Review

Particularities of Fungicides and Factors Affecting Their Fate and Removal Efficacy: A Review

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Abstract: Systemic fungicide use has increased over the last decades, despite the susceptibility of resistance development and the side effects to human health and the environment. Although herbicides and insecticides are detected more frequently in environmental samples, there are many fungicides that have the ability to enter water bodies due to their physicochemical properties and their increasing use. Key factors affecting fungicide fate in the environment have been discussed, including the non-target effects of fungicides. For instance, fungicides are associated with the steep decline in bumblebee populations. Secondary actions of certain fungicides on plants have also been reported recently. In addition, the use of alternative eco-friendly disease management approaches has been described. Constructed Wetlands (CWs) comprise an environmentally friendly, low cost, and efficient fungicide remediation technique. Fungicide removal within CWs is dependent on plant uptake and metabolism, absorption in porous media and soil, hydrolysis, photodegradation, and biodegradation. Factors related to the efficacy of CWs on the removal of fungicides, such as the type of CW, plant species, and the physicochemical parameters of fungicides, are also discussed in this paper. There are low-environmental-risk fungicides, phytohormones and other compounds, which could improve the removal performance of CW vegetation. In addition, specific parameters such as the multiple modes of action of fungicides, side effects on substrate microbial communities and endophytes, and plant physiological response were also studied. Prospects and challenges for future research are suggested under the prism of reducing the risk related to fungicides and enhancing CW performance.

Keywords: constructed wetlands; fungicides; water contamination; plant physiological responses; microbiome

1. Introduction

Fungi pathogens can cause significant crop losses and consequently an essential reduction in the global food supply. Grains, fruits, and vegetables are amongst the crops demanding extensive use of fungicides during the growing season in order to be protected from diseases [1]. Furthermore, their application is very common in postharvest packaging plants, parks located in urban areas, and protected forest areas. Fungicide use has increased rapidly over the last decade. Approximately four hundred thousand tons of fungicides are applied globally, which represents 17.5% of global pesticide applications [2]. However, fungicide sales exceed 40% of the total pesticide sales in the European Union; the sales of inorganic fungicides comprise 54%, and organic ones 46%, of which 14.1% are (dithio)carbamates, 6.7% imidazoles and triazoles, 1.3% benzimidazoles, 0.8% morpholines, and 23.1% other fungicides and bactericides [3].

Fungicides can enter natural waters through agricultural wastewater from washing or loading of spraying equipment, leaks occurring due to improper maintenance of empty

containers (point source pollution), and diffusion through run-off, spraying drift, leaching, and subsurface drainage [1].

Fungicides include a broad range of compounds with different modes of action belonging to various chemical classes. Acute and/or chronic toxicity of organic fungicides to aquatic or terrestrial organisms have been reported in many studies. The extensive use of chemical pesticides in agriculture also raises concerns for public health. Exposure experiments in rats showed endocrine-disrupting, biochemical, histopathological, and hematological effects [4]. Several fungicides are characterized as hazardous chemicals by the World Health Organization (WHO) and are banned in the European Union.

Several factors, such as intensive farming, resistance management, market needs, new diseases, phytotoxicity, and safety to humans and other organisms, drive companies to invest heavily in innovative fungicide formulations. Therefore, the registration of new fungicides is constant, and the addition of innovative characteristics such as systemicity, persistent activity, low resistance development risk, and public health and environmental safety, is necessary. Some fungicides can also act against fungi, indirectly influencing positively the host plant physiological responses.

The introduction of alternative organic fungicide formulations promises various advantages, such as higher efficacy and lower risk for pathogens to develop resistance to fungicides. Disease management has improved due to the recent introduction of nanoscience and the development of nanofungicides. The main advantages of these nanometer particle sized formulations are the lower application dose of active ingredients, higher effectiveness, pathogen target specificity, and lower distribution to the environment [5]. However, nanofungicides can cause side effects on non-target organisms, and remediation techniques have not been developed, as nanofungicides' environmental fate has not been studied at a large scale [6]. Another recent advance in disease management is the introduction of chiral fungicides; however, both the European Commission and the United States Environmental Protection Agency (US EPA) point out that crucial information gaps exist in their environmental risk assessment [7]. The more recent use of chemical plant defense or resistance activators is another plant antifungal approach based on plant immunity activation rather than targeting the fungi directly [8].

Biofungicides are proposed as another alternative environmentally friendly, non-chemical approach to plant disease control, avoiding many of the associated side effects [9]. Biofungicides consist of two groups: microorganism-based pesticides (microbial fungicides) and plant extracts or plant-based-product pesticides (biochemical fungicides). Both of these groups can successfully manage various pathogen species, such as Botrytis spp., Sclerotinia sclerotiorum, Monilinia spp., and Phytophthora spp. [10,11]. Biofungicides are reported as eco-friendly compounds that do not present phytotoxic and other adverse effects. Their antifungal effectiveness depends on interactions with the host plants [12]. Another low environmental risk strategy is the use of chelating agents, which are known as fertilizer products; they can increase the bioavailability of fungicides to pathogens. Recent studies indicate that chelation is a promising tool for disease management [13,14].

The development of novel fungicides is dynamic. As a result, new prospects and challenges have arisen regarding their environmental fate and removal from contaminated systems by remediation techniques such as constructed wetlands (CWs). Various researchers have reported that CWs can effectively manage pesticide contamination, including fungicides [15–17]. Pesticide fate in the CW environment is a result of different natural processes such as biodegradation, hydrolysis, photolysis, adsorption, plant uptake, and sedimentation. The efficiency of CWs on fungicide removal depends on the physicochemical properties of the target compound, such as the half-life in water and soil (DT50), the affinity of fungicides to organic carbon Koc, octanol/water partition coefficient (Kow), and water solubility. Plant species, hydraulic retention time, vegetation mass, hydraulic loading rate, microbial biofilm, and porous composition can be classified as the key CW characteristics that can determine their efficiency [18–20]. However, CW system performance can be limited by low plant uptake and the inhibition of microbial activity. There is recent evidence

that favors the induction of microorganisms to a CW system. The bioaugmentation of CWs is a recent regulation strategy for enriching or protecting microbial activity and enhancing plant metabolism functions against xenobiotics [17,19].

Studies on fungicides' environmental fate and ecological risk assessments for the non-target organisms are not as extensive as for herbicides and insecticides. As a result, researchers underestimate the remediation strategies related to fungicide removal. In the last decade, several review studies have described the environmental fate and the side-effects on non-target organisms caused by conventional fungicide use, while novel fungicides, such as nanofungicides and chiral fungicides, have not been thoroughly investigated. Furthermore, the recent introduction of plant metabolism boosters in the agricultural sector, for instance biofungicides and exogenous phytohormones, gives insights into their possible utilization in CWs to improve the removal performance and their interactions between them and CW biological parameters. Consequently, the aim of this study is to point out possible research gaps or underreported issues in environmental risk assessments and the respective mitigation attempts using CWs. Additionally, this study aims to highlight potential CW strategies for fungicide removal, focusing on interactions between CW plants and microorganisms and fungicide exposure.

2. Environmental Fate and Risk of Chemical Fungicides

2.1. Inorganic Fungicides

The most studied and used inorganic fungicides are copper and sulfur. Copper and sulfur are presented in numerous forms and are applied in various crops to control important foliar fruit diseases. Various copper and sulfur formulations for organic farming have been authorized by the European Union. Following their biogeochemical cycle, inorganic fungicides can run off to surface water and be adsorbed in the soil and sediments. Copper and sulfur are important trace metals for organisms' fundamental functions, yet large concentrations can be harmful [21].

When copper oxide is dissolved in water, the dominant and biocidal oxidation ion is Cu^{2+} [22]. Acidity and salinity play an important role in aquatic biota toxicity. High pH values result in a reduction of available hydrogen ions, which leads to copper toxicity. Therefore, copper ions can be attached at aquatic organisms' cells. Other physicochemical factors that influence the toxicity levels are the dissolved organic matter and dissolved water organic carbon content [21,23]. As Beck and Saundo-Wilhelmy [24] have reported, the tendency of sediments to adsorb heavy metals is high, and thus sediments can facilitate the availability of toxic chemicals in the water and aquatic organisms. Some species have a high level of sensitivity to copper, whereas others can efficiently overcome it. Copper is bioaccumulated in fish, decapod crustaceans, and algae and stored in bivalves, barnacles, and aquatic insects. The most sensitive species to copper exposure are cyanobacteria, while coccolithophores and dinoflagellates have a lower sensitivity to copper, and diatoms present resistance to copper [25].

Copper cannot be degraded in soil but can be accumulated through copper-based degradation compounds occurring in different forms. Copper's mobility in the soil profile is characterized as medium to low. A recent study reported that the high concentrations of copper in vineyards soils and groundwater was caused mainly by copper-based fungicide use, negatively affecting water quality and food safety [26]. Copper residues in soil could cause toxic effects on macro- and microorganisms, adversely influencing the various beneficial interactions in soil, such as pesticide biodegradation, soil structure, nutrition availability for plants, and pathogen resistance [27]. Element copper is able to cause toxicity to beneficial bacteria and fungi in the environment [28]. Diaz-Ravina et al. [29] reported that the microbiocidal activity in vineyard soil can be significantly reduced by high application rates and prolonged use of copper-based pesticides. For instance, high-dose application of Cu-based pesticides can have negative effects on arbuscular mycorrhiza fungi (AMF) [30]. Schoffer et al. [31] reported that copper soil pollution is more common in countries or

regions that have not enacted regulations for copper-based pesticides applications, which consequently follow only commercial formulation guidelines.

Sulfur can be found in various forms in the environment, such as gas (i.e., SO_3) and salt (i.e., $MgSO_4$), which are created through bacterial physiological processes. In sediments and soils, sulfur can be found as a trace element or in an inorganic form. Sulfur can cause toxicity to bacteria and fungi that are beneficial to the environment, which are not considered as crop pests. In addition, studies indicate that sulfur can be phytotoxic to some plants, such as cucurbits, apricots, and raspberries [32,33]. Kuklinska et al. [28] also reported that *Vibrio fischeri* is sensitive to sulfur exposure. The available information regarding sulfur interaction with organisms, its toxicity threshold, and its environmental fate is limited compared to copper.

2.2. Organic Fungicides

The environmental fate of organic fungicides (Table 1) depends on various physico-chemical parameters, such as ionization (pk_a), water solubility, volatility, K_{ow}, and half-life in soil and water (DT_{50}). Soil texture, organic carbon content, pH, clay mineral type, dissolved organic matter, and cation exchange capacity also play an essential role in the environmental fate of fungicides, defining processes such as run-off to surface water, adsorption, or leaching. In addition, rainfall, irrigation, microbiological degradation, hydrolysis, photolysis, and application rate could affect fungicide fate [34,35].

Table 1. List of common chemical fungicides [36,37].

Chemical Family	Group Name	Active Substances	Target Site	Mode of Action
Acylalanines	Phenyl Amides (PA)	metalaxyl	RNA polymerase I	Disruption of nucleic acid synthesis-RNA polymerase 1
Thiophanates	Methyl Benzimidazole Carbamates (MBC)	thiophanate	protein B1: ß-tubuline assembly in mitosis	Inhibition of mitosis and cell division (Beta-tubulin assembly in mitosis)
Pyridine-carboxamides	Succinate-dehydrogenase inhibitors (SDHI)	boscalid	complex II: succinate-dehydrogenase	Inhibition of mitochondrial ATP production in fungal cells
Pyridinyl-ethyl-benzamides	Succinate-dehydrogenase inhibitors (SDHI)	fluopyram	complex II: succinate-dehydrogenase	Succinate dehydrogenase inhibition within mitochondria blocking electron transport
Methoxy-carbamates	Quinone outside Inhibitors (QoI)	pyraclostrobin	complex III: cytochrome bc1	Respiration inhibitor of QoI
Dicarboximides	dicarboximides	iprodione	MAP/Histidine-Kinase in osmotic signal transduction	Signal transduction inhibitor
Triazoles	De-Methylation Inhibitors (DMI)	tebuconazole	C14- demethylase in sterol biosynthesis	Sterol 14-demethylase enzyme inhibition in membranes
Ethyl phosphonates	phosphonates	fosetyl-Al	phosphonates	Mycelial growth and spore production—Plant's defense elicitor
Dithio-carbamates and relatives	dithio-carbamates and relatives	mancozeb	multi-site contact activity	Chemicals with multi-site activity

Fungicide residues in surface water (e.g., streams, lakes, rivers) and groundwater have been detected by many monitoring studies worldwide. The majority of these studies were focused on a few fungicides of local importance. The extensive (multiple applications and high doses) use of fungicides in specific crops (e.g., vineyards, horticulture, orchards, etc.) can lead to pollution of nearby natural waters from fungicide residues. Hence, the spatial and temporal distribution of fungicide residues in surface waters varies throughout the year and amongst agroecosystem compartments. Usually, the highest concentrations of curative fungicides are detected during growing or preharvest seasons, whereas preventative fungicides are found at early plant growth stages and during the winter period. Regions planted with grape and tree crops have received high application doses of fungicides, resulting in high detection frequency and high concentrations of fungicides in the ecosystems [1,38].

The presence of various pesticides has been investigated in vineyard groundwater bodies in northern Italy. The environmental quality standard set by the EU (0.1 µg/L) was exceeded by five fungicides (metalaxyl–M, fluopicolide, penconazole, tetraconazole, and dimetomorph), presenting significantly high concentrations. The maximum concentrations of metalaxyl–M and penconazole were 8.015 µg/L and 18.72 µg/L, respectively [35]. In addition, a similar monitoring study was conducted in Spanish vineyards, where the detection frequency of metalaxyl, dimethomorph, and penconazole reached 50%. Moreover, the highest concentration was observed for same fungicides (metalaxyl and penconazole) [39]. These results indicate that the extensive use of fungicides in vineyards can cause an essential surface and groundwater pollution.

Papadakis et al. [34] conducted a pesticide monitoring study in two river basins in North Greece, with corn, cotton and cereals as the main crops, over a two-year period. Twenty-nine fungicides were detected at least once, while multiple detections (7 to 10 times) of boscalid, diphenylamine, etridiazole, and hexachlorobenzene were also observed. Extremely high concentrations for seven fungicides (azoxystrobin, diphenylamine, etridiazole, propiconazole, tebuconazole, quintozene, and difenoconazole), ranging from 0.153 to 0.819 µg/L, were identified. In the worst-case scenario, the risk quotient index was higher than one for four fungicides. The results showed that fungicides contribute to ecotoxicological risk for river basins.

The presence of 24 fungicides was investigated in the surface water and sediments of a horticulture area in Australia. The agricultural activity of the studied area included tree fruits, bulbs, vineyards, vegetables, and herbs. Although the authors reported that the individual fungicide residues did not pose environmental risks, due to low ecotoxicological endpoints, several fungicides were detected in concentrations above 0.2 µg/L (iprodione, myclobutanil, pyrimethanil, cyproconazole, trifloxystrobin, and fenarimol) and others had a detection frequency ranging between 18 and 36% (myclobutanil, trifloxystrobin, pyrimethanil, difenoconazole, and metalaxyl). The temporal distribution of residues was affected by the chemical class of the fungicides. Preventing fungicides were detected across the whole season, and curative fungicides mostly in March or October [40]. Although agricultural activity is the main source of pollution, urban and industrial activities can pollute the environment as well. Merel et al. [41] confirmed that the presence of carbendazim in the Rhine river (west Germany) originated from industrial wastewaters.

Recently, new ecotoxicological endpoints have been introduced for many fungicides due to their secondary side effects. The majority of studies for toxicological effects on non-target organisms have been conducted on a laboratory scale, using model organisms such as *Lemna* spp., *Daphnia* spp., and *Dario* spp. [1]. *Dario rerio* is an essential organism for toxicological studies, as *Dario* is sensitive to the exposure of toxic compounds. Endocrine dysfunction, oxidative stress, and immune system disorders were observed when zebrafish were exposed to carbendazim during larval and fetal stages at concentrations above 4000 ng/L [42]. Apart from carbendazim, tebuconazole caused adverse effects on the congenital system of Zebrafish, limiting locomotion at concentrations 4 and 6 mg/L [43]. The acute and chronic toxicity of strobilurins kresoxim-methyl, pyraclostrobin, and trifloxystrobin were investigated in *D. magna* neonates and embryos by Cui et al. [44].

The results showed that Daphnia embryos are more sensitive to fungicide exposure than neonates, presenting 157.3 μg/L, 3.9 μg/L, and 1.7 μg/L 48-h EC_{50} for kresoxim-methyl, pyraclostrobin, and trifloxystrobin, respectively. In addition, the lowest-observed-effect concentrations were similar to the environmental concentrations, and thus the authors reported that the studied fungicides were very toxic for *D. magna*.

There are available studies that indicate *Lemna* spp. sensitivity to fungicide exposure [45]. However, many researchers demonstrate that *Lemna* spp. can efficiently remediate contaminated natural waters and thus investigate improvement approaches. Walsh et al. [46] reported that the density over which the plants can grow on the surface of the wastewater, i.e., how much of the surface of the medium they cover, is a crucial parameter for duckweed-mediated remediation. As density increases, *L. minor* growth and TN and TP removal rates decline. To understand the remediation rate of duckweed in wetlands, total petroleum hydrocarbons in wetlands and tissues of duckweed were studied, and the experimental data were applied to the first-order kinetic rate model. After 120 days, *L. paucicostata* had successfully removed 97.91% percent of hydrocarbons from wetlands [47]. Regarding fungicides, a study showed that *L. minor* cultures could remove up to 76% of copper and 40% of dimethomorph after 96 h, suggesting *L. minor* is a suitable macrophyte plant for utilization in phytoremediation systems [48]. Many researchers have investigated the fungicides' side-effect toxicity, which can be increased when used in pesticide mixes due to synergistic interactions with other pesticides [49]. Synergy raises serious concerns for public health and environmental safety globally. Interactions between fungicides and insecticides, as well as how honeybees are affected, are of particular interest to researchers [50]. Individually, each fungicide may cause low acute toxicity to honeybees. However, a fungicide's toxicity effect could be increased when mixed with insecticides. Several studies have shown that the toxicity effects of specific pyrethroid, neonicotinoid, and organophosphate insecticides can be enhanced by combining sterol biosynthesis-inhibiting (SBI) fungicides. The combined exposure of honey bees to the fungicide propiconazole and the neonicotinoid insecticide clothianidin and a mixture containing acetamiprid and propiconazole resulted in increased mortality rates compared to exposure only to insecticides [51]. Based on their mode of action (fungicides and insecticides), similar interactions are expected to other non-target organisms. In addition, the toxicological effects of common fungicides and insecticides on honeybees were investigated during almond bloom. The insecticides chlorantraniliprole, diflubenzuron, and methoxyfenozide were tested on worker bee adults, and the fungicides iprodione and propiconazole, and a mixture of two fungicides pyraclostrobin and boscalid, were applied individually or in fungicide-insecticide mixtures to larvae. Increased larvae mortality was observed when chlorantraniliprole was applied with iprodione or propiconazole. The chlorantraniliprole-propiconazole combination was also highly toxic to adult workers. Besides the combination of chlorantraniliprole-fungicides, no synergistic effects were reported [52].

Moreover, a recent study showed that copper hydroxide is non-toxic to *Clarias gariepinus*, but mild toxicity effects were observed when it was combined with glyphosate [53]. In addition, synergistic interactions between active substances and adjuvants or inert ingredients have been reported in the literature. Pesticide commercial formulations are often thought to be more hazardous to bees than the active ingredients alone. For instance, the oral toxicity to bees of Bravo Weather Stik® (a chlorothalonil commercial formulation) showed a four-fold higher toxicity in comparison with active ingredient chlorothalonil alone [54].

Several researchers suggest that AMF symbiosis with plants in root systems has beneficial impacts on increased nutrient uptake, drought resistance, and resistance to pathogens. Similarly, plant growth-promoting rhizobacteria (PGPR) can affect plants beneficially, improving root physiology and enhancing plant growth, since they colonize the rhizosphere of plants. AMF and PGPR can be exposed (directly or indirectly) to fungicides though soil application, seed treatment, foliar spray, and wash-off from plant leaves and then drift to the soil. Thus, the physiological interactions between AMF and PGPR and host plants can be affected. Therefore, researchers focus on the combination of the advan-

tages of AMF and PGPR with a suitable chemical protection, friendly to AMF and PGPR colonies [55,56]. The impact of azoxystrobin and flutolanil (Amistar and Monarch) on the AMF *Rhizophagus irregularis* MUCL 41,833 in potatoes was studied. The applied recommended doses of azoxystrobin and flutolanil to control *Rhizoctonia solani* in potato crops and their effects against the spore germination, root colonization, extraradical mycelium development, and spore production of AMF *R. irregularis* MUCL 41,833 were assessed. Flutolanil did not cause any impact on spore germination or extra-radical development, whereas azoxystrobin significantly reduced spore germination and extra-radical development. Further, root colonization and arbuscule formation was negatively affected only by flutolanil [57]. In another study, strains of the PGPR *Pseudomonas* spp. showed tolerance when exposed to high concentrations of carbendazim and hexaconazole. The results also showed that fungicides can adversely affect the germination efficiency, growth, and physiological development of *Raphanus sativus*, but the combined application of PGPR controlled the adverse effects [56].

2.3. Chiral Fungicides

Many fungicides have an asymmetric center, which can provide two types of stereoisomers: enantiomers and diastereomers. Enantiomers have identical physicochemical properties but behave differently in asymmetric environments, such as in their biochemical processes. Enantiomers also show different biological activity, environmental fate, and toxicological profile. Diastereomers may not have identical physicochemical properties, and their biological activity usually varies [58].

Stereoselective fungicides differ in terms of toxicity, bioaccumulation, and bioavailability on non-target organisms [58]. Deng et al. [59] investigated the toxicity of four stereoisomers of metconazole to the aquatic algae *Chorella pyrenoidosa*. The results showed that the 96 h EC_{50} values were different, following the pattern cis-1S,5R-Z > trans-1S,5S > trans-1R,5R > cis-1R. In addition, the photosynthesis dysfunction, the generation of reactive oxygen species (ROS), and the antioxidant response were induced more drastically by 1S,5S. In a similar study, three enantiomers of epoxiconazole were tested for their toxicological impact on the green alga *Scenedesmus obliquus*. The EC_{50} values followed the order (+)-epoxiconazole > (−)-epoxiconazole > rac-epoxiconazole, whilst different effects on the determined chlorophyll contents, malondialdehyde contents, and antioxidant enzyme activities of algae cells were observed [60].

The environmental behavior of chiral fungicides has mainly been studied by evaluating their half-lives in crops and soils. The half-life values can provide interesting information about the potential biodegradation and the persistence of the studied compounds [54]. While fungicide enantiomers may present different half-life values from the racemic mixture, similar values were observed in other cases. The half-life of penconazole enantiomers in plant tissues and soil was determined in a field experiment. The results showed that the penconazole enantiomer (−) was degraded significantly faster than its (+) isomer in grapes and soil [61]. On the contrary, propiconazole stereoisomers were studied under aerobic, anaerobic, and sterile conditions by incubating the stereoisomers in three different types of soil, with the study investigating the dissipation process. The results showed no significant stereoselectivity under anaerobic and sterile conditions in all tested soil after 200 days of incubation, which is in contrast with the aerobic conditions where significant stereoselectivity was identified [62].

2.4. Nanofungicides

A fungicide is classed as nanofungicide if the size of the active ingredients ranges between 10 and 100 nm. The use of nanoparticles in fungi disease management can be divided in two categories: nanoparticles as protectants (alone) and as carriers for organic fungicides [63]. The main advantages of nanoparticles as carriers for organic fungicides are the improvement of persistence and activity of the active ingredient, the increased ability

for translocation within plants, the confrontation of the low-water-solubility problems, and the achievement of slow release.

Preventative nanofungicides can be applied directly to roots, leaves or seeds. Copper, silver, zinc oxide, and titanium dioxide are amongst the most studied nanofungicides. The effectiveness of ZnO, Ag, CuO, and Cu nanoparticles was compared with a commercial formulation containing $Cu(OH)_2$ against common fungi strains such as *Bacillus cinerea*, *Alternaria alternata*, etc. The comparison evaluated mycelial growth, colony formation, seed germination, and the hyphal and spore morphology of the fungi. Mycelial growth of fungi strains was inhibited in vitro by all the nanoparticles, but the most effective were Cu and ZnO. In addition, the nanoparticles were more lethal at the spore germination stage [64]. Shyla et al. [65] investigated the antifungal activity of zinc oxide, silver, and titanium dioxide particles against *Macrophomina phaseolina*, which can infest oilseed and pulse crops. At lower concentrations, Ag nanoparticles were more effective than ZnO and TiO$_2$ against target fungi. In general, silver presented the highest antifungal activity from the other metals. Silver ions can cause dysfunction in thiol groups of fungal cell walls. As a result, the electron transport chain, energy metabolism, and transmembrane function are disrupted. Furthermore, fungal DNA can be mutated, respiratory chain dissociated, membrane permeability decreased, and cell lysis affected by silver-based fungicides.

Another popular nanoparticle fungicide with low toxicity risk to human health and the environment is chitosan. Chitosan can block nutrient supply, prevent the biosynthesis of mRNA and proteins, disrupt the cell membrane, and inhibit H+-ATPase of fungi. Some of the fungi that can be managed by chitosan are Fusarium crown rot, root rot in tomato, gray mold of grapes, and rice blast disease in rice [66]. Chitosan–lactide copolymer nanoparticles were used as carriers for pyraclostrobin, a low-water-soluble fungicide. The carrier was tested against *Colletotrichum gossypii* at different concentrations and compared to a commercial formulation of pyraclostrobin. The results showed that nanofungicide effectiveness did not exceed the commercial one at three and five days post-application. Nevertheless, the nanofungicide antifungal activity was increased at day 7 post-application [67]. Janatova et al. [68] achieved a successful *Aspergillus niger* control by formulating five individual essential oils with silica material MCM-41 in nanocapsules. Their effectiveness was reported to be higher than commercial oils at 14 days post-*Aspergillus niger* infection.

Despite the advantages of nanofungicides, these compounds can enter natural waters through leaching, run-off, or spray-drift. Soil properties such as surface charge, cation species, and the type of soil can define the mobility of nanoparticles in the soil. In addition, the nanoparticles can modify the soil sorption capacity of pesticides, resulting in the fluctuations of their toxicity severity. As a result, toxicity effects have been observed in humans, plants, microorganisms, and vertebrates due to their exposure to nanofungicides [69]. According to Ameen et al. [70], the exposure of nanopesticides can have a different impact on plant growth depending on application conditions such as application rate and size and type of nanomaterial. Nanoparticles can be taken up and cross the plasma membrane through various processes, such as endocytosis, pore formation, and carrier proteins [71]. Plants can activate defense systems and overcome stress parameters (including nanoparticles). However, there is the possibility for plants to fail to overcome toxicity effects, showing symptoms such as damaged DNA, reduced rate of transpiration, and others [72]. For instance, decreased content of leaf photosynthetic pigment (chlorophyll a and b) and reduced biomass (17–20%) have been observed in maize after application of the nanofungicide $Cu(OH)_2$ [73]. In addition, nanofungicides have the potential to harm beneficial soil bacteria and fungus. Abd-alla et al. [74] reported that high concentrations of Ag-nanoparticles reduced mycorrhizal colonization, glomalin content, and mycorrhizal responsiveness of AMF *Glomus aggregatum*. Hence, the nitrogen-fixing *Azotobacter vinelandii* presented various toxicity symptoms under Ag-nanoparticle presence, such as deduced cell number, apoptosis structural damage, inhibition of biological nitrogen fixation, and ROS generation [75].

Furthermore, various aquatic organisms have been investigated for their responses to nanoparticle exposure. Mortality, hatching delays, and various developmental malformations were shown when zebrafish embryos were exposed to nanoparticles [76].

2.5. Chemical Plant Defense Activators

Chemical plant defense activators constitute another group of fungicides with novel mode of action. Acibenzolar s-methyl (ASM) is a compound that can induce plants' defense mechanisms, such as systemic acquired resistance, with salicylic acid taking part in the process. ASM can be used as an alternative solution to common bactericides and fungicides. Many researchers report that ASM is able to effectively manage various diseases in different crops, e.g., onion and tomato [77]. In addition, ASM induces the production of enzymes and phytoalexins when the plant is chemically, biologically, or physically stressed. However, ASM has been identified as phytotoxic, has been linked to production losses, and in some situations, may exacerbate other pest assaults [78]. Potassium phosphate (PP) is a salt that is applied in cultures as a foliar fertilizer. Plant defense function is also stimulated by PP use. PP is characterized by high mobility and solubility. As a result, harmful oomycetes are successfully controlled in different cultures, such as papaya, tomato, and potato [78,79]. Another salt, fosetyl-Al, is a worldwide broad-spectrum fungicide that is commonly used in horticulture. Its action is based on preventing the development of fungi spores and mycelium, inhibiting the pathogen penetrating into the plant. It was also documented that fosetyl-Al plays a role in plant defense mechanism activation [80].

The environmental fate and toxicological effects of chemical plant activators to non-target organisms have not been extensively studied. The effects of fosetyl-Al on model species *Danio rerio* in water and *Enchytraeus crypticus* in soil were evaluated at a laboratory scale. The ecotoxicological assessment showed that fosetyl-Al is not considered safe for *D. rerio* and *E. crypticus* for concentrations higher than the PECs, which are 1.067 mg/kg for soil and 0.06496 mg/L for surface water [81]. In the case of ASM, Guziejewski et al. [82] reported that it is moderately to highly toxic to fish, moderately toxic to invertebrates. and highly toxic to aquatic plants.

3. The Role of Vegetation and Microbial Communities on Fungicide Removal in CWs and Other Phytoremediation Systems

Phytoremediation is a technology that uses plants and microorganisms located in the rhizosphere in order to remove, mitigate, break down, and retain pollutants such as pesticides in soils, surface water, and groundwater. However, phytoremediation processes can be adversely affected by pesticides, which can cause phytotoxicity, as plants are exposed to stressful conditions. CWs are a type of phytoremediation system is based on wetland plant species, which usually grow in soil or gravel substrate [83].

Among other factors, the vegetation and its related functions are crucial for pesticide removal in CW systems. Vegetation provides pollutant uptake, phytoaccumulation, degradation, and sorption through rhizosphere, flocculation, sedimentation, and suitable conditions for enhanced microbial activity [84] Therefore, an efficient phytoremediation process in CWs depends on two main factors: the tolerance of plants to pollutants and the presence of favorable conditions for microorganism growth in the rhizosphere, contributing to contaminant degradation [19]. In most studies, phytoaccumulation and plant uptake are associated with K_{ow} of each compound. High or low $LogK_{ow}$ values may facilitate uptake or translocation, respectively. However, the optimum $LogK_{ow}$ values for uptake, translocation, and accumulation range between 3.0 and 4.0 [85]. Furthermore, researchers [18] have reported that macrophytes such as *Typha latifiola*, *Phragmitis australis*, and others have high potential to absorb various pesticides, accumulating them in roots, stems, and leaves. In addition, the phytoavailability of a pesticide is determined by its molecular size (weight). A tiny molecule pesticide (Mr 500 Da) is often absorbed passively through diffusion, whereas a pesticide with a molecular weight more than 500 usually requires ATP hydrolysis to drive absorption [86].

Plants have established complex mechanisms for degrading xenobiotics like pesticides into detoxified compounds. Glycosyltransferase in plants catalyze the conjugation of sugars with endogenous metabolites or exogenous compounds. The purpose of glycosylation is to make substrates more water soluble, making them easier to degrade [86]. Many GTs s have been reported to protect plants from the toxicity of fungicides by O–glycosylation. The O–glycosylation products of their hydroxylated metabolites have been found in grape and strawberry for the fungicides thiabendazole, pyrimethanil, and cyprodinil [87].

Microbial diversity and richness have a dominant role in the stability and maintenance of CW treatment efficacy. Fungicide-degrading microorganisms (beneficial for plant growth) can be found either in filter bed material (porous media) or in plant roots. In addition, epiphytic or endophytic microorganisms can colonize wetland plants. The pesticide biotransformation, through microbial communities, is mainly conducted at the rhizosphere, which is favored by the release of oxygen and organic exudates of plants [88]. The combination of phytoremediation with bioaugmentation improves treatment efficiency compared to individual approaches. Therefore, researchers have recently focused on microcosmos functions and the potential amplification of microbiota activity [89].

The contribution of vegetation and the associated microorganisms to fungicide removal through CWs and other plant-based remediation systems is descried below, presenting various related studies (Table 2).

Table 2. The use of constructed wetlands for fungicide removal.

Target Fungicide	Vegetation	Microbial Changes/Contribution	Plant Removal	Wastewater Type	CW Type	Reference
Fluopyram	*Phragmites australis, Typha latifiola*	bioaugmentation with *Pseudomonas spp*	efficiency	synthetic	pilot scale HSF	[19]
Tebuconazole	*Juncus effuses, Berula erecta, Iris pseudacorus, Phragmites australis, Typha latifiola*	not specified	P. australis absorbed higher amount of fluopyram than T. latifiola	synthetic	pilot scale HSF, FWS	[90]
Boscalid	*Phragmites australis*	not specified	B. erecta achieved significantly higher removal efficiency than the other plant species	synthetic	pilot scale HSF	[15]
Chlorothalonil	*Phragmites australis*	response to fungicide exposure: non-optimal bacteria group growth	the presence of vegetation greatly enhances boscalid removal	synthetic	pilot scale HSF	[91]
Tebuconazole	*Juncus effuses, Berula erecta, Iris pseudacorus, Phragmites australis, Typha latifiola*	plants promoted higher microbial activity than unplanted CWs	non-specified	synthetic	pilot scale HSF, FWS, VFS	[92]
Tebuconazole, imazamil	*Juncus effuses, Berula erecta, Iris pseudacorus, Phragmites australis, Typha latifiola*	nitrifying bacteria may play an active role in biodegradation	B. erecta achieved significantly higher removal efficiency than the other plant species	synthetic	pilot scale HSF, FWS	[93]

HSF: horizontal subsurface flow; FWS: free water-surface system; VFS: vertical flow system.

3.1. Storbilurins

The action of strobilurins against fungal mitochondrial respiration is based on the electron transport block in the cytochrome bc_1 complex (complex III), between cytochrome b and cytochrome c_1, at the Q_o site. Therefore, ATP synthesis (energy supply) is blocked, causing oxidative stress and fungus cell death [94]. Pyraclostrobin ($LogK_{ow}$ = 3.99) and azoxystrobin ($LogK_{ow}$ = 2.50) are the best sellers among strobilurin fungicides and are mainly applied to soybean, grape, wheat, and corn crops. Other commonly used strobilurin fungicides are tryfloxystrobin, picoxystrobin, kresoxim-methyl, and fluaxastrobin, with log K_{ow} values of 4.5, 3.6, 3.4, and 2.86, respectively, and their water solubility inversely proportional to $LogK_{ow}$ values [87,95].

Maillar et al. [96] indicated that a stormwater wetland achieved 100% removal of kresoxim methyl and 93% of azoxystrobin. *P. Australis* (70–80%) was the main wetland vegetation during the monitoring period. Other plants tested were *T. latifiola* and *Choenoplectus lacustris.* Although plant uptake was not quantified, vegetation was assumed to contribute to fungicide removal due to the optimum Log K_{ow} values of the tested compounds.

In addition, the phytoaccumulation ability of three plants (*Juncus effusus*, *Pontederia cordata* and *Sagittaria latifolia*) against azoxystrobin was assessed in order to be used in wetland remediation systems. Plants were planted in sandy soil, with azoxystrobin being applied to every two months. Researchers quantified the azoxystrobin residues in plants and soil during the experiment. *P. cordata* achieved the highest removal rate (51.7%). Particularly, the root of *P. cordata* contained up to 39.8% of the total absorbed azoxystrobin [97]. Furthermore, Elsaesser et al. [98] supported that the presence of the submerged macrophyte *Elodea nuttallii* (Planch) increased the removal efficiency of a vegetated flow-through stream system in comparison with an unplanted one, achieving more than 90% removal of the initial concentration of trifloxystrobin.

The complex between cytochrome b and cytochrome c_1, which is unsettled by strobilurins, appears in all eukaryotic organisms, including plants. Thus, the exposure of CWs plants to strobilurins may cause reduced plant growth and thus decreased phytoaccumulation ability. Pedersen et al. [99] tested the response of isolated mitochondria from wheat and showed that the electron transport in the cytochrome bc_1 was blocked.

3.2. Demethylation Inhibitors (DMI)

The DMI fungicide group consists of various chemical classes, such as triazoles and imidazoles, which have a common mode of action. DMIs inhibit the cytochrome P450, which is responsible for ergosterol production and the synthesis of the cell wall of fungi [100]. Difenoconazole, tebuconazole, imazalil, epoxiconazole, and cyproconazole are considered as commonly used members of the DMI group, and their respective $LogK_{ow}$ values are 4.36, 4.1, 3.89, 3.3, and 3.09 [84].

Lv et al. [92] studied the removal efficiency of five different CWs planted with *T. latifolia* (cattail), *P. australis* (common reed), *I. pseudocorus* (yellow flag), *J. effusus* (soft rush), and *B. erecta* (water parsnip) against imazalil and tebuconzole. Planted CWs presented much higher removal efficiency than unplanted ones during the summer period. Despite the low phytoaccumulation of fungicides, the plants contributed to fungicide biodegradation, though the active microbial community hosted in their rhizosphere. Both fungicides were mainly phytoaccumulated by *B. erecta*, while *J. effuses* has shown significantly greater plant uptake in the winter. During the experiment, the CW vegetation accumulated only 5–6% of the initial applied fungicides (nominal concentrations). Another study indicated that the tebuconazole uptake by plants was quite low, ranging between 2.1 and 12.5%. However, the role of plant metabolism in tebuconazole dissipation was remarkable [89]. Furthermore, the role of three macrophytes in difenoconazole removal was investigated. Researchers suggested that the two main factors contributing to difenoconazole removal were the physicochemical properties of the tested compound and the biomass of the macrophytes [101].

3.3. Other Chemical Fungicides

Boscalid is a relatively new succinate dehydrogenase inhibitor (SDHI), with high effectiveness and a broad spectrum. Its mode of action is based on the inhibition of fungal respiration by blocking the ubiquinone binding site [102]. Papaenvagelou et al. [15] demonstrated that the moderately lipophilic boscalid was bioaccumulated by *T. latifolia* and *P. australis*, increasing the total removal efficacy of CWs. In addition, the lower uptake ability of plants during the winter period was attributed to a lower activity of plants when compared with the summer period.

The environmental fate studies of chloronitriles are focused on the fungicide chlorothalonil. Chlorothalonil can bind and deplete cellular glutathione (GSH) and can inhibit glycolysis by binding with glyceraldehyde 3-phosphate dehydrogenase (GAPDH), causing cell death [103]. A study related to chlorothalonil removal using CWs showed that the fungicide removal was correlated with the presence of bacteria *Pseudomonas* spp., which were favored by *P. australis* [90].

As mentioned before, high copper residues in vineyard soil could have toxicological side effects. Hyperaccumulators can absorb high amounts of copper, especially in their shoots. The *Brassicaceae* family contains several plants able to accumulate significant amounts of copper. However, hyperaccumulators present low plant growth and thus low plant biomass, which is strongly correlated with copper plant uptake. Therefore, the choice of an appropriate plant is mainly based on the shoots' ability to absorb high copper amounts [104].

Anilinopyrimidine fungicides might inhibit methionine biosynthesis. In addition, several researchers have shown that anilinopyrimidine fungicides can prevent the secretion of fungal hydrolytic enzymes such as laccases, lipases, and proteases [105]. Dosnon-Olette et al. [106] tested the potential toxicity effects of pyrimethanil on five macrophytes, with their removal performance also investigated. Among the tested species, *L. minor* achieved the higher phytoaccumulation of pyrimethanil (17.1%). Moreover, *L. minor* presented high tolerance to pyrimethanil exposure. A similar study was conducted using the macrophyte species *L. minor* and *S. polyrhiza.* The target compound was the morpholine fungicide dimethomorph. Both plants were not affected by fungicide exposure, with their removal rate reaching up to 18% [107].

Ag nanoparticles are possible carriers of fungicides, and thus their fate was investigated in CW systems. The effects of Ag nanoparticles on microbial communities in the CW substrates and the contribution to nanoparticle removal of CW vegetation were examined. The results showed that Ag nanoparticles caused changes in microbial community and also in the abundance of the key functional bacteria, decreasing the removal efficiency of the system. In addition, the plants of CW (*Iris wilsonii*) absorbed low amounts of Ag nanoparticles. However, the removal efficiency of Ag nanoparticles was evaluated at 95.72%, which indicates that the CW could effectively remove Ag nanoparticles [108]. Similarly, Cao et al. [109] investigated the removal performance of Ag nanoparticles though CWs. *I. pseudacorus* was planted in CWs and took part in the removal of Ag nanoparticles. Their residues were detected in the roots and leaves of plants. Roots could accumulate significantly higher amounts than leaves, with an overall removal performance higher than 98%.

4. Tools, Technologies, and Methodologies for Fungicide Phytoaccumulation Improvement

4.1. Plant-Growth Regulators and Phytohormones

The recent introduction of plant metabolism amplifiers, such as biofungicides and exogenous plant hormones, in the agricultural sector to control plant pathogens has given rise to speculation about their potential application in CWs to improve removal performance, as well as their interactions with CW vegetation and microbial communities. PGPR (Plant Growth-Promoting Rhizobacteria), phytohormones, chelators, and other biotechnological tools are considered as Low Risk Pesticides (LRPs) or eco-friendly disease management

approaches. In addition, under field conditions, or in various remediation techniques, PGPR, phytohormones, and chelators interact with chemical fungicides and affect their fate and removal efficacy.

Phytohormones are known as small organic molecules, which are involved in various growth and development processes of plants and also in plant immunity, supporting biotic or abiotic stress control [110]. Among the identified nine categories of phytohormones, ethylene (ET), salicylates (SA), jasmonates (JA), and cytokinins (CK) act as defense regulators in plant immunity against various pathogens, including fungi [111]. Researchers report that the exogenous application of plant hormones can enhance plant resistance against fungi pathogens [112].

Melatonin was first discovered in plants in 1995, prompting a surge of research on the hormone's role and activities in plants. Nowadays, researchers conduct studies in order to examine the impacts of melatonin in agriculture. Increase of the biomass production, improvement of seed germination, and photosynthesis activity and tolerance to biotic stress was also reported as one of the benefits of melatonin presence in plants. As a result, the exogenous application of melatonin against fungi was studied [113]. Zhang et al. [114] reported that melatonin could successfully control the infection of *Phytophthora infestans* in potato cultures. The melatonin treatment caused ultrastructure cell changes, lower pressure resistance of *P. infestans*, and an underdeveloped mycelium. Interestingly, melatonin acted synergistically with a commercial fungicide containing fluopicolide and propamocab hydrochloride, indicating that the reduction of chemical fungicide use is possible. The combined application of classical fungicides, nanofungicides, plant growth regulators, chemical plant activators, microbial fungicides, and nutrients obfuscates the study of their environmental fate and ecotoxicity issues. The use of melatonin could enhance the fungicide removal performance of CW vegetation. Melatonin influences numerous gene expressions in different plant growth stages and physiological stages. Melatonin can act as a regulator for these plant hormones, increasing or inducing their beneficial effects on plants. Furthermore, the regulation of primary or secondary metabolism and osmosis has been reported after melatonin application. In addition, melatonin interferes with the redox network within plants, balancing both reactive nitrogen and reactive oxygen species (ROS), such as hydrogen peroxide, hypochlorous acid, and nitric oxide, which occasionally can be harmful to plants [115]. Yan et al. [116] reported that exogenous melatonin limited the phytotoxicity effects of carbendazim on tomatoes and increased plant resistance to fungicide exposure. In particularl, ROS levels were decreased, antioxidant enzymatic activity was enhanced, and the induced production of glutathione contributed to fungicide detoxification.

Local and systemic acquired resistance was achieved by SA exogenous application against various fungi, such as *Fusarium oxysporum*, *A. alternata*, *Magnaporthe grisea*, and *Colletotrichum gloeosporides* [117]. The application of 2 mM of SA was enough to reduce *B. cinerea* severity in tomato by 67% [118]. The JA application can induce plant defense, inhibit the death of plants cells, and prevent the expansion of fungi infection [119]. According to Zalewski et al. [120], a treatment of Winter Triticale with 1 mM of methyl jasmonate in specific growth stages controlled a further expansion of various triticale grain fungi pathogens, such as *A. alternata* and *Cladosporium cladosporioides*. However, a higher application dose of methyl jasmonate was correlated with higher disease severity, caused by mycotoxin-producing fungi.

Auxins are organic compounds with low molecular weight. Their presence within plants can enhance cellular and plant growth. Among them, indole acetic acid (IAA) is the most essential [121]. Auxins are demonstrated as successful contributors to phytoremediation performance. Rostami et al. [122] reported that the auxin treatments of phytoaccumulators enhances the biomass of the roots and stems. The root system of treated plants presented higher growth than other plant parts and simultaneously an increased secretion of exudates from plant root to rhizosphere. In addition, a well-developed root system provides favorable conditions for microorganism growth, as well as increased microbial

population and activity. IAAs can be produced with the involvement of various bacterial species, such as *Bacillus* spp., *Acinetobacter* spp., *Pseudomonas* spp., *Azospirillum* spp., and *Azotobacter* spp. The amount of produced auxins depend on the genus and species of the bacteria and their growth conditions [123].

Gibberellins, such as gibberellic acid, are crucial for various growth and development processes of plants. Many plant species enhance the production of amine proline acid and protectant compounds. Proline can protect vital macromolecules such as proteins and increase enzymatic activity under stressful conditions. The application of exogenous gibberellins promotes proline synthesis in plant tissues, resulting in increased plant defense and a positive plant growth regulation. Apart from proline production, gibberellins can enhance the chlorophyll content and plant biomass when plants are exposed to toxic compounds [124,125].

Salicylic acid is a phenol compound that promotes plant defense response against biological or non-biological stresses and reduces the effects of toxic compounds, as a curative. It is also considered a preventive compound for the toxic effects of xenobiotics on plants. Plant physiological processes such as bud growth, membrane permeability, mitochondrial respiration, stomatal closure, material transfer, photosynthesis, growth rate, and ion absorption are affected by salicylic acid presence [126]. Salicylic acid causes metabolic reactions and thus physiological changes to plants, which are adopted by plants. These changes strengthen plant tolerance to various stressful environmental factors [127]. The exogenous salicylic acid application was tested for phytoremediation systems targeting copper. The results showed increased plant resistance to copper and a reduction of the adverse effects of copper [128].

A major function of cytokinins (CK) is to synthesize chlorophyll. The continuous chlorophyll production through CK keeps the leaves "young", collecting free radicals and transforming ethioplasts to chloroplasts. As a result, plants develop adaptations and tolerance to environmental conditions. In addition, studies showed that CK interact with plant defense systems, increasing glutathione production and eventually plant tolerance to contaminants. Moreover, CK application can enhance the plant biomass [120].

The favorable effects of plant growth regulator (PGR) treatments in the phytoremediation of heavy-metal-contaminated soil were reported by Rostami and Azhdarpoor [120]. However, the potential positive effects of PGR as an eco-friendly treatment for pesticides have not been investigated in CW vegetation. Moreover, many fungicides have a pivotal role in plant physiology and the production/regulation of phytohormones.

4.2. Chelation

Many researchers report that the use of polysaccharides as chelating agents for vital elements can enhance nutrient bioavailability for plants, contributing to their uptake, translocation, and utilization within the plants. In addition, amino acid complexes with micronutrients can increase plant growth and yields through photosynthesis process improvement [129]. Nowadays, similar chelates are examined for their ability to stimulate plant immunity or for their direct effects against fungi. Buzón-Durán et al. [130] investigated the antifungal ability of chitosan oligomers (COS) and four amino acids—cysteine, glycine, proline, and tyrosine—against *Fusarium culmorum* in Spelt using field trials and in vitro seeding assays. The results showed that the COS–tyrosine mixture was the most effective in fungal growth inhibition. In field studies, the COS–tyrosine mixture reduced the disease severity by 83.5%. In addition, a mixture with chitosan and riboflavin achieved satisfactory control of *Penicillium digitatum* in in vitro experiments, promoting a potentially alternative fungicide for citrus fruit postharvest treatment, with a low environmental risk [131].

Bloem et al. [132] reported on another chelating agent, Ethylenediaminetetraacetic acid (EDTA), which is a compound mainly used in micronutrients and as a fertilizer component. The application of EDTANa$_2$ controlled *Fusarium graminearum* in wheat, by up to 90% in

field experiments. In in vitro assays, the presence of EDTANa$_2$ inhibited the deoxynivalenol production and chitin synthase activity of *Fusarium* spp. [14].

Chelators have also been studied for use in phytoremediation systems. Chelator addition (e.g., EDTA) may increase the removal of pollutants by plants, with reduced plant growth observed at the same time. In addition, these compounds have high half-life time values and are persistent in the environment; thus, the exposure of high concentrations of chelating agents to plants and soil microorganisms can be toxic [133]. Following these studies, researchers have recently focused on more eco-friendly chelating agent applications. The application of the degradable chelators glutamic acid, nitrilotriacetic acid, ethylenediamine disuccinic acid, and citric acid were examined on their own and in combination to increase the phytoextraction effectiveness of amaranth (*Amaranthus hypochondriacus* L.) in two Cd-contaminated agricultural soils. First, the plants were resistant to the chelators that were used, and the addition of glutamic acid and nitrilotriacetic acid effectively aided plant biomass production. Additionally, the combination of glutamic acid and nitrilotriacetic acid showed significantly higher soil enzyme activity compared with individual applications [134]. Despite the lack of similar studies related to fungicide removal, the use of chelators in CWs is a promising tool for enhanced plant uptake and phytoaccumulation in CWs for fungicide removal [135].

Bioaugmentation with PGPR Plant Growth-Promoting Rhizobacteria and AMF Arbuscular Mycorrhizal Fungi

In the field of agriculture, some isolated beneficial microorganisms, plant extracts, and essential oils can have lethal effects on crop pathogens (Table 3). Consequently, various biofungicides have been formulated and registered [9–11].

Table 3. List of common biofungicides [37].

Group Name and Mode of Action	Chemical/Biological Family	Organism Origin	Target Site
	Polypeptide	Extract from lupine plantlets	Multiple effects on ion membrane
Plant extracts, Biologicals with multiple modes of action	Phenols, sesquiterpenes, triterpenoids, and coumarins	Extract from *Swinglea glutinosa*	Affects fungal spores and germ tubes, induces plant defense
	Terpene hydrocarbons, terpene alcohols, and terpene phenols	Extract from *Melaleuca alternifolia*	Competition, cell membrane disruption, induced plant defense
Microbial, Biologicals with multiple modes of action	Bacterial *Bacillus* spp.	*Bacillus amyloliquefaciens* strain QST713	Competition, mycoparasitism, antibiosis, induced plant defense
	Bacterial *Pseudomonas* spp.	*Pseudomonas chlororaphis* strain AFS009	
	Fungal *Trichoderma* spp.	*Trichoderma atroviride* strain I-1237	

The application of several microbial-based fungicides is called, by many researchers, "augmentative biological control" [136]. Plant Growth Promoting Microorganisms (PGPM) are among the most popular microbial-based fungicides that can control disease directly or indirectly. Moreover, PGPM are able to increase crop yield by enhancing nutrient uptake, improving disease tolerance and enhancing abiotic or biotic stress adaptation. Plants can host PGPM in plant parts such as the rhizosphere and the endosphere. The most commonly applied microbial inoculants are the PGPR (e.g., *Pseudomonas* spp., *Bacillus* spp., and *Rhizobia* spp.), followed by the AMF (e.g., *Glomous* spp. and *Rzizofagous* spp.). Numerous studies reported successful applications of PGPM against plant diseases. *Bacillus amyloliquefaciens* (former subtilis) is a rhizobacterium that can produce endospores and

antibiotics. The mode of action is based on pathogen cell membrane disruption, and it is mainly used for *B. cinerea* on horticultural species [137]. Ongena et al. [138] reported that Bacillus amyloliquefaciens has the potential to induce plant defense mechanisms of disease-affected plants.

PGPR promote the production of vital compounds, including organic acids, sideroormones, antibiotics, enzymes, and phytohormones. These compounds are responsible for various beneficial impacts on the vegetation of phytoremediation systems, which improve pollutant removal efficiency, including greater plant biomass, tolerance development under abiotic (e.g., weather conditions) or biotic (e.g., pathogens) stressful conditions, higher nutrient uptake, higher microbial activity on the root system, increase of pesticide biodegradation, and pesticide bioaccumulation [139–142]. In addition, PGPR can reduce ethylene production through enzyme 1-aminocyclopropane-1-carboxylate (ACC) deaminase synthesis, which dissipates the ethylene precursor ACC, achieving a significant plant growth enhancement [143]. Furthermore, DalCorso et al. [144] suggests that plant growth promotion and phytoaccumulation improvement can be achieved by bacterial auxin (IAA), which is stimulated by PGPR. Despite the lack of studies related to acibenzolar-S-methyl fate in phytoremediation systems, some studies prove its translocation ability within plant tissues and its interactions with PGPR strains. For instance, the PGPR strains *Bacillus subtilis* GB03 and *Bacillus pumilus* SE34 had a significant influence on ASM translocation in tomatoes, promoting higher concentrations of fungicide in aerial parts compared with non-PGPR treated plants [145].

Xiao et al. [146] investigated the remediation ability of hyperaccumulator *Sedum alfredii* to remove the benzimidazole fungicide carbendazim. The plantation of *S. alfredii* was combined with carbendazim-degrading bacterial strains (*Bacillus subtilis*, *Paracoccus* spp., *Flavobacterium* spp., and *Pseudomonas* spp.). The removal performance was increased by 32.1–42.5% when inoculated with bacteria *S. alfredii* treatments. Additionally, bacterial inoculation improved the microbial activity and structure of soil and enhanced carbendazim biodegradation. Parlakidis et al. [19] investigated the influence of bioaugmentation of PGPR *Pseudomonas putida* on *P. australis* growth and uptake ability in CWs, targeting the fungicide fluopyram. The results showed that the inoculated plants absorbed higher concentrations of fluopyram, and they had higher plant biomass compared with the non-bioaugmented plants.

Furthermore, PGPR can be directly involved in fungicide biodegradation. The influence of *Bacillus subtilis* on the fungicide penthiopyrad was investigated on a laboratory scale. *B. subtilis* can enhance by approximately 5% the dissipation rate of penthiopyrad. However, its combination with fungi *Trichoderma harzianum* increased the degradation by 29.1% [147]. Myresiotis et al. [148] studied the interactions between various PGPR strains inoculated in soil and fungicides propamocarb hydrochloride and acibenzolar-S-methyl. In all cases, soil inoculated with PGPR showed a remarkable dissipation rate of acibenzolar-S-methyl, approximately six times higher than non-inoculated soils. From all tested strains, *Bacillus amyloliquefaciens* strain IN937a and *Bacillus Pumilus* strain SE34 had the most significant impact on propamocarb hydrochloride degradation.

Another essential microbe group that can be bioaugmented in CW plants is the AMF. AMF presents similar benefits to PGPR. The increased production of phytohormones, which enhance plant growth and contaminant plant uptake, was associated with AMF inoculation in accordance with Liao et al. [149]. Furthermore, Göhre and Paszkowski [150] demonstrated that plant rhizosphere growth and the nutrients and water adsorption by plant roots was much greater in inoculated AMF plants as compared to untreated plants.

5. Conclusions, Perspectives, and Challenges

Fungicides are considered a vital tool for agriculture, protecting crops against fungal diseases and therefore securing high agricultural productivity. Nowadays, the evolution of technology can provide novel chemical fungicides, such as nanofungicides and chiral fungi-

cides, to address plant resistance development. However, the extensive use of chemical fungicides leads to a risk for public health, natural waters, and non-target organisms.

Various studies indicate that CWs can prevent the distribution of pesticides to the natural environment, but few of them target fungicides. Fungicides can have adverse impacts on plants and beneficial microorganisms in CWs. As a result, plant accumulators and microbial communities may have a low contribution to fungicide removal. In the agricultural industry, microbial formulations (e.g., PGPR and AMF) are proposed as an alternative eco-friendly solution for plant diseases. Similarly, synthetic plant growth regulators, chelators, and phytohormones have a beneficial effect on plants under biotic or abiotic stress, showing much promise as an effective anti-fungal strategy. Their mode of action is based on plant defense induction, enhanced plant biomass, and production of vital compounds. Recently, these formulations have been investigated in phytoremediation systems, presenting effective removal of organic pollutants, metals, and nutrients. This review demonstrates strong evidence to suggest that the addition of exogenous microorganisms, plant growth regulators, and phytohormones can overcome the fungicide toxicity side-effects for CW vegetation and microbial communities and enhance fungicide removal. However, there are information gaps regarding their interactions with chemical fungicides within CWs.

The exogenous application of PGRs can be used to improve phytoremediation, but there is still a lack of information on the appropriate application stages and dosages. Hence, the synergistic effects of indigenous and exogenous melatonin on toxic compounds are still unclear. The application of chelating agents in CWs could be an efficient strategy to remove inorganic fungicides and nanofungicides. However, low-biodegradable chelators at high doses can have a toxic effect on CW vegetation and microbial communities. Therefore, the choice of plant species, chelator type, and dose treatment are critical for optimum removal performance.

The microbial populations in the substrate or water of the CW systems, as well as those in the plant material, could be altered by inoculation. Many studies found that the inoculation strains were persistent (e.g., [151]), while some investigations found that the density of the inoculated strains decreased over time (e.g., [152]). In addition, the length of the study appears to have an effect on the outcomes. The inoculation process can be done immediately, or waiting for the system to be stabilized [89]. Hussain et al. [151] found that removal performance of the tested bioaugmented CWs was optimum in the first three months, but then deteriorated in the following months. Plant health declined at the same time, with plant shoots beginning to become yellowish.

However, available data for the microbial inoculation effects on microbial communities in CW system are provided mostly by molecular fingerprinting such as restriction fragment, length polymorphism, real-time quantitative PCR, etc., which indicate only the dominant members of the microbial communities. Next-generation sequencing techniques are necessary to determine the population size of inoculants, their competition with indigenous microorganisms, and their interactions with the fungicides, reaching taxa identification. Furthermore, the hydrological conditions of CWs have received little attention, which could have a crucial impact on microbial development, considering that free water surface CWs are mostly aerobic, whereas HF CWs are mostly anoxic/anaerobic.

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