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Review

Nanomaterials and Their Role in Constructed Treatment Wetlands

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Abstract

The long-term treatment performance of constructed wetlands (CWs) is constrained by substrate reactivity and biological processes. Nanomaterials offer routes for enhancement, yet the links between material properties, ecological responses, and system-level environmental benefits remain insufficiently understood. This review examines how nanomaterial synthesis and incorporation influence pollutant removal, substrate–microorganism–plant interactions, and the broader functions of CWs. Iron-based nanomaterials provide complementary pathways for nutrient removal by supporting nitrogen transformations through electron donation and interfacial electron transfer, while immobilizing phosphate through surface complexation and precipitation. Supported nanocomposites extend substrate functionality by coupling pollutant adsorption, catalytic reactions, and biofilm formation. These effects interact with changes in microbial activity, root physiology, and nutrient uptake to influence treatment performance. Such interactions also offer opportunities to improve stormwater runoff treatment, resource recovery, and greenhouse gas mitigation. However, nanoparticles retained within wetland substrates and biofilms may prolong the exposure of microorganisms and plant roots. High concentrations or prolonged exposure may impair microbial activity and plant function, potentially reducing treatment performance. Nanoparticle release may pose additional ecological risks. Future research should integrate long-term operational monitoring, ecological safety assessment, and life cycle assessment to establish trade-offs between treatment gains and environmental burdens. This review informs nanomaterial selection and operational optimization to advance water purification, resource utilization, and low-carbon operation in CWs.

Keywords: constructed wetlands; nanotechnology; nanomaterials; pollutant removal; resource recovery; greenhouse gas mitigation

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1. Introduction

Constructed wetlands (CWs) are ecological treatment systems that remove pollutants through the combined action of substrates, microorganisms, and plants [1,2]. Their low energy requirements, straightforward operation and maintenance, and multiple ecosystem services have supported their widespread application in treating domestic wastewater, wastewater treatment plant effluent, agricultural runoff, and selected industrial wastewaters [3]. Treatment performance depends not only on direct pollutant retention and immobilization by substrates but also on attached biofilm activity

and plant rhizosphere processes [4]. However, limited substrate adsorption capacity, insufficient electron donors at low carbon-to-nitrogen ratios, and variations in pollutant loading and environmental conditions continue to constrain treatment performance [5]. These limitations pose challenges to the sustained removal of nitrogen, phosphorus, and certain recalcitrant emerging contaminants. Material modification that enhances both substrate interfacial reactivity and biological processes has consequently become an important research direction for improving CW performance.

Nanomaterials offer new opportunities for CW enhancement owing to their large specific surface areas, abundant surface-active sites, and tunable adsorption, catalytic, and redox properties [6,7]. At appropriate doses, nanoscale zero-valent iron (nZVI) and Fe_3O_4 nanoparticles (NPs) can improve nitrogen and phosphorus transformation and removal by enhancing substrate interfacial reactions, facilitating electron transfer, and modulating extracellular polymeric substance secretion, enzyme activity, and functional microbial community composition [8,9]. However, prolonged exposure to materials such as silver nanoparticles (AgNPs) and nickel oxide nanoparticles (NiO NPs) may inhibit key enzyme activities and functional gene expression, alter microbial communities, and induce oxidative stress in plants, thereby impairing treatment performance [10–12]. Nanomaterials can also be retained by substrates and biofilms and subsequently transported and redistributed among substrates, biofilms, and plants, with their environmental fate and biological effects depending on particle properties and exposure duration [13,14]. Assessing their potential applications in CWs therefore requires an integrated evaluation of treatment performance, underlying mechanisms, and long-term ecological effects.

This review aims to examine the applications, mechanisms, and sustainability implications of nanomaterials in CWs. Specifically, it focuses on: (1) reviewing green synthesis routes and functional material designs, and examining how adsorption, catalysis, redox reactions, and interfacial processes contribute to pollutant removal; (2) assessing interactions among nanomaterials, substrates, microorganisms, and plants, with particular attention to their effects on treatment performance and system stability; and (3) evaluating long-term performance, ecological risks, resource recovery potential, and economic feasibility for future research and implementation. By linking material properties and biological responses with operational benefits and constraints, this review can provide a reliable and environmentally sustainable basis for improving CW treatment.

During the preparation of this manuscript, the authors used Midjourney 7 to generate some elements in the figures. The authors have reviewed and edited the output and take full responsibility for the content of this publication.

2. Literature Retrieval and Research Landscape

2.1. Literature Search and Screening

This literature search was conducted in the Web of Science Core Collection through 23 July 2026 to identify studies on the application and environmental effects of nanomaterials in CWs. Search terms combined constructed-wetland terms ("constructed wetland*" and "constructed wetlands") with nanomaterial-related terms, including "nanomaterial*," "nanoparticle*," "nanoscale zero-valent iron," "nZVI," "Fe_3O_4", "silver nanoparticle*," and "graphene oxide." Studies were included if nanomaterials were directly added to CWs, loaded onto substrate materials, or incorporated as composite media, and if pollutant removal or system responses were reported. Studies limited to conventional water treatment or adsorption experiments, or examining NPs solely as environmental contaminants without their application in CWs, were excluded. After deduplication and screening of titles, abstracts, and full texts, 50 studies were retained for analysis.

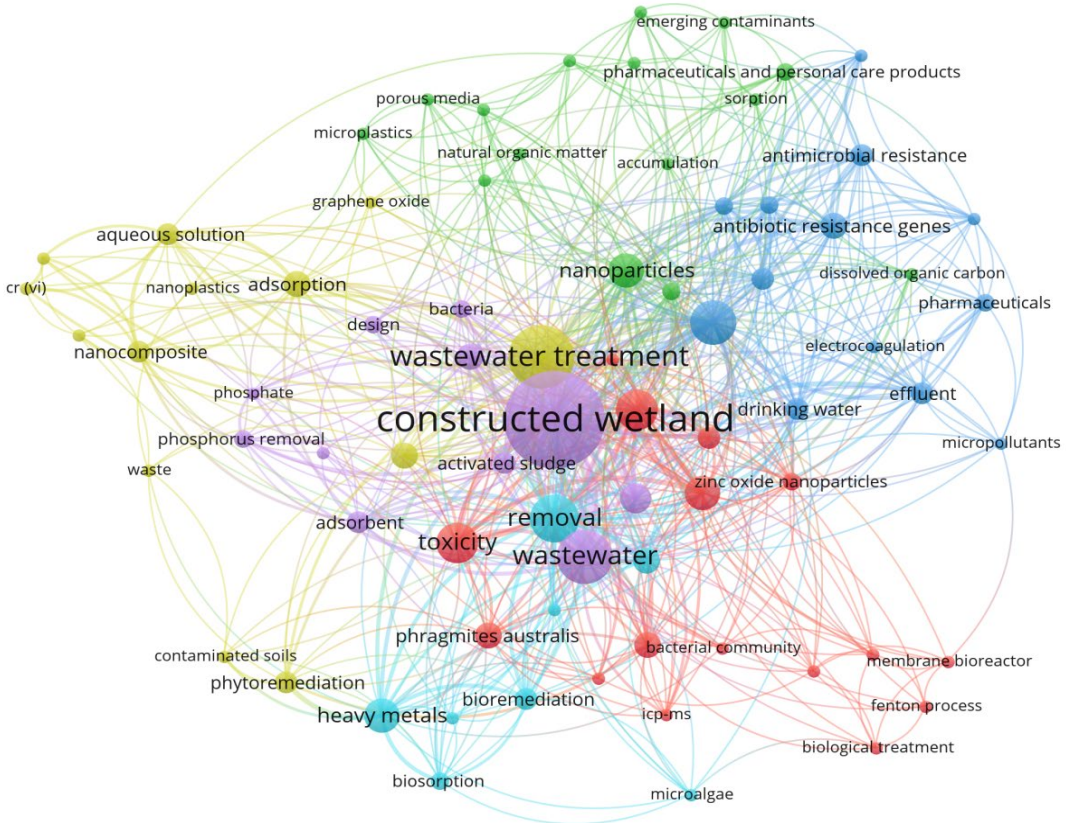
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2.2. Bibliometric Overview

To characterize the thematic structure and temporal distribution of research on nanomaterials in CWs, keyword co-occurrence, clustering, and timeline analyses were conducted using VOSviewer1.6.13 and CiteSpace 2.6.R2. As shown in Figure 1a, the VOSviewer co-occurrence network comprises 76 keywords grouped into six clusters. The clusters are interconnected, and the central keywords exhibit dense co-occurrence links. "Constructed wetland" and "pollutant removal" occupy central positions in the network and are linked to themes concerning nanomaterials, treatment targets, biological responses, and environmental risks. The six clusters can be broadly characterized as: (1) materials and pollutant removal; (2) phosphorus removal and emerging contaminants; (3) microbial, plant, and ecological responses; (4) adsorption and nanocomposites; (5) pollution remediation and bioremediation; and (6) environmental risks and exposure. This network structure indicates that research on nanomaterials in CWs addresses both pollutant removal and biological or ecological responses, in relation to specific materials, contaminants, and treatment contexts.

The CiteSpace timeline (Figure 1b) shows that earlier keywords included "constructed wetland," "nanoparticles," and "phosphorus removal." Subsequent keywords included "adsorption," "silver nanoparticles," and "phytoremediation," whereas more recent terms include "microbial community," "toxicity," "plant–microbe interactions," "resource recovery," and "circular economy." The temporal distribution of these keywords indicates a broadening of research topics from material application and pollutant removal to biological responses, environmental risks, and resource recovery. The following sections examine pollutant-removal performance in CWs where nanomaterials have been applied, interactions between nanomaterials and biological processes, and material fate and ecological effects under long-term operating conditions.

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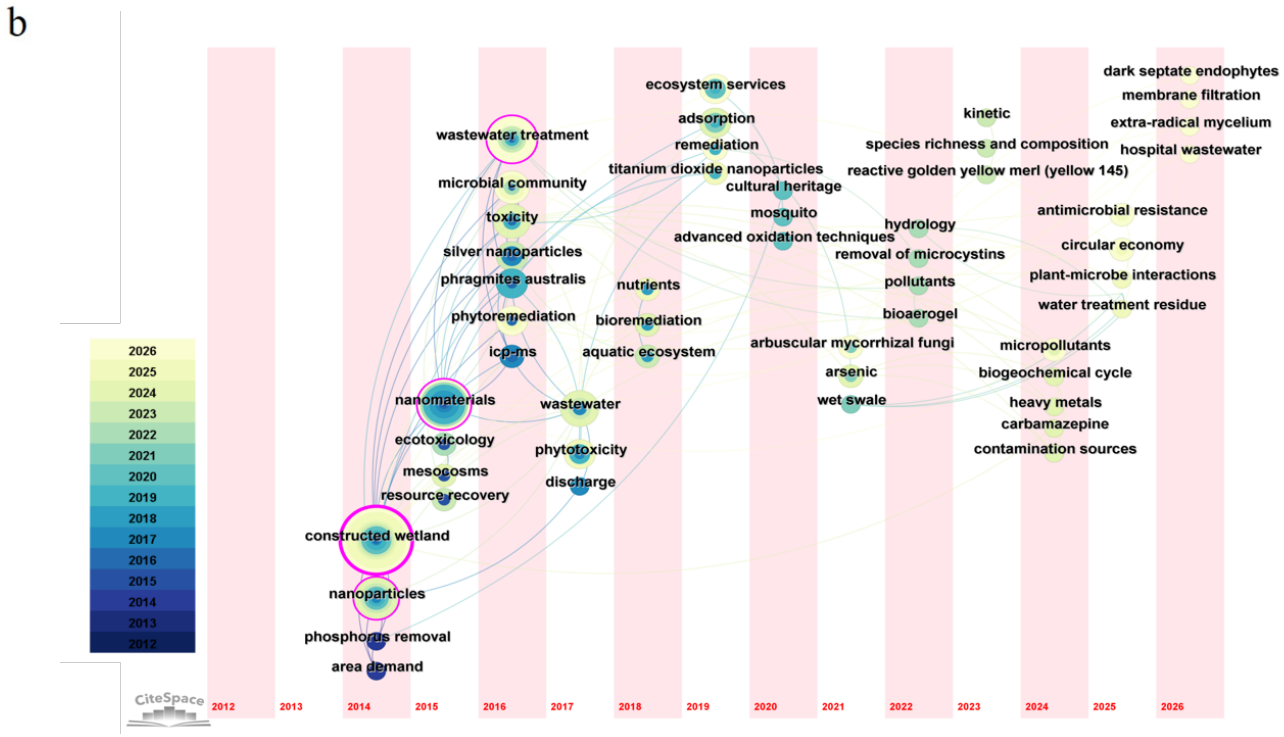


Figure 1. Bibliometric landscape of nanomaterials in CWs research: (**a**) keyword co-occurrence network; (**b**) temporal evolution of research topics.

3. Green Synthesis and Functional Design of Nanomaterials for CWs

3.1. Green Synthesis Routes

Green nanotechnology has emerged as a critical frontier in the field of sustainable development, with its core objective being the design of cleaner, energy-efficient, and environmentally friendly nanomaterial synthesis processes [15], demonstrating considerable potential in areas such as water treatment, climate change mitigation, renewable energy, and pollutant removal [16].

Biological synthesis is one approach within green nanotechnology. This approach employs bioactive metabolites derived from biological resources—such as plant extracts or microorganisms including bacteria, yeasts, fungi, and algae—as natural reducing and stabilizing agents to convert metal ions (e.g., Ag^{+}, Au^{3+}, Zn^{2+}, Fe^{3+}) into metallic or metal oxide NPs [17]. NPs, as the most fundamental and widely applied units of nanotechnology, encompass a broad range of types, including metals, metal oxides, carbon-based materials, and polymers [18]. Their defining feature—a high surface-area-to-volume ratio—confers remarkable surface reactivity, enabling efficient molecular-level interactions with contaminants. This property underpins their superior performance in catalytic, adsorptive, and chemical transformation processes [7].

During synthesis, these biomolecules induce nucleation and promote the growth of NPs through redox reactions, while simultaneously forming a capping layer on the particle surface to prevent aggregation, thus enhancing NP stability and dispersibility [19]. This bio-mediated process can typically occur under ambient temperature and pressure without the need for strong reducing agents or organic solvents, potentially reducing the use of hazardous reagents and energy relative to some conventional synthesis routes [20]. Depending on the reaction system, NPs may form extracellularly within the reaction medium or intracellularly, followed by separation and purification through centrifugation and cell disruption. Moreover, by tuning parameters such as reaction time, metal salt concentration, and biological source, it is possible to control NP size and morphology to

a certain extent. Owing to its mild reaction conditions, its high ecological compatibility, and the excellent biocompatibility of the products, green nanomaterial synthesis offers a potentially more sustainable alternative to traditional physical and chemical routes.

Currently, biological synthesis pathways for green nanomaterials can be broadly categorized into four major approaches: microorganism-mediated synthesis, fungi- or yeast-assisted synthesis, plant extract-assisted synthesis, and algae-mediated synthesis. The advantages and disadvantages of each approach are summarized in Table 1. Bacterial-mediated synthesis utilizes reductase enzymes secreted during cellular metabolism to react with metal ions, enabling both intracellular and extracellular NP formation characterized by rapid reaction kinetics and low cost [21]. Fungal- and yeast-mediated synthesis relies on their rich extracellular enzymatic systems, often yielding NPs with potential stability and compatibility with large-scale cultivation. Plant extract-assisted synthesis employs natural phytochemicals such as phenolics, flavonoids, and polysaccharides derived from leaves, roots, flowers, and fruits as reducing and stabilizing agents, offering broad resource availability, operational simplicity, and environmental safety [19]. Algae-mediated synthesis, in contrast, leverages the high growth rate and strong metal-ion adsorption capacity of microalgae, enabling the efficient biosynthesis of metallic and metal oxide NPs. Although each biological system exhibits distinct advantages and limitations in terms of reduction capacity, reaction rate, and control over particle morphology, all share key characteristics of greenness, low energy consumption, and renewability. These features collectively provide diverse and sustainable pathways for the large-scale production of environmentally benign nanomaterials.

Table 1. The advantages and disadvantages of synthesizing green nanomaterials through different methods.

Synthesis Method	Advantages	Disadvantages	References
Bacterial-mediated synthesis	Fast cultivation rate with relatively low cost. Nanoparticles can be synthesized either intracellularly or extracellularly. Microorganisms naturally reduce metal ions to form stable NPs.	Strain selection may require strict aseptic conditions. Risk of contamination during cultivation. Limited control over NPs morphology and size. Complicated purification process, particularly for intracellular synthesis.	[22]
Fungal/Yeast-mediated synthesis	Fungi and yeasts possess extensive extracellular enzyme systems suitable for large-scale synthesis. NPs produced often show high stability and excellent biocompatibility due to natural biomolecule capping.	Long cultivation period required. High post-processing cost for intracellular products.	[23]
Plant extract-assisted synthesis	Abundant, renewable, and eco-friendly raw material sources. Simple operation and relatively low cost. Can proceed under mild conditions, suitable for environmental applications.	Extraction efficiency and composition may vary with conditions. Difficult to achieve product uniformity and large-scale reproducibility. Requires precise control over reaction parameters.	[19]

Algae-mediated synthesis	Rapid growth rate, easy cultivation, and potential for large-scale biomass production. Capable of producing a wide range of metal/metal oxide NPs with bio-functional surface coatings.	The reaction process is sensitive to light and growth conditions. Limited to aquatic biological [24] systems. Challenges in downstream recovery and purification.	

3.2. Functional Properties and Modes of Incorporation into CWs of NPs

Green-synthesized NPs generally exhibit a high surface-area-to-volume ratio and pronounced surface reactivity, allowing efficient molecular-level interactions with pollutants [25], as shown in Table 2. Their principal environmental functions include: (i) adsorption, through surface-active sites that capture heavy metals and organic contaminants; (ii) catalysis, as ZnO and TiO_2 NPs can degrade recalcitrant organics and play a catalytic role; (iii) antimicrobial activity, with silver NPs (Ag NPs) disrupting bacterial membranes and inhibiting pathogenic growth; and (iv) magnetically assisted catalysis and recovery, where magnetic NPs such as Fe_3O_4 may influence nitrogen transformation and permit magnetic separation under suitable conditions.

Table 2. Application of nanomaterials in CWs.

Nanoparticle Type	Nanocomposite	Key Function	CW Configuration and Key Conditions	Target Pollutants	Main Finding	References
Metallic NPs	Zeolite-supported nZVI	Biological N-removal enhancement	CW columns	NH_4^+–N; NO_3^-–N; TN	Removal: NH_4^+–N 86.56%; NO_3^-–N 66.42%; TN 69.92%.	[26]
	nZVI amendment	Microbial and enzyme stimulation	CW columns; PFOA: 1 mg/L	NH_4^+–N; TP under PFOA stress	Improved nutrient removal; enhanced substrate enzyme activity and EPS production.	[8]
	Chitosan–nano-FeS/peanut-shell biochar (CFP)	Electron donation; denitrification	VF-CW; Acorus calamus; 120 d	NH_4^+–N; NO_3^-–N; TN; Pb	Electron donation and enhanced microbial N removal; maximum TN removal: 54.23%.	[27]
	Starch–nano-FeS/peanut-shell biochar (SFSP)	Electron donation; denitrification	VF-CW; Iris pseudacorus; HRT: 72 h; SFSP: 40%	NH_4^+–N; NO_3^-–N; Pb	Electron-donor-supported denitrification; improved N removal under Pb stress.	[28]
	Alginate-immobilized biochar/nano-FeS	Electron donation; autotrophic denitrification	CW columns; 8–13 °C; composite dosage: 30%	NO_3^-–N; TN	Predominantly autotrophic denitrification; removal: NO_3^-–N 93.59%; TN 80.06%.	[29]
Metal Oxide NPs	ZnO-, CuO-, MgO- and MnO-coated biochar		VF-CW; pH: 6.9–7.4	Reactive Yellow 145	Enhanced dye removal; CuO/biochar performed best.	[30]
	Fe_3O_4/pumpkin biochar (PK400Bio/MAG)	Catalytic oxidation; adsorption; biodegradation	Solar-assisted vertical subsurface-flow CW; pH 6–7; H_2O_2	Procion Blue R: 50 mg/L	96–98% dye removal versus 70–75% in the conventional CW.	[31]

			30–40 mg/L; 35–40 °C			
Carbon-based NPs	Sr–TiO_2-coated porous ceramic media	UV photocatalysis	Unplanted VF-CW model; surface catalyst-media layer: ~1 cm; UV: 8–10 h/d; ~160 d	Organic matter; nutrients	UV-assisted photocatalysis; illuminated surface media.	[32]
	BC–$CaCO_3$/TiO_2	Adsorption/precipitation; pH buffering	CW columns; Typha latifolia and unplanted controls; synthetic acid mine drainage	Cu; Fe; Mn; Pb; Zn	pH buffering and metal retention; >99% Cu, Fe and Zn removal in the planted system.	[33]
Polymeric NPs	Biopolymer–AgNP-functionalized cork	Antibacterial activity	Material assay under simulated CW conditions	*E. coli*; *S. aureus*	Sustained antibacterial activity during a 5-day assay.	[34]

In recent years, such green-synthesized NPs have been increasingly integrated into CWs for pollutant remediation. Loading NPs onto porous supports such as biochar, or incorporating them into wetland substrates as composite media or surface coatings, can improve particle dispersion and facilitate pollutant removal through adsorption, redox reactions, and catalysis [35]. For example, nZVI donates electrons during oxidation, promoting the reductive transformation of contaminants. Under suitable reaction conditions, nZVI-based materials can also activate oxidants such as H_2O_2 to generate reactive species that promote organic contaminant degradation [36]. Luo et al. [26] incorporated zeolite-supported nZVI into CW substrates, achieving removal efficiencies of 66.42 ± 1.33%, 86.56 ± 0.93%, and 69.92 ± 0.56% for NO_3^--N, NH_4^+-N, and total nitrogen, respectively. TiO_2-modified media can likewise be incorporated into wetland substrate beds or immobilized on supports such as sand or biochar to combine pollutant adsorption with catalytic oxidation of organic contaminants [35].

TiO_2-modified media can be immobilized on supports such as sand or biochar. Overall, by enhancing pollutant removal efficiency, promoting plant biomass growth, and optimizing overall water/wastewater treatment processes, green nanotechnology may strengthen the environmental remediation capacity and sustainability of CWs [37]. Green-synthesized NPs combine catalytic, adsorptive, and antimicrobial properties with biocompatibility and sustainability, positioning them as promising candidates for advancing wastewater treatment in CWs.

4. Nanomaterials Effects on Wetland Plant Growth and Biomass Production

Nanomaterials have shown considerable potential in stimulating wetland plant growth and enhancing biomass accumulation [38]. Acting as novel nutrient carriers or growth stimulants, NPs can significantly improve the uptake efficiency of essential nutrients such as nitrogen and phosphorus by wetland plants [39]. On the one hand, NPs can promote the uptake, transport, and assimilation of nitrogen and phosphorus by modifying root architecture (increasing root length, root surface area, and root tip number), enhancing root and enzyme activities, and regulating the expression of nutrient transporter genes [40]. On the other hand, nanomaterials have the capacity to modulate rhizosphere microbial communities by stimulating beneficial microbial populations, which in turn promote plant metabolism and stress tolerance [41]. These responses may support that wetland plants exhibit accelerated growth and increased biomass production.

The elevated biomass not only strengthens ecosystem resilience but also expands the available surface area for pollutant adsorption and transformation, thereby enhancing the overall purification performance of CWs [42].

4.1. Targeted Impacts of Different Nanomaterial Classes

Different classes of nanomaterials exhibit distinct advantages in promoting plant growth and facilitating pollutant removal, as summarized in Table 3. Metal NPs (e.g., Ag, Au, Fe) can catalyze the degradation of organic contaminants while enhancing plant uptake of heavy metals [43]. Metal oxide NPs (such as TiO_2, ZnO, and Fe_3O_4) are particularly effective due to their catalytic and equilibrium properties, contributing both to pollutant degradation in aquatic systems and the regulation and buffering of the water environment [33,44]. Carbon-based nanomaterials, including fullerenes, carbon nanotubes, and GO, possess exceptionally high surface areas and strong adsorption capacities, enabling efficient sequestration of heavy metals and organic pollutants [45]. In contrast, polymer-based NPs can be engineered as delivery systems, providing targeted transport of nutrients or growth factors directly to the rhizosphere [37].

Table 3. Effects of different nanomaterials on plant growth.

Nanomaterial Type	Specific Effects on Plant Growth	Key Parameters Affected		References
Chitosan–nano-FeS/biochar composite	Alleviated Pb stress and supported Acorus calamus growth.	Plant growth and Pb-stress response	Vertical-flow CW microcosms; Acorus calamus; 120-day experiment; N/Pb-containing wastewater.	[27]
TiO_2 NPs	Prolonged exposure increased Phragmites australis photosynthesis, stomatal conductance, transpiration and root activity; system nitrogen removal nevertheless declined.	Photosynthesis, gas exchange and root activity	CW planted with Phragmites australis; TiO_2 exposure 1 and 50 mg/L; short- and long-term comparison.	[46]
Graphene oxide (GO)	At 20–140 mg/L, increased Iris pseudacorus dry biomass by 37–84% and pigment contents by 26–178%; 80 mg/L gave the strongest response.	Biomass, photosynthetic pigments, PSII performance and nutrient contents	Hydroponic experiment; Iris pseudacorus; GO 1, 20, 80 and 140 mg/L; 15 weeks.	[47]
Fe3O4 NPs	Bioaugmented Canna indica floating wetlands showed improved root/shoot growth relative to non-inoculated plants under ciprofloxacin stress.	Root/shoot length and dry biomass	Floating treatment wetland; Canna indica; 20-L tanks; ciprofloxacin 100 mg/L; 20-day batch experiment.	[48]
Carbon nanotubes (CNTs)	CNTs decreased biomass in some plant monocultures; species mixtures mitigated this inhibition, and mixtures including Arundo donax supported higher biomass	Plant biomass, species interaction and greenhouse-gas emissions	Vertical subsurface-flow CW microcosms; species included *Arundo donax*, *R. carnea*, T. *fluminensis* and *O. javanica*.	[49]

	and improved N/gas outcomes.			
Ag, TiO_2 and CeO_2 nanoparticles	AgNPs inhibited aquatic-plant photosynthesis and root activity; TiO_2 NPs enhanced photosynthesis and root activity after 60 d; CeO_2 effects shifted from positive at 5 d to negative at 60 d.	Photosynthesis, root activity, antioxidant enzymes, lipid peroxidation and C/N/P contents	Wetland-plant exposure experiment; AgNPs, TiO_2 NPs and CeO_2 NPs at 1 and 50 mg/L; 5- and 60-day exposures.	[46]

Among wetland plants, *Phragmites australis* (common reed) serves as a representative species [50]. Reeds not only directly assimilate nutrients (nitrogen and phosphorus) from wastewater but also provide a favorable rhizospheric environment for nitrification, denitrification, and organic matter degradation [51]. Moreover, their root systems exhibit strong accumulation capacities for heavy metals including cadmium, lead, copper, and chromium [52]. The application of nano-TiO_2 has been shown to further enhance the ecological functions of reeds by nearly doubling their biomass, thereby significantly improving pollutant removal and ecological restoration in both CWs and natural aquatic systems. Field experiments demonstrated that TiO_2 NP treatment increased reed biomass by 97.5%, plant height by 23.3%, and photosynthetic rate by 88.3% compared to controls [53]. The same study also reported that TiO_2 application suppressed weed growth, indirectly strengthening the competitive dominance of wetland plants.

4.2. Nanotechnology Enhanced Phytoremediation Pathways

Nanotechnology plays a pivotal role in enhancing plant functional performance [37]. As illustrated in Figure 2, nanomaterials contribute through multiple mechanisms. Firstly, they can adsorb environmental contaminants, thereby reducing phytotoxicity and mitigating risks to plant growth [54]. Secondly, their catalytic properties facilitate the accelerated breakdown of pollutants within plant tissues or wetland substrates, converting harmful substances into less toxic or innocuous forms [55]. In addition, nanomaterials can function as delivery systems, enabling the targeted transport of nutrients or growth-promoting compounds to the rhizosphere, thus improving nutrient uptake efficiency and stress tolerance. More importantly, nanotechnology can reinforce intrinsic phytoremediation pathways by promoting pollutant uptake through roots, accelerating enzymatic degradation of organic contaminants, enhancing the volatilization of certain compounds, or immobilizing pollutants within soils to restrict their diffusion and bioavailability.

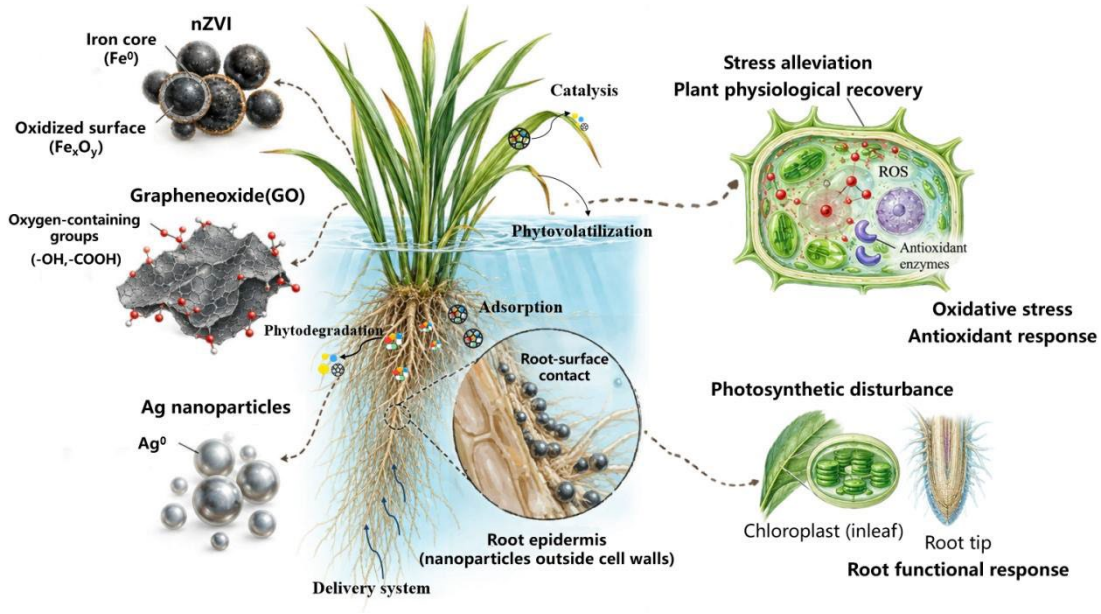


Figure 2. Schematic diagram of the effects of nanomaterials on wetland plant functions.

Nanotechnology acts through synergistic mechanisms that not only increase the efficiency of plant-based remediation but also extend its applicability in CW systems. Recent studies further highlight that some metal oxide NPs, such as ZnO, can supply zinc, an essential micronutrient, whereas silver-based materials can exert antimicrobial effects; this response establishes a net benefit to wetland plants, thereby promoting both plant health and productivity [56]. For instance, ZnO NPs markedly improved early-stage rice growth under salt stress: treatment with 50 mg/L ZnO enhanced germination rates, seedling development, photosynthetic pigment levels, and antioxidant enzyme activities [57]. Similarly, Ag NPs have been shown to stimulate seed germination and increase yields of both crops and wetland macrophytes [56]. Collectively, these findings demonstrate that selected nanomaterials may influence wetland plant growth and biomass accumulation by enhancing root architecture, nutrient transfer, and stress resilience.

5. Application of Green Nanomaterials in Substrate Optimization of CWs

Integrating nanomaterials into CW substrates has emerged as a promising approach to enhance the treatment efficiency of CWs. Due to their high surface-to-volume ratio and unique surface chemistry, NPs may modify substrate surface properties and promote the attachment and proliferation of functional microbial communities, and thereby significantly strengthen pollutant removal performance [58]. Fe_3O_4 NPs, nZVI, and their supported composites have been used to modify CW substrates, showing potential to enhance the removal of nitrogen, phosphorus, and selected emerging contaminants [59], as illustrated in Figure 3.

For instance, the incorporation of magnetic Fe_3O_4 NPs into CW substrates can increase the available reactive surface area, providing a favorable habitat for microbial colonization and consequently enhancing the degradation of organic matter as well as nitrogen and phosphorus pollutants [60]. Experimental studies have shown that adding Fe_3O_4 NPs to CWs increases the removal efficiencies of ammonium nitrogen, nitrate nitrogen, and total phosphorus to 95.9%, 83.8%, and 90.4%, respectively, which are substantially higher than those observed in unmodified systems [60]. CWs incorporating zeolite-supported nZVI achieved removal efficiencies for NO_3^--N, NH_4^+-N, and TN that

exceeded those of conventional gravel-based systems by 40.77, 18.34, and 35.73 percentage points, respectively [26]. Beyond conventional pollutants, iron-based nanomaterials show potential for controlling emerging biological contaminants such as ARGs. Lu et al. [61] demonstrated that nZVI bound ARG-bearing plasmid DNA through Fe–O–P coordination, with an adsorption capacity of 4.29 $mg \cdot g^{-1}$. DNA recovered by desorption was fragmented, indicating that nZVI-mediated removal involved structural damage in addition to adsorption. Furthermore, a 56-day landfill leachate exposure experiment showed that nZVI decreased ARG abundance, primarily in association with a reduction in mobile genetic elements (MGEs) [62].

In addition, nano-sized iron oxide particles (n-Fe_2O_3) have been reported to stabilize the Anammox process under near-anaerobic conditions by generating ROS, thereby further improving system efficiency [63]. In addition to directly contributing to pollutant removal through adsorption, complexation, precipitation, and redox reactions, nanomaterials can alter electron transfer at the substrate–biofilm interface, EPS secretion, and functional microbial community composition [26]. For instance, iron-based nanomaterials stimulate microbial activity and EPS production by improving energy availability and metabolic activity. In oligotrophic water, silica-coated nZVI increased ATP levels and nitrate/nitrite reductase activities, suggesting enhanced energy supply and denitrifying metabolism that support EPS biosynthesis and secretion [64]. Meanwhile, Fe^0 oxidation and Fe^{2+}/Fe^{3+} interconversion may facilitate interfacial electron transfer. Consistently, Fe^0-driven denitrification studies show that corrosion-derived Fe^{2+} and Fe^{3+} stimulate EPS formation, while EPS itself may contribute to electron mediation [65]. On the other hand, nZVI generates Fe^{2+} and H_2O_2 that participate in surface-associated Fenton reactions, with ROS production influenced by pH and iron-complexing ligands through their effects on iron availability and reactivity [66]. They can also influence wetland plant physiology, thereby affecting overall treatment performance [67].

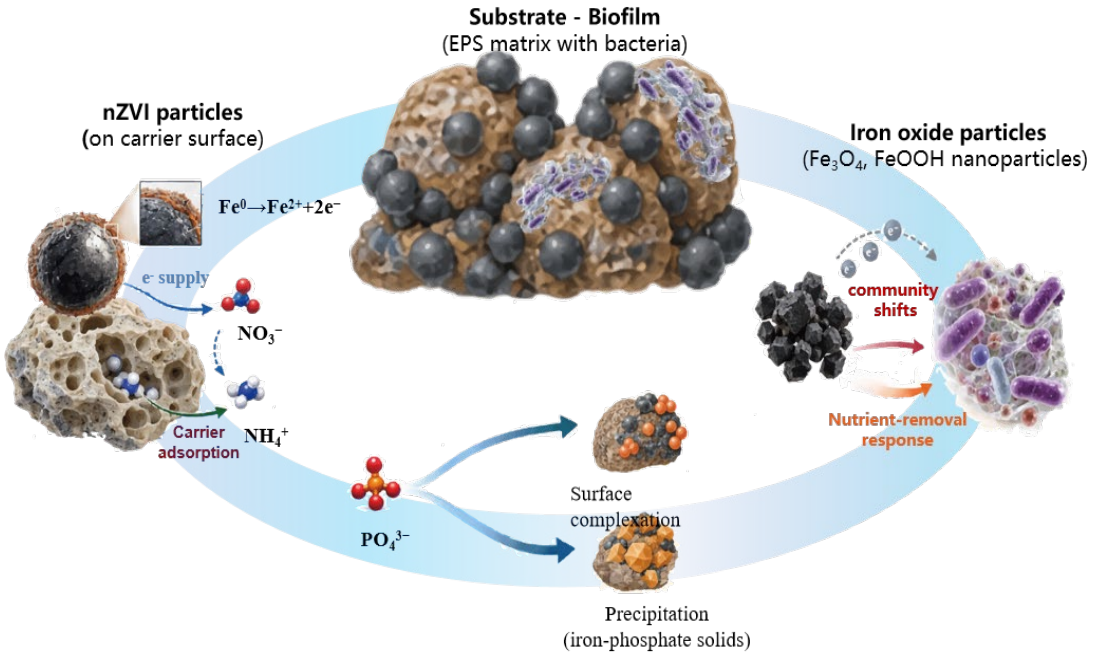


Figure 3. Iron-based nanomaterials act on CW substrate to promote nitrogen conversion and phosphorus fixation.

In addition to metal oxides, carbon-based nanomaterials have also demonstrated remarkable performance in CW substrate modification. Graphene, carbon nanotubes, and biochar-based materials possess excellent adsorption capacities, efficiently capturing

organic pollutants while providing electron transfer pathways for electroactive microbes, thereby enhancing denitrification and phosphorus removal [68]. For example, composites of biochar with semiconductor NPs such as TiO_2 or ZnO not only retain the high porosity of biochar but also exhibit catalytic activity, facilitating the degradation of recalcitrant organic compounds via catalytic oxidation, Fenton-like reactions, and electron transfer processes [69]. ZnO/biochar composites show enhanced adsorption affinity due to surface functional groups, whereas Fe_3O_4/biochar composites combine efficient adsorption with magnetic separability, offering potential for recovery and recycling. In addition, the applications of carbon-based nanomaterials extend to ARG control. Xu et al. [70] demonstrated that GO interacted with plasmid DNA, disrupted base stacking and double-helical structure, and inhibited extracellular ARG transformation. Specifically, GO with a lateral area of 0.08 μm^2 inhibited *aphA* transformation by approximately 50% at 25 $\mu g \cdot mL^{-1}$. In addition, Zhong et al. [71] achieved a 4.3-log_{10} reduction in antibiotic-resistant bacteria in real wastewater effluent using graphitic carbon nitride (g-C_3N_4) under simulated solar irradiation for 60 min, accompanied by extracellular ARG damage and decreased abundance. Nanotechnology enhances the capacity of CWs to control emerging biological contaminants through the complementary mechanisms of interfacial DNA fragmentation and inhibition of horizontal gene transfer (HGT) [72].

The contaminant removal mechanisms of these nanomaterial-modified composites typically involve ion exchange, electrostatic interactions, π–π stacking, electron transfer, inner-sphere complexation, oxidation reactions, and hydrophobic interactions [73]. These mechanisms are illustrated in Figure 4. For instance, the incorporation of TiO_2 into biochar can enhance the adsorption capacity and mineralization rate of sulfamethoxazole, with degradation efficiencies maintained at 90–92% [74]. Similarly, ZnO/biochar and Fe_3O_4/biochar composites further improve the removal efficiencies of organic pollutants, anions, and heavy metals by optimizing the materials' porosity and surface charge characteristics [75].

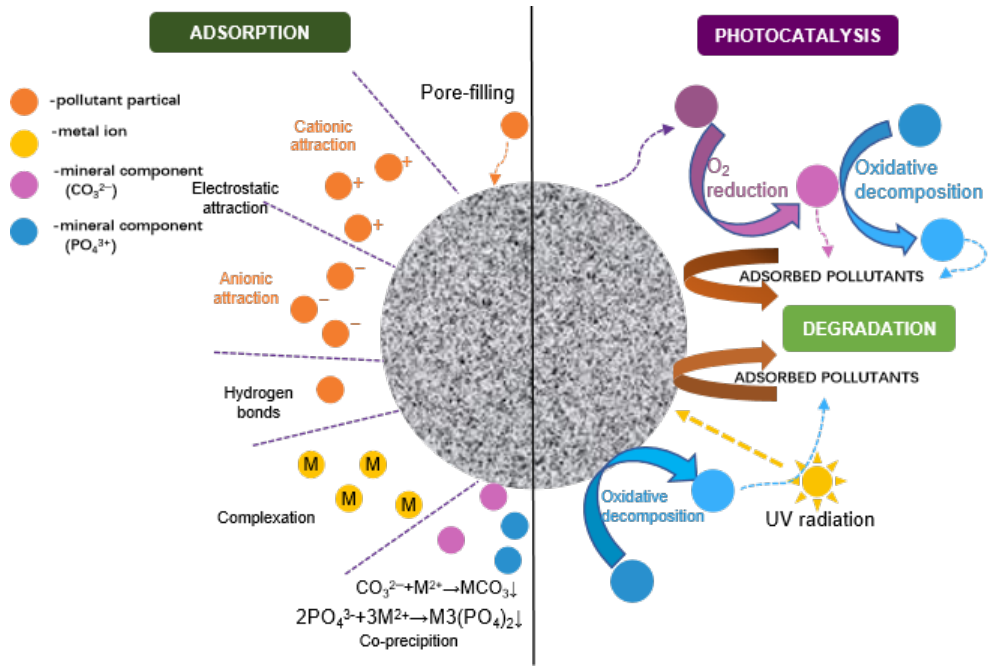


Figure 4. Nanocomposites act on CWs substrate to promote contaminant removal.

Notably, the effects of nanomaterials in CWs are strongly dose- and exposure-dependent. At appropriate doses, iron-based NPs may enhance electron transfer, enzyme activities, and the abundance of nitrogen- and phosphorus-transforming microorganisms.

In contrast, excessive or prolonged exposure may cause particle aggregation, metal-ion release, oxidative stress, and inhibition of functional genes [76]. Therefore, NP dosage should be regarded as an operational variable rather than merely a material property, and future applications require a careful balance between maximizing treatment efficiency and ensuring ecological safety.

Beyond optimizing dosage, the application of nanomaterial-modified substrates at larger scales requires evaluating their performance under the hydraulic and mass-transfer conditions of full-scale CWs. Wetland studies have shown that flow velocity and solute exchange between mobile and immobile regions influence removal kinetics and pollutant residence times [77,78]. These findings suggest that preferential flow and limited water exchange in larger beds may reduce effective contact with modified media, while diffusion resistance within carrier pores may limit access to internal reactive sites. Increasing nanomaterial loading may therefore not yield proportional gains in treatment capacity. Future studies should compare identical modified media at laboratory and pilot scales to determine how feeding patterns and media placement affect residence-time distributions and pollutant breakthrough, thereby informing full-scale design.

6. Enhancement of CWs as Green Infrastructure Through Nanomaterials Synergy

CWs serve as a critical component of urban green infrastructure, contributing to stormwater management, water/wastewater treatment, ecological restoration, resource recycling, and carbon sequestration, with their potential being increasingly enhanced through the integration of green nanotechnology [79].

6.1. Stormwater Management and Ecological Restoration

In urban stormwater management, CWs mitigate flood risks by storing runoff, attenuating peak flows, and filtering sediments and pollutants through vegetation and sedimentation processes [80]. The incorporation of functional nanomaterials, such as metal oxides, into wetland substrates can further enhance adsorption capacity and structural resilience, ensuring sustained treatment efficiency during peak runoff events. Additionally, coating substrates with catalytic nanofilms (e.g., TiO_2 NPs) may enable the degradation of recalcitrant organic pollutants, achieving a synergistic effect between physical and chemical treatment processes and offering potential for water quality improvement.

Beyond stormwater management, CWs play an indispensable role in ecological restoration and biodiversity conservation. The dense vegetation and aquatic habitats within CWs provide essential refuges for wildlife, thereby promoting biodiversity, and form integral components of urban ecological corridors that attenuate runoff peaks while offering recreational spaces for the public [81]. The integration of nanotechnology can further enhance dissolved oxygen levels, mitigate eutrophication, and improve the functional performance of microbial communities, thereby strengthening ecological stability and biodiversity services. In this context, nanomaterials function not only as tools for pollutant regulation but also as key agents for overall ecosystem improvement.

It is well known that CWs have been widely applied worldwide for various wastewater treatments, such as chemical oxygen demand, organic matter, nitrogen, phosphorus, and heavy metals, exhibiting remarkable purification performance. Specifically, well-designed CW systems can achieve average removal efficiencies of over 80–90% for TN and TP [82]. Meanwhile, with the increasing complexity of aquatic pollution, emerging contaminants such as antibiotics, organic micropollutants, ARGs, and persistent pollutants (e.g., Perfluoroalkyl & Polyfluoroalkyl Substances, PFAS) have

become major environmental concerns. Studies have shown that in some highly efficient CW systems, the removal efficiencies for 14 types of antibiotics and 60 types of organic micropollutants can exceed 90%, while the removal of PFAS can reach 39–97% or even higher through the incorporation of modified substrate systems [83]. During these processes, nanomaterials—such as Fe_3O_4 NPs and metal-based composites—have demonstrated the capacity to significantly enhance nutrient (N and P) removal by increasing the specific surface area and providing additional reactive sites [60]. They also facilitate chemical transformation and reduction reactions, thereby improving the operational resilience and purification efficiency of CW systems through substrate modification. As a result, the integration of nanomaterials into CWs can boost treatment performance and enhance the economic feasibility and practical applicability of the system.

6.2. Potential for Resource Recovery and Greenhouse Gas Mitigation

CWs can support resource recovery through the integrated reuse of treated water, plant biomass, and nutrients. Treated effluent can be reused for irrigation or ecological replenishment, while harvested plants can be converted into organic fertilizers, soil amendments, biochar, or bioenergy. Plant biomass valorization has been reported to reduce system environmental impacts and operating costs by approximately 85% and 65%, respectively. Anaerobic digestion followed by pyrolysis of wetland plants can also produce phosphorus-rich biochar containing 19.52–27.53 mg $P \cdot g^{-1}$ [52]. Magnetic nanocomposites offer potential for enhanced nutrient adsorption and subsequent recovery by magnetic separation. Fe_3O_4, nZVI iron, and Fe(II)/Fe(III)-modified carbonaceous materials can enhance phosphorus capture through surface complexation, electrostatic adsorption, and Fe–P precipitation, depending on material properties and reaction conditions. For example, Fe(II)/Fe(III)-modified biochar derived from emergent plant residues supported Fe_3O_4 and FeO(OH), exhibiting enhanced phosphorus adsorption and magnetic separability [84]. Converting plant residues into magnetic phosphorus sorbents, followed by separation, regeneration, or fertilizer use of phosphorus-loaded materials, could therefore link biomass management with phosphorus removal and nutrient recovery in CWs. Nevertheless, harvested biomass should be assessed for the accumulation of metal ions or nanoparticles prior to resource recovery. Increased biomass alone does not establish whether nanoparticles have accumulated in plant tissues or whether the harvested material is safe for reuse. Where accumulation is detected, its suitability for reuse should be evaluated based on contaminant concentrations and forms, potential release during processing and use, and the intended recovery pathway.

Nanomaterial amendments have shown potential for mitigating greenhouse gas emissions from CWs by regulating microbial carbon and nitrogen transformations. Bi et al. [85] reported that adding 1% and 2% biochar-supported nZVI reduced mean CH_4 emission fluxes by 59.8% and 35.6%, respectively, relative to gravel controls, with the reductions associated with enhanced methane oxidation. Furthermore, Kong et al. [86] found that biochar-supported sulfidated nanoscale zero-valent iron (S-nZVI/BC) achieved nitrate removal efficiencies of up to 100% while reducing N_2O emission fluxes by 24.17–36.63%. These findings demonstrate that nanomaterials have potential to mitigate greenhouse gas emissions and regulate carbon and nitrogen cycling in CWs, offering practical benefits for urban low-carbon strategies.

In summary, the integration of CWs with green nanotechnology may influence multiple ecosystem services, including stormwater regulation, water quality improvement, ecological restoration, resource recovery, and greenhouse gas mitigation. Such integration transforms CWs from single-function pollutant control units into

multifunctional ecological platforms. Through careful design and scientific management, CWs are poised to play an increasingly prominent role within future urban green infrastructure networks.

7. Challenges and Future Trends

7.1. Environmental Fate and Long-Term Stability Risks of Nps

Although green nanotechnology offers numerous advantages for CWs, its long-term stability and ecological safety require thorough evaluation. Several studies have reported short-term improvements in pollutant removal after NP addition; evidence for sustained performance remains limited. Long-term application may result in NP aggregation, surface passivation, pore blockage, loss of catalytic activity, and saturation of adsorption sites. These changes can progressively reduce treatment performance and may increase the risk of particle or metal-ion release. Yang et al. [87] reported that long-term exposure to TiO_2 NPs reduced nitrogen removal efficiency in CWs systems by 35–51% and disrupted the expression of nitrogen metabolism-related genes. Ag NPs exposed for 450 days in plant roots and topsoil were found to impair photosynthetic activity, root functionality, and biofilm metabolic performance [12]. Yan et al. [13] conducted a 120-day GO exposure experiment in CWs planted with *Iris pseudacorus*. At concentrations of 0.5 and 5 $mg \cdot L^{-1}$, GO was effectively retained by biofilms but underwent limited biodegradation. Exposure was also associated with oxidative stress in plants and reduced nitrogen removal performance [13].

Similarly, carbon-based NPs can accumulate in organisms and mammalian tissues, exerting ecotoxicological effects such as oxidative stress, DNA damage, immune modulation, and shifts in community composition [88]. Algae and crustaceans are particularly sensitive to metal oxide NPs, including TiO_2, ZnO, and CuO [89]. Nevertheless, some studies suggest that at current environmental concentrations, most engineered NPs are unlikely to cause significant ecological harm. Given the limited available data and the challenges of characterizing NP behavior in complex environmental matrices, further investigation of their transport, transformation, and mechanisms of toxicity in wetlands is essential for identifying and mitigating potential ecological risks.

7.2. Safety Management Frameworks and Regulatory Standards

With the evolution of industrial practices, the emergence of novel contaminants has posed increasing challenges for wetland remediation. Catalytic NPs (e.g., TiO_2) have demonstrated the capability to degrade such recalcitrant pollutants; however, their extensive application underscores the urgent need for long-term safety assessment and regulatory oversight [90]. The widespread use of nanomaterials further highlights the necessity of establishing robust safety evaluation frameworks. Current regulatory systems are often adapted from conventional particulate standards and lack specific criteria and risk assessment methods tailored to the unique properties of NPs [91].

In the European Union, the European Commission adopted Regulation (EU) 2018/1881 on 3 December 2018, introducing Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) requirements for nanoform characterization and chemical safety assessment, applicable since 1 January 2020. In the United States, the Environmental Protection Agency established reporting and recordkeeping requirements for certain nanoscale chemical substances under Section 8(a) of the Toxic Substances Control Act (TSCA) in 2017. Covered manufacturers and processors are required to report chemical identity, production volume, manufacturing and processing methods, exposure and release information, and available health and environmental effects information.

For environmental testing, the Organisation for Economic Co-operation and Development (OECD) published Test No. 318: Dispersion Stability of Nanomaterials in Simulated Environmental Media in 2017 and the Guidance Document for the Testing of Dissolution and Dispersion Stability of Nanomaterials, and the Use of the Data for Further Environmental Testing and Assessment in 2020. These documents support evaluation of particle behavior but do not establish CW-specific safe doses.

Beyond material safety assessment, particle release and dissolution from metal-containing nanomaterials also raise effluent-management concerns during CW operation. Where released metals are regulated by local discharge standards or permits, the corresponding requirements apply. The US EPA's 1996 guidance, The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion, explains the conversion of dissolved-metal water-quality criteria into total recoverable metal permit limits but is not specific to nanomaterials. Compliance with applicable metal limits therefore does not, by itself, establish nanoparticle ecological safety. Therefore, this review recommends evaluating nanoparticle release, dissolution, and biological effects under actual CW operating conditions to inform safety management frameworks and regulatory standards.

7.3. Economic Feasibility and Life Cycle Assessment

Beyond safety considerations, the cost-effectiveness of nanomaterials is a critical factor for their large-scale application. The synthesis, dispersion, and recovery of nanomaterials require additional investment, necessitating comprehensive economic evaluations. Life cycle assessments (LCAs) can quantify the environmental impacts associated with substrate sourcing, processing, use, and disposal, particularly for materials intended for large-scale or long-term application in CWs.

The synthesis route can substantially affect the production cost and environmental impacts of nanomaterials. Martins et al. [92] reported that plant-extract synthesis reduced the estimated production cost of nZVI from €0.95 to €0.11 per gram compared with sodium borohydride synthesis. Under the Portuguese electricity scenario, the plant-extract route also achieved an approximately 50% lower aggregate LCA impact score covering human health, ecosystem quality, climate change, and resource consumption. Similarly, Patiño-Ruiz et al. [93] reported lower assessed environmental impacts for plant-extract synthesis of iron oxide nanoparticles than for coprecipitation, including global warming potential and freshwater ecotoxicity, although ethanol and electricity use remained important contributors. For CW applications, production-stage comparisons should be extended to an equivalent treatment service, such as a defined wastewater volume treated to the same effluent target over a specified operating period. Future research should focus on optimizing the economic feasibility of nanomaterial production and application, aiming to achieve high-efficiency, low-cost operation of CWs without compromising environmental safety.

7.4. Intelligent Monitoring and Smart-Responsive Management Systems

The research trends are moving toward smart-responsive and multifunctional nanomaterials, such as composite structures integrating adsorption, catalysis, and sensing functionalities [94]. Simultaneously, the integration of advanced sensing and information technologies could enable real-time monitoring and precise management of nanomaterials within CW systems. At the policy level, the establishment of standards and environmental monitoring frameworks is essential to balance risks and benefits and to support the sustainable application of green nanotechnology in wetlands.

8. Conclusions

Nanomaterials can enhance CW treatment through complementary physicochemical and biological pathways. Iron-based materials support nitrogen transformation through electron supply and interfacial electron transfer while retaining phosphate through complexation and precipitation. Supported nanocomposites combine adsorption and catalytic functions with biofilm development, but their treatment benefits depend on microbial and plant responses. Experimental evidence of greenhouse gas mitigation, together with potential benefits for stormwater management and resource recovery, extends the value of nanomaterials in CWs beyond pollutant removal. Material aging, prolonged exposure, or particle release may compromise initial gains. Future studies should prioritize long-term operation under realistic wastewater conditions, jointly assessing treatment performance, biological compatibility, material fate, and greenhouse gas emissions. Life cycle and economic assessments are needed to determine whether these improvements justify the additional material and operational inputs.

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