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Review

Floating Aquatic Macrophytes in Wastewater Treatment: Toward a Circular Economy

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Abstract: Floating aquatic macrophytes have a high level of proficiency in the removal of various contaminants, particularly nutrients, from wastewater. Due to their rapid growth rates, it is imperative to ensure the safe removal of the final biomass from the system. The ultimate macrophyte biomass is composed of lignocellulose and has enhanced nutritional and energy properties. Consequently, it can serve as a viable source material for applications such as the production of bioenergy, fertilizer and animal feed. However, its use remains limited, and in-depth studies are scarce. Here, we provide a comprehensive analysis of floating aquatic macrophytes and their efficacy in the elimination of heavy metals, nutrients and organic pollutants from various types of wastewater. This study offers a wide-ranging scrutiny of the potential use of plant biomasses as feedstock for bioenergy generation, focusing on both biochemical and thermochemical conversion processes. In addition, we provide information regarding the conversion of biomass into animal feed, focusing on ruminants, fish and poultry, the manufacture of fertilizers and the use of treated water. Overall, we offer a clear idea of the technoeconomic benefits of using macrophytes for the treatment of wastewater and the challenges that need to be rectified to make this cradle-to-cradle concept more efficient.

Keywords: floating aquatic macrophytes; pollutant removal; bioenergy; biofertilizer; circular economy

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Citation: Sayanthan, S.; Hasan, H.A.; Abdullah, S.R.S. Floating Aquatic Macrophytes in Wastewater Treatment: Toward a Circular Economy. *Water* **2024**, *16*, 870. https://doi.org/10.3390/w16060870

Academic Editor: Andrea G. Capodaglio

Received: 10 February 2024
Revised: 7 March 2024
Accepted: 8 March 2024
Published: 18 March 2024

1. Introduction

Water is the most critical natural resource on the planet [1]. The global water crisis has been highlighted as a highly serious ongoing and future issue in the global risk report from the World Economic Forum [2]. Additionally, it has also been anticipated that two-thirds of the world's population is supposed to face a water shortage within the next two decades [1]. The rapid increase in anthropogenic activities to compensate for the water demand of the growing population has intensified the withdrawal of fresh water [3]. This has resulted in water quality impairment and increased effluent quantities [4,5]. Currently, we are witnessing a universal trend of water mining and usage, taking the line of least resistance regarding water scarcity and substandard effluent quality [6,7].

Wastewater consists of organic matter, nutrients, heavy metals, explosives, radioactive elements and specific organic and inorganic chemicals, including micropollutants and microorganisms, that are above the permissible level unless they pass through a treatment system [8–10]. Wastewater, according to its origin, can be broadly categorized as domestic, industrial, agricultural, leachate and stormwater discharge [9]. Domestic wastewater, also known as household sewage, is comprised of waste from the kitchen, shower, toilet, washbasin and laundry. Since the solid content is approximately 0.1%, the availability of toxicants and the huge quantity of water being expelled make domestic sewage treatment more challenging [1,11]. Industrial wastewater is more difficult to treat as it contains various toxicants at high concentrations, and the constituents of industrial wastewater vary depending on the industry [12]. Agricultural runoff is generally the outlet water from farmlands and contains toxicants conveyed from residual fertilizers and other chemicals used in agriculture [11]. Landfill leachate has negative impacts on the environment because of its high levels of organic nitrogen and ammonia [13]. Water flowing across terrestrial areas after rain or snowmelt is considered stormwater runoff; as it does not originate from a single channel, its constituents can largely vary.

When wastewater reaches the environment without prior removal of or reduction in contaminants, it can threaten living organisms [14]. In general, water bodies are the ultimate sites of effluent discharge [15], and therefore, wastewater plays a significant role in controlling the quality of water bodies by influencing their water quality parameters [16]. Toxified water with high organic matter and nutrient levels will lead to oxygen depletion in water bodies due to the stimulated growth of microbes and aquatic macrophytes, technically termed "eutrophication". Eutrophication is characterized by abrupt algal growth, the development of plankton scum, the death and replacement of fish and other organisms and increased water sedimentation and turbidity. This facilitates the development of pathogenic microorganisms, resulting in the spread of waterborne diseases [17]. Specifically, the availability of nitrogen above the threshold level in water bodies causes blue baby syndrome in infants [18].

The occurrence of heavy metals in water bodies may cause either acute or chronic diseases [19]. After consumption, heavy metals will not be localized to the primary consumer but transmitted to different levels of consumers from their prey in the food chain via biomagnification [20], resulting in the death of the end consumer. Overall, pollutants in water bodies will adversely affect the aquatic ecosystem and result in the collapse of biodiversity, which is not limited to aquatic ecosystems [21].

Globally, it is estimated that approximately 80% of wastewater is disposed of without any adequate treatment [22]. This practice is more prevalent in developing countries because of insufficient treatment and disposal systems [23,24]. Hence, both the scientific community and industrial units must collaborate to develop efficient wastewater treatment and disposal systems.

The treatment of wastewater before its mixing with water bodies is indispensable for a safer environment. Treatments remove or reduce contaminants from wastewater and recover resources whenever possible. Pollutant removal can be accomplished by different treatment methods, such as physical, chemical and biological processes, as shown in Table 1. Each method consists of a variety of treatment techniques [25,26].

Table 1. Different wastewater treatment methods and respective processes.

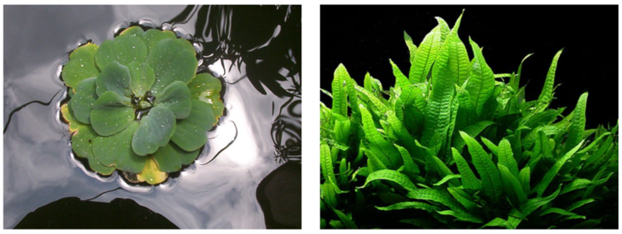
Physical Methods	Chemical Methods	Biological Methods
Reverse osmosis	Neutralization	Activated sludge
Comminution	Flocculation and coagulation	Aerated lagoons
Sedimentation	Oxidation	Trickling filter
Filtration	Ion exchange	Rotating biological contactors
Skimming electrolysis	Ozonation	Stabilization pond
	Chlorination	Phytoremediation

The selection of an appropriate treatment method is critical as it needs to meet the selection criteria; predominantly, the treatment should be efficient, economically viable and environmentally friendly. According to a previous study, biological treatment methods are generally more adaptable than other methods [25]. Economic advancement due to no or low energy consumption, eco-friendly attributes and operating flexibility make the biological treatment more feasible despite its minimal shortcomings [27,28]

Phytoremediation is a biological treatment method using plants to eliminate contaminants from wastewater, groundwater and soil [29,30]. Subsequently, wherever possible, the extracted resources, along with the plants, will be used for other purposes, such as animal feed production [8], drug formulation [31], bioenergy production [32] and soil fertility improvement and reclamation [33]. The suitability of macrophytes in post-treatment resource recovery and product development frames the floating phytoremediation process as a cradle-to-cradle (C2C) design, which is a novel approach to eliminate waste and create a circular economy. In this context, floating phytoremediation is regarded as an efficient and environmentally friendly method for the treatment of wastewater [34]. In this paper, we discuss the use of selected floating aquatic macrophytes (FAMs) in the removal of various pollutants and present the post-treatment potential of selected FAMs regarding their contribution to a circular economy. This approach can validate the effects of combining macrophytes with other treatment methods for the protection of water bodies.

1.1. Aquatic Macrophytes

Aquatic macrophytes are a set of diverse photosynthetic organisms that can be seen by the naked eye and belong to different divisions of the kingdom Plantae, such as Chlorophyta, Bryophyta, Pteridophyta and Spermatophyta [35]. The availability of aquatic macrophytes from more primitive divisions is lower than that of vascular macrophytes. As shown in Figure 1, aquatic macrophytes are generally categorized based on their growth forms, such as emergent macrophytes (pickerelweed, tape grass), submerged macrophytes (American pondweed, *Chara*), free-floating macrophytes (duckweed, pistia) and floating leaf macrophytes (fragrant waterlily, spatterdock) [36].


(a) *Pistia stratiotes* (b) *Microsorum pteropus*


(c) *Nymphaea alba* (d) *Pontederia cordata*

Figure 1. Different types of aquatic macrophytes.

Aquatic macrophytes use the nutrients available in the water bodies and convert them into biomass [37]. This capacity has been studied in detail to investigate their capability to thrive under various nutrient and pollutant conditions in view of their application in wastewater treatment. As a result, few plant species with remediating potential have been identified so far [38]. The recommended macrophytes are expected to possess some additional qualifications, such as (1) the capability to extract and accumulate, transform, degrade or volatilize contaminants; (2) high growth rates; (3) the simultaneous remediation of multiple pollutants; (4) dense root and shoot systems to support bioaccumulation and biosorption; (5) resistance to pests and disease; and (6) unattractiveness to animals to ensure the cessation of toxicant transformation through the food chain [39–42].

Macrophytes can remove, transform or stabilize nutrients [43], heavy metals [44], pharmaceutical compounds [45], endocrine-disrupting chemicals (EDCs) [46], radionuclides [47] and microorganisms [26]. This can be achieved via five different phytoremediation techniques, namely phytoextraction, rhizofiltration, phytostabilization, phytodegradation and phytovolatilization [48,49].

Via phytoextraction, the accumulated contaminants are eliminated by harvesting the biomass [50,51]. Phytoextraction is either a continuous process, using hyperaccumulating or fast-growing plants, or an induced process, using chelates to improve the bioavailability of the metals [52,53]. Rhizofiltration is related to the absorption, concentration and precipitation of inorganics (metal ions) and organics [54] through plant roots over a certain period [55,56]. Phytostabilization occurs through sorption, precipitation, complexation and metal valence reduction. Traits, genotypes and root physiology control the mobility and bioavailability of contaminants [50,57,58]. Phytovolatilization deals with eliminating the absorbed contaminants in gaseous form to the atmosphere via evapotranspiration [59].

In phytodegradation, the contaminants are either accumulated in the plant tissue and converted into less toxic compounds through metabolic activities or directly decomposed with the help of enzymes released by the plant roots [60,61]. In addition, the capability of improving dissolved oxygen, competing with microorganisms for food and sunlight and the physical filtration capacity using the dense root system make them more efficient in treating the various types of wastewater efficiently. Macrophytes are proficient in transforming oxygen through roots into the constructed wetland systems, which can accelerate the organic waste degradation and reduce the pollutant loads [62]. On the basis of previous studies, macrophytes can directly absorb organic matter [63] and can also reduce sunlight penetration [64] into the wastewater treatment systems, thereby reducing the establishment and multiplication of pathogenic microorganisms and supressing harmful algal blooming. Physical filtration is another mode of supportive mechanism in the wastewater treatment rendered by macrophytes [65], in which the dense and complex fibrous root systems can filter and trap various sizes of particles.

As phytoremediation processes do not require external energy, macrophyte-based treatment is economically viable and sustainable [38,66–68]. This approach can be seen as an alternative to chemical and physical treatments because of the possibility to meet the desired standards established for primary, secondary and tertiary effluents [69]. Macrophytes have been used for the treatment of wastewater for more than four decades [40]. Currently, this method is gaining considerable attention, making it an emerging technology [38].

1.2. Floating Aquatic Macrophytes

Floating macrophytes (FAMs) are a distinctive category of aquatic macrophytes as they are exposed to the atmosphere and can exist as producers either in turbid or high-water-depth conditions. They generally prefer water areas with little or no movement [36] and use phytoextraction, phytodegradation, phytovolatilization and rhizofiltration to remove contaminants [70]. Further, they support microbial decomposition in water bodies by associating with secondary carbon sources and facilitating nitrogen removal through denitrification [71]. Regardless of some drawbacks, such as preventing the photosynthesis of submerged organisms and being a barrier to oxygen dissolution from the atmosphere to the water bodies [36], FAMs play a crucial role in pollutant removal, producing biomass with a high nutritive value [69–72].

According to previous studies, FAMs can scavenge metal ions [73–76]. Specifically, the roots are involved in the active uptake of metal ions and their translocation to other tissues [77,78]. The roots also play a key role in facilitating microbial growth by providing a high specific surface area. Passive metal-ion uptake is dominated by the aerial parts that are in contact with the wastewater [77]. In this regard, the most common FAMs, such as water hyacinth, water fern and duckweed, have been extensively studied for their ability to improve wastewater quality. Their rapid growth, hyperaccumulation and availability favour their use in remediation projects [49,79,80].

Water hyacinth (*Eichhornia* sp.) is a floating aquatic weed, shown in Figure 2a, that belongs to the family Pontederiaceae and is the most commonly used macrophyte due to its high availability and adaptability and high growth rate [81]. Native to South America, it now occurs in almost all tropical countries. Significant amounts of money have been used to control the spread of water hyacinth. The genus Eichhornia contains seven species, namely *E. azurea*, *E. crasspes*, *E. diversifolia*, *E. heterosperma*, *E. natans*, *E. paniculata* and *E. paradoxa*. Among them, *E. crassipes* is the most common one [82]. The species of this genus can thrive in hazardous environments and produce biomass amounts of 60–100 t/ha/yr, making them highly effective in treating wastewater and predominant in subsequent resource recovery [83,84].

Figure 2. Predominant strains of floating aquatic macrophytes.

Duckweed is one of the most abundantly available small angiosperms, shown in Figure 2b, without any distinctive systems or leaves. It belongs to the family Lemnaceae and includes four genera, namely *Lemna*, *Spirodela*, *Wolffia* and *Wolfiella*, with a total of 37 species [85]. The growth rate of duckweed is higher than that of other large macrophytes. Ziegler, et al. [86] reported that under in vitro conditions, the doubling time of duckweed varies from 1.34 to 4.54 days, with an annual biomass output of 39.2–44 t dw/ha/yr. Duckweed is becoming increasingly popular due to its growth habits and capacity to withstand highly toxic conditions. It can accumulate heavy metals and serves as a metal indicator [87], making it an important plant in the treatment of heavy-metal-contaminated sites [88].

Water fern, also known as mosquito fern, is a tiny aquatic macrophyte, shown in Figure 2c, that occurs in both tropical and sub-tropical regions. It belongs to the genus *Azolla* and the family Salviniaceae, with two subgenera and six species. Duckweed can fix atmospheric nitrogen through a symbiotic relationship with *Anabaena azollae*, allowing it to survive in sites with low nitrogen levels [89]. This macrophyte can take up different heavy metals from wastewater streams [90–92] and remove large amounts of nitrogen and phosphorous, as high as 2.6 t N/ha/yr and 0.434 t P/ha/yr, and has been effectively used in phytoremediation [93,94]. *Azolla* is one of the fastest growing aquatic genera, with a doubling time from 5 to 7 days and a biomass production of 93.4–100 t dw/ha/yr [81,95]. Floating aquatic plants can grow in vertical as well as horizontal directions, thereby increasing their photosynthetically active surface area, making them some of the most productive communities [96].

2. Pollutant Removal

Macrophytes have been used in the removal of toxic compounds individually or as components of constructed wetlands to purify various wastewater types [97]. Based on recent studies on the use of macrophytes, there is a trend toward the simultaneous removal of multiple pollutants [22,98]. Different macrophytes have been studied regarding their potential to remove various pollutants, organic matter, nutrients, heavy metals and pathogens. Factors such as plant tolerance, the feasible range of toxicants that plants can accumulate, the concentration of toxicants in the medium and environmental factors largely impact the remediation capability of macrophytes [99]. It is not always appropriate to use living aquatic macrophytes for the continuous removal of harmful pollutants. After becoming saturated with pollutants, pollutant uptake decreases, and the plant will eventually perish due to the detrimental effects of the pollutants on plant growth and metabolism [100]. Therefore, although macrophytes are widely used in wastewater treatment, the application of dead or inactive parts or any substances obtained from biological sources is a better choice in continuous wastewater treatment.

When the biomass is alive during the treatment of wastewater, the process is denoted as “bioaccumulation”, whereas the use of dead biomass is termed “biosorption” [101]. During the former process, the toxic compounds attach in an inter- and intracellular manner, whereas in biosorption, such attachment is extracellular. Absorption, a double-stage active process, is responsible for pollutant removal via bioaccumulation, whereas in biosorption, a single-stage passive process, adsorption controls pollutant removal. Further, while desorption is only partially possible for bioaccumulation, biosorption also includes desorption. Generally, the removal performance is higher in biosorption than in bioaccumulation [102,103].

Water hyacinth can effectively be used in the removal of pollutants by chemical, biological, mechanical or hybrid means [104]. It can eliminate inorganic nitrogen [nitrate (NO3-N), ammonium (NH4-N), and total N)] and phosphorus (PO4−3-P and total P) from nutrient-rich wastewater [96]. Duckweed is another promising macrophyte with high potential in the removal of a wide spectrum of pollutants (organic pollutants, heavy metals, agrochemicals, pharmaceuticals and personal care products, radioactive waste, nanomaterials and hydrocarbons) from wastewater and can thrive in highly contaminated water [96]. Duckweed has been used in the treatment of low-strength domestic wastewater to high/severe-strength industrial wastewater streams to obtain clean, non-potable water [105,106]. Some authors recommend the use of duckweed after the removal or conversion of organic sludge into simple organic and inorganic molecules as they can be easily taken up by this macrophyte [107]. Another aquatic macrophyte with a high potential for pollutant removal is *Azolla* [108]. In combination with *Anabaena azollae*, it efficiently removes nutrients even after complete nitrogen depletion. The species *A. pinnata* can effectively be used in the treatment of domestic and industrial effluents [8,109,110].

Since FAMs grow rapidly and eliminate large amounts of pollutants with high removal rates through their extensive fibrous root system and aerial parts [111], they have been studied extensively regarding the removal of different pollutants such as heavy metals, nutrients and different organic compounds in wastewater. In the following section, we discuss in detail the capacity of different FAMs to remove various pollutants.

2.1. Heavy Metal Removal

Heavy metals are major pollutants in aquatic environments due to their high toxicity, non-degradable nature and bioaccumulation and biomagnification [10,112–114]. Aquatic macrophytes play a crucial role in the removal of heavy metals from the aquatic environment [115]. Table 2 shows the heavy metal uptake capacities of different FAMs, either via bioaccumulation or biosorption [101,116,117]. During the uptake of heavy metals at the whole plant and cellular level, plants absorb the metals based on the negative charges of their cell walls. Subsequently, the metals are transported into the cell cytoplasm and partitioned into cell organs or excreted [118]. Plants can accumulate 100,000 times higher concentrations of heavy metals compared to the effluent concentration [119].

Table 2. Heavy metal uptake by different floating aquatic macrophytes.

Macrophyte	Wastewater	Removal Performance	References
Eichhornia crassipes	River water	Al—63%, Zn—62%, Cd—47%, Mn—22% and As—23% in seven hours of exposure time	[120]
Eichhornia crassipes	Aquas solution	Adsorption of Pb—29.83 mcg/g, Cr—24 mcg/g Zn—29.94 mcg/g, Cd—28.41 mcg/g	[121]
Eichhornia crassipes	Synthetic wastewater	In 4 mg/L solution of Cd, the accumulation in root Cd—2044 mg/kg, in shoot Cd—113.2 mg/Kg In 40 mg/L solution of Zn, the accumulation in root Zn—9652.1 mg/Kg, in shoot Zn—1926.7 mg/Kg	[122]
Eichhornia crassipes	Synthetic wastewater	Adsorption of Cr^{3+}—99.8% and Cr^{6+}—89.15	[123]
Eichhornia crassipes	Industrial wastewater	Adsorbed 99.5% of chromium in 15 days of exposure time	[124]
Eichhornia crassipes	Synthetic wastewater	Zn—95% and Cr—84% in 11 days of exposure time	[98]
Eichhornia crassipes	Domestic wastewater	Fe reduced from 1.25 mg/L to 0.36 mg/L, Cu reduced from 0.3 mg/L to 0 mg/L, Mn reduced from 0.5 mg/L to 0.08 mg/L, Pb reduced from 0.2 mg/L to 0.01	[125]

Table 2. *Cont.*

Macrophyte	Wastewater	Removal Performance	References
Eichhornia crassipes	Hydroponic medium	Accumulation of mercury ion in root part—1.99 mg/g, in leaf part—1.74 mg/g and in petiole part—1.39 mg/g	[126]
Eichhornia crassipes	Synthetic wastewater	Absorption of Cd—59.4%, As—60.8%, Pb—92.4%, Zn—60.2% and Cu—60.7% during 30 days of exposure time.	[127]
Lemna	Synthetic wastewater	Bioaccumulation of Pb—62.8%	[128]
Lemna gibba	Synthetic wastewater	Cr removal varied from 37.3% to 98.6% Cd removal varied from 81.6 to 98.6%	[129]
Lemna minor	Synthetic wastewater	Se—19.5 mg/g when exposed for 20 days	[130]
Lemna minor	Synthetic wastewater	As—5% when exposed for 21 days	[131]
Lemna minor	Synthetic wastewater	Co—72%, Cd—66%, Zn—91%, Cr—26%, Ni—50%, Cu—91%, Fe—66% and Mn—89%	[132]
Lemna minor	Industrial wastewater	Cd—44.93%, Cr—32.26%, Ni—74.48% and Pb—79.1%	[133]
Lemna gibba	Synthetic wastewater	Removal of Pb ranged from 60.1% to 98.1% Removal of Cd ranged from 41.6% to 84.8%	[134]
Lemna minor	Coal mine effluent	Fe—19 mg/g	[135]
Lemna minuta	Synthetic wastewater	Al—97%, Fe—60% and Cr—4.9%	[136]
Azolla filiculoides	Synthetic wastewater	Inactivated Azolla with methanol: Pb^{2+}—36%, Cd^{2+}—33%, Ni^{2+}—34% and Zn^{2+}—24% Inactivated Azolla with ethanol: Pb^{2+}—41%, Cd^{2+}—36%, Ni^{2+}—38% and Zn^{2+}—31%.	[137]
Azolla filiculoides	Synthetic wastewater	Al—96%, Fe—90% and Cr—8.3%	[136]
Azolla filiculoides	Synthetic wastewater	Co—65%, Cd—61%, Zn—87%, Cr—19%, Ni—30% Cu—92%, Fe—70% and Mn—87%	[132]
Azolla pinnata	Industrial wastewater	Cd—57.3%, Cu—53.9%, Cr—58.1%, Fe—56.1%, Pb—72.4% and Zn—60%	[138]
Azolla filiculoides	Industrial wastewater	Biosorption of Cr^{6+}—83.341%	[139]
Azolla pinnata	Industrial wastewater	Removal of Hg ranging from 80% to 94% Removal of Cd ranging from 70% to 91%	[116]
Azolla pinnata	Synthetic wastewater	Fe—92.7%, Zn—83%, Cu—59.1%, Mn—65.1%, Co—95%, Cd—90%, Ni—73.1%	[140]

Live water hyacinth can remove large amounts of heavy metals through absorption and translocation to shoots and other tissues [141]. Dried water hyacinth and ash obtained from water hyacinth have also been used to adsorb heavy metals from waste streams [121,142,143].

Jones, et al. [120] conducted a study in the British River and reported the most pronounced heavy metal removal (21 heavy metals) using water hyacinth. After an exposure period of 7 h, 63% of Al, 62% of Zn, 47% of Cd, 22% of Mn and 23% of As were removed. Under in situ conditions, the authors reported the removal of Mn, Zn and Cd at 6%, 11% and 15%, respectively.

Bais [144] explored the biosorption ability of the shoots and roots of water hyacinth in the rainy season as well as in winter and summer. Based on the findings, during winter, 31% of Cd was removed via the shoots and 41% via the roots. Bianchi, et al. [136] reported that A. filiculoides can efficiently eliminate Fe and Al, with removal rates of 92% and 96%, respectively, whereas only 10% of Cr could be removed.

When comparing the biosorption capacities of *Azolla ficuloides* and *Hydrilla verticillata* regarding the removal of Cu(II), Cr(VI), As(III) and Pb(II), Bind, et al. [145] found that Pb was effectively absorbed by both species, with removal rates of 81.4% and 84.3%, respectively, from a synthetic wastewater stream containing Pb at a concentration of 10 mg L1. The adsorption capacity followed the order Pb(II) > Cu(II) > As(III) > Cr(VI).

Chaudhary and Sharma [129] investigated the efficiency of *Lemna gibba* in removing Cr and Cd from solutions with varying concentrations under laboratory conditions. The experiments were carried out for 7 and 15 days, and the removal rates were 37.3% to 98.6% for Cr and 81.6% to 94.6% for Cd. The removal capacity of this species decreased with increasing metal concentrations.

Yilmaz and Akbulut [146] evaluated the efficiencies of two different species of duckweed, namely *L. minor* and *L. gibba*, regarding metal removal under aeration. The removal rates were Pb 57%, Ni 60%, Mn 60% and Cu 62% for *L. minor* and for *L. gibba*. Aeration and the combination of these species increased the removal rates.

2.2. Nutrient Removal

In water bodies, nutrients are essential for the survival of aquatic biomes. However, above certain thresholds, they can become toxic to various organisms. Since aquatic plants can thrive in high nutrient concentrations and produce large amounts of biomass, they remove nutrients from wastewater. Table 3 shows the nutrient uptake capacities of different FAMs. Nitrogen and phosphorous are the key nutrients, accompanied by carbon at a certain level. Excess nitrogen and phosphorous accumulation results in water eutrophication, with negative impacts on ecosystem health. To satisfy the physiological requirement of macro- and micronutrients and to support the epiphytic biofilm growing on the surface, macrophytes will consume nutrients through assimilative uptake, which is the direct method of nutrient removal [147]. Further, the macrophytes can additionally support the treatment system indirectly in nitrogen removal by enhancing the nitrification and denitrification process through generating a spatial oxygen gradient across the treatment system [148].

Table 3. Nutrient uptake by floating aquatic macrophytes.

Macrophyte	Wastewater	Removal Performance	References
Azolla filiculoides	Aqua culture wastewater	NH_4^+—95% PO_4^{3-}—31%	[149]
Azolla filiculoides	Petroleum refinery wastewater	N—36% P—44%	[150]
Azolla pinnata	Domestic wastewater	Soluble reactive P—60.21% Total N—23.97%	[151]
Azolla microphylla	Pond water mixed with domestic wastewater	NO_3^-—57% NH_4^+—62% PO_4^{3-}—80%	[152]
Azolla pinnata	Dairy wastewater	TKN—73.25% TP—65.37%	[22]
Azolla pinnata	Industrial wastewater	TKN—81.94% TP—60.04%	[138]
Azolla filiculoides	Livestock wastewater	NH_4^+—52.7%	[153]
Lemna minor	Dumpsite leachate	TN—79.77% TP—75.75%	[154]
Lemna aequinoctialis	Anaerobically digested swine wastewater	TP—98.65% NH_4^+—68.16%	[155]
Lemna minor	Livestock wastewater	NH_4^+—66.4%	[153]
Lemna minor	Palm oil mill effluent (POME)	NH_4^+—95.5% (5% POME dilution) PO_4^{3-}—86.7% (10% of POME dilution)	[156]
Lemna minor	Domestic wastewater	Soluble reactive P—69.66% Total N—25.57%	[151]
Lemna minor and *Lemna punctata*	Swine wastewater	NH_4^+—67.84% PO_4^{3-}—11.2 ± 0.74 mg/L to 0.03 ± 0.02 mg/L	[157]
Eichhornia crassipes	Pond water mixed with domestic wastewater	NO_3^-—74% NH_4^+—67% PO_4^{3-}—71%	[152]
Eichhornia crassipes	Domestic wastewater	TN—76.61%, TP—44.84% NH_4^+—72.48%, PO_4^{3-}—38.69%	[158]
Eichhornia crassipes	Swine wastewater	In hot season, NH_4^+—97.5% PO_4^{3-}—81.4% In cold season, NH_4^+—67.5% PO_4^{3-}—56.2%	[159]
Eichhornia crassipes	Domestic wastewater	NH_4^+—89%	[160]
Eichhornia crassipes	Rice mill wastewater	TP—80% TN—70%	[161]
Eichhornia crassipes	Sewage contaminated pond water	TN—47.42% TP—53.44%	[162]
Eichhornia crassipes	Domestic wastewater	NH_4^+—63.26 ± 10.47% PO_4^{3-}—61.96 ± 12.11%	[163]

Kadir, et al. [156] carried out a preliminary study to determine the appropriate dilution of palm oil mill effluent (POME) to successfully grow L. minor and A. pinnata and to evaluate the corresponding nutrient removal rates. Both species showed high ammonia removal, with rates of 98% and 95.5%, respectively, in 5% POME. Phosphate removal was higher in 10% POME, with 93.3% removal by A. pinnata and 86.7% by L. minor. Overall, A. pinnata showed a significant nutrient reduction in 2.5% POME.

In another study, the authors performed a 2-week experiment to test the nutrient removal capacities of *L. minor* and *A. filiculoides* from textile, distillery and domestic wastewater mixtures. There were no significant differences in the nutrient removal rates between the species; *A. filiculoides* removed 94.6% of phosphorous, and *L. minor* removed 92% of phosphorous. Total nitrogen was more efficiently removed by *A. filiculoides* (94.6%) compared to *L. minor* (92%) [132]. Similarly, Verma and Suthar [164] investigated the capacity of *L. gibba* to treat sewage; *L. gibba* removed 42–64% of nitrate and 37–54% of total phosphorous.

Singh, et al. [165] investigated the potential of *Eichhornia crassipes* in removing nitrogen and phosphorous from glass industry effluent (GIE). This study was supported by a response surface methodology and an artificial neural network for optimization and prediction. Diluting the GIE to 60% and treating it with GIE showed the best results in terms of the removal of total Kjeldahl's nitrogen (93.9%) and total phosphorus (87.4%).

2.3. Organic Contaminant Removal

Organic pollutants are broadly categorized into two major groups: oxygen-demanding waste and synthetic organic pollutants. Wastewater from municipalities and the food industry, paper mill effluent and animal farm wastewater contain more biodegradable compounds that can be degraded by microorganisms, resulting in a higher oxygen demand and, ultimately, in anoxic conditions. Plants can effectively remove simple organic matter, which requires high oxygen demand during decomposition, and their effectiveness was tested by several researchers. El-Kheir, et al. [166] used *L. gibba* to treat primary treated sewage and observed BOD (biological oxygen demand) and COD (chemical oxygen demand) decreases by 90.6% and 89.0%, respectively. Another study was carried out by Bhagavanulu, et al. [167] to evaluate the biosorption capacity of the root, stem and leaf powder of water hyacinth. Root and stem powder were effective in turbidity management. The maximum BOD reduction of 49.2% was observed when the root powder was used for 30 min. A COD reduction was observed when a combination of leaf and root powder, in equal amounts, was used. Sahi and Megateli [168] investigated the ability of L. minor to reduce the COD in real dairy wastewater (RDW) and synthetic dairy wastewater (SDW) over a period of 10 days, and this species was more effective in removing COD from RDW (60%) compared to SDW (55.5%). Mamat, et al. [169] determined the efficacy of Azolla pinata in the treatment of palm oil mill wastewater and reported that this species effectively removed 85.89% of the BOD and 80.58% of the COD.

Synthetic organic compounds are produced by synthetic detergents, agrochemicals, specific food additives, pharmaceuticals, synthetic fibers and plastics [170]. Organic pollutants of the category persistent organic pollutants (POPs) are more dangerous because they can remain in the food chain and have a longer half-life [171]. Endocrine disruptive chemicals are a subdivision of synthetic organic compounds with the capacity of creating hormonal imbalances and affecting reproduction development or behaviour in animals and causing irregular endocrine behaviour and cancer in humans [172]. The increase in the amounts of endocrine-disrupting chemicals in most waste streams has resulted in public concerns regarding their elimination [173]. Chlorophenols, bisphenol A, dichlorodiphenyltrichloroethane (DDT), chlorpyrifos, atrazine, 2, 4-D and glyphosate are widely available endocrine-disrupting chemicals [108,174].

Pharmaceuticals are another subclass of synthetic organic pollutants, and their use has increased recently. Anti-inflammatories, antidepressants, antiepileptics, lipid-lowering drugs, β-blockers, anti-ulcer agents, antihistamines and antibiotics [175] are organic pollutants derived from the pharma industry. As an example, diclofenac, a nonsteroidal anti-inflammatory drug, has gained attention because it persists in municipal wastewater [176].

Table 4 shows the capacities of different FAMs to take up organic pollutants. Campos, et al. [177] investigated the efficiency of *E. crassipes* and *Cyprus isocladus* in different constructed wetlands to eliminate endocrine disruptors from synthetic municipal wastewater. The removal rates varied from 9.0 to 95.6% for ethinyl estradiol, 29.5 to 91.2% for bisphenol A and 39.1 to 100.0% for the progestin levonorgestrel. Zazouli, et al. [108] reported the removal of bisphenol A by Azolla, with removal rates from 60 to 90%. In a study by Bianchi, et al. [136], by using *L. minuta* and *A. filiculoids*, diclofenac was removed at removal rates below 10%, whereas higher rates were observed for the removal of levofloxacin, with rates of 50% and 60%, respectively. Xia and Ma [178] investigated the removal of the phosphorus pesticide ethion with water hyacinth. The plant accounted for 69% of the removal of ethion from the waste stream through uptake and phytodegradation, but the roots and shoots emitted ethion at levels of 74–81% and 55–91%, respectively, in ethion-free medium after a growth period of 7 days. In a study by Balarak [179], 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP) were removed from agropharma waste using *Azolla*, with removal rates of 71% and 85%, respectively. Garcia-Rodríguez, et al. [180] tested the potential of duckweed to remove carbamazepine, acetaminophen, propranolol, ibuprofen, diclofenac, caffeine, bisphenol A, and 17-a-ethinylestradiol from secondary treated wastewater, and the observed removal rates are promising.

Table 4. Organic pollutant uptake by floating aquatic macrophytes.

Macrophytes	Pollutants	Removal Performances	References
Lemna minor	Zeta-cypermethrin (concentration was 300 ppb)	Maximum 95.9% removal was observed at the 96th h.	[181]
Lemna minor and *Lemna punctata*	Ibuprofen (10 µM) and fluoxetine (10 µM)	Ibuprofen—47.5 ± 3.9% in 9 days Fluoxetine—55.6 ± 3.9% after 1 day	[182]
Lemna gibba	Acetaminophen, diclofenac, and progesterone at 1000 µg/L	Acetaminophen—66.12 ± 1.4%, diclofenac—47.50 ± 2.0% and progesterone—66.50 ± 1.7% after 4 days of treatment	[183]
Lemna minor	Landfill leachate	COD—39%, BOD—47% in 15 days of treatment	[184]
Lemna minor	Cefadroxil, metronidazole, trimethoprim, and sulfamethoxazole	Cefadroxil—100% in 14 days; metronidazole—96%, trimethoprim—73%, and sulfamethoxazole—59% in 24 days	[185]
Lemna minor	Acid blue 113 (5.0 mg/dm^3), Reactive blue 198 (5.1 mg/dm^3), Basic red 46 (5.1 mg/dm^3), and Direct orange 46 (5.0 mg/dm^3)	Acid blue 113—32% Reactive blue 198—19% Basic red 46—51% Direct orange 46—4%	[186]
Eichhornia crassipes	2,4-dichlorophenoxy acetic acid (2,4-D) at 4 g/L	Removal was 91% through biosorbent method	[187]
Eichhornia crassipes	Chlorpyrifos (0.1, 0.5, 1.0 mg/L)	0.1 mg/L solution—81 ± 1.8% 0.5 mg/L solution—91 ± 2.6% 1.0 mg/L solution—82 ± 1.6%	[188]
Eichhornia crassipes	Cotton red dye, Cotton blue dye and Cotton yellow dye were maintained at 10 mg/L	Water hyacinth stem powder treated with phosphoric acid at the rate of 10 mg/25 mL used Cotton red dye—82.54 ± 1.2% Cotton blue dye—51.37 ± 0.7% Cotton yellow dye—78.65 ± 0.45%	[189]
Eichhornia crassipes	Sulfadiazine at 1 mg/L	Removed 83.5% when exposed for 25 days	[190]
Eichhornia crassipes	Industrial mine wastewater	BOD—50% COD—34%	[124]
Eichhornia crassipes	Formaldehyde at 200 mg/L	Removed 93% of pollutant when exposed for 10 days	[191]
Azolla filiculoides	Polyphenols and COD in two different olive mill wastewaters Initial COD—92,000 ± 2200 and 44,400 ± 800. Initial polyphenols—7360 ± 290 and 4367 ± 130.	COD—52% and polyphenols—53% (wastewater from traditional extraction system) COD—95% and polyphenols—65% (wastewater from continuous extraction system)	[192]
Azolla filiculoides	Acid green 3 at 10 mg/L concentration	99.1% when absorbent concentration was 4 g/L and the exposed time was 90 min.	[193]
Azolla filiculoides	Ampicillin at 100 mg/L concentration	0.8 g/L activated carbon prepared from *Azolla filiculoides* was proficient to remove 96.84% of ampicillin with a contact time of 60 min.	[194]
Azolla filiculoides	Pyrocatechol at 5 ppm of concentration.	Removed more than 90% after 14 days of duration	[195]
Azolla pinnata	Palm oil mill effluent Concentration of effluent varied from 10% to 60%	BOD—92.98% (35% concentration), COD—86.01% (60% of concentration), and oil and grease—79.74% (35% concentration).	[169]

Dyes are another group of organic pollutants in the wastewater stream and are mainly derived from industrial plants and households. According to Kant [196], around 8000 chemicals are associated with dyeing processes and pose risks to environmental and human health. For example, crystal violet, a commonly used dye, is mutagenic and carcinogenic. Color removal from dyes is a serious problem as it consumes more oxygen and increases the BOD value in the waste stream [197]. Kulkarni, et al. [197] studied the biosorption capacity of water hyacinth root powder for the decolorization of crystal violet dye and obtained a Langmuir monolayer biosorption capacity of 322.58 mg/g. These authors further examined the influence of initial pH, initial dye concentration, biosorbent dosage, contact time and temperature on dye removal and found that water hyacinth was an effective biosorbent to remove crystal violet dye from an aqueous solution. Nath, et al. [198] investigated the biosorption capacity of water hyacinth in the removal of industrial dyes such as methylene blue, Congo red, crystal violet and malachite green from aqueous solutions at laboratory scale and observed maximum removal rates of 90%, 88%, 92% and 90%, respectively. According to Padmesh, et al. [199], *Azolla* can efficiently be used in the removal of acid blue 15 and eliminated 61.3% of this dye from an aqueous solution through biosorption. Durairaj [200] and Imron, et al. [201] tested the effectiveness of L. minor in removing methylene blue and textile acid orange 10, respectively, with contact times of 1 day for methylene blue and 4 days for acid orange. The removal rates were 80.66% for methylene blue and 82.9% for acid orange.

3. Circular Economy in Phytoremediation

The current production perspectives are directly linked to resource extraction and product transformation, which are not sustainable as these resources are limited [202]. Rather than such a linear economy concept, which is based on "take–make–dispose", the circular economy running in closed loops is more effective in terms of resource sustainability [203]. According to Webster [204], a circular economy is one that is restorative by design and that aims to keep product components and materials at their highest utility and value at all times. Cradle-to-cradle principles and the laws of ecology are the main pillars supporting this concept [205,206]. Regarding the wastewater sector, the circular economy emphasizes the extraction and use of possible resources, including water, as shown in Figure 3.

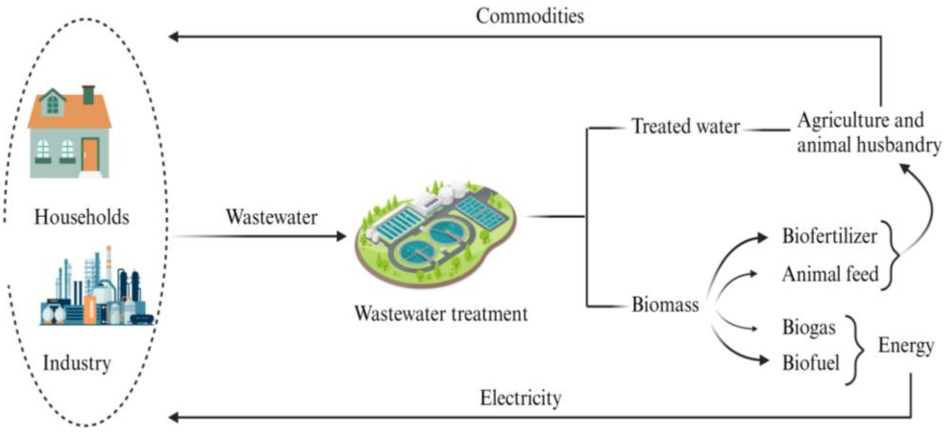


Figure 3. Implementation of circular economy in FAM wastewater treatment.

Wastewater may contain different components such as energy, nutrients, heavy metals, biopolymers and antibiotics [207–209]. Effluents from different sources are rich in different resources, depending on the point of waste generation. Hence, it is obvious that wastewater is a potential source of various resources, and different chemical and physical methods have been employed to extract these resources. For example, Yangui and Abderrabba [210] extracted polyphenols from olive oil wastewater via adsorption, and Li, et al. [211] separated proteins from soybean wastewater using complexation. Li, et al. [212] removed heavy metals using calcination with nitrogen, using magnesium chloride as an additive. However, these processes and energy demanding and not environmentally friendly, calling for "greener" alternatives.

Although macrophytes are commonly used for wastewater treatment, the disposal of the harvested biomass is challenging [213,214]. Since the harvested biomass is rich in nutrients and can be used to produce energy via thermochemical and biochemical processes, it can be directly used to generate fuel, feed or fertilizer [215]. Water hyacinth, Azolla and duckweed are predominant aquatic weeds in Asian countries, with a high potential to remove nutrients from waste streams and to produce high biomass amounts [89]. The biomass production of prominent FAMs is shown in Table 5. Biomass production varies depending on the plant type and the prevailing environmental circumstances. Based on the table, *Eichornia crassipes* has the highest biomass production capacity, whereas Lemna sp. has the lowest one.

Table 5. Productivity of prominent floating aquatic macrophytes.

Floating Aquatic Macrophytes	Productivity (ton/ha/yr)	Reference
Eichornia crassipes	60–100	[82]
Eichornia crassipes	456	[216]
Eichornia crassipes	106	[217]
Lemna sp.	39.2–44	[218]
Lemna sp.	481–730	[164]
Azolla sp.	33–35	[219]
Azolla sp.	100	[218]
Azolla sp.	93.4–100	[220]

3.1. Bioenergy Production

Excessive consumption, the emission of toxic substances and global warming are major concerns related to the use of fossil fuels [221]. The Paris Climate Agreement of 2015 emphasizes that nations should limit temperature rise to 1.5 °C by any means possible. Due to the high global demand for energy, the production of fossil fuels continues to dominate the energy section, accounting for 81% [222]. However, after continuous growth, the fossil fuel industry, which contributes remarkably to CO_2 emissions, is expected to decline. It has been anticipated that 56% of fossil methane gas, 58% of oil and 89% of coal have to be limited to the percentages available in 2018 to ensure a probability of 50% in achieving the Paris Climate agreement of 2015 [223]. This scenario will create a gap between the demand for and supply of global energy. Therefore, to avoid energy shortages, it is crucial to propose alternative energy sources [224]. In this context, the use of renewable energy resources appears to be an effective solution.

Bioenergy can be seen as one of the potential players in the renewable energy context [225]. There are sets of bioenergy production technologies, such as the production of bioethanol, biodiesel and biomethane, that receive more attention in substituting traditional energy sources. Currently, it is difficult to find biomass feedstock of high quality and quantity to produce bioenergy. This trend has shifted the search for biomass away from edible feedstock to lignocellulosic or algal biomass [226]. Several authors encourage the usage of macrophyte biomass as an alternative for first-generation feedstock to produce biofuel. The ability of macrophytes to proliferate rapidly and produce higher biomass amounts via sequestering nutrients from effluents makes them potentially suitable for bioenergy production [89]. The desired biomass constituents, such as proteins, lipids and carbohydrates, along with low lignin and higher cellulose and hemicellulose contents, as shown in Table 6, are advantages [227–229]. Macrophytes, which perform well in nutrient uptake from wastewater and are capable of producing efficient biomass feedstock, can potentially be applied in integrated wastewater treatment and bioenergy production [89]. In recent years, bioenergy production via biochemical and thermochemical processes in aquatic macrophytes has received increased attention.

Table 6. Lignocellulosic biomass composition of specific floating aquatic macrophytes.

Biomass	Cellulose (%)	Hemicellulose (%)	Starch (%)	Lignin (%)	Reference
Water hyacinth	24.5	34.1	NA	8.6	[230]
Water hyacinth	36.84 ± 0.8	27.7 ± 0.2	NA	7.93 ± 0.5	[231]
Water hyacinth (root)	24.34	54.95	NA	14.44	[232]
Water hyacinth	13.24	64.54	NA	8.19	[232]
Water hyacinth	24.8	30	NA	5.6	[233]
Azolla	21.8	13.5	NA	10.3	[218]
Azolla pinnata	12.76	10.20	NA	28.24	[234]
Azolla	5.6–15.2	9.8–17.9	NA	9.3–34.8	[235]
Azolla pinnata	28.87 ± 0.64	11.11 ± 0.29	NA	8.07 ± 0.25	[236]
Azolla pinnata	26.00 ± 0.31	14.00 ± 0.31	NA	7.00 ± 0.11	[237]
Duckweed	10–24.5	3.5	5–70	3.1	[238]
Duckweed	55.2	33.6	NA	12.2	[225]
Duckweed	43.7	3.5	20	2.4	[239]
Duckweed	29.4 ± 1.8	24.6 ± 2.2	NA	23.8 ± 1.3	[240]
Duckweed	11.9	13.8	3.2	3.2	[241]

3.1.1. Biochemical Conversion

Biochemical conversion is a prominent technology used to produce multiple biofuels, such as bioethanol, biomethanol, biodiesel, Fischer–Tropsch diesel and gaseous fuels such as biomethane and biohydrogen. These end products can be attained through the anaerobic digestion, alcoholic fermentation and acidogenic fermentation of aquatic macrophyte feedstock. Hossain, et al. [242] conducted a study on ethanol production using a biomass of water hyacinth (*E. crassipes*) and *Azolla* sp. (*A. pinnata*) as feed stock for fermentation. Water hyacinth showed a higher ethanol yielding capacity (0.32 g/g) than *Azolla* sp. (0.20 g/g ethanol). Magdum, et al. [243] and Das, et al. [244] used *Pichia stipitis* for the production of ethanol from the hydrolysate of water hyacinth and obtained 19.2 and 10.44 g/L, respectively. Su, et al. [245], using duckweed as a substrate for producing higher alcohols, reported that duckweed is a suitable fermentation biomass substrate that requires basic pre-treatment, without the need for supplementary nitrogen or strengthening with redox agents; the production of biofuel from duckweed could be achieved through bioconversion by *Clostridium acetobutylicum* and *Escherichia coli*. The biofuels produced are not limited to traditional forms of energy, such as ethanol, and higher-energy alcohols with higher energy yields can also be produced. Xu, et al. [246] investigated the capacity of duckweed to produce ethanol after transferring it from piggery farm effluent to well water and sustaining it for 10 days. The final ethanol production was 6.42 × 103 L/ha, which is 50% higher than that obtained with the use of maize produced in the same area.

Singhal and Rai [247] investigated the biogas production from water hyacinth. The plants were allowed to grow in pulp and paper mill effluent and distillery effluent at various dilutions. Parallel experiments used deionized water as a control. Biogas production was higher in phytoremediation plants than in deionized water plants, and water hyacinth cultivated in 20% pulp and paper mill effluent showed the highest biogas output (23,650,141.4 cc/kg dry weight).

Ramaraj and Unpaprom [248] examined duckweed biogas production at different temperatures. Based on their results, the total biogas yield at ambient temperature was 7863.69 mL/L, whereas the yield under mesophilic conditions (35 °C) was 10,376.59 mL/L, and that under thermophilic conditions (50 °C) was 9981.08 mL/L, with a maximum methane concentration of 64.47%. This study emphasizes that duckweed biomass substrate has the highest biogas production rate in the mesophilic temperature range.

Patil, et al. [249] explored the biogas production efficiency of water hyacinth treated with NaOH, combined with poultry waste and primary sludge. Fresh water hyacinth was used as a control. The highest cumulative biogas yield of 0.38 L/g was obtained from water hyacinth combined with poultry waste. A high methane percentage of 71% was found in the treatment using water hyacinth pretreated with NaOH. Other studies investigating bioenergy production through biochemical conversion are listed in Table 7; most of them focused on biogas production.

Table 7. Use of floating aquatic macrophytes in bioenergy production.

Macrophyte	Form of Energy	Description of Produced Bio-Energy	References
Water hyacinth	Bioethanol	185 mg/g of dry WH bioethanol was produced during fungal and acid-treated usage.	[250]
Water hyacinth	Bioethanol	*E. crassipes* without chromium adhered performed higher (12,100 mg/L) in producing bioethanol than that of chromium adhered (8000 mg/L).	[251]
Water hyacinth	Biodiesel	Biodiesel content of water hyacinth was susceptible for different season. It varied between 3.32 and 6.36%. The content was highest in summer season (6.36%).	[252]
Water hyacinth	Biogas	At the end of the 50th day, pretreated water hyacinth produced 3737 ± 21 mL of biogas, whereas non-pretreated water hyacinth produced 3038 ± 13 mL.	[231]
Water hyacinth	Biogas and bioelectricity	The maximum cumulative bio-H_2 production was 904.24 ± 40.69 mL/L within 14 h of fermentation. The bio-methane production improved with time and stopped on the 18th day. The highest cumulative CH_4 produced was 796.73 ± 18.62 mL/L. The maximum power density obtained using fuel cells was 18.81 ± 0.75 W m^{-3}.	[233]
Azolla filiculoides	Biodiesel	Produced biodiesel characteristics matched well and had an estimated density of 880 ± 2.9 kg m^{-3}, cetane number of 63 ± 4.0 and an iodine value of 80 ± 15.	[253]
Azolla pinnata	Biogas	1 L of slurry made from *Azolla pinnata* and cow dung produced 3571.14 mL of biogas, where methane percentage was 55.62%	[254]
Azolla filiculoides	Bioethanol	*Azolla filiculoides* hydrolysate used to produce ethanol with different microbes, among them, Kluyveromyces marxianus, produced the highest bioethanol (26.8 g/L) within 60 h.	[255]
Azolla filiculoides	Biogas	Highest cumulative methane yield was 280.9 mL/g volatile solid in lipid free sample.	[256]
Azolla spp.	Bio-oil	38.5% (weight basis) bio-oil was obtained.	[257]
Lemna gibba	Biogas	Methane yield ranged between 60 and 468 mL/g of volatile solid in pretreated duckweed, and for non-pretreated duckweed it was between 9 and 76 mL/g of volatile solid.	[258]
Lemna spp.	Biogas	The maximum cumulative biogas production was 11,695 mL for mixure of cattle manure and duckweed in the ratio of 1:1.	[225]
Lemna minor	Biogas	The reactor with the highest specific biogas output, 0.16 L/g of organic carbon, was found to have a duckweed biomass/inoculum/food waste ratio of 1:1:1.	[259]
Spirodela polyrrhiza	Ethanol	Ethanol yield of 12.0 ± 0.6 g/100 g dry ground sample of duckweed with conversion efficiency of 90.8%	[260]
Lemna spp.	Bio-oil	The bio-oil yield was 40% of dry duckweed in weight basis.	[261]

3.1.2. Thermochemical Conversion

Thermochemical conversion is the process of decomposing biomass into solid, liquid and gaseous fuel products via thermal processing. It encompasses gasification, pyrolysis and hydrothermal liquefaction techniques. Pyrolysis is an anoxic thermochemical process through which the biomass is converted into bio-oil, carbon-rich solids and volatile matter [262]. Gasification is the process of incompletely burning biomass to produce CO, H_2 and CH_4. The produced mix is called producer gas and used as fuel for engines [263]. Hydrothermal liquefaction is another novel technique for thermochemical conversion in which the biomass is depolymerized to produce biocrude oil and chemicals at a moderate temperature and high pressure [264].

Miranda, et al. [218] explored the influence of temperature on the bio-oil production efficiency of *A. filiculoides* through hydrothermal liquefaction after participation in treating selenium-rich synthetic wastewater (SeSW). After 5 days of treatment with SeSW, the produced total bio-oil accounted for 15.8%, 21.5% and 16.0%, respectively, at 260, 280 and 300 °C for 15 min. Biswas, et al. [257] investigated the pyrolysis of *Azolla* sp., *Sargassum enerrimum* and water hyacinth using a fixed-bed reactor at different temperatures in the vicinity of nitrogen. *Azolla* sp., *S. tenerrimum* and water hyacinth produced 38.5, 43.4 and 24.6 weight percentages of liquid yield, respectively, at 400, 450 and 400 °C.

Muradov, et al. [265] analyzed the pyrolysis products of *L. punctata* and *A. filiculoides* after their use in swine wastewater treatment. The authors concluded that *Azolla* and algae produced similar spectra of bio-oils, which were different from the products obtained from duckweed samples. The wide range of petrochemicals and straight-chain C10 and C21 alkanes obtained can be used directly as diesel fuel supplements or as a glycerine-free biodiesel component. Golzary, et al. [266] and Singh, et al. [267] reported the efficient thermochemical conversion of *Azolla* and water hyacinth to biocrude oil, respectively, with yields of 39% and 29% and 23% and 24.6%, respectively, via hydrothermal liquefaction and pyrolysis.

3.2. Feed Production

With deforestation and the introduction of dwarf plant species, the area of grazing land has declined, along with a decrease in fodder availability.

Commercial feed supplements are being released at a high price to compensate for natural feeding, resulting in increased costs for animal products. In addition, commercial feeds have negative effects on product quality and animal health [268]. When searching for long-term animal feed, macrophytes have been found as a viable alternative to conventional feeds, with promising nutritional values (Table 8) and a high biomass production capacity. In general, it has been evidenced that the control of aquatic weeds consumes more money. Hence, utilizing the macrophytes in animal feed formulations after effective wastewater treatment would be an ideal choice instead of spending more money on both the production of plants, such as maize, sorghum and vegetables, and specialized animal feed and on the control of aquatic weeds [269]. According to de Queiroz, et al. [270], after lifecycle analysis (LCA), they declared that the production of animal feed would be more effective in mitigating freshwater eutrophication and climate change compared to the production of biofuel and biofertilizer production. Therefore, it can be said that the effective utilization of macrophytes or the combination of macrophytes and other nutritional sources in the formulation of the ration would be a more socially, economically and environmentally viable approach.

Table 8. Nutrition composition of some floating aquatic macrophytes on dry matter basis.

Macrophytes	Protein	Lipid	Ash	Total Carbohydrate	References
Azolla filiculoides	19.70	4.20	18.50	NA	[271]
Azolla pinnata	26.84 ± 0.70	5.55 ± 0.70	18.37 ± 0.10	NA	[272]
Azolla	27.1	6.37	14.29	45.86	[273]
Azolla japonica	23.7–31.2	6.0–6.7	9.0–9.5	NA	[274]
Azolla pinnata	21.4	NA	16.2	NA	[234]
Lemna minor	28.00	5.00	25.00	42.00	[275]
Lemna minor	NA	3.1	NA	51.2	[239]
Lemna sp.	16.0	9.0	26	35.0	[276]
Lemna gibba	21.5	4.5	20.1	NA	[277]
Lemna punctata	16.3	NA	3.5	24.5	[278]
Eichornia crassipes	17.93	16.62	8.85	49.05	[279]
Eichornia crassipes	10.5	1.5	12.4	NA	[280]
Eichornia crassipes	8.53 ± 0.43	1.42 ± 0.01	20.12 ± 0.12	NA	[281]
Eichornia crassipes	10.4	1.66	24.6	NA	[282]
Eichornia crassipes	13.88	4.89	24.16	NA	[283]

The protein content of Azolla on a dry weight basis can reach 25.4%, with an amino acid profile of 10.2%. However, the carbohydrate and oil contents are comparatively low [284]. Duckweed has a high protein content, which can reach 41% in nutrient-rich media [285,286]. According to its amino acid profile, it is rich in leucine, threonine, valine, phenylalanine and lysine [287]. Specifically, the concentration levels of lysine are close to those of animal protein [288].

The high cellulose and hemicellulose contents of water hyacinth make this plant an energy source for ruminants [289]. In addition, most of these aquatic macrophytes are rich in minerals and vitamins that are essential for the normal functioning of the body. Numerous studies have confirmed the suitability of feeding duckweed, Azolla and water hyacinth to various farm animals such as ruminants, pseudo-ruminants, non-ruminants and fish and shrimp [286,290–294].

3.2.1. Ruminants

Although farmers, particularly in Southeast Asia and probably elsewhere, have developed the use of *Azolla* as a source of nutrients for livestock, controlled experiments to develop commercial crops are lacking. There are, however, some reports on the use of *Azolla* as feed supplement for fish and livestock, focusing on fish and domestic animals in which normal feed protein sources have been replaced by *Azolla* meal on an iso-nitrogenous basis. However, studies on the use of *Azolla microphylla* as supplementation in the diet of cross-bred cattle are scarce [295].

Pillai, et al. [284] identified an increase in overall milk yield in cattle of up to 15% when they were fed 1.5–2 kg of fresh *Azolla* per day along with regular feed. Further, the researchers concluded that the increment in milk yield is not only due to the nutrient content of *Azolla* but also to other components, such as carotenoids, biopolymers and probiotics. An attempt was made to gauge the nutritional impact of *Azolla* meal in a total mixed ration (TMR) at various dietary levels on the nutrient use and metabolic condition of goats. To this end, goat kids were fed different inclusion levels of *Azolla* meal (0%, 20% and 40%) mixed with a concentrate mixture and green fodder berseem. The inclusion of 20% *Azolla* meal resulted in the highest digestibility, and the final weight gain of the goat kids was also significantly higher [296].

The use of duckweed as a ruminant feed source has not received much attention, mainly because of the challenge of gathering enough duckweed for a reliable feed trial. More ruminant studies are, however, expected as the popularity of duckweed grows. Duckweed meal has not been extensively studied as a fodder supplement for ruminants, although duckweed can potentially supply minerals, particularly P and N. A meal for ruminants that includes both fresh duckweed and crop waste may have a balanced nutrient level and can be used in livestock production systems for cattle, sheep and goats [297]. Babayemi, et al. [298] conducted a study in African dwarf goats to determine the potentiality of aquatic fern and duckweed as a protein source for ruminants. According to the initial preference test, goats were more likely to consume dried and fresh duckweed than water fern. Based on the outcomes, in the next step, a balance trial was conducted. Duckweed supplementation considerably increased nitrogen retention compared to the control diet, which consisted of guinea grass only. Another study was conducted to determine the potential use of duckweed in goat nutrition. In this experiment, five different levels of fermented duckweed were incorporated into the diet of goats, namely 0%, 15%, 30%, 45% and 60%. According to the results, a 45% inclusion level resulted in a high efficiency in goats, and it is assumed that such a level can guarantee the supply of sufficient energy and balance the concentration of ammonia and volatile fatty acids in the rumen, thereby optimizing rumen microbial activity [299].

Water hyacinth contains high levels of cellulose and hemicellulose, which could serve as energy sources for ruminants. Fresh water hyacinth has been used as a partial replacement for para grass in diets for cattle [300,301]. The use of wilted water hyacinth in a rice-straw-based diet had a positive effect on feed intake and growth in beef cattle [302]. Water hyacinth can be successfully ensiled with the addition of molasses, rice bran, cassava root and organic acids, and the silages are generally accepted by ruminants. In one study, feeding an ensiled mixture of water hyacinth, rice straw, urea and molasses to dairy cattle resulted in a higher milk yield [303]. Islam, et al. [302] conducted a study on bull cattle to investigate the effect of feeding wilted water hyacinth on growth and nutrient use. Three groups of cattle were fed three different rations (treatments), namely 100% rice straw, 75%

rice straw + 25% wilted water hyacinth and 50% rice straw + 50% wilted water hyacinth, along with 2 kg of fresh German grass, 300 g of mustard oil cake and 50 g of common salt per 100 kg of body weight. The daily dry matter intake did not vary significantly among the treatments and fluctuated between 3.15 and 3.41 kg. The authors concluded that the total and daily live weight gain were significantly higher in groups that were given wilted water hyacinth supplementation.

3.2.2. Fish

Water hyacinth, *Azolla* and duckweed have been recommended as dietary supplements for herbivorous and omnivorous freshwater fish [271,304,305]. However, when the fiber content is above the permissible limit, the corresponding macrophyte will not be recommended [306]. Datta [271] conducted a feeding trial to examine the efficiencies of different inclusion levels of dried *Azolla*, such as 15%, 25% and 35%, in the diet of *Labeo rohita*. The inclusion of 25% *Azolla* resulted in the highest specific growth rate of 0.75%/day and the most pronounced weight gain. The obtained condition factor of all fish involved in the experiment ranged between 1.224 and 1.233, whereas the recommended condition factor is between 0.964 and 1.896. This indicates the good condition of the experimental fish. Additionally, a reduction in fat content was observed with the incorporation of *Azolla*.

Talukdar, et al. [307] investigated the effect of duckweed as a feed on fish polyculture. One treatment was the control (T2), and in the other treatments, the fish were additionally supplied with duckweed daily at 50% of their body weight (T1). Fish from T1 showed a higher survival rate (90%) than those from T2. The net production from T1 was 6.25 t/ha/yr, and that of T2 was 2.84 t/ha/yr. This study emphasizes the use of duckweed as an economically viable feed in fish polyculture. Along these lines, Kabir, et al. [305] determined the consequences of duckweed supplementation in polyculture diets, using ponds fertilized with cow dung, urea and triple superphosphate to grow silver carp, Thai sharputi, tilapia, common carp and mrigal for 90 days with and without duckweed supplementation. Fish from the pond supplied with duckweed exhibited a higher net production compared to the control.

3.2.3. Poultry

Alalade, et al. [308] explored the effects of supplementing *Azolla* in the diets of growing pullets, using a complete randomized design for 10 weeks with 120 Nera brown pullets. *Azolla* meals were incorporated at levels of 0%, 5%, 10% and 15% (treatments) with a regular diet. Weight gain (WG), feed intake, feed conversion ratio, packed cell volume, red blood cell, hemoglobin and white blood cells were not significantly different among the treatments. Age at first lay and egg quality characteristics, except egg yolk weight, were similar for all treatments. Yolk weight was lower in hens fed Azolla meal. Based on these findings, *Azolla* meal can be added to the diet of growing pullets up to a level of 15%. Basak, et al. [309] reported that *Azolla* in the ration of broilers improves the live weight gain, production number and protein efficiency of broilers at an inclusion level of 5%.

Khandaker, et al. [310] suggested that incorporating 15% duckweed into the diet of laying ducks, instead of mustard oil cake (MOC), has economic benefits. To determine the optimal amount of duckweed to include, the authors used a group of 84 laying Jinding ducks over a period of 75 days. The diet initially consisted of 15% MOC, which was subsequently modified by duckweed in a progressive manner to 5%, 10% and 15%. The addition of duckweed did not result in any notable decline in live weight gain, egg weight or feed conversion efficiency. However, it did lead to an increase in egg production and overall profitability. Conversely, Men and Yamasaki [311] indicated that modifying a commercial diet by adding 5–25% fresh water hyacinth has a detrimental effect on the growth of ducks. However, from a financial perspective, such a modification would still be considered acceptable.

3.3. Fertigation

With the initiation of the green revolution, the negative impacts of certain agricultural practices have become obvious, with widespread diseases and ecosystem degradation. Intense agriculture has promoted the usage of agrochemicals and artificial fertilizers to obtain higher outputs in limited areas, thus causing soil degradation, water depletion and climate change, among other consequences. Apart from their negative impacts on ecosystems, chemical fertilizers are also costly. The energy requirement for producing 1 kg of nitrogen fertilizer ranges from 51 to 68 MJ [312]. The cost of energy, along with other fixed and variable costs, accounts for a large proportion of the money used for fertilizers and other agrochemicals, which is reflected in the price of agricultural products.

The implementation of a sustainable agriculture can reduce the negative impacts on intensive agricultural systems. Sustainable agriculture is a series of agronomic practices that are eco-friendly, economically viable and socially acceptable. Reducing chemical fertilizer usage and adopting organic farming practices are key strategies of sustainable agriculture. According to Tuomisto, et al. [313] organic farming is the best way to attain sustainability in agriculture because it has the capacity to maintain production, along with a healthier soil and biosphere.

Numerous studies emphasize the potential of macrophytes in the production of organic fertilizer. When considering macrophytes as biofertilizer, they are low cost and eco-friendly. According to de Queiroz, et al. [270], from their LCA analysis, producing biofertilizer will mitigate terrestrial acidification and ozone layer depletion more than producing animal feed. If a community wastewater treatment system persists with FAMs, the end of the treatment of the community itself can utilize the macrophytes for biofertilizer production and can try to be a self-sufficient community.

Azolla spp. is one of the vital species which can be processed as biofertilizer, green manure, compost and biochar. The symbiotic relationship with *Anabaena azollae* facilitates the plant's ability to fix atmospheric nitrogen and serve as a nitrogen source [314]. In addition to supplying nitrogen, it can supply other essential elements, vitamins, minerals, essential amino acids, growth promoters and organic compounds [284].

Yao, et al. [315] examined the efficiency of *Azolla* substitution as a biofertilizer in rice fields instead of synthetic nitrogen fertilizer in a field experiment over 3 years with five treatments, namely control without urea (CK), farmers' nitrogen practice (FN), farmers' nitrogen practice combined with Azolla biofertilizer (FNA), reducing the nitrogen level by 25% (RN) and substituting *Azolla* biofertilizer for 25% nitrogen (RNA). The nitrogen use efficiency was high in RNA and FNA, with 52% and 31%, respectively, and both treatments showed reduced nitrogen loss by 48% and 26%, respectively, along with lower ammonia losses. Treatments with Azolla showed increased nitrogen uptake, with levels 17% (RNA) and 33% (FNA) higher than those observed for FN. In addition, the RNA and FNA treatments showed 8% and 14% higher rice yields compared to the yield observed for FNA.

Duckweed is another floating macrophyte that can thrive in environments with high nitrogen and phosphorous levels. Healthy duckweed can be compared to commercial fertilizer in terms of nitrogen availability and used to increase plant productivity in a sustainable manner. Kreider, et al. [316] incorporated dried duckweed into the soil in microcosm, column and field trials and compared it to compost, diammonium phosphate (DAP) and amendment-free soil (control) in terms of biological nitrogen cycling, nutrient retention and crop yield. According to the results, duckweed N mineralization (25 ± 13%) was higher than that of compost (11 ± 12%) and lower than that of DAP (107 ± 21%) in microcosm tests. In the column study, 2% of the added nitrogen was leached out in the duckweed treatment, whereas 60% of N was leached out from the DAP treatment. Regarding the leaching of phosphate, the duckweed treatment showed a higher level of leaching (56%) than compost (27%) and a lower level than DAP (78%). Crop yield was measured in a field after application to sorghum, and the dry mass yield of forage sorghum was highest in the DAP plots (8.69 ± 0.90 Mg ha^{-1}), followed by the duckweed (8.36 ± 1.26 Mg ha^{-1}) and the amendment-free plots (7.93 ± 0.73 Mg ha^{-1}).

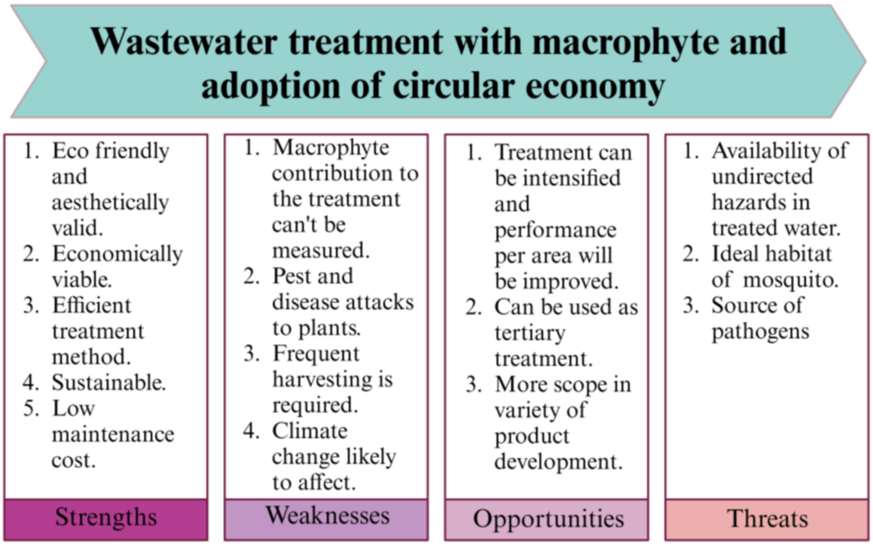
Water hyacinth is another potential macrophyte that is also capable of thriving in a wide range of water quality conditions and can absorb nutrients from water. Since it produces large amounts of biomass, it can become noxious if left in the ecosystem after water treatment. Composting and direct use as green manure would therefore be appropriate methods. Lata and Veenapani [317] prepared manure from water hyacinth by processing it for 3 months and 10 days and investigated the efficiency of incorporating water hyacinth manure (WHM) into the soil by determining the growth parameters of *Brassica juncea*. Different combinations of water hyacinth were prepared as follows: 100% WHM (1:0), 50% WHM (water hyacinth manure + garden soil, 1:1), FYM'W (water hyacinth manure + farmyard manure,1:3) and CNTR (control; no water hyacinth manure, only garden soil, 0:1). The different treatments differed significantly in terms of plant growth and yield parameters. Maximum yield was obtained in 100% WHM, along with the highest values of some growth parameters, such as the number of inflorescences per plant, number of seeds per plant, root weight and dry weight of pods. The 50% WHM treatment also showed the highest values in shoot, root and whole-plant length. Hence, it was concluded that higher levels of WHM inclusion promote the yield and growth attributes of plants.

3.4. Water Usage

Wastewater treated with macrophytes can be a good water source for agriculture and landscape irrigation, washing, cleaning, industrial purposes and groundwater replenishment [318]. Currently, there is a trend towards the reuse of treated wastewater. According to Galkina and Vasyutina [11], the usage of treated wastewater was nearly eight million cubic meters per day in 2017, with an annual increase of 15%. There are several advantages of the use of treated wastewater for purposes other than drinking, such as the maintenance of available freshwater resources without pollution, the reduction of fertilizer use and economic viability [319].

4. Challenges and Recommendations

Although the use of macrophytes in wastewater treatment and subsequent resource recovery are prominent and productive, there are still opportunities, limitations and threats, as shown in Figure 4. While the strengths and opportunities of this treatment process are obvious, the weaknesses and threats of this treatment method can be seen through a common frame as disadvantages.



Wastewater treatment with macrophyte and adoption of circular economy

Strengths	Weaknesses	Opportunities	Threats
1. Eco friendly and aesthetically valid. 2. Economically viable. 3. Efficient treatment method. 4. Sustainable. 5. Low maintenance cost.	1. Macrophyte contribution to the treatment can't be measured. 2. Pest and disease attacks to plants. 3. Frequent harvesting is required. 4. Climate change likely to affect.	1. Treatment can be intensified and performance per area will be improved. 2. Can be used as tertiary treatment. 3. More scope in variety of product development.	1. Availability of undirected hazards in treated water. 2. Ideal habitat of mosquito. 3. Source of pathogens

Figure 4. SWOT analysis of using floating aquatic macrophytes for wastewater treatment and consequent product development.

The common drawback of using macrophytes in wastewater treatment is the complexity of finding the influential depth of the macrophytes in wastewater treatment. In general, the treatment potential of the macrophytes is the sum of the activities of microorganisms, natural decomposition and plant activities. Taking nitrogen as an example, macrophytes are capable of taking up ammonia and nitrate from the wastewater; simultaneously, the algae present in the water use both forms of nitrogen and reduce the nitrogen content. However, the level of ammonia in wastewater is controlled by ammonification and decomposition, and the nitrate concentration in the wastewater is determined by nitrification and denitrification. Therefore, the influence of biotic and abiotic factors makes it more difficult to determine the contribution of macrophytes in pollutant removal [320]. In this case, each component influencing pollutant removal in different types of wastewater should be studied separately.

One of the major issues is the susceptibility of macrophytes to environmental changes; in addition, they are prone to insect and pest attacks. Temperature, relative humidity, sunlight and wind speed are the most influential factors determining the growth of plants. Under sub-optimal conditions, the results are not adequate. Any pest species should therefore be adequately managed to ensure a high efficiency. In most cases, the reason behind the failure of large-scale treatment plants, even if the system worked successfully on a laboratory scale, is the influence of biotic and abiotic factors [321]. To solve these issues, the location of the wastewater treatment plant should be feasible for optimizing the climate to a certain range (e.g., natural shade and accessibility of sprinklers). Furthermore, seasonal variations should be considered when selecting macrophyte species. To overcome the issue of pests and diseases, some plants, such as Chrysanthemum indicum, can be used as border crops, along with organic pesticides, fungicides and bactericides for control.

Various hazards have also been reported when using the products of treated wastewater. As these macrophytes can only treat wastewater up to a certain extent, irrigation using the treated water will result in the accumulation of contaminants in the soil and disturb the soil ecosystem, with potential transfer along the food chain. The use of macrophytes is also risky regarding the production of feed for animals. As an example, duckweed has the capacity to accumulate a variety of heavy metals, which will be transferred along the food chain, threatening human health [297,322]. Macrophytes should therefore be used with caution, and depending on the requirement, treated wastewater can be used.

Although macrophytes are high in nutrients, they may be low in some amino acids such as tryptophan and methionine, necessitating supplementation [323,324]. Another challenge in dealing with macrophyte for wastewater treatment is the fast growth rate [325]. Although they facilitate wastewater treatment, their biomass needs to be removed safely, which is time- and labour-intensive. The need for more space is another issue related to macrophyte growth, and treatment systems can only be used in designated regions and not continuously [286]. To maintain the macrophytes within a defined boundary, continued removal is essential. To this end, an automated system can be fixed to harvest the macrophytes, depending on the time or morphological characteristics.

5. Conclusions

Floating phytoremediation is a green trend to eliminate contaminants from wastewater. This method is more effective than conventional treatment methods as it is economically viable, effective in contaminant removal and environmentally friendly. Aquatic macrophytes can remove various pollutant types, including organic and inorganic compounds. Several macrophytes have been used to decontaminate wastewater in the secondary and tertiary stages of treatment. Floating aquatic macrophytes such as *Azolla*, duckweed and water hyacinth are the key players in removing contaminants and can be efficient via bioaccumulation and biosorption. The produced macrophyte biomass can, however, threaten environmental health if not handled properly. In some cases, it can be used for the production of bioenergy, animal feed and fertilizer, facilitating a circular economy.

Author Contributions: Conceptualization, S.S. and H.A.H.; methodology, S.S. and H.A.H.; resources, S.R.S.A.; data curation, S.S. and H.A.H.; writing—original draft preparation, S.S.; writing—review and editing, S.S. and H.A.H.; supervision, H.A.H. and S.R.S.A.; funding acquisition, H.A.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Universiti Kebangsaan Malaysia with Geran Universiti Penyelidikan (GUP-2022-028).

Data Availability Statement: Data sharing is not applicable to this article.

Acknowledgments: The authors would like to acknowledge the Universiti Kebangsaan Malaysia for funding this research project through the Geran Universiti Penyelidikan with grant no. GUP-2022-028.

Conflicts of Interest: The authors declare no conflict of interest.

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