

Article

Pyraclostrobin Removal in Pilot-Scale Horizontal Subsurface Flow Constructed Wetlands and in Porous Media Filters

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Abstract: Pyraclostrobin is a fungicide extensively used for the control of various fungal diseases and is frequently detected in environmental samples. Natural systems, such as constructed wetlands (CWs) and gravity filters, are effective and environmentally friendly treatment systems, which can reduce or eliminate pesticides from the environment. The aim of this study was to investigate the capacity of two pilot-scale CWs (porous media: cobbles and fine gravel, planted with *Phragmites australis*) and six gravity filters (filling material: bauxite, carbonate gravel and zeolite) to remove pyraclostrobin from polluted water originating from spraying equipment rinsing sites. For this, experiments were conducted to test the performance of the above natural systems in removing this fungicide. The results showed that the mean percent pyraclostrobin removal efficiencies for cobbles and fine gravel CW units were 56.7% and 75.2%, respectively, and the mean percent removals for HRTs of 6 and 8 days were 68.7% and 62.8%, respectively. The mean removal efficiencies for the bauxite, carbonate gravel and zeolite filter units were 32.5%, 36.7% and 61.2%, respectively, and the mean percent removals for HRTs 2, 4 and 8 days were 39.9%, 43.4% and 44.1%, respectively. Regarding the feeding strategy, the mean removal values of pyraclostrobin in gravity filter units were 43.44% and 40.80% for continuous and batch feeding, respectively. Thus, these systems can be used in rural areas for the treatment of spraying equipment rinsing water.

Keywords: pesticides; fungicide removal; phytoremediation; hydraulic residence time; constructed wetlands



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1. Introduction

Modern agriculture depends on the use of pesticides to increase crop yields, but their residues may pose a serious threat to aquatic and terrestrial ecosystems. Pesticides may end up in different environmental compartments through diffuse or non-point and point sources. The amounts of fungicides applied to large-scale crops have increased rapidly over the last two decades [1].

Synthetic strobilurin fungicides are analogous to the natural products isolated from the fungi of the genus *Strobilurus*; due to their high efficacy, they have quickly become the most important chemical group of fungicides [2,3]. Pyraclostrobin is a strobilurin fungicide discovered by BASF in 2000; it has been registered to protect grapes, peppers, tomatoes, wheat, potatoes, sugarbeets, carrots and soybeans against diseases caused by ascomycetes, basidiomycetes, deuteromycetes, and oomycetes [4]. The main mode of action of pyraclostrobin involves the inhibition of mitochondrial respiration by blocking the electron transfer at the outer side of the cytochrome-bc1 complex. Moreover, pyraclostrobin

application is related to the activation of the physiological regulation of plants and the promotion of plant growth [5,6]. Following its first inclusion in Annex I of Directive 91/414/EEC in 2005, pyraclostrobin was registered in more than 50 countries, and with sales of more than 1 billion US\$ in 2016, it was the best-selling fungicide [7]. Because of the extended application, pyraclostrobin is also one of the most frequent residues in food [8,9] and environmental matrices (soil, water, sediment and biota) [10–15]. The environmental fate and dissipation of pyraclostrobin depend on the exposure conditions ($DT_{50(\text{field})} = 33.3$ days) [4]. Various metabolites were identified during pyraclostrobin hydrolysis and photolysis, and some of them could be more toxic, compared to their parent compound [16,17]. Pyraclostrobin is applied to crops throughout the growing season, which may result in the exposure of non-target organisms within or near agroecosystems. Various laboratory and field studies have reported that pyraclostrobin may accumulate and be toxic to fish, amphibians, amphipods, algae, *Daphnia magna* and mussels [7,18–26] at environmentally relevant concentrations, and has been classified among the 10 compounds with the highest risk to aquatic organisms [27]. In addition, pyraclostrobin can negatively impact honey bee and other pollinators [28–30]. Recently, various nanomaterials were tested for the controlled release of pyraclostrobin and the reduction of its environmental impact [31–33].

Point-source and diffuse pesticide contamination in water has become a serious environmental problem, which is increasing due to the absence of effective and low-cost remediation techniques. Agricultural wastewater from the mixing, loading and washing of spray equipment and improper handling of tank mix leftovers contribute to point-source pollution [34–37]. Several treatment technologies have been suggested for the removal of pyraclostrobin, such as photocatalytic degradation with TiO_2 as a photocatalyst [38], UV radiation [16], ozone and solar still decontamination systems [20], and simultaneous microbial decomposition and Fenton oxidation [39]. However, their high operation and maintenance costs make these technologies non-sustainable and non-preferable options. Therefore, alternative, more environmentally friendly technologies are recommended. The use of natural treatment systems, such as constructed wetlands (CWs), gravity filters, vegetated buffer strips and ponds, provides an effective practice of mitigating or eliminating nutrients, pesticides and emerging pollutants in an environmentally friendly manner [40–50]. Constructed wetlands (CWs) constitute an effective natural treatment technology, with low operation and maintenance cost, simple operation, and low environmental impact [43,51]. CWs have been successfully used for the treatment of several pollutants, and there are several studies in the literature regarding their performance and removal mechanisms [47,48,50]. In the wetland environment, pesticide removal occurs through physical (settling, adsorption), chemical (oxidation, hydrolysis, photolysis) and biological (plant uptake, metabolism, microbial degradation) processes. In the literature, there are studies regarding the removal of some pesticides from surface runoff using CWs [34–37,48]. However, there is lack of research regarding the treatment of water contaminated with pyraclostrobin by using CWs and gravity filters.

The aim of this study was to investigate the removal efficiency of pyraclostrobin originating from spraying equipment rinsing sites by the use of the following: two mature pilot-scale constructed wetlands (CWs) containing fine gravel and cobbles as porous media, planted with common reed (*Phragmites australis*); and six gravity filters with filling materials of bauxite, carbonate gravel and zeolite.

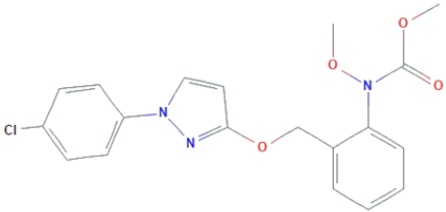
2. Material and Methods

2.1. Properties of Pyraclostrobin

Pyraclostrobin (IUPAC name: methyl-N-[2-[[1-(4-chlorophenyl)pyrazol-3-yl]oxymethyl]phenyl]-N-methoxycarbamate) is a wide spectrum and effective fungicide used to control major plant pathogens in cereals (including wheat, barley, and oat) and other crops (forage and grain maize, triticale, sugarbeet, potatoes, vegetables including brassicas, carrot, beans, vining peas, fruits including strawberry, etc.). It acts against a wide range of fungal dis-

eases, including powdery mildew, Septoria, Rusts, leaf blight, anthracnose and brown spot. The behavior of pesticides and their distribution among the environmental compartments (i.e., water, soil, air, plants and other biota) is a complex process, affected by the application strategy and the physicochemical properties of pesticides, such as water solubility, octanol–water partition coefficient (LogK_{ow}), vapor pressure, soil adsorption coefficient (K_d or K_f or K_{oc}) and degradation time. Based on its physicochemical properties (Table 1), pyraclostrobin is characterized as non-volatile (Henry’s Law constant is lower than $0.1 \text{ Pa m}^3/\text{mol}$), moderately persistent (soil degradation $\text{DT}_{50,\text{field}}$ is between 30 and 100 days) and highly bioaccumulating, as its LogK_{ow} value is higher than 3.0 [4]. Concerning its toxicological profile, pyraclostrobin exhibits high (fish, invertebrate) to moderate (sediment dwelling organisms, aquatic plants, algae) aquatic ecotoxicity.

Table 1. Pyraclostrobin properties.

Parameter	Value
Formula	$\text{C}_{19}\text{H}_{18}\text{ClN}_3\text{O}_4$
Substance group	Strobilurin
Molecular structure	
Molecular weight (g/mol)	387.82
Water solubility at 20 °C (mg/L)	1.9
Octanol–water partition coefficient LogK_{ow} at pH 7 and 20 °C	3.99 (high bioaccumulation)
Vapor pressure at 20 °C (mPa)	2.60×10^{-5}
Sorption coefficient K_{oc} (L/kg)	9304 (non-mobile)
Henry’s Law constant at 25 °C ($\text{Pa m}^3/\text{mol}$)	5.31×10^{-6} (non-volatile)
Soil degradation $\text{DT}_{50,\text{field}}$ ¹ (days)	33.3 (moderately persistent)

¹ half-life for field studies.

2.2. Experimental Systems Description and Operation

Two pilot-scale horizontal subsurface flow (HSF) CWs and six porous media filters (gravity filters) were used. Figure 1a presents a schematic section of each pilot-scale unit, which was a rectangular tank of dimensions 3.0 m long, 0.75 m wide and 1.0 m deep. The thickness of the porous media was 45 cm. The CW units with code names FG-R and CO-R contained fine gravel (code name FG: $D_{50} = 6 \text{ mm}$) and cobbles (code name CO: $D_{50} = 90 \text{ mm}$) as porous media, respectively, which were igneous rocks obtained from a riverbed. The pilot-scale CW units were both planted with *Phragmites australis* (code name: R) and were described in more detail by Akratos and Tsihrintzis [52].

Pyraclostrobin-enriched water at a concentration of 1.3 mg/L , which was used to simulate agricultural wastewater from point sources of pollution, was prepared every day and was used for loading the CW units. Based on our previous experience in respective experiments (i.e., removal of pesticides and pharmaceuticals using CWs), two hydraulic residence times (HRTs) of 6 and 8 days were applied [34–36,53–55]. The loading period lasted from April 2015 to October 2015 with daily loading of 53 and 40 L to achieve HRT of 6 and 8 days, respectively. The design and operational characteristics of the CW units and gravity filters are summarized in Table 2. For the acclimatization of the units, sampling started one month after loading i.e., from May 2015. Water samples from the inlet and outlet of each CW unit were taken every 10 days from May 2015 and were analyzed to determine pyraclostrobin concentration. In order to find the fungicide accumulation in the plants, at the end of the experimental period, roots, shoots and leaves from plants of

both FG-R and CO-R units were collected and analyzed to determine the pyraclostrobin concentrations.

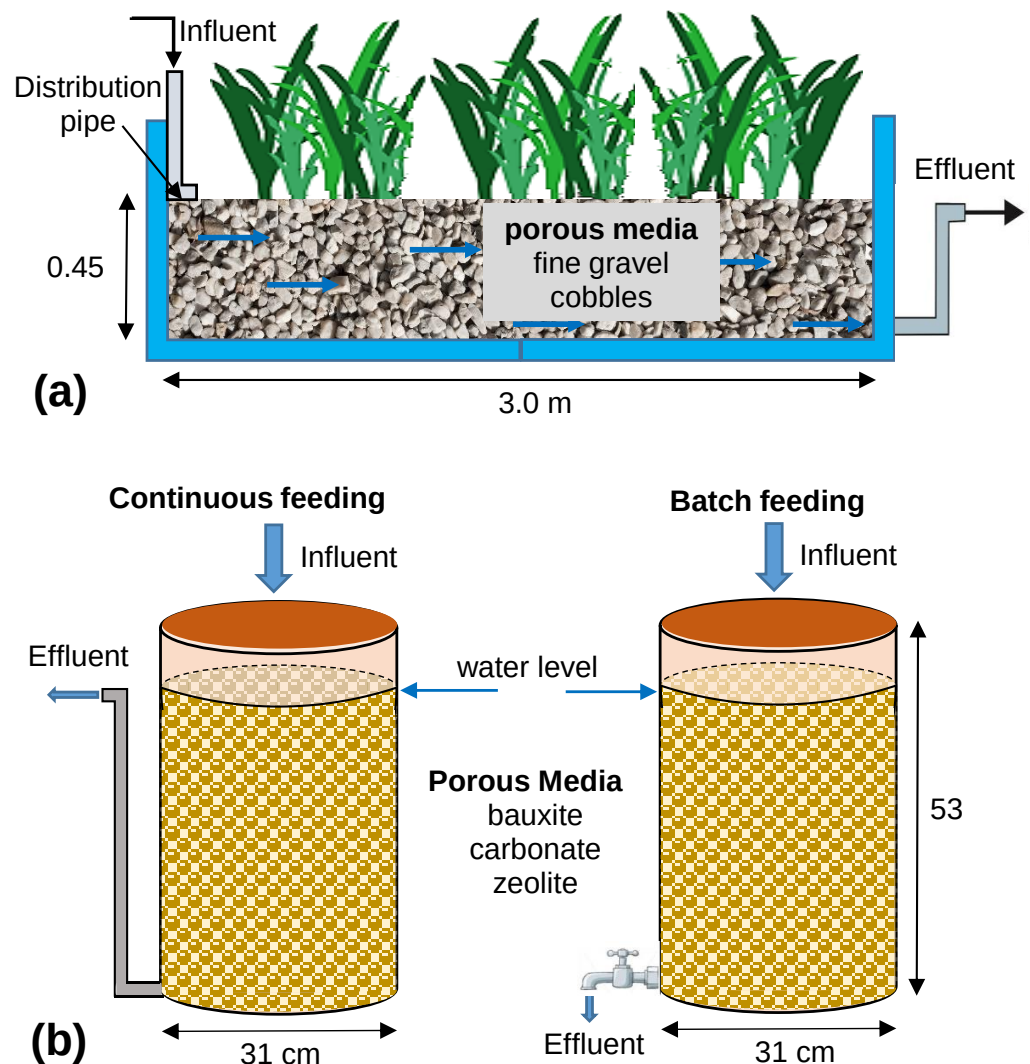


Figure 1. Schematic layout (not to scale) of: (a) pilot-scale CW unit; (b) gravity filters.

The six gravity filters were cylindrical tanks of diameter 31 cm, height 53 cm and nominal volume 40 L; three of them were used for continuous feeding (named: FB-C, FC-C and FZ-C) and the remaining three (named: FB-B, FC-B and FZ-B) for periodic (batch) feeding. A flow control valve was installed at the base of the batch-feeding filters, which was always closed and opened only for emptying the filter. In the continuous feeding filters, a vertical pipe was connected to the bottom of the tank and ended at the height of the surface of the porous media (Figure 1b). The tube was always open and was used to maintain the water level in the filter tank at the upper level of the porous media at all times. So, all filters operated at full saturation conditions, as the water level was always up to the surface of the porous media. For each type of filter, three different porous media were used, i.e., fine bauxite (FB: $D_{50} = 6$ mm; range 2.5–16.0 mm), fine carbonate gravel (FC: $D_{50} = 6$ mm; range 2.5–16.0 mm) and fine zeolite (FZ: $D_{50} = 6$ mm; range 2.5–16.0 mm). The volumes of the filter material and the pore water were 26 and 8 L, respectively. Pyraclostrobin-enriched water at a concentration of 1.3 mg/L was added to the top of the filters. The continuous feeding filters were loaded daily with volumes of 4.0, 2.0 and 1.0 L in order to achieve HRTs of 2, 4 and 8 days, respectively (Table 2). Regarding the batch feeding filters, they were loaded once with 8 L of the above solution, which remained in the filter tank for HRTs of either 2 or 4 days (Table 2). Then, the valve at the bottom of the tank was opened to drain

the solution (water enriched with pyraclostrobin). The tank filter was then refilled with 8 L of fresh solution.

Table 2. Design and operational characteristic of HSF-CWs and gravity filter units.

Constructed Wetlands					
CW Unit	Porous Media	Plant Species	HRT (d)	Q _{in} (L/d)	HLR (mm/d)
CO-R	Cobbles	<i>Phragmites australis</i>	6	53	23.6
			8	40	17.8
FG-R	Fine gravel	<i>Phragmites australis</i>	6	53	23.6
			8	40	17.8
Gravity Filters					
Continuous Feeding			Periodical (batch) Feeding		
Filter Unit	Porous Media	HRT (days)	Filter Unit	Porous Media	HRT (days)
FB-C	Bauxite	2, 4, 8	FB-B	Bauxite	2, 4
FC-C	Carbonate	2, 4, 8	FC-B	Carbonate	2, 4
FZ-C	Zeolite	2, 4, 8	FZ-B	Zeolite	2, 4

HRT: hydraulic residence time, Q_{in}: influent rate, HLR: hydraulic loading rate.

Water samples from the inlet and outlet of each filter were collected every seven days from the continuous filters and on the day of loading from the batch filters for the determination of the pyraclostrobin concentration. During the experiment, all filter tanks were kept closed to prevent evaporation. Physicochemical parameters, such as temperature (T), pH, dissolved oxygen (DO) and electrical conductivity (EC), were measured in situ at the inlet and outlet of the two CWs and the six filters, using a portable measuring device (WTW, series 197i, Germany).

2.3. Methodology for Pyraclostrobin Determination

Water samples (200 mL) from the inlet and outlet of the CWs and the filters were first filtered (0.7 µm), and within 24 h, the solid phase extraction (SPE) was performed by using C18 (500 mg/6 mL) cartridges, following the method described by Papaevangelou et al. [34]. Instrumental analysis was performed on a HPLC-PDA (Thermo Finnigan, Surveyor system equipped with LC solvent pump, degasser, auto-sampler and photodiode array detector). The Hypersil Gold 100 × 4.6, 5 m HPLC column was used for chromatography. The mobile phase of the HPLC system consisted of an acetonitrile: water gradient program from 20% to 95% acetonitrile in 11 min followed by a hold period of 9 min, after which the system was returned to the initial conditions for equilibration. The flow rate of the mobile phase was 1 mL/min. The acquisition of the data was made at 230 and 275 nm, and quantification was conducted at 275 nm. The pyraclostrobin limit of detection and limit of quantification were 0.1 and 1 µg/L. Recoveries were tested at 3 levels (800, 100 and 10 µg/L) and ranged from 84% to 105% with RSD lower than 10%. Pyraclostrobin concentration on plants of *Phragmites australis* was determined by the “QuEChERS acetate” methodology, as presented by Liu et al. [56] and Gikas et al. [35].

2.4. Statistical Analyses

The SPSS 25.0 statistical package was used for statistical analyses. Levene’s test was used to test the data for normality and variance homogeneity. The Student’s *t*-test was used in order to compare the capacity of the CW units and evaluate the contribution of porous media and HRT on the overall removal. In addition, the *t*-test was used to assess the feeding strategy of filter units. Differences in removal efficiencies of pyraclostrobin among the three gravity filters (with different porous media) were estimated using the Kruskal–Wallis test. In cases where the Kruskal–Wallis test indicated significant differences

between filters, pairwise comparisons were evaluated using the Mann–Whitney U-test. The statistically significant level was set at $p = 0.05$.

3. Results and Discussion

3.1. Physicochemical Parameters in Constructed Wetlands

Figure 2 presents box–whisker plots of physicochemical parameters of the inflow and outflow of CW units. The median value is indicated by the line inside the box, the upper (75th) and the lower (25th) quartiles are denoted by the caps of the box, and the minimum and maximum values are indicated by the whiskers of each box. The mean temperature (T) of the influent water in the CW units was $25.3\text{ }^{\circ}\text{C}$, showing a low increase at the outlet of the units (Figure 2a). The average temperatures of the effluent water of CO-R and FG-R units were 27.6 and $27.5\text{ }^{\circ}\text{C}$, respectively. The pH values of water at the inlet and outlet of the CW units were in the neutral range (7.0 ± 0.4) without remarkable fluctuations (Figure 2b). The mean pH value of the influent was 7.3 , and of the effluent, 7.0 and 6.9 for CO-R and FG-R units, respectively.

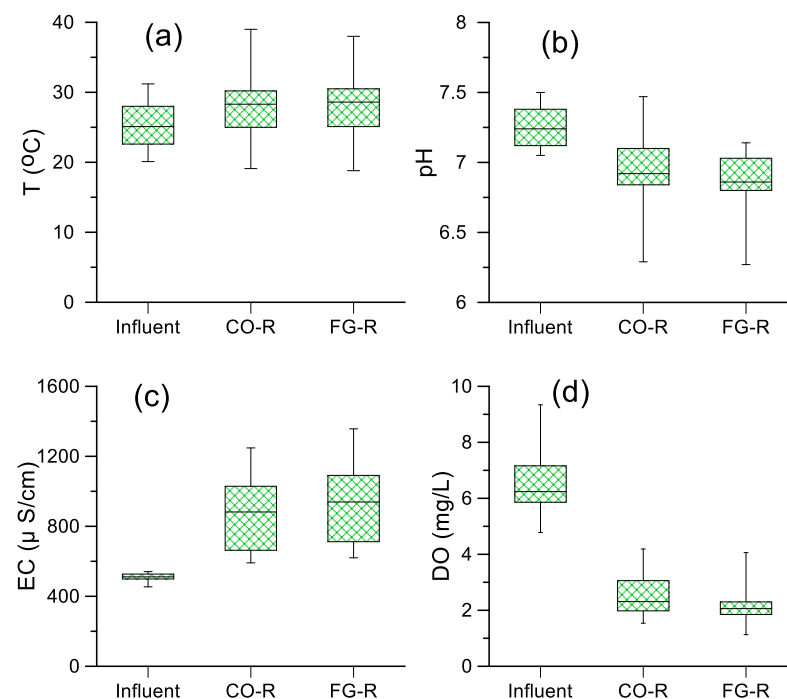


Figure 2. Box–whisker plots of physicochemical parameters in the CWs units: (a) temperature; (b) pH; (c) electrical conductivity; (d) dissolved oxygen. The line inside the box denotes median values, the upper and lower box frames denote the 75 and the 25 percentiles, respectively, and the whiskers denote the maximum and minimum values.

The EC values of water in the effluent of the CW units were higher than those in the influent (Figure 2c), which may be attributed to the release of ions in the substrate from the plant (*Phragmites australis*) root system, as well as to condensation due to evapotranspiration, especially in the period (mainly on summer months) when the air temperature is high [54]. The mean EC value of the influent was $509.5\text{ }\mu\text{S}/\text{cm}$, and those of the effluent were 866.5 and $901.7\text{ }\mu\text{S}/\text{cm}$ for CO-R and FG-R units, respectively. The mean DO concentration in the influent ($6.6\text{ mg}/\text{L}$) was higher than the values in the effluents of the CW units (Figure 2d) due to the consumption by microorganisms, even though the plants transfer oxygen to the rhizosphere [57]. The mean DO concentrations in the effluent were 2.5 and $2.2\text{ mg}/\text{L}$ for CO-R and FG-R, respectively.

3.2. Pyraclostrobin Removal in the CW Units

Figure 3 presents the concentrations and the percent removal of pyraclostrobin at the inlet and outlet of the CO-R and FG-R units throughout the experimental period. The influent and effluent pyraclostrobin concentrations did not indicate any seasonal fluctuation. The influent pyraclostrobin concentration range for both CW units was 1.01–1.40 mg/L and the effluent concentration range was 0.40–0.59 mg/L and 0.20–0.38 mg/L for CO-R and FG-R units, respectively. The mean influent value for both CW units was 1.21 mg/L, and the mean effluent values for CO-R and FG-R units were 0.52 and 0.30 mg/L, respectively. The two pilot-scale units showed satisfactory pyraclostrobin removal throughout the experimental period. Mean removal efficiencies were 56.7% and 75.2% for CO-R and FG-R units, respectively. Box-whisker plots of removal capacity (Figure 4a) showed a difference between the two units for the entire period. The *t*-test analysis indicated statistically significant differences for the mean removal efficiencies between CO-R and FG-R units ($p < 0.05$). This means that the CW with fine gravel as the porous media was more effective in removing pyraclostrobin than the CW with cobbles, indicating that the grain size of the porous medium is an important design parameter in the CWs.

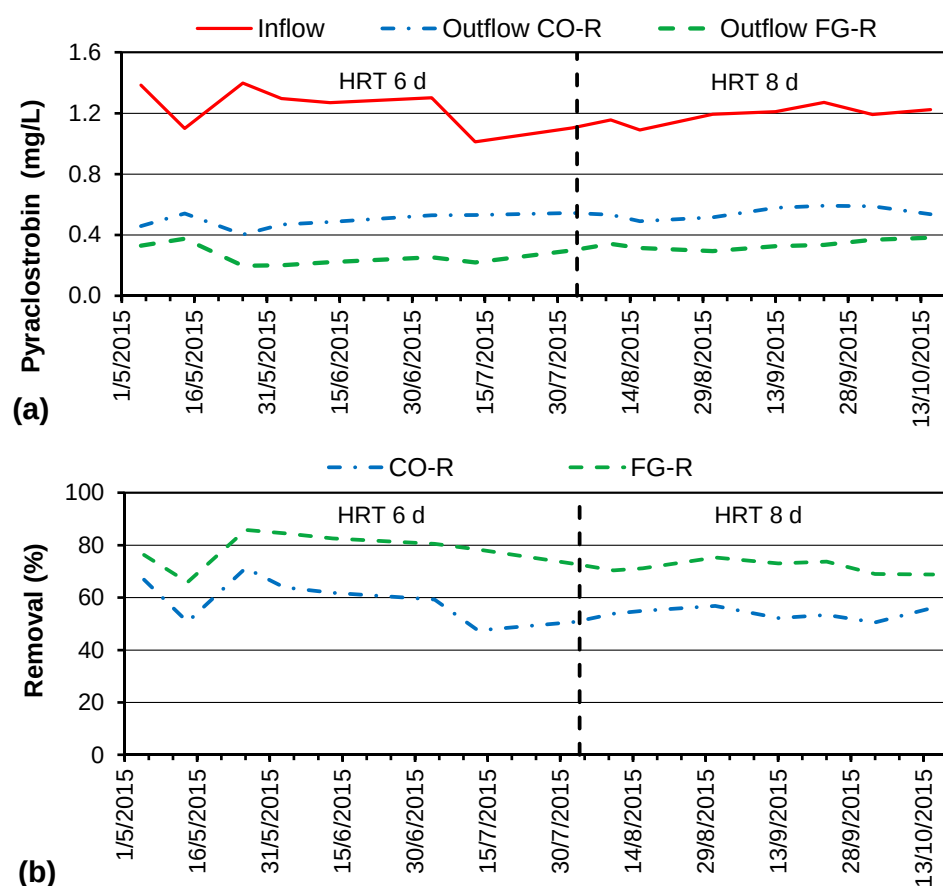


Figure 3. (a) Variation of pyraclostrobin concentration in pilot-scale CW influent and effluents; (b) removal efficiencies (%).

The effectiveness of constructed wetlands is affected by HRT, with higher removal of pesticides relating to longer HRT, particularly for hydrophobic compounds ($\text{LogK}_{\text{ow}} > 4$). High HRT favors processes such as adsorption of pesticides on porous media and precipitation, resulting in their removal from the aqueous phase [58]. In the present study, two HRTs of 6 and 8 days were applied. Figure 4b presents the pyraclostrobin removal in the two pilot-scale CW units for HRTs of 6 and 8 days. The comparison of the two HRTs is valid because there was minor difference in the water temperature at the effluent of the CW units, with the mean temperatures being 28.2 and 25.7 °C for HRTs of 6 and 8 days, respectively.

The box–whisker plot shows that there was a minor difference between removals with mean percent removals of 68.7% and 62.8% for HRTs of 6 and 8 days, respectively. The *t*-test showed that there was no statistically significant difference in removals between the two HRTs ($p > 0.05$). These results suggest that 6-day HRT may be sufficient for pyraclostrobin removal (Figure 4b). Similar results were reported for boscalid, terbuthylazine, S-metolachlor and fluopyram with LogK_{ow} of 2.96, 3.4, 3.05 and 3.3, respectively [34–36,55].

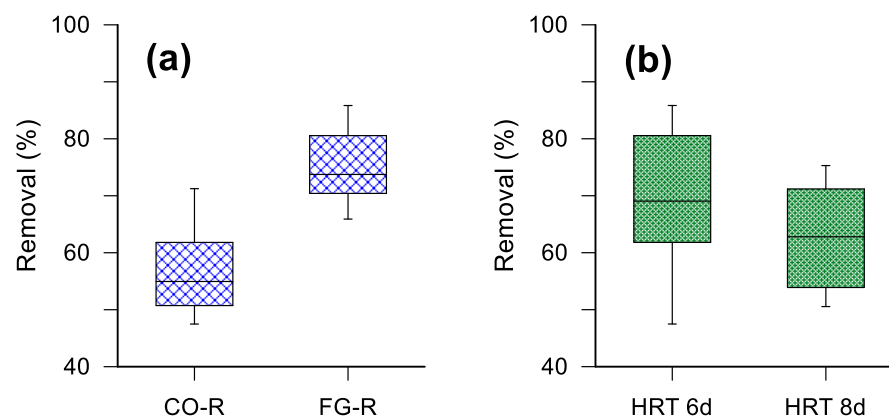


Figure 4. Box–whisker plots of pyraclostrobin removal efficiencies for the entire experimental period: (a) overall for each CW unit; (b) for HRTs of 6 and 8 days.

In the constructed wetlands environment, the main processes for pesticides elimination or removal are physicochemical processes, such as volatilization, hydrolysis, photolysis and adsorption on substrate, and biological processes, such as plant absorption and biodegradation [54,59]. Therefore, in the present study, the removal of pyraclostrobin due to volatilization is considered negligible, as the Henry’s Law constant is less than $0.1 \text{ Pa m}^3/\text{mol}$ and the vapor pressure $< 5.0 \text{ mPa}$ (Table 1), indicating that pyraclostrobin is nonvolatile [4].

Hydrolysis experiments in aqueous solution of pyraclostrobin at concentration of 10 mg/L and at pH 5.0, 7.0, and 9.0, and in rain water with pyraclostrobin concentration of 5 mg/L and pH 6.2 to 7.9 were conducted by Zeng et al. [16]. The results indicated that pyraclostrobin was very stable at pH 5.0. The half-life values of pyraclostrobin in aqueous solutions at pH 7.0 and 9.0 were 99.02 and 46.21 days, respectively. In rain water, the half-life was 115.5 days, and the presence of microorganisms did not affect the pyraclostrobin hydrolysis rate. In the present study, the pH values of water in the CW pilot-scale units ranged between 6.6 and 7.4 (Figure 2b), and the HRT was 6 and 8 days; therefore, the removal of pyraclostrobin by hydrolysis is considered negligible.

Photocatalytic degradation in an aqueous solution of pyraclostrobin (2.3 mg/L) with the presence of TiO_2 (0.5 g/L) as a photocatalyst and UV light irradiation for 60 min was conducted by Lagunas-Allué et al. [38]. Results showed that about 99% of pyraclostrobin was degraded, which was 15 times faster than direct photolysis. Zeng et al. [16] also reported that the degradation rate of pyraclostrobin in aqueous solution under the irradiation of UV light was faster than that under sunlight. The half-life values of pyraclostrobin in aqueous solutions at pH 5.0, 7.0 and 9.0 under UV light were 2.42, 1.47 and 1.32, and under sunlight, they were 11.2, 3.29 and 3.69 h, respectively. In the present study, the loading solution was prepared daily and shortly before loading the units, and the water level in the CWs was always below the substrate surface. Moreover, the existing vegetation further reduced the penetration of sunlight. Therefore, photodegradation is considered to have little contribution to pyraclostrobin removal in the pilot-scale CW units.

The plant uptake and phytoaccumulation of pesticides are dependent on both the plant species and the pesticide characteristics, such as octanol/water partition coefficient (LogK_{ow}). Pesticides with LogK_{ow} values ranging from 3.0 to 4.0 have higher accumulation in plant tissue compared to those with a LogK_{ow} value greater than 4.0 [13,60]. Additionally, chemical compounds with LogK_{ow} values ranging between 0.5 and 3.0 are more hydrophilic

and show the best accumulation in plants through root absorption [61]. Pyraclostrobin with LogK_{ow} value of 3.99 (Table 1) is moderately hydrophobic [4], and therefore, high accumulation on plant tissue of pyraclostrobin is expected. However, research on the ability of plants to remove pyraclostrobin is limited. At the end of the experimental period, plant analysis was performed, and the concentration of pyraclostrobin in the roots, shoots and leaves was determined. The mean pyraclostrobin concentrations were 0.3, 0.7 and 4.9 mg/kg dry weight for the leaves, shoots and roots, respectively, showing that a higher pyraclostrobin accumulation occurs in the root of *Phragmites australis*. Previous studies also reported that the roots of macrophytes (i.e., *Phragmites australis*, *Typha latifolia*, etc.) accumulate the highest amounts of pesticides [36,54,59]. The phytoremediation process is considered effective when pesticide entrapped in the roots (belowground biomass) can be translocated to shoots and leaves (aboveground biomass). The ability of plants to transfer pesticides from underground to aboveground biomass is provided by the translocation factor ($\text{TF} = C_a/C_b$; C_a and C_b is the pesticide concentration in aboveground and belowground plant tissues). In the present study, the TF was found to be 0.2 (less than 1), which means that the pyraclostrobin is accumulated in the belowground biomass (rhizome). Higher TF values (3.9 and 1.8 for imazalil and tebuconazole, respectively) in *P. australis* were reported by Lv et al. [59].

The pyraclostrobin biodegradation half-life of 33 days in soil (Table 1) indicates that biodegradation may be an important process for pyraclostrobin removal. According to Chen et al. [62], the microbial metabolism is one of the main pathways responsible for the degradation of strobilurins (i.e., pyraclostrobin and azoxystrobin) in the soil. Strobilurin-degrading microbes include *Bacillus*, *Pseudomonas*, *Klebsiella*, *Stenotrophomonas*, *Arthrobacter*, *Rhodanobacter*, *Cupriavidus*, and *Aphanoascus* [63]. Biodegradation studies of pyraclostrobin by bacteria from orange growing plots were conducted by Biroli et al. [64]. The results showed that the biodegradation rate is mainly affected by the initial concentration of pyraclostrobin, which showed a positive contribution, and secondly by the temperature, which showed a negative contribution. Thus, increasing the concentration of pyraclostrobin increases the biodegradation percentage, and increasing the temperature decreases the biodegradation. Considering the previous discussion, adsorption on substrate, phytoaccumulation and microbial biodegradation can be key factors in the overall pyraclostrobin removal in the pilot-scale CW units.

Based on the literature, various metabolites have been identified during pyraclostrobin hydrolysis, photolysis and biodegradation. Photocatalytic degradation of pyraclostrobin in the presence of TiO_2 as a photocatalyst and UV light irradiation was conducted by Lagunas-Allué et al. [38]. Based on the results of the experiments, possible photodegradation pathways were proposed with the main steps as follows: hydroxylation of the aromatic rings followed by the loss of the N-methoxy group, substitution of chloride atom by a hydroxyl group, rupture of the pyrazol and phenyl bond, and the scission of the oxygen and pyrazol bond. In addition, the hydrolysis and photolysis of pyraclostrobin in paddy water were studied, and the metabolites of pyraclostrobin were identified by Zeng et al. [16]. Two and three metabolites were detected and identified in hydrolysis and photolysis, respectively, and the results showed that the metabolites have completely different hydrolysis and photolysis processes. Furthermore, the biodegradation of pyraclostrobin by bacteria from orange cultivation plots was studied by Biroli et al. [64]. They proposed a new biodegradation pathway with 15 identified metabolites. The five metabolites with small molecules from the pyraclostrobin biodegradation produced were 1-(4-chlorophenyl)-1H-pyrazol-3-ol, phenylmethanol, benzaldehyde, acetamide and formamide.

An operational problem that may occur during the operation of HSF-CWs is the clogging of the porous media. The clogging is mainly due to suspended solids. The experimental findings of this study can help in designing HSF CWs for treating, for example, spraying tank rinsing water or agricultural runoff, which is usually discharged untreated directly to nearby streams. In an actual design project, engineering solutions can be provided to remove the suspended solids of the spraying tank rinsing water or the agricultural

runoff. Proper design of the porous media (or pretreatment of the wastewater in case of high suspended sediment concentrations) can be employed to effectively address this potential problem and increase the lifespan of the system.

3.3. Pyraclostrobin Removal in the Gravity Filters

Statistics (mean value, standard deviation, minimum and maximum values) of influent and effluent concentrations of pyraclostrobin in the filter units for each HRT are presented in Table 3. The mean pyraclostrobin concentration at the inlet of the filters was between 1.15 and 1.25 mg/L; the mean concentrations at the outlet ranged between 0.41 and 0.92 mg/L. They were generally lower than those at the inlet, indicating the ability of the filters to remove pyraclostrobin. The lowest mean effluent values for the entire experimental period were 0.48 mg/L (range 0.34–0.70 mg/L) and 0.49 mg/L (range 0.24–0.68 mg/L) in filters FZ-C and FZ-B, respectively (Table 3). Table 3 also presents the statistics of removal efficiencies of pyraclostrobin for all filters and for each HRT. The filters with fine zeolite as porous media for both continuous and batch feeding strategies showed the highest efficiency in pyraclostrobin removal, which ranged between 49.7% and 69.2% for the FZ-C filter, and between 49.4% and 79.8% for the FZ-B filter. As in the case of the CW units, the removal of pyraclostrobin in the filter units by volatilization, hydrolysis and photolysis, as well as plant uptake is negligible due to the absence of plants. Therefore, adsorption on porous media and microbial degradation can be key processes for pyraclostrobin removal in gravity filters.

Table 3. Statistical data of influent and effluent of pyraclostrobin in filter units.

Continuous Feeding												
Influent Concentration (mg/L)				Effluent Concentration (mg/L)								
				FB-C			FC-C			FZ-C		
	2 d	4 d	8 d	2 d	4 d	8 d	2 d	4 d	8 d	2 d	4 d	8 d
Mean	1.23	1.25	1.19	0.82	0.84	0.80	0.80	0.78	0.75	0.52	0.47	0.45
SD	0.13	0.07	0.06	0.12	0.06	0.05	0.08	0.09	0.05	0.10	0.05	0.04
Max	1.40	1.40	1.27	0.95	0.94	0.89	0.94	0.92	0.81	0.70	0.53	0.52
Min	1.01	1.10	1.10	0.63	0.73	0.75	0.70	0.68	0.66	0.34	0.40	0.38
Removal (%)												
Mean				33.10	32.31	32.93	34.95	36.98	37.35	58.32	62.66	62.58
SD				11.10	6.55	6.69	8.18	7.37	4.41	5.84	3.05	3.79
Max				54.51	43.58	40.96	47.93	45.53	45.00	69.18	68.00	66.61
Min				17.82	21.00	19.76	25.36	24.18	32.55	49.68	58.90	56.68
Batch Feeding												
Influent Concentration (mg/L)				Effluent Concentration (mg/L)								
				FB-B		FC-B		FZ-B				
	2 d	4 d		2 d	4 d	2 d	4 d		2 d	4 d		4 d
Mean	1.29	1.15		0.92	0.82		0.86	0.76		0.57		0.41
SD	0.13	0.12		0.05	0.09		0.03	0.08		0.10		0.12
Max	1.50	1.37		0.97	0.96		0.89	0.87		0.68		0.57
Min	1.09	1.01		0.82	0.66		0.79	0.62		0.39		0.24
Removal (%)												
Mean				28.04	28.47		32.51	33.15		56.03	64.49	
SD				8.42	7.31		8.04	9.38		6.36	9.59	
Max				40.87	39.69		42.82	44.90		68.70	79.84	
Min				16.52	19.04		19.72	15.40		49.42	51.24	

SD: standard deviation, Max: maximum value, Min: minimum value.

The effect of the design parameters on pyraclostrobin removal in gravity filters is presented in Figure 5. The mean removal values of pyraclostrobin in gravity filter units were 43.44% and 40.80% for continuous and batch feeding, respectively, without statistically significant differences between them (t -test: $p > 0.05$). Similar results were reported for the removal of fluometuron in gravity filters by Gikas et al. [37]. The filters with fine zeolite showed higher removal capacity than the other filters (Figure 5b). The mean removal values for FB, FC and FZ filters were 32.5%, 36.7% and 61.2%, respectively. The pyraclostrobin removal efficiency in FZ filters was statistically significantly higher than those in FB ($p < 0.05$) and FC ($p < 0.05$). Previous studies indicated that the presence of zeolite in CW and in gravity filters as porous media increased the pesticide adsorption [37,55,65–67]. In the present study, three HRTs of 2, 4 and 8 days were applied at the continuous filters and two HRTs of 2 and 4 days at the batch filters. Figure 5c presents the pyraclostrobin removal in the filter units at HRTs of 2, 4 and 8 days. The mean removal values of pyraclostrobin were 39.9%, 43.4% and 44.1% for HRTs of 2, 4 and 8 days, respectively, without statistically significant differences between them (Kruskal–Wallis test: $p > 0.05$). The difference in the mean removal of pyraclostrobin between HRTs of 2 and 4 days was 3.5% and that between HRTs of 4 and 8 days was 0.7%, suggesting that an HRT of 4 days may be sufficient for pyraclostrobin removal in gravity filters. These results are in agreement with those of a previous study on the removal of fluometuron in gravity filters [37].

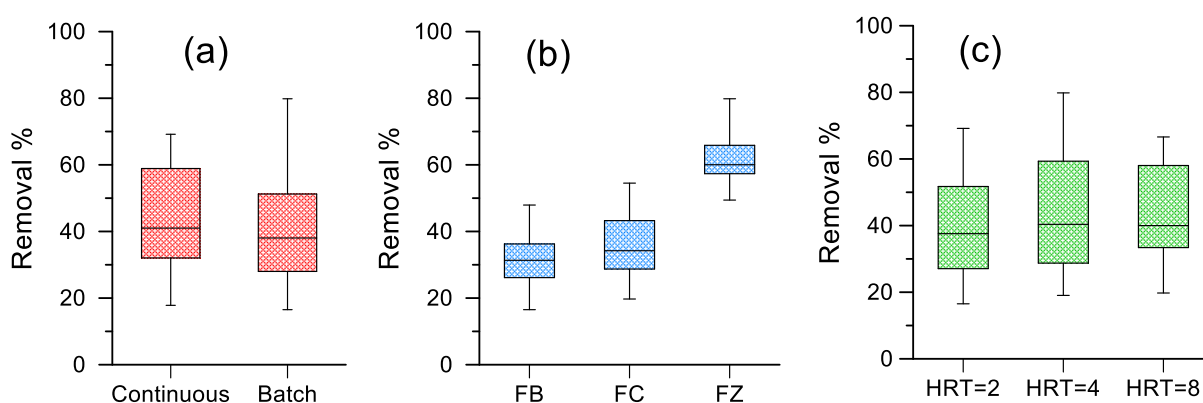


Figure 5. Effect of design parameters on pyraclostrobin removal in gravity filters: (a) feeding strategy; (b) porous media; (c) hydraulic residence time.

4. Conclusions

Two low-cost natural systems—constructed wetlands and gravity filters—were employed in the removal of pyraclostrobin from polluted water. Plant absorption in CWs, and microbial degradation and adsorption on the substrate in both CW and filter systems were the main processes for pyraclostrobin removal, while in both systems, its removal by volatilization, hydrolysis and photolysis was negligible. The FG-R unit with porous media fine gravel achieved the highest removal efficiency of pyraclostrobin of 75.2%, indicating that the grain size of the porous medium is an important design parameter in the CWs. According to the findings of the present study, pyraclostrobin is accumulated in the rhizome of *Phragmites australis*. An HRT of 6 days is sufficient for pyraclostrobin removal. On the other hand, the filters with fine zeolite as porous media, for both continuous and batch feeding strategies, showed the highest pyraclostrobin removal; in contrast to the feeding strategy, the HRT was found to have a great effect on fungicide removal. Hybrid systems combining CW and filters could be placed in series to increase pesticide removal from agricultural runoff and improve water quality. The installation and operation of such systems at point sources of pollution (e.g., sites where equipment for mixing and spraying pesticides is washed) would be one measure to effectively mitigate the pesticide risk to surface and groundwaters in agricultural areas at low cost.

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