in marine or freshwater ecosystems [90]. Those toxins, now classified as emergent contaminants, exhibit high toxicity to both animals and plants. There is currently considerable concern regarding crop irrigation and household use of cyanotoxins-contaminated water, as those compounds can result in economic losses and impact human health [91]. Different techniques, including ozonation, chlorination, and photocatalysis, have been tested and utilized in water treatment installations to eliminate cyanotoxins, although the costs of those treatments (as well as the generation of toxic breakdown products) have limited their use on commercial scales [5]. Calado et al. [78] demonstrated in laboratory tests the efficiencies of the macrophytes Egeria densa, C. demersum, and M. aquaticum for completely removing Microcystin-LR (MC-LR—2030  $ng\cdot L^{-1}$ ), a hepatotoxin produced by the cyanobacterium Microcystis aeruginosa. On the other hand, the terrestrial plant Iris pseudacorus was not found to be efficient for removing Microcystin-LR in vertical flow wetland systems [27], since no significant differences were observed between planted and non-planted wetland systems. The presence of living vegetation, however, reduced nutrient concentrations in the water that contribute to eutrophication [27]. In spite of the importance of cyanotoxins, few studies have investigated the capacity of wetland systems to remove them, although laboratory experiments have clearly demonstrated the phytoremediation potentials of macrophytes.

## 4.6. Nanoparticles

Nanotechnology involves the fabrication and use of structures produced at nanometric scales, and that technology has now expanded to many diverse areas [92]. Nanoparticles are currently used for commercial and industrial purposes in the production of pharmaceuticals, therapeutic compounds, cosmetics, electronics, construction materials, and even foods for human consumption [93]. Hand-in-hand with their increased production and use, large quantities of nanoparticles have been discarded into the environment, especially in surface waters [94]. Although such studies are only incipient, there is evidence for the environmental toxicity of nanoparticles [64,95], and concern about how their subsequent physical, chemical, biological transformations will affect the environment [96].

Bao et al. [63] evaluated the efficiency of vertical flow wetland systems in removing silver nanoparticles. A wetland system planted with *P. australis* demonstrated the ability to remove 78.53% of waterborne nanoparticles, as compared to a 40.96% removal efficiency in a non-planted system, resulting in the final removal by the plants of 37.57% of the nanoparticle [63]. *P. australis* did not, however, demonstrate high efficiency for removing cerium nanoparticles [64], with those plants removing only up to 17.9% of the nanoparticles (which were largely accumulated in their roots). Most of the nanoparticles were held in the system's biofilms, and their toxicity to both plants and microorganisms was quite evident [64].

Huang et al. [65] likewise reported high efficiency in the removal of silver nanoparticles (approximately 96%) in a vertical flow wetland system planted with *Iris pseudacorus* and observed the reduction of COD compounds (83%), total N (61%), ammonia (42%), and total P (70%). As with cyanotoxins, there have been only limited studies examining the removal of nanoparticles by wetland systems and the roles of plants in that process. Published studies have only been of isolated experiments, without examining interactions with other environmental elements, as would occur under natural conditions [96].

## 5. Wetland System Biomass Management and Destination

Wetland systems require defined management strategies for collecting and disposing of the biomasses produced that will avoid the propagation of potentially invasive species, while at same time guaranteeing efficient pollutant removal [97].

The final destination of the macrophyte biomasses generated by wetland systems must be well-planned, as their content of diverse contaminants must not be allowed to return to the environment. If allowed by law, the biomass may be used as animal feed or fertilizer, or in the generation of bioenergy through direct combustion or for biogas or bio-ethanol production [57,98]. When determining the type of use for the biomass, its contaminant content must be kept in mind to avoid possible future problems related to simply shifting the contaminants removed from the water to the soil or to other organisms. As such, processes that involve combustion and/or the direct use of intact biomass (such as wood) should be given priority.

Roj-Rojewski et al. [99] tested the potential of some wetland system species to produce biogas, in light of the fact that *P. australis* (the common reed) produces more energy than other species, and those authors noted the potential of using those systems as economically viable sources of renewable energy. A study undertaken by Licata et al. [57] determined that it was possible to use the biomass of *A. donax* to produce bioenergy, although its cost-effectiveness remains to be determined. The biomass of *Eichhornia crassipes* (water hyacinth) derived from a hybrid wetland system was suggested for use in civil construction through the incorporation of its fibers into concrete blocks (for added strength) [100]. A similar concept was put forward for *T. latifolia* biomass, whose fibers could be used to improve the thermal and elastic properties of clay construction bricks [101].

In addition to the correct final destination of wetland system biomasses, their living maintenance must also be considered—as there could be second rounds of water contamination depending on the degradation rates of the system's constituent plants [102]. Yang et al. [102] analyzed four species of submerged macrophytes (*Najas guadalupensis, Hydrilla verticillata, Chara* spp. and *Potamogeton illinoensis*) and observed that their decay rates varied widely and depended on the nutritional composition of each; they also stressed the importance of studies of all of the species employed in wetland systems in order to adequately manage them.

We highlight that it is important to consider the use of non-indigenous plant species when planning the setup of constructed wetlands. Invasive species generally respond favorably to altered hydrological regimes, changes in water quality, eutrophication and substrate disturbance [103]. Some of these species present great efficiency of water depuration associated with valuable biomass. However, invasive exotic wetland species cause substantial loss of native wetland species and greatly alter wildlife habitat [103]. It is the case of the purple loosestrife (*Lythrum salicaria*), a wetland plant native to Europe and Asia brought to North America the early 1800s. This species is commonly used in constructed wetlands in Europe, but as a prolific invasive species, purple loosestrife sprouted aggressively, disrupting wetland communities and becoming an ecological problem in USA and Canada [104].

## 6. Conclusions

As life can imitate art (and art can imitate life), wetland systems emerged from observations that naturally swampy areas can filter contaminants, guaranteeing the quality of one of our most precious sources of life: water. In spite of mounting evidence of their functionality and effectiveness, there is still not any single wetland system model capable of clearing all types of water contaminants. That lacuna is largely due to our incapacity to closely replicate natural ecosystems at small scales. Additionally, the water volume/area ratios of constructed wetlands tend to be greater than natural sites, while their water retention times are shorter. Edaphoclimatic factors such as solar radiation, pH, and temperature, as well as system architectures, flow types, substrates, and vegetation also affect constructed wetland efficiencies. Complex interactions between those factors, together with the diversity of target substances to be cleared, present essentially limitless possibilities for wetland studies. As reviewed here, the chemical proprieties of the contaminants in water also play a role in the efficiency of planted systems. Generally, plants in wetlands increase metal removal from water in relation to non-planted systems, but it is not the case for organic contaminants. Plants in constructed wetlands were not efficient for the removal of some pesticides (chlorpyrifos), pharmaceutical compound

(acetaminophen) and cyanotoxins. In those cases, therefore, more studies using different flow systems and plant species must be performed aiming to maximize the constructed wetland efficiency.

One of the greatest questions associated with constructed wetlands is related to the capacities of their constituent plants to clear waterborne contaminants, which will directly affect the efficiencies of those systems. Within that context, there are still questions about which plant species should be used to obtain the greatest decontamination efficiency. In most cases, the species that have been studied are those that occur in natural wetlands, but numerous investigations have demonstrated the high tolerance and remediation capacity of a wide variety of macrophyte species when exposed to different contaminant substances [16,83,105]. Moreover, the use of exotic species in constructed wetlands can become an ecological problem. Although they can show great tolerance and removal capacity, their aggressive sprout and competitive characteristics can disrupt wildlife habitats. In that context, attention has recently been focused on the use of ornamental species having commercial value, thus combining environmental with economic benefits. Marín-Muniz et al. [26], for example, tested the use of Canna hybrid, Alpinia purpurata and Hedychium coronarium in monoculture or poly-culture systems treating domestic sewage, and observed that those species demonstrated significant capacities for removing contaminants (fluorides, chlorides, nitrates, ammonia, phosphates, sulfates and total and volatile solids) and for producing commercially valuable flowers. Within that context, attention should also be given to the use of commercial species that generate little methane  $(CH_4)$ , as wetland vegetation can produce, transport, and liberate that greenhouse gas into the environment [106]. Those species to be introduced into wetland systems must also be previously vetted to ensure that there exists no interspecific competition between them that could affect system performance [62]. Another advantage of the use of ornamental species in wetland systems is the possibility of removing one of the principal management concerns—the final destination of plant biomass. The correct destination of plant biomass must avoid the return of the captured contaminants to the natural environment, so that destinations such as the manufacture of construction material, fertilizers and bioenergy and biogas production should be considered (even though there have so far been very few studies in that context).

Although wetland system construction represents a promising technology, existing systems should be closely studied to avoid future environmental impacts. In addition to the emission of greenhouse gases [106], recent studies have shown that the adhesion, internalization, and colonization of *Salmonella napoli* on the macrophyte *P. australis* could make that plant a source of propagation and transmission of pathogens in watercourses and create risk situations for human and animal health [107]. As such, the importance of detailed studies of wetland system species and their management before their use and implantation must be stressed—although the elevated efficiency and low costs of wetland systems as compared to other processes for the remediation of contaminated waters makes them very attractive alternatives. More detailed investigations into the different types of constructed wetland systems, especially focusing on the use and management of the plant biomass generated, will aid in refining those systems and moving towards their large-scale use.

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