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Review

Impact of Heavy Metal Sequestration During Phytoremediation of Textile Wastewater on Biogas Yield of Aquatic Plants: A Review

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Abstract

The textile industry consumes a significant quantity of water and produces effluent containing water-soluble dyes and heavy metals such as Lead (Pb), Cadmium (Cd), Chromium (Cr), Copper (Cu), and Zinc (Zn), among others. Heavy metal contamination of water bodies and their impact on aquatic life, as well as on human health, is of prime importance. This review examined the potential of phytoremediation, a low-cost and eco-friendly process for removing contaminants from textile effluent. This review also investigated the impact of heavy metal toxicity on aquatic plants used for biogas production post phytoremediation application. This review evaluated textile effluent characteristics, efficiency evaluation of phytoremediation of textile wastewater, metal uptake mechanisms of aquatic plants, and anaerobic digestion processes with emphasis on Water hyacinth (*Eichhornia crassipes*), Duckweed (*Lemna minor*), and Water lettuce (*Pistia stratiotes*). The findings indicated that these aquatic plants possess immense potential for removing heavy metals and other impurities by employing phytoextraction and rhizofiltration methods. Their rapid growth rate makes them preferred candidates for anaerobic digestion. However, accumulation of heavy metals in plant tissues inhibits microbial activities during anaerobic digestion, resulting in fluctuations in biogas and methane production. Findings also showed that these aquatic plants are efficient in the removal of heavy metals in water while yielding considerable biomass that can be used to produce bioenergy through anaerobic digestion. However, the sequestration of heavy metals in plant biomass may affect the rate of methane generation efficiency. The findings of this review suggest that phytoremediation has promising potential for the recycling of textile wastewater and, when coupled with biogas production, contributes towards a circular bioeconomy, an approach that integrates closed-loop resource utilization with renewable biological systems to minimize waste.

Keywords: anaerobic digestion; biogas yield; heavy metals; phytoremediation; textile wastewater; water hyacinth

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1. Introduction

Water contamination is a significant global challenge and is one of the leading causes of diseases and deaths worldwide. The textile sector is a key player of the global economy, estimated at around $1.16 trillion in 2025 and expected to grow to $1.74 trillion by 2035 [1]. Globally, this large sector offers more than 60 to 70 million jobs, especially in developing countries, where it serves as a main contributor to gross domestic product (GDP). The quantity of toxic metal pollution in the biosphere has risen markedly since the Industrial Revolution. Textile industries demand a significantly large quantity of water for their production purposes and often do not fully reveal the chemicals used in dyeing, which are the main causes of pollution. Pollutant concentrations in textile wastewater fluctuate depending on how wastewater is managed and how much of it is diluted after manufacturing. The most used chemicals in the textile industry are textile dyes. Around 10,000 unique dyes can be found in the market, with an annual global output exceeding 7×10^5 metric tons. Textile dyes pose a significant threat to human health as they contain heavy metals, which fall under the most dangerous toxic pollutant category according to the Agency for Toxic Substances and Disease Registry (ATSDR), maintained by the US Department of Health and Human Services. Annually, between 2000 and 3200 tons of metallic chromium (Cr) escape into India's environment. Heavy metals, such as Lead, Arsenic, Chromium, Nickel, Copper, Cadmium, Mercury, and Zinc, are naturally occurring but can accumulate in environmental matrices due to industrial usage. Concern about heavy metals and their pollution is global due to their impact on water bodies and human health [1,2]. Textile industries account for almost 20% of worldwide industrial water pollution and utilize about 93 billion cubic meters of water each year. In areas such as West Bengal, India, and the Mekong Delta, the release of untreated wastewater from numerous dyeing facilities has resulted in the noticeable presence of heavy metals in nearby food chains, affecting surface and groundwater [3].

Human population growth and worldwide industrial development have resulted in the enhancement of heavy metal contamination of the world's water bodies. Before exploring biological solutions, it is important to recognize that the traditional chemical and physical methods used for heavy metal removal include processes like chemical precipitation, ion exchange, and membrane filtration. Though efficient at the removal of these harmful elements from the environment, these techniques frequently demand costly chemical reagents and produce toxic secondary sludge that needs additional hazardous waste management. Conversely, phytoremediation provides a non-invasive, visually appealing, and economical option, frequently costing just one-third of conventional physical methods [4].

Phytoremediation can be an ideal and cost-effective method for removing heavy metals from polluted water directly. Many plants have been used for heavy metal removal from wastewater, such as duckweed, water hyacinth, hydrilla, and water cabbage, among others [2,5].

1.1. Importance of Textile Wastewater Management

The management of textile wastewater is a worldwide environmental concern because of the significant volume and harmfulness of the industrial effluents. Worldwide, the textile sector accounts for roughly 20% of industrial water pollution and uses around 93 billion cubic meters of water each year [6]. In key production centers such as India and Southeast Asia, more than 80% of textile wastewater is released untreated into nearby water bodies, damaging thousands of kilometers of essential waterways like the River Ganges [5]. This absence of management imposes a significant financial strain; for instance, the worldwide

economy suffers an approximate loss of $500 billion each year because of inadequate recycling and management of textile waste and water [7].

A case study on the Noyyal River, a tributary of the Kaveri River in Tamil Nadu, India, starkly illustrates the impacts of untreated textile wastewater. Tiruppur, India, is referred to as the "Knitting City" and contains more than 800 bleaching and dyeing facilities that have traditionally released around 87 to 90 million liters of untreated wastewater each day directly into the river basin [8,9].

The impact of heavy metal contamination on human life cannot be overemphasized. Human exposure to heavy metals significantly impacts the skin, respiratory, and cardiovascular organs [10]. In textile industries, heavy metals often enter the wastewater stream because of the dyeing process, where they are widely used as mordants and fixatives to enhance dye–fiber interactions. This is necessary because many dyes, especially natural dyes and some synthetic classes, exhibit low inherent affinity toward textile fibers, particularly cellulosic materials such as cotton. At the molecular level, metal ions (e.g., Cr^{3+}, Cu^{2+}, Fe^{2+}/Fe^{3+}, Al^{3+}) function by forming coordination complexes between the dye molecules and the fiber substrate. These metals act as a bridging agent, simultaneously interacting with functional groups in dyes (-OH, -COOH, $-NH_2$), and reactive sites in fibers (e.g., amino and carboxyl groups in wool, hydroxyl groups in cellulose).

This results in the formation of a stable dye–metal–fiber complex, which significantly improves dye fixation (binding strength), color fastness (resistance to washing, light, and rubbing), color intensity, and shade variation. Furthermore, metallic mordants can alter the electrical structure of dye molecules, resulting in color variations due to changes in light absorption capabilities. This explains why the same dye can yield different shades depending on which metal is used [11].

The presence of organic dyes can have a significant impact on metal bioavailability from textile effluents. This is because dye molecules possess groups capable of forming complexes with metal ions, thus reducing the free concentration of the metals. The complex metals can also remain stable in the water phase, affecting their bioavailability to plants. This will also have an impact on both the phytoremediation process and anaerobic digestion [11].

Apart from heavy metals, the textile effluents also contain large quantities of synthetic dyes released during the dyeing process. The presence of these dyes in wastewater has a detrimental effect on the photosynthetic processes of plants. Additionally, they degrade aquatic habitats by limiting light penetration and increasing oxygen use. The presence of heavy metals and chlorine in some dyes can be hazardous to many aquatic organisms. As complex organic molecules, dyes are highly visible and recalcitrant; they degrade aquatic habitats by limiting light penetration and increasing oxygen use, leading to a spike in biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [12]. Furthermore, suspended particles can clog fish gills, causing death. The ability of algae to produce food and oxygen is also diminished. Moreover, dyes have been found to interfere with specific municipal wastewater treatment processes, including ultraviolet disinfection [12].

Despite the clear advantages of using biological systems for remediation, a significant research challenge remains. While the technical capacity of aquatic plants to sequester metals is well-established, the most critical knowledge gap lies in the economic viability of anaerobic digestion when utilizing this toxic biomass as a feedstock. Transitioning from successful phytoremediation to a sustainable energy recovery model requires overcoming the financial and operational hurdles caused by metal-induced microbial inhibition. Addressing this gap is essential for determining if such integrated systems can move beyond laboratory success to become economically feasible industrial solutions.

1.2. Objectives and Scope of This Study

This review explored the environmental and energy recovery dimensions of treating textile wastewater through phytoremediation, focusing on the potential of aquatic plants to clean contaminated wastewater and to subsequently serve as substrates for biogas generation. This review investigated biological and plant-based approaches, such as phytoremediation, to eliminate hazardous dyes and chemicals from textile effluents. This study highlighted water-saving technologies and process upgrades that can reduce both consumption and wastewater generation. This review also emphasized eco-conscious waste handling practices that support long-term resource conservation and promote circular bioeconomy principles through energy recovery from biomass. The aim of this review was to identify knowledge gaps in metal accumulation and biogas output to examine how the sequestration of heavy metals by phyto-remediating plants influences anaerobic digestion efficiency and biogas (methane) yield. Finally, this review assessed implications for integrated wastewater treatment and biogas recovery, like how coupling phytoremediation with biogas production can offer a dual-benefit approach to pollution control and sustainable energy generation.

2. Textile Wastewater: Composition and Contamination

Textile wastewater is a harmful composition that includes dyes, surfactants, and heavy metals. When aquatic plants are used for phytoremediation and further processing of textile wastewater, they tend to sequester heavy metals, altering the characteristics of biomass and influencing biogas production. Figure 1 shows the trend and the process of the key stages of the textile manufacturing process, which can be an influential part.

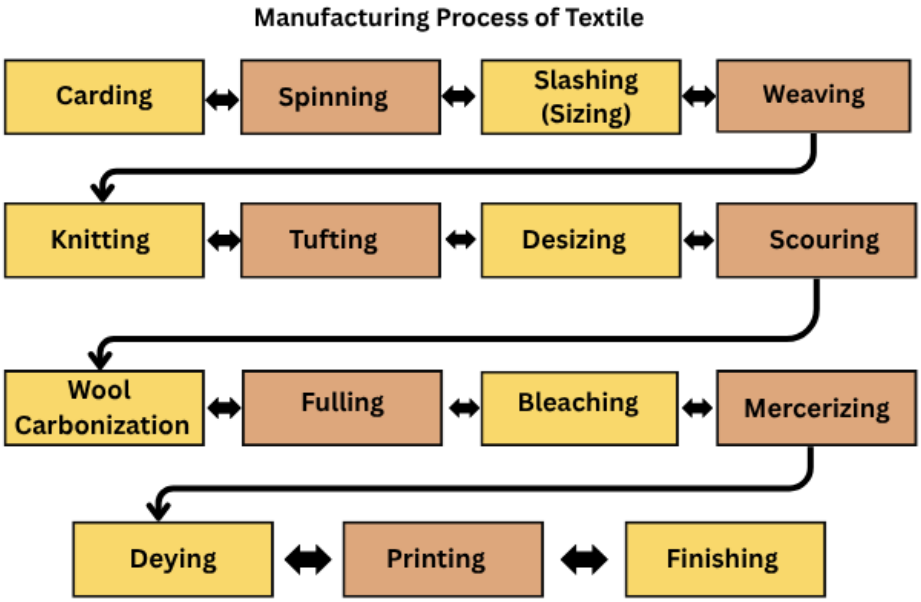


Figure 1. Key stages in the textile manufacturing process, from raw fiber preparation to finishing.

Table 1 contains the typical effluent characteristics from major textile processes such as desizing, bleaching, and dyeing, and provides a benchmark for assessing wastewater composition and treatment requirements [13]. Table 2 documents all heavy metals commonly used in the textile industry along with their respective impact on human and environmental health.

Table 1. Effluent characteristics from major textile processes [13,14].

Process	Nature of Effluent	Typical COD and BOD Levels	Treatment Strategies
Sizing	Starch, waxes, binders, polyvinyl alcohol (PVA)	COD: 1500–3000 mg/L; BOD: 600–1200 mg/L	Enzymatic hydrolysis for starch removal - Screening and sedimentation for suspended solids - Biodegradation for organic binders
Desizing	High BOD, COD, turbidity, color	COD: 5000–12,000 mg/L; BOD: 2000–6000 mg/L	Biological treatment (activated sludge, trickling filters) - Coagulation–flocculation - Aerated lagoons
Scouring	Suspended solids, high pH, COD, oil, and grease	COD: 3000–8000 mg/L; BOD: 1000–3500 mg/L	Neutralization (acid dosing) - Oil–water separators - Sedimentation and filtration
Bleaching	Alkalinity, residual chlorine, medium COD, high TDS	COD: 1000–3000 mg/L; BOD: 100–500 mg/L	Dechlorination (using sodium bisulfite) - Reverse osmosis or nanofiltration - pH adjustment
Mercerizing	Alkali content, high pH, low COD and conductivity	COD: 300–800 mg/L; BOD: 50–200 mg/L	Caustic recovery systems - Ion exchange or membrane filtration - Equalization tanks
Dyeing	Strongly colored, medium COD, low TDS, heavy metals	COD: 1500–6000 mg/L; BOD: 300–1500 mg/L	Adsorption (activated carbon, biosorbents) - Advanced oxidation processes (AOPs) - Membrane filtration
Printing	Pigments, metals, waxes, binders, softeners, urea, thickeners, medium COD	COD: 2000–5000 mg/L; BOD: 500–1500 mg/L	Electrochemical treatment - Photo-catalytic degradation - Foam fractionation and coagulation

Table 2. Health and environmental risks associated with various heavy metals commonly used in the textile industry.

Metal	Use in the Textile Industry	Health and Environmental Impact	References
Cadmium (Cd)	Used in dyes and coatings	Highly toxic, accumulates in organs, carcinogenic, bioaccumulates in the food chain	[15–18]
Lead (Pb)	Present in compounds like lead nitrate, molybdate, and acetate, used during dyeing	Affects nervous, circulatory, and immune systems; impairs development in children; inhibits plant growth	[17,19]
Zinc (Zn)	Used as ZnO in pigments and antimicrobial finishes	Essential in trace amounts; excess causes immune disruption, fertility reduction, which accumulates in crops	[20]
Nickel (Ni)	Used in dyeing processes with cobalt and chromium	Causes allergies, fibrosis, organ damage, cancer, and genetic changes	[16]
Copper (Cu)	Used in bright-colored pigments	Excess causes nausea, liver/kidney damage, and water pollution; linked to Wilson's Disease	[21,22]
Chromium (Cr)	Catalyst, a mordant for dyeing wool, is used in leather processing	Skin and respiratory carcinogens contribute to major water pollution	[22]
Arsenic (As)	Historically used in green dyes; now in residual wastewater	Bioaccumulates in organs, causing cancer, crop toxicity, and needs stricter waste management	[23,24]

Recent studies consistently report textile effluents to be predominantly alkaline, with pH often ranging from 7 to 13 and COD frequently exceeding 3000 mg/L, particularly in bleaching and printing operations. Elevated total dissolved solids further reflect the extensive use of salts and processing chemicals. Among heavy metals, chromium, copper, zinc, and nickel are most commonly detected, largely due to their association with dyes, catalysts, and fixing agents used during textile processing. Studies from South Asia, especially Bangladesh and India, indicate concerning levels of toxic metals such as Pb and Cd, often exceeding recommended limits and posing significant environmental and health risks. Overall, the data highlight substantial variability in effluent composition depending

on process type, while reinforcing the persistent challenge of high organic load and metal contamination in textile wastewater. (Table 3).

Table 3. Comparative analysis of pH, organic load (COD), and toxic heavy metals in textile wastewater from various global studies.

Country	Textile Process Type	pH	COD (mg/L)	TDS (mg/L)	Pb (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Zn (mg/L)	Ni (mg/L)	As (mg/L)	Key Notes	References
Bangladesh	Mixed discharge (dyeing + tanning)	7.6–9.4	NR	NR	0.08–4.77	0.01–0.16	0.04–12.03	0.01–0.13	0.08–1.02	0.01–0.05	NR	Elevated Pb, Cd, Cr pose health risks	[25]
India (Gujarat)	Bleaching, mercerizing, Printing, Washing	12.3–13.1	3926–4449	18,720–21,989	NR	NR	NR	NR	NR	NR	NR	Alkaline effluent with high dissolved solids	[26]
Turkey	Dyeing/ finishing	3–5	NR	NR	50–500	NR	NR	NR	NR	NR	NR	Pb concentration increased on dyes addition.	[27]
India (South 24 Parganas, West Bengal)	Small-scale textile unit effluents	NR	NR	NR	0.07–1.84	NR	NR	NR	0.07–0.94	0.05–0.09	NR	Severe contamination in real effluent context	[3]

NR = Not Reported; COD = Chemical Oxygen Demand; TDS = Total Dissolved Solids.

Figure 2 illustrates the environmental and health risks arising from the discharge of textile industry effluents into the environment, showing both direct impacts like esthetic issues and water pollution, and indirect impacts such as eutrophication and adverse effects on human health.

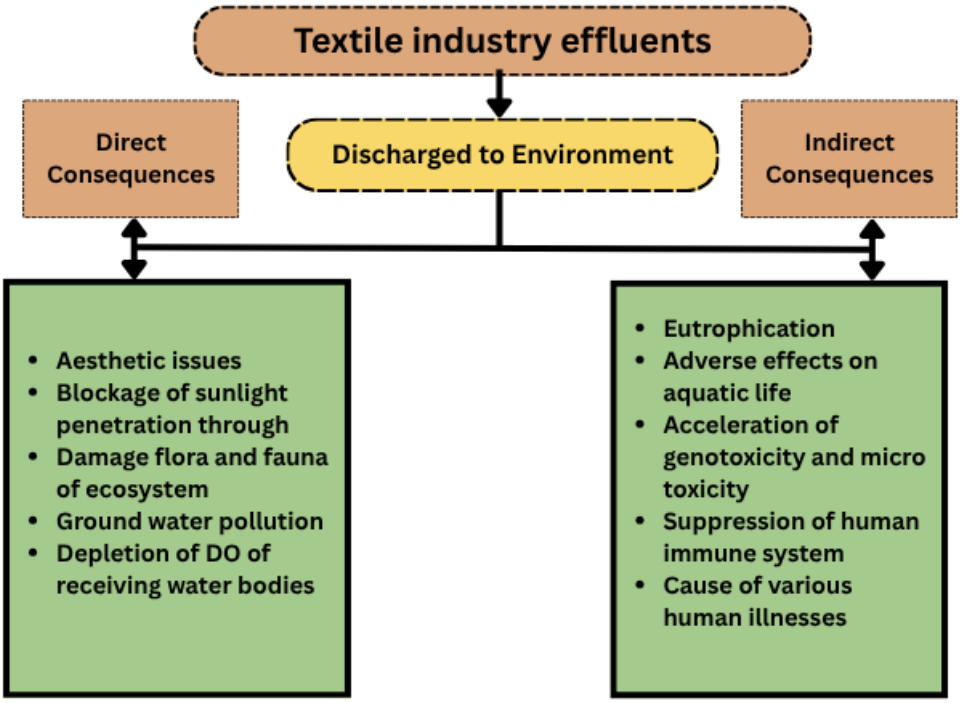


Figure 2. Direct and indirect consequences of discharging textile industry effluents into the environment.

3. Phytoremediation of Textile Wastewater

3.1. Concept and Mechanisms of Phytoremediation

Phytoremediation is an eco-friendly technique that relies on the natural abilities of plants to clean up pollution from soil and water. This method includes five main strategies, each working in a unique way to remove or neutralize contaminants. Phytoextraction involves plants pulling heavy metals or other inorganic toxins from the soil through their roots. These pollutants are then stored in the plant's shoots or leaves, making them easier

to remove later. Phytostabilization helps trap pollutants in the soil by binding them into substances like lignin or humus. This prevents them from spreading through the air or water. Phytovolatilization allows certain plants to absorb pollutants and convert them into less toxic forms, which are then released as gases into the atmosphere. Phytodegradation (also called Phytotransformation) uses enzymes produced by plants to break down harmful chemicals in both soil and water. Rhizofiltration focuses on using plant roots to filter out contaminants, especially heavy metals, from polluted water, absorbing and concentrating them within the root system. Together, these phytoremediation techniques offer a sustainable and cost-effective way to restore polluted environments using the power of plants [4,28,29].

3.2. Types of Phytoremediation Techniques

One promising, affordable, and environment-friendly technique for treating wastewater from the textile industry is phytoremediation. The efficiency of various plant species in eliminating textile dyes and wastewater varies. The efficacy of phytoremediation is influenced by the molecular weight and chemical makeup of contaminants. Textile wastewater treatment can be made more effective by combining chemical treatments and phytoremediation. An efficient method for treating textile wastewater at the source is in situ phytoremediation. Textile dye phytoremediation research has mostly stayed in the laboratory.

3.3. Selection Criteria for Aquatic Plants

Plants must be able to withstand and flourish in the presence of various contaminants found in textile effluent, such as dyes, heavy metals, and other chemicals. Different plants have different capacities for withstanding textile dyes. During the selection process, the wastewater's predominant pigments should be considered [30]. Rapid development guarantees prompt pollution absorption and effective wastewater treatment. More biomass increases the surface area available for the absorption and buildup of pollutants [31]. A healthy root system increases the plant's ability to absorb pollutants from the water and sediment [32]. The selected plant species must be able to adapt to the aquatic conditions of the treatment set up for a phytoremediation system to work efficiently [33]. Additionally, the treatment system's long-term viability and operational cost reduction depend on its ease of cultivation and maintenance [34]. Choosing plants that are native and plentiful in the area guarantees improved climate suitability and lowers transportation costs [35].

Lastly, the plant must not discharge any toxic materials into the environment while in use or after being disposed of. In certain situations, the plant's esthetic appeal should be taken into consideration, particularly if the treatment system is open to the public [36].

Among the aquatic macrophytes native to or naturalized in Indian freshwater ecosystems, *Lemna minor*, *Eichhornia crassipes*, and *Pistia stratiotes* best satisfy the above criteria, combining ecological dominance with demonstrated tolerance of nutrient-enriched and heavily polluted water bodies. These free-floating macrophytes exhibit rapid growth rates, high biomass productivity, and ease of harvesting, making them more suitable for large-scale phytoremediation and bioenergy applications than many submerged or emergent aquatic species. Compared to other local aquatic plants, these species are also better adapted to high pollutant loads and have been extensively studied in the Indian context, ensuring data availability and reliability.

Additionally, the management of *Eichhornia crassipes* and *Pistia stratiotes* often requires removal of plant biomass from water bodies. The removed biomass are suitable candidates for biogas production via anaerobic digestion, therefore, provide a sustainable valorization pathway, aligning wastewater treatment with renewable energy generation within a circular bioeconomy framework

4. Aquatic Plants in Phytoremediation

Phytoremediation uses diverse plant species to extract, degrade, and detoxify organic contaminants [37–39]. According to several studies, aquatic plants can effectively remove heavy metals from contaminated water compared to terrestrial plants due to their rapid growth rates, higher pollutant uptake capacity, and significant biomass production [40–45]. Furthermore, these species require only simple mineral nutrients and exhibit high photosynthetic efficiency, allowing them to thrive under a wide range of sunlight intensities, from full tropical exposure to partially shaded conditions [46]. This adaptability, combined with the direct and continuous contact between their root systems and the contaminated water, results in significantly improved purification effects compared to soil-based plants.

4.1. Common Aquatic Plants Used

The selection of Duckweed (*Lemna minor*), Water Hyacinth (*Eichhornia crassipes*) and Water Lettuce (*Pistia stratiotes*) for this review is based on their status as some of the most effective natural filters found in tropical and subtropical aquatic environments (Figure 3). Unlike other aquatic flora, these three species exhibit exceptionally high growth rates and a unique physiological capacity to bioconcentrate heavy metals such as Lead, Arsenic, and Chromium within their extensive root systems [13]. Table 4 lists these three commonly used aquatic plants for phytoremediation, providing a comparative study of their physiological traits and specific contaminant removal capabilities.



(a) (b) (c)

Figure 3. Three aquatic plants selected for this review: (**a**) Duckweed (*Lemna minor*), (**b**) Water Hyacinth (*Eichhornia crassipes*), and (**c**) Water Lettuce (*Pistia stratiotes*).

The selection of these specific aquatic plants is driven by their dual role in environmental cleaning and renewable resource production. While these plants are highly effective at removing pollutants from textile wastewater, the process creates a large volume of plant biomass that contains the absorbed contaminants, which must be handled responsibly. Instead of treating this leftover material as waste, these species serve as excellent raw materials for anaerobic digestion (AD). This is primarily due to their physical structure, which is rich in fermentable components like hemicellulose and cellulose but low in complex structural lignin, making them very easy for natural bacteria to break down.

By combining water treatment with anaerobic digestion, the system transforms a pollution problem into a circular economic benefit. During this process, organic parts of the plant are converted into renewable energy (biogas), which helps offset the energy costs and carbon footprint of the textile manufacturing process. While the heavy metals are safely concentrated into a much smaller and manageable volume of digestate (leftover solids). This integrated approach provides the textile industry with a sustainable way to treat toxic water while simultaneously generating renewable energy [13,14,47].

Table 4. A comparative summary of the phytoremediation potential of three aquatic plants: Duckweed, Water Hyacinth, and Water Lettuce.

Feature/Parameter	Duckweed (*Lemna minor*)	Water Hyacinth (*Eichhornia crassipes*)	Water Lettuce (*Pistia stratiotes*)	References
Growth Form	Free-floating; tiny roots on or below the water surface.	Free-floating with aerial rosettes and long submerged roots.	Free-floating with rosette leaves and hanging roots.	[48,49]
Growth Rate	Rapid, tolerant to various conditions.	Extremely fast-growing; biomass doubles in days.	Fast-growing but slower than hyacinth.	[50]
Metal Tolerance	High tolerance; some species grow better at low metal concentrations.	High tolerance, but excessive metal concentrations may reduce growth.	Moderate to high; effectiveness varies by metal and conditions.	[51,52]
Heavy Metals Removed	Pb, Ni, Cr, Cu, Zn, Cd, U, B, As.	Fe, Cu, Zn, Cr, Mn, Cd, Hg, Pb, As.	Cd, Cu, Fe, Pb, Zn, Mn, Cr, Hg, Al.	[53–57]
Notable Removal Efficiency	99.3% Ni in 28 days (*L. minor*); 95% Pb and 84% Cr in 12 days (*L. gibba*); 62.8% Pb in 3 days.	96% Pb in 12 days (2 ppm); BCF: Fe > Cd > Cu (up to 3622.86).	>85% removal of Pb, Cr, Mn, Zn (in 24 h); Higher Pb and Fe uptake than *E. crassipes*.	[57–62]
Bioconcentration Factor (BCF)	Pb > Mn > Cu > Zn.	Fe (3622.86) > Cd (439.74) > Cu (233.33).	Zn > Cd (2.3) > Ni (2.2); BCF > 1 for many metals.	[54,61,63–67]
Organic Pollutant Removal	Dimethomorph, Flazasulfuron, Copper sulphate.	Endocrine disruptors, neonicotinoids, insecticides (e.g., mevinphos), and herbicides (e.g., ethion).	Chlorpyrifos (82%), Cu^{2+}, Hg^{2+}, Fe^{3+}.	[55,68–72]
Influence of Nutrients	Nutrient enrichment improves metal tolerance and growth but may reduce metal accumulation at high levels.	Excessive metals can reduce growth and phytoremediation efficiency.	Efficiency influenced by pH, metal concentration, and exposure duration.	[51,52,73,74]
Cold Tolerance	High (better than water hyacinth); suitable for colder climates.	Low; less suited for colder environments.	Moderate; more tolerant than hyacinth but less than duckweed.	[75]
Other Features	High starch and protein content in biomass; Ideal for biorefinery applications.	Can also treat organic pollutants; Invasive species; Can choke wetlands if not managed.	Effective against both metals and pesticides; May be more effective in combination with other aquatic plants.	[74,76–78]
Best Use Case	Industrial effluents, textile wastewater, cold climates, and integrated phytoremediation-biorefinery.	Polluted wetlands, large-scale contaminated water bodies, and heavy organic pollutant load.	Shallow ponds, pesticide-affected water, combined with other aquatic plants, for broader remediation spectrum.	[53,61,74,78–81]

4.2. Mechanisms of Metal Uptake and Accumulation in Aquatic Plants

Plants need certain heavy metals like copper, molybdenum, zinc, iron, manganese, and nickel for healthy growth. However, they are also surprisingly good at dealing with non-essential and potentially toxic metals such as cadmium, chromium, lead, silver, and mercury, when these are present in high concentrations [82,83]. In aquatic plants, heavy metal removal mainly occurs through a process called phytofiltration, which includes rhizofiltration and shoot filtration [84,85].

In water, metals exist in different chemical forms. Plant roots absorb these metals and transport them into cells, where they are either neutralized or stored. To manage toxic metals like lead, cadmium, and mercury, plants bind them with special proteins or peptides [86]. Organic compounds like citrate and malate also help, especially in acidic conditions that make metals more bioavailable to plants [87]. For example, nickel is often stored in vacuoles bound to citrate, and zinc forms stable bonds with citrate and oxalate [88,89].

Plants also face oxidative stress due to metal exposure, which they counter using antioxidant enzymes and compounds [90,91]. Detoxification involves either locking metals in vacuoles or embedding them in cell walls. Phytochelatins (PCs), a group of metal-binding peptides inside plant bodies, play a vital role, especially in removing cadmium by trans-

porting it into vacuoles [92,93]. Additionally, a member of the cation diffusion facilitator transporter gene family, Metal Tolerance Proteins (MTPs), helps store metals like zinc and nickel inside plant cells, improving their ability to survive in polluted environments. MTPs are proteins found in membranes that promote the sequestration and detoxification of metal ions in the cells of plants. MTPs move metal ions such as zinc, manganese, iron, and cadmium to vacuoles, hence lowering cytotoxicity and keeping the cell in balance. As MTPs control the distribution of metal ions in plant cells, their presence not only ensures that essential metabolic processes remain undisturbed but also affects the process of phytoremediation in general. Within the scope of anaerobic digestion, when the metal ions are bound in the plant tissues via MTP-mediated sequestration, there is no inhibition of microbes [92].

While many studies showed that metals tend to accumulate mostly in plant roots [94,95], they are also found in shoots, especially depending on the type of metal and plant species [96,97]. Some metals move directly into the leaves through water contact, while others are absorbed by roots and transported upward. Aquatic plants can store metals like iron, manganese, zinc, copper, chromium, nickel, lead, and cadmium in their leaf tissues as well [98,99].

Several aquatic plants are known for their remarkable ability to clean up polluted water. *Lemna minor*, also known as Duckweed, is excellent at absorbing metals, especially iron, copper, and zinc in its leaves [98]. In systems where multiple metals are present, it has shown high uptake of cadmium and copper without much stress [100]. *Eichhornia crassipes*, also known as Water Hyacinth, is a fast-growing plant that mostly accumulates metals in its roots, reducing the amount that reaches its leaves [52]. This strategy helps it survive in highly polluted environments. It also efficiently moves nitrogen to its shoots, aiding in rapid growth [29,101]. Another commonly used plant species is *Pistia stratiotes*, also known as Water Lettuce, which can store high levels of copper in its leaves and tolerates metal exposure without showing signs of damage [64,100]. It adapts well to different conditions and remains healthy even under heavy metal stress. The success of these aquatic plants in removing heavy metals depends on several factors, including the type of metal, its concentration, the plant species, and environmental conditions like pH and exposure duration. Despite these variables, duckweed, water hyacinth, and water lettuce remain promising, sustainable tools for cleaning up contaminated water bodies.

An important but often overlooked dimension of metal accumulation in these macrophytes is the partitioning of sequestered metals between roots and shoots, which has direct implications for the fate of metals when plant biomass enters the biodigester. A recent review of floating macrophytes, which includes *Lemna minor*, *Pistia stratiotes*, and *Eichhornia crassipes*, reports that approximately 75–90% of absorbed metals are retained in roots, with only 10–25% translocated to shoots under most conditions and for most metals [102]. Root/shoot ratio analysis further indicates that approximately 80% of several metals (Cr, Cu, Fe, Ni) are retained in roots when the root/shoot ratio is ≥ 6, while Fe shows an even stronger root preference at root/shoot ratios exceeding 17 [102]. As a working design assumption for typical phytoremediation conditions, approximately 80–90% of total metal mass resides in roots and 10–20% in shoots, unless a species or metal combination exhibits hyperaccumulator behavior with high translocation capacity. Table 5 summarizes the approximate root versus shoot metal partitioning for the three macrophytes examined in this review.

Table 5. Approximate roots versus shoots metal partitioning for three floating macrophytes.

Species	Typical Metal Share in Roots	Typical Metal Share in Shoots	References
Lemna minor	~75–90% of metal mass	~10–25%	[100,102]

Table 5. *Cont.*

Species	Typical Metal Share in Roots	Typical Metal Share in Shoots	References
Eichhornia crassipes	~70–90%	~10–30%	[102–105]
Pistia stratiotes	~60–80% (often higher)	~20–40%; in some cases, ~50%	[102,103,106]

4.3. Efficiency of Different Aquatic Plants in Metal Sequestration

Among the most studied aquatic plants for phytoremediation are *Lemna minor*, *Eichhornia crassipes*, and *Pistia stratiotes*, all known for effectively removing heavy metals from water [107]. Their performance varies with metal type, concentration, and exposure time. Generally, *E. crassipes* is the most effective, followed by *P. stratiotes*, and then *Lemna minor* [57,108].

E. crassipes shows high heavy metal removal efficiency, which is up to 97% Cu, 96% Pb, and 89% Fe [60,109,110]. In textile effluent, the bioconcentration factor (BCF) for *E. crassipes* follows Fe > Cd > Cu, and *P. stratiotes* is for Pb, Cd, and Cu removal [57,61].

P. stratiotes removes 24–80% of metals from leachate and accumulates more Pb and Fe than *E. crassipes* in some cases [57,111]. It effectively removes Pb (70.7%) and Cu (66.5%) and can act rapidly, with significant removal in 24 h [62,112]. Its BCF trend is Zn > Cd > Ni [64].

Studies showed that *Lemna minor* removed 99.3% Ni in 28 days and 62.8% Pb in 3 days [58,113]. *L.* spp. removed 95% Pb and 84% Cr in 12 days [59]. In multi-metal systems, *L.* spp. showed high Cd^{2+} and Cu^{2+} accumulation [100], with a typical BCF order of Pb > Mn > Cu > Zn [63]. Ultimately, plant selection depends on the target metals and environmental conditions such as pH, metal concentration, and exposure duration.

Among the abiotic factors governing metal sequestration efficiency, the pH of textile effluent warrants particular attention. Textile effluents are typically alkaline (pH 8–11), yet *L. minor*, *E. crassipes*, and *P. stratiotes* perform optimally under near-neutral conditions (pH ≈ 6–7.5), where metal solubility and root bioavailability are greatest. This mismatch between effluent pH and plant physiological optima has direct consequences for remediation performance. Under alkaline conditions, metals such as Pb, Cu, and Cr tend to form insoluble hydroxide precipitates, reducing their bioavailable fraction despite potentially high total concentrations in the effluent. Concurrently, elevated pH suppresses proton-driven ion transport mechanisms at the root surface, restricting active metal uptake even when soluble metal fractions remain present. Studies have demonstrated that all three macrophytes exhibit measurably reduced uptake of metals such as Cd and Cu under alkaline conditions relative to near-neutral pH, despite their otherwise high accumulation capacity. In contrast, near-neutral pH promotes favorable metal–root interactions by maintaining metal speciation in soluble, plant-accessible forms, while strongly acidic conditions risk phytotoxicity and structural root damage. These pH-driven shifts in both metal speciation and root physiology are therefore critical determinants of phytoremediation efficiency in textile wastewater systems and underscore the practical importance of pH pre-adjustment as a preparatory step before introducing macrophytes into textile effluent treatment [102,114].

5. Biogas Production from Aquatic Plants

5.1. Overview of Biogas Production

Biogas is a clean and renewable fuel generated through the anaerobic digestion (AD) of organic waste [115]. As a sustainable alternative, it offers a way to replace conventional fossil fuels [116]. Aquatic macrophytes are important components of aquatic habitats. Among the best-suited materials for biogas production are aquatic macrophyte plants like *Eichhornia crassipes*, *Pistia stratiotes*, and *Lemna minor*, as they are fast growing, have high cellulose and hemicellulose content, and low lignin levels [117–119]. These plants are often

more productive than land-based feedstocks and have a favorable carbon-to-nitrogen ratio, making them ideal for energy recovery [120,121].

Aquatic macrophytes are typically viewed as appropriate for anaerobic digestion because of their relatively low to moderate lignin levels compared to terrestrial lignocellulosic biomass, which improves biodegradability [122]. However, differences can be found between species; for example, duckweed has moderate lignin content, which is lower than usual terrestrial biomass but might be greater than that of other aquatic plants [123].

Moreover, the biomass collected from phytoremediation, where these plants are used to clean industrial wastewater, can also be converted into biogas, improving the cost-effectiveness and sustainability of the entire process (Figure 4a,b) [85]. This strategy also helps control invasive aquatic weeds, which otherwise pose ecological problems [120].

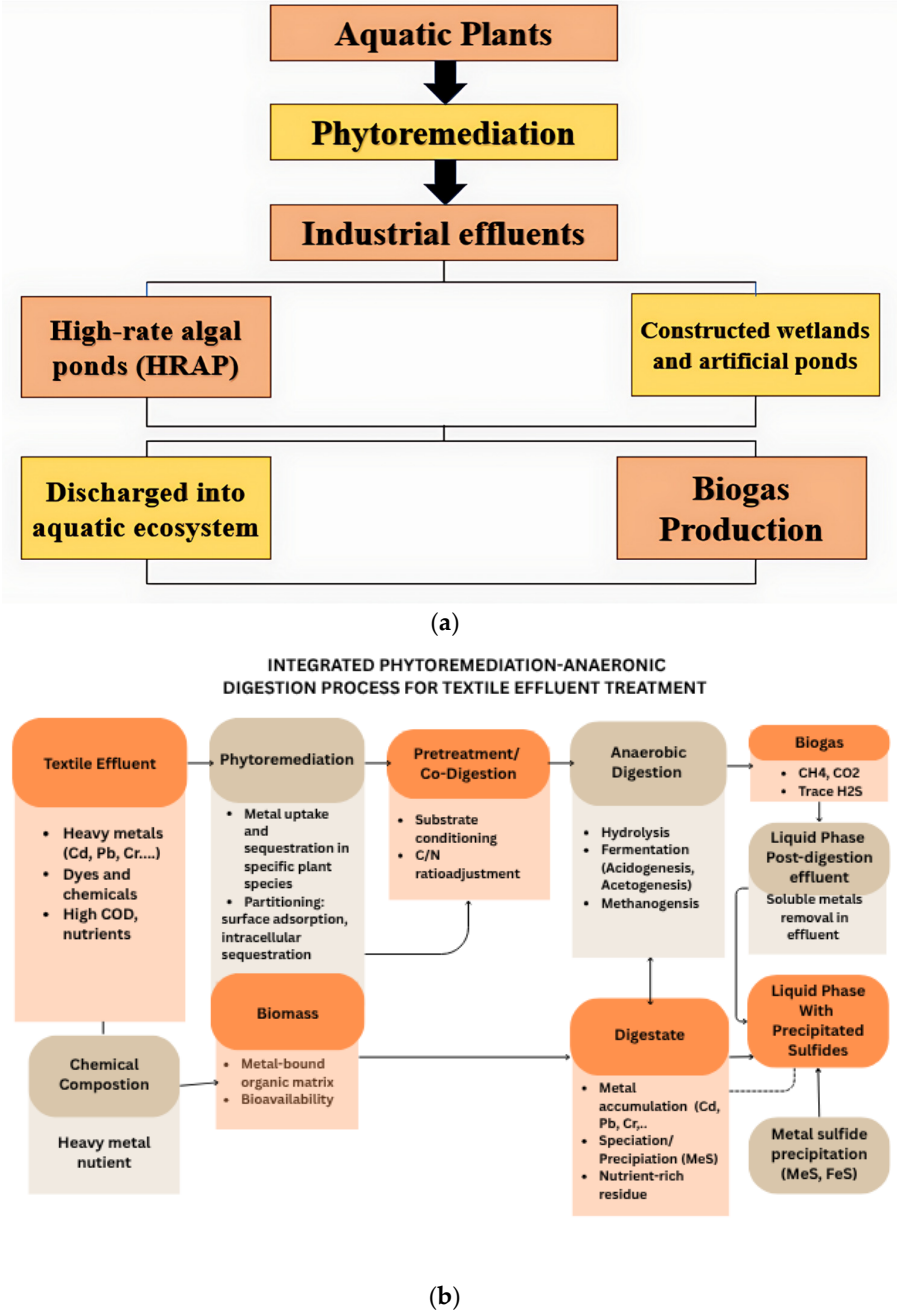


Figure 4. (**a**) A process flow for treating industrial effluents using aquatic plants for phytoremediation. (**b**) Schematic Flow of Metal Fate during Textile Effluent Bioprocessing.

In India and elsewhere, aquatic plants like *Pistia stratiotes*, *Eichhornia crassipes*, and *Lemna Minor* are commonly used for biogas generation [124]. Research shows that plants such as *Eichhornia crassipes* and *Pistia stratiotes* degrade easily and yield significant amounts of biogas during digestion [125]. The resulting biogas can be used directly for cooking, heating, or even power generation using engines or fuel cells [121,126].

5.2. Role of Organic Matter in Biogas Production

Biogas production is based on anaerobic digestion (AD), which is a natural process where organic materials like sludge, agricultural residues, and crop waste are broken down into methane-rich biogas [127]. Growing concerns about environmental damage and food security have pushed biofuel research toward non-edible, lignocellulosic feedstocks [128]. A key challenge in this process is hydrolysis, the rate-limiting step where complex organics are broken into simpler compounds [129]. However, it is not just carbohydrates and proteins; lipids also play a crucial role in digestibility and methane generation, particularly in the case of microalgae [130]. To boost efficiency, pretreatment techniques like ultrasound are being used to enhance the solubility of organic matter [131].

Aquatic plants such as water hyacinth, water lettuce, and duckweed are often considered environmental nuisances due to their rapid growth, which can be converted into valuable bioenergy through AD, dark fermentation, and co-digestion [132]. Water hyacinth (*Eichhornia crassipes*) is an invasive species widely studied for both biogas and bioethanol production. It is also known for its ability to remove heavy metals from polluted water [133–137]. Water lettuce (*Pistia stratiotes*), aside from being used in traditional medicine, is effective in removing pollutants from sewage sludge. Its high carbohydrate, protein, and fiber content make it a strong candidate for biogas feedstock [138–141]. Duckweeds (*Lemna minor*) are known for limiting evaporation and sunlight penetration, which benefits water conservation [142]. Their composition includes pectin, hemicellulose, and lipids that support their use in biogas and biodiesel production [143,144].

With rising interest in diverse organic wastes for energy recovery, improvement in the hydrolysis stage and considering all key biomass components, carbohydrates, proteins, and lipids, are vital steps for maximizing biogas output and effective waste treatment [127,145].

5.3. Biogas Yield from Aquatic Plants

Aquatic plants offer a renewable and eco-friendly biomass source for biogas production, with their fast growth rates and suitable chemical composition [146]. Their high productivity and widespread availability make them ideal candidates for sustainable energy generation. Table 6 lists the biogas production potential of duckweed, water hyacinth, and water lettuce.

Table 6. Biogas production potential of three aquatic plants: Duckweed, Water Hyacinth, and Water Lettuce.

Aquatic Plant	Key Characteristics	Biogas Yield	Methane Content (%)	Process Optimization and Key Findings	References
Lemna minor (Duckweed)	High starch, cellulose; rapid growth; low lignin	1250–10,377 mL total biogas; 390 ± 0.1 mL CH_4/g VS	Up to 85.48% (with co-digestion)	44% higher gas yield; reduced digestion time (~15 days); co-digestion with cow dung enhances methane; integrated bioethanol–biomethane process increases energy output by 70.4%	[147–154]

Table 6. *Cont.*

Aquatic Plant	Key Characteristics	Biogas Yield	Methane Content (%)	Process Optimization and Key Findings	References
Eichhornia crassipes (Water Hyacinth)	High cellulose and hemicellulose; low lignin; balanced C/N ratio	Up to 812 L/kg VS; 0.36 L/kg VS	49–68.89%	5% NaOH pretreatment improves yield (142.61 L/kg VS, 64.59% CH_4); co-digestion (swine dung, banana peel, cow dung) enhances methane (~65%); digestate is useful as fertilizer	[136,155–161]
Pistia stratiotes (Water Lettuce)	Moderate lignin concentration, Moderate cellulose; produces VFAs; suitable for phytoremediation	234–321 mL/g VS; up to 17,570 mL total	48–79.7%	Acid/enzymatic pretreatment improves biomethane (234 mL/g VS); stable methane production with inoculum; adaptable across 35–65 °C; HSAD systems show high yield	[138,162–166]

Plant Type and Biomass

Submerged species like *Myriophyllum spicatum*, *Egeria densa*, and *Hydrilla verticillata* form dense underwater beds with substantial biomass accumulation [167]. Floating plants, particularly fast-growing species such as *Pistia stratiotes* and *Eichhornia crassipes*, are not only abundant but also useful in controlling eutrophication in aquatic systems [168,169]. Emergent plants from wetland areas like *Scirpus lacustris*, *Typha latifolia*, and *Phragmites australis* are commonly utilized for biogas production and contribute additional benefits such as erosion control and soil quality improvement [170–172].

The efficiency of biogas production from these aquatic plants largely depends on the availability of digestible organic compounds like sugars and the plant's moisture content. To ensure economic viability, proper methods of harvesting, storage, and transport are essential. Furthermore, pretreatment techniques such as grinding, ensiling, or enzymatic hydrolysis can significantly improve the digestibility of plant matter and enhance methane yield [173].

Recent studies emphasized the potential of integrating aquatic macrophytes into decentralized biogas systems, especially in rural and peri-urban settings, to improve waste management and energy access [174].

In the rural regions of the Vietnamese Mekong Delta (VMD), small-scale pig farmers commonly rely on household-scale biogas digesters as an alternative to grid electricity and traditional firewood. While these systems offer clear energy benefits, the discharged effluent often remains rich in nutrients, particularly high chemical oxygen demand (COD) and ammonia, raising concerns about secondary environmental impacts. A recent study investigated whether water lettuce (*Pistia stratiotes* L.) cultivated in biogas effluent ponds could serve as a viable feedstock for further anaerobic digestion [175]. The 75-day experimental study maintained optimal conditions favorable for methane production. Interestingly, 50% of the total methane yield was produced within a relatively short window of time between days 17 and 42, indicating a rapid and efficient digestion phase. Peak daily biogas production reached 0.12 L/g VS on day 16, while the highest daily methane yield was recorded at 0.052 L/g VS. Hydrogen sulfide (H_2S) concentrations, an important indicator of gas quality, peaked at 28 ppm between days 14 and 21. Another study demonstrated the dual role of water lettuce as it not only reduced the pollutant loads from wastewater, but when co-digested with pig manure during anaerobic digestion, it also boosted overall biogas output [175]. These findings suggest that water lettuce has potential as both a

promising feedstock for anaerobic digestion and a positive co-substrate for generating renewable energy in integrated farming systems.

Unchecked proliferation of water hyacinth (*Eichhornia crassipes*) posed a serious environmental challenge at Lake Chivero, the primary water source for Harare, Zimbabwe. Over the years, the lake has experienced severe eutrophication, largely driven by excessive nutrient inputs that have led to rapid growth of water hyacinth, which has disrupted ecosystem balance and compromised water quality. To address this issue, a study investigated whether harvested water hyacinth could serve as a viable feedstock for biogas production [176]. Through controlled laboratory-scale anaerobic digestion experiments, it was demonstrated that the plant biomass generated biogas with a notably high methane content, indicating its potential as a renewable energy resource. The findings illustrated a compelling circular approach: transforming an invasive species responsible for ecological degradation into a source of clean energy.

The characteristics of a species of Duckweed (*Lemna gibba)* and its performance during anaerobic co-digestion with waste activated sludge under mesophilic conditions were also studied [177]. Methane yields were particularly favorable when duckweed constituted approximately 40–50% (*v*/*v*) of the feed mixture, indicating that balanced substrate ratios are important to optimize gas production. These observations were aligned with existing studies that highlighted the advantages of co-digestion strategies in enhancing process stability and methane output.

By comparing the biogas output before and after phytoremediation, it has been noted that the dual benefit of pollution control and renewable energy generation. Aquatic plants growing in polluted waters tend to absorb heavy metals, which supports environmental cleanup but may influence the quality and digestibility of the harvested biomass intended for anaerobic digestion. Several aquatic species are known for their ability to absorb heavy metals, including submerged plants like *Hydrilla verticillata*, *Ceratophyllum demersum*, and *Potamogeton malaianus* [178–180], emergent plants like *Typha latifolia*, and floating plants such as water hyacinth (*Eichhornia crassipes*) [181–183].

After phytoremediation, the chemical composition of these plants can change. In some cases, a rise in lignin content may make them harder to break down, reducing biogas yield. The use of plants to extract heavy metals has a long history and is often referred to as different terms like agro-remediation, green remediation, and vegetative remediation [184–187].

Ultimately, how phytoremediation affects biogas production depends on various factors, such as plant species, the types and levels of pollutants involved, the duration of exposure, and the digestion conditions, among others [188]. Therefore, although phytoremediation improves environmental remediation, it also converts plant material into a substrate containing metals, which needs careful assessment prior to anaerobic digestion to prevent negative impacts on biogas production [189].

5.4. Factors Influencing Biogas Production

Process Conditions

Maximizing biogas production from aquatic plants requires careful optimization of key process parameters. Temperature plays a critical role, with mesophilic conditions (around 32–35 °C) being most effective for microbial activity and methane production [190,191]. Water hyacinth, in particular, performs best within this range [192]. pH should be maintained between 6.5 and 7.5. Methane production drops sharply outside this range, especially below pH 5.5, which can halt the process entirely [193]. In water hyacinth digestion, pH tends to decline during fermentation, which requires constant monitoring [194]. An ideal carbon-to-nitrogen (C/N) ratio generally falls between 20:1 and 30:1, although values

between 16:1 and 25:1 are frequently observed for substrates based on aquatic plants, depending on co-digestion and system parameters. Imbalances may result in ammonia accumulation or nitrogen shortage, each of which decreases gas production [195]. Other supporting indicators like biochemical oxygen demand (BOD), chemical oxygen demand (COD), and volatile solids (VSs) also influence performance [196]. Retention time, a parameter refers to how long the biomass stays inside the digester, typically ranges from 10 to 30 days for aquatic plants. Shorter durations may not allow full digestion, while longer ones require more reactor space. For lignocellulosic plants, 2–3 weeks retention time is often ideal [197–199]. Hydraulic retention time (HRT) refers to how long biodegradable material stays in the digester. Its influenced by temperature and reactor design, typically ranging from 10 to 40 days for mesophilic systems and around 14 days for thermophilic ones. If HRT is too short, beneficial microbes may get flushed out; if it is too long, it increases reactor size and cost. For lignocellulosic biomass, an optimal HRT is about 2–3 weeks for efficient breakdown and methane production [199]. Adding an inoculum rich in diverse microbes like bacteria, fungi, and archaea can significantly boost biogas yield and speed up digestion [200]. While bacterial and archaeal populations shift with chemical changes, fungi remain relatively stable and play a key role in breaking down complex plant material [201]. Table 7 explains the key parameters such as chemical, physical and biological parameters and their ranges which influence the production of biogas.

Table 7. Key parameters that influence biogas production.

Parameters	Impact on Biogas Production	References
Organic Matter Content	Higher organic matter enhances microbial decomposition, increasing biogas yield.	[115]
C: N Ratio	Ideal ratio (~20:1–30:1) depending on substrate type supports microbial activity; imbalance leads to ammonia inhibition or nitrogen limitation.	[195]
Temperature	Higher temperature boosts gas production but may lower methane content.	[190,202]
pH	Optimal pH is crucial; extremes hinder microbial activity and reduce biogas yield.	[193]
Retention Time	Adequate time ensures complete decomposition and maximum gas output.	[199]
Inhibition	Presence of toxic substances like heavy metals inhibit microbial processes.	[203]
Microbial Diversity	A diverse microbial population improves substrate breakdown and gas generation.	[201]
Plant Species	Different plants vary in digestibility and biogas potential.	[204]
Pretreatment	Methods like chopping or chemical treatment enhance substrate digestibility and gas yield.	[205,206]

6. Impact of Heavy Metal Sequestration on Biogas Yield

It is crucial to differentiate between the buildup of metals in plant biomass during phytoremediation and the changes in metal forms occurring inside the anaerobic digester. Metals stored in plant tissues before digestion could have inhibitory effects depending on their binding format (e.g., cell wall-bound, complexed, or precipitated forms), as these influence their release during biomass degradation. In contrast, inside the digester, metals can experience changes in their speciation, such as precipitation (e.g., as metal sulfides), which can lower their bioavailability and toxicity. Therefore, the effect of metals on biogas production is influenced not just by their concentration but also by their location and chemical form [207,208].

The output of biogas during anaerobic digestion can be complicated and multidimensionally affected by heavy metal sequestration. While some of the metals might have positive impact but others have negative impact on the overall process. The shift from stimulation to toxicity is influenced by the type of metal and its levels; for example, Iron (Fe) and Nickel (Ni) serve as essential co-factors for methanogenic enzymes, whereas non-essential metals such as Mercury (Hg) and Cadmium (Cd) act as a strict inhibitor [209,210]. Accumulating metals in phytoremediated biomass before anaerobic digestion can pose challenges, as these metals might be released during the digestion process and hinder microbial activity, depending on their concentration and form [208].

On the positive side, the anaerobic digester can immobilize metal compounds (e.g., via precipitation or complexation) can lessen the negative impacts of heavy metals on microbial communities by lowering their bioavailability. This creates a favorable environment for beneficial microbes to flourish, increasing both their activity and the quantity of biogas generated [211]. It also helps maintain just the right levels of essential trace metals that microbes need to stay healthy [212]. Additionally, keeping toxic metals in check through sequestration can make the digestion process more stable and reliable, ultimately leading to better methane yields [213]. The type and quality of the feedstock also play a major role in determining how much biogas can be generated [214,215].

However, there are disadvantages, as sequestration can sometimes lock away not only toxic metals but also important micronutrients, making them unavailable to the microbes that need them. This can slow down or even reduce biogas output [216]. High levels of certain metals can be especially problematic. For instance, copper (Cu) at 281.25 mg/L reduced biogas production by as much as 77% [203]. Heavy metals like mercury (Hg), cadmium (Cd), and chromium (Cr) are particularly harmful to methanogenic bacteria, with mercury being the most toxic. This can severely limit the efficiency of the digestion process [217]. Moreover, strategies like bioaugmentation used to improve digestion can sometimes increase metal concentration in the leftover digestate, posing risks if its used as fertilizer [216,218].

A recent study showed how trace metals influence methane production during anaerobic digestion of organic solid waste (e.g., agricultural and food waste). It was found that certain trace elements, such as iron (Fe), cobalt (Co), molybdenum (Mo), and nickel (Ni), are vital for microbial enzyme systems when added in the right dosage. Optimal ranges (e.g., ~0.56–1.67 mg Fe/g VS, ~0.01–0.1 mg Co/g VS) were associated with significantly higher methane yields, but excessive dosing led to inhibition, consistent with Haldane-type kinetics. This highlights that enough trace metals are needed to support digestion, but at higher concentration they harm the microbial communities [209].

6.1. Speciation of Heavy Metals in Plant Biomass and Its Influence on Bioavailability

To distinguish between metal sequestration in plants and the transformations that occur during anaerobic digestion, it is essential to consider the chemical forms in which metals are stored in phytoremediated biomass. During phytoremediation, metals do not exist as free ions but are instead immobilized via various mechanisms, such as binding to components of the cell wall (e.g., pectin, cellulose), storage within vacuoles inside the cell, binding with organic compounds (phytochelatins and proteins), and forming stable compounds such as metal phosphates or sulfides [219].

These various forms influence how much metals become available during anaerobic digestion. Metals loosely attached to cell walls or found in exchangeable fractions are more easily released during hydrolysis, while metals existing as insoluble precipitates (e.g., Metal sulfides or phosphates, or strongly complexed forms, remain less available to organisms [220].

During anaerobic digestion, variations in pH, redox potential, and sulfide levels have an additional impact on metal speciation. Under reducing conditions, metals can form sulfides (e.g., FeS), reducing their toxicity. However, disruptions in digester conditions can cause these metals to become mobile again, resulting in abrupt rises in their bioavailability and inhibiting microbial activity [220,221].

Therefore, the effect of heavy metals on biogas production is influenced not just by their overall concentration, but also by their transformation from plant-bound forms into bioavailable forms inside the digester.

6.2. Metal Contamination Impact

Heavy metal contamination poses a serious challenge to biogas production from aquatic plants. Since anaerobic digestion depends on microbial activity, the presence of key heavy metals like lead, cadmium, chromium, and mercury (Table 6 for threshold ranges) can disrupt bacterial functions, significantly lower methane yields and in some cases halt the digestion process altogether [216,222,223].

Moreover, the digestate and the leftover material from biogas production can retain these heavy metals. When this byproduct is used as fertilizer, it can introduce harmful contaminants into agricultural soil and potentially enter the food chain, raising environmental and health concerns [224,225]. In addition to affecting microbes, heavy metals can also impair the growth and physiology of aquatic plants, ultimately reducing the biomass available for digestion.

Therefore, understanding the concentration and behavior of heavy metals in aquatic ecosystems is essential. Monitoring elements such as lead, arsenic, cadmium, chromium, and mercury helps anticipate their potential impacts on both plant growth and biogas generation efficiency [25]. It is of utmost importance to pre-assess biomass quality before digestion to reduce the risks associated with heavy metal interference in biogas systems [184].

6.3. Levels for Metal-Specific Toxicity and Inhibition

Heavy metals can notably affect biogas generation by altering the development and function of microbial populations essential to the anaerobic digestion process. As outlined in Section 6.2, these effects are heavily influenced by the initial metal composition in plant biomass and their conversion into bioavailable forms during digestion and differ according to chemical form, length of exposure, and substrate properties. Although some trace metals serve as vital micronutrients, high levels can result in toxicity and hinder processes [226,227].

Trace elements like iron (Fe), cobalt (Co), and nickel (Ni) are essential in methanogenic processes, functioning as cofactors for important enzymes that participate in methane production. However, when present in amounts exceeding optimal levels, these metals can interfere with enzyme function and disrupt microbial equilibrium. In contrast, non-essential metals like cadmium (Cd), lead (Pb), and mercury (Hg) show toxicity even at low concentrations, significantly suppressing methanogenic activity [216,217,228,229].

To better differentiate between helpful and harmful levels, Table 8 outlines the micronutrient needs and toxicity limits for essential metals, including their chemical forms, the microorganisms they affect, and the usual environments in which they are found [209,219].

Table 8. Micronutrient and Toxicity Limits for Heavy Metals in Anaerobic Digestion.

Heavy Metal	Beneficial Range	Inhibitory Range	Chemical Species (If Known)	Affected Microbial Group	Substrate Type/Context	References
Iron (Fe)	0.56–1.67 mg/g VS	>5 mg/g VS (excess leads to imbalance)	Fe^{2+}, Fe^{3+}, FeS	Methanogens (enzyme activation)	Organic waste, sludge	[209,212]

Table 8. *Cont.*

Heavy Metal	Beneficial Range	Inhibitory Range	Chemical Species (If Known)	Affected Microbial Group	Substrate Type/Context	References
Nickel (Ni)	0.005–0.5 mg/L	>10 mg/L	Ni^{2+}	Methanogens (cofactor in enzymes)	Agricultural waste, manure	[209,230]
Cobalt (Co)	0.01–0.1 mg/g VS	>5 mg/L	Co^{2+}	Methanogens (vitamin B_{12} synthesis)	Food waste, sludge	[209]
Copper (Cu)	Trace (<1 mg/L)	~281 mg/L (up to 77% inhibition)	Cu^{2+}	Methanogens, acidogens	Textile wastewater biomass	[203]
Zinc (Zn)	<5 mg/L	>150 mg/L	Zn^{2+}	Enzymatic systems (general microbes)	Mixed substrates	[217]
Chromium (Cr)	Trace amounts	>100 mg/L (35–50% reduction)	Cr^{3+}, Cr^{6+} (Cr^{6+} highly toxic)	Methanogens	Industrial effluents	[217]
Cadmium (Cd)	None (non-essential)	>1–10 mg/L	Cd^{2+}	Methanogens (highly toxic)	Contaminated biomass	[216,230]
Lead (Pb)	None (non-essential)	>50 mg/L (process instability)	Pb^{2+}	Methanogens	Phytoremediated plants	[229]
Mercury (Hg)	None (non-essential)	>1 mg/L (severe inhibition)	Hg^{2+}, methyl-Hg	Methanogens (enzyme inhibition)	Industrial sludge	[217,231]

The impact of heavy metals on anaerobic digestion is influenced by their dual function as necessary micronutrients and possible inhibitors. Trace elements such as Fe, Co, and Ni are necessary for enzymatic activity in methanogenesis, while non-essential metals like Cd, Pb, and Hg are toxic even at low concentrations. Toxicity is significantly affected by the form of metals present, as soluble ionic species tend to be more harmful compared to precipitated forms (e.g., metal sulfides). Table 6 provides an overview of the beneficial and inhibitory ranges for important metals, as well as their microbial targets and common substrate environments [203,209,216,217,229].

Among frequently documented inhibitory impacts, copper (Cu) has been recognized as extremely harmful to methanogens, with levels approximately 281.25 mg/L decreasing biogas production by as much as 77% [203]. Chromium (Cr), especially in its hexavalent form (Cr^{6+}), is notably more toxic than Cr^{3+}, and levels exceeding 100 mg/L can cause a 35–50% reduction in methane production [202]. The increased toxicity of Cr^{6+} relative to Cr^{3+} is mainly because of its higher solubility and ability to move through microbial cell membranes. Cr^{6+} usually occurs as chromate (CrO_4^{2-}), which can enter microbial cells through sulfate transport systems due to its structural similarity. Once inside the cell, Cr^{6+} is reduced intracellularly to Cr^{3+}, producing reactive oxygen species (ROS) during the process. These ROS cause oxidative stress, which harms DNA, proteins, and membrane lipids, eventually interfering with microbial metabolism. In contrast, Cr^{3+} is less bioavailable because it tends to form stable, insoluble complexes, which restrict its entry into cells and reduce its toxicity [208,232].

Likewise, zinc (Zn), despite being a necessary micronutrient, can become inhibitory when its concentration surpasses 150 mg/L. Lead (Pb), often found accumulated in phytoremediated biomass like water hyacinth, can lead to process instability even at concentrations as low as 50 mg/L in its soluble form [229].

In addition to overall concentration, the specific chemical forms of metals significantly influence toxicity, as soluble ionic forms are more readily available to organisms and more inhibitory than precipitated forms like metal sulfides. This distinction is especially significant in systems that use phytoremediated biomass, as metals might be slowly released during digestion, from specific plant-bound forms (e.g., exchangeable vs. precipitated fractions), affecting their availability and influence on microbial communities [208].

6.4. Link Between Metal-Sequestered Biomass and Anaerobic Digestion

A major challenge in combining phytoremediation with biogas production is how heavy metals stored in plant biomass impact anaerobic digestion (AD). During phytoremediation, aquatic plants absorb metals into their tissues by binding them to cell walls, storing them in vacuoles, and forming complexes with organic ligands. This changes the biomass composition by raising the ash content and lowering the biodegradable volatile solids, which may have a negative impact on methane production [222].

In AD systems, trace metals like Fe, Co, and Ni are crucial for the activity of methanogenic enzymes, although excessive buildup, especially of Cd, Pb, and Hg can hinder microbial metabolism. Unlike external contamination, metals in phytoremediator biomass are internally bound and may be gradually released during hydrolysis, resulting in delayed toxicity and decreased process stability [233].

Furthermore, metal stress during plant growth may elevate lignin and phenolic compound levels, which can decrease substrate biodegradability and hinder hydrolysis, the rate-limiting stage in AD [234].

Metal speciation also affects toxicity, as soluble forms are more harmful than precipitated or complexed forms [233,235]. In general, how phytoremediation-derived biomass affects biogas production is influenced by the type, amount, and availability of metals present, highlighting the need to assess biomass quality before digestion [233].

6.5. Disruption in Microbial Activity

Heavy metals also affect microbial communities by altering their diversity and composition, which can lead to reduced biogas production and overall process instability [203,230]. Elevated levels of Cadmium (Cd) and Nickel (Ni) have been demonstrated to alter the microbial community from methanogens to more robust but slower-growing hydrogenotrophic methanogens, resulting in overall process instability and decreased cumulative gas production [230]. Over time, this disturbance makes it more difficult to maintain ideal operating conditions.

In addition to changes within the community, heavy metals directly disrupt functional gene expression and the enzymatic processes involved in methane production. Important genes, including mcrA (methyl-coenzyme M reductase), which play a crucial role in methane production, are suppressed when toxic metals such as Cd, Hg, and Pb are present. Likewise, genes linked to acetate usage (e.g., Ack and PTA) along with hydrogenotrophic pathways are suppressed, resulting in lower metabolic efficiency [66,222].

Heavy metals can also attach to sulfhydryl (-SH) groups in enzymes, altering protein structure and reducing enzyme function. For instance, Ni and Co are necessary for the production of cofactors (e.g., coenzyme F430 and vitamin B_{12}), but high levels can interfere with their own metabolic pathways via feedback toxicity. Moreover, metals-triggered oxidative stress results in the production of reactive oxygen species (ROS), which cause additional harm to microbial DNA, proteins, and cell membranes, disrupting gene expression and cellular processes [222,227].

Over time, this disturbance makes it more difficult to maintain ideal operating conditions. In addition to impacting methane production, heavy metals also affect biogas quality, especially the concentration of hydrogen sulfide (H_2S). Sulfate-reducing bacteria (SRB), which compete with methanogens for substrates, may be encouraged in specific metal-stressed environments, resulting in higher H_2S production. High H_2S levels are problematic as they lead to corrosion in biogas engines, pipelines, and storage systems, which in turn decreases equipment lifespan and raises maintenance expenses. On the other hand, certain metals like iron (Fe) can lower H_2S levels by creating insoluble metal sulfides (e.g., FeS), thus enhancing gas quality. Therefore, the presence and types of metals have a

dual effect on controlling both methane production and hydrogen sulfide levels, directly impacting the efficiency and lifespan of biogas systems [222,236].

6.6. Interpretation and Permanent Environmental Effects

Long-term consequences include the buildup of heavy metals in the digestate and sludge [216], which can impact its quality as a fertilizer and pose environmental risks [231]. Due to the non-biodegradable nature of metals, they build up in the solid fraction of the anaerobic digestion process. This buildup affects the quality of the digestate as a fertilizer; for instance, Mercury (Hg) levels surpassing 1.0 mg/kg dry matter frequently make the byproduct legally unsuitable for use on agricultural land according to environmental safety regulations [231].

The bioavailability and toxicity of metals are determined by their chemical form, or speciation, with some forms being more easily absorbed by microbes. Other factors like temperature, metal content, and pH can also influence how microbes absorb heavy metals [230,237]. In an anaerobic setting, sulfides can lead to the precipitation of metals as metal-sulfides, making them less bioavailable and consequently less toxic to the microbes. Nonetheless, elements such as variable pH and temperature can cause the re-mobilization of these metals, resulting in toxicity shocks to the environment [230,237].

7. Challenges and Research Gaps

7.1. Technical and Operational Challenges

The integration of phytoremediation for textile wastewater treatment with subsequent biogas production from plant biomass is a promising circular economy approach, but it presents several technical and operational challenges.

Although aquatic plants are effective at sequestering heavy metals, high metal concentrations in their biomass can inhibit anaerobic digestion, reducing biogas yields. Metals interfere with the metabolic processes of biogas-producing microbes [238]. The severity of this inhibition depends on the type, concentration, and soluble form of heavy metal. High heavy metal levels can also negatively impact microbial respiration and plant health [239] and can lead to serious health issues for humans if they subsequently enter the food chain [240].

Textile effluent changes the biochemical composition of aquatic plants, affecting their suitability for anaerobic digestion. Alterations in cellulose, hemicellulose, and lignin content can impact biogas yields [241,242]. While lignocellulosic wastes are often a disposal problem, their varied structures can affect biodegradability [243].

Maintaining stable anaerobic digestion is challenging due to potential changes in wastewater composition and metal concentrations. Ideal conditions, including pH, temperature, and nutrient balance, must be maintained [244]. A further challenge is managing the digestate, which may contain residual metals, necessitating careful disposal to prevent environmental contamination. Although anaerobic digestion is vital for a sustainable bioeconomy, digestates must be monitored to prevent the release of contaminants like antibiotic resistance genes into the environment [245].

A study showed that the risk of spreading antibiotic resistance genes (ARGs) through contaminated digestate could be a major concern. Current models do not adequately predict biogas yield based on the heavy metal content and biochemical changes in aquatic plant biomass after phytoremediation.

Even though there are technological options for the recovery of metals from digestants, such technologies tend to be very expensive and specific. In most instances, digestion sludge contaminated with metals will need to be disposed of at designated sites

7.2. Limitations of Current Phytoremediation Practices

Textile effluent, a complex mixture of contaminants, can hinder plant growth, thereby reducing the effectiveness of phytoremediation [246]. While plant-based methods such as rhizofiltration and phytoextraction are utilized, the process in aquatic media is limited by factors such as wastewater physicochemical properties (pH, salinity, and COD), metal bioavailability, and the specific plant's capacity to detoxify complex dyes

Phytoremediation is a slow process that can take years, especially for heavily polluted sites. Its effectiveness is limited to the root zone, making it challenging to remove contaminants deep underground [247]. Furthermore, the number of plants that can be grown limits the land area that can be efficiently treated.

The ability of plants to collect metals varies. While hyperaccumulators exist, many species may not efficiently collect metals or may become toxic at high concentrations. Despite these drawbacks, phytoremediation is considered an environmentally friendly method for removing contaminants from industrial, residential, and agricultural discharges. After phytoremediation, the hazardous biomass from hyperaccumulator plants must be repurposed into circular bioeconomy byproducts like biochar or biogas, rather than leaving them as a source of pollution [248].

The efficacy of phytoremediation is highly dependent on environmental variables like climate, soil pH, and pollutant type [249]. Not all plants can accumulate or break down every type of pollutant, and excessive pollutant levels can be toxic to the plants themselves [250]. Additionally, there is a risk of pollutants entering the food chain if animals consume the contaminated plants [251]. Since accumulated pollutants are transferred to the biomass, the contamination problem is not entirely resolved but rather moved, necessitating proper disposal [252].

7.3. Gaps in Understanding the Interaction Between Metal Sequestration and Biogas Production

Research on biogas production from aquatic plants highlights several gaps. While low concentrations of metals can stimulate biogas production and high concentrations can inhibit it, the exact threshold values for various metals and microbial communities are not fully understood. There is also a need for more research on the long-term effects of continuous metal exposure on the stability and resilience of microbial communities.

Additionally, most studies focus on total metal concentrations, but more research is needed to understand how different metal species, which affect toxicity and bioavailability, impact microbial activity and biogas production. The dynamics of complex microbial communities are also a key area for future study, as metals can selectively inhibit or stimulate certain groups like acidogens and methanogens.

Finally, further research is required to optimize pretreatment methods for biomass from metal-sequestering plants to manage metal release. It is also crucial to assess the economic and practical feasibility of scaling these findings from lab-based studies to large-scale biogas production systems.

7.4. Crisis Management Strategy

This strategy involves emergency actions like diluting the hazardous feed material, regulating the pH value, temporarily decreasing the rate of organic load, and adding buffers/adsorbers. Moreover, techniques such as co-digesting the hazardous feed material with fresh organic material, along with the employment of metal-resistant microbes, have also been recommended.

8. Conclusions

Investigating the use of phytoremediation in treating textile wastewater and its subsequent impact on biogas production reveals a promising sustainable approach to tackling heavy metal pollution while harnessing renewable energy. As toxic heavy metals, including lead, cadmium, chromium, and arsenic, pose serious risks to human health and the environment, they must be removed from textile effluent. Employing aquatic plants like water lettuce (*Pistia stratiotes*), water hyacinth (*Eichhornia crassipes*), and duckweed (*Lemna minor*), phytoremediation presents an applicable and cost-effective strategy for extracting these contaminants from polluted water sources. This review demonstrates how aquatic plants may effectively absorb and accumulate heavy metals through a variety of processes, such as phytoextraction, rhizofiltration, and phytostabilization. Beyond their role in cleansing water bodies, these plants yield substantial biomass, which can serve as a feedstock for anaerobic digestion (AD), a process that generates biogas. By combining the generation of biogas and phytoremediation, a system of circular economy that combines energy recovery and waste treatment is promoted, reducing environmental degradation and our reliance on fossil fuels.

Despite the benefits of using aquatic plants for phytoremediation, their tissues' ability to sequester metals could prevent the formation of biogas. Heavy metals present in the plant biomass can hinder the activity of microorganisms crucial for efficient methane generation during anaerobic digestion. However, strategies such as pre-treating the biomass, co-digesting it with other organic materials, and utilizing microbial communities with a higher tolerance for metals can help mitigate these adverse effects.

This review highlighted a number of real-world instances that show that biogas generation and phytoremediation are possible. Notably, water hyacinth and duckweed have exhibited promising biogas yields, attributed to their high organic matter content and rapid growth rates. Their effectiveness in both removing heavy metals from wastewater and generating biogas highlights their potential in sustainable wastewater treatment and renewable energy production. The impact of metal accumulation on biogas yield is a critical consideration. While metal uptake by plants aids in environmental remediation, it can influence the subsequent anaerobic digestion process. Elevated metal concentrations within the plant biomass can lead to microbial inhibition, potentially resulting in a decrease in biogas production.

In summary, this review showed how aquatic plants may provide a dual strategy for handling effluent from textile wastewater and generating clean energy. Utilizing the resultant plant biomass to produce biogas is consistent with the goals of sustainable energy, complementing the successful removal of environmental contaminants through phytoremediation. Nevertheless, further research and innovation are essential to address current operational and technological hurdles. Future efforts should prioritize the development of advanced biomass pretreatment methods, assess the long-term environmental consequences, and optimize the interplay between metal accumulation in plants and the efficiency of anaerobic digestion. By following these paths, the textile sector may embrace more environmentally friendly wastewater treatment techniques and help the world transition to renewable energy sources.

Executive Conclusions

- The phytoremediation approach using aquatic plants is an effective and economical way of removing heavy metals from textile effluents.
- Some of the promising plants include *Pistia stratiotes*, *Eichhornia crassipes*, and *Lemna minor*.
- By integrating phytoremediation with anaerobic digestion, we can achieve wastewater management and energy production through biogas production.

- However, the presence of heavy metals in plant biomass may hinder microbial metabolism, hence reducing biogas production.

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