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Enhanced Removal of Ibuprofen, Paracetamol, and Caffeine in Vertical Constructed Wetlands Using Biochar and Zeolite as Support Media

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Abstract

Pharmaceuticals such as ibuprofen, paracetamol, and caffeine are commonly found in wastewater due to incomplete removal in conventional treatment systems. This study evaluated three vertical constructed wetland (V-CW) configurations: V1 (gravel–sand with vegetation), V2 (biochar–zeolite with vegetation), and V3 (biochar–zeolite without vegetation). All systems achieved high removal efficiencies for organic matter (Chemical Oxygen Demand (COD): 89.4–91.7%, Biochemical Oxygen Demand over 5 days (BOD_5): 93.3–93.8%, Total Suspended Solids (TSS): 94.5–96.6%) and pharmaceuticals (ibuprofen: 81.8–91.5%, paracetamol: 90.0–94.3%, caffeine: 93.1–97.2%). Statistical analysis showed that substrate type significantly influenced ibuprofen (p = 0.0035) and caffeine (p = 0.0436) removal, while vegetation had no significant effect (p > 0.266). The enhanced performance of biochar and zeolite can be attributed to their high adsorption capacity and microbial support, with adsorption and biodegradation identified as dominant removal mechanisms, as reported in previous research. These findings highlight the importance of engineered substrates in optimizing constructed wetlands for wastewater treatment to improve the removal of emerging contaminants. Future research should focus on long-term substrate performance, cost-effectiveness, and field-scale validation, particularly in regions with vulnerable groundwater systems such as the Yucatán Peninsula.

Keywords: adsorption; biodegradation; decentralized sanitation; emerging contaminants; pharmaceutical wastewater treatment; tropical climate

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1. Introduction

The occurrence of pharmaceuticals in aquatic environments has emerged as a critical environmental and public health concern worldwide. Widely consumed compounds, such as ibuprofen, paracetamol, and caffeine, are consistently detected in wastewater effluents and surface waters due to their extensive use and incomplete removal in conventional wastewater treatment plants [1,2].

Their presence has been associated with ecotoxicological effects on aquatic organisms, alterations in microbial community structure, endocrine disruption, bioaccumulation, and the promotion of antimicrobial resistance, all of which pose risks to both ecosystem health and human safety [3,4]. Additionally, caffeine is widely used as an indicator of pharmaceutical pollution in aquatic environments due to its anthropogenic nature, distinctive origin, environmental destination, and elevated consumption [5]. Its persistence and correlation with other pharmaceuticals make it a reliable tracer for anthropogenic contamination.

The urgency of developing effective treatment strategies is particularly evident in vulnerable regions such as the Yucatán Peninsula aquifer, one of the world's largest karstic groundwater systems. Its highly permeable limestone geology, lack of natural filtration, limited wastewater infrastructure, and pressures from agriculture and tourism make it highly susceptible to contamination by pharmaceuticals and other emerging pollutants [6]. Protecting this critical water resource requires innovative, low-cost, and environmentally sound treatment approaches.

Traditional wastewater treatment technologies are often ineffective at removing pharmaceuticals, necessitating the development of sustainable and low-cost alternatives. In this context, constructed wetlands (CWs) have gained increasing attention as nature-based treatment systems capable of eliminating a diverse range of pollutants through a combination of adsorption, biodegradation, phytoremediation, and sedimentation [7,8]. Among CW designs, vertical flow constructed wetlands (V-CWs) offer distinct advantages, including enhanced oxygen transfer, efficient pollutant removal, reduced land footprint, and cost-effectiveness, making them highly suitable for treating wastewater contaminated with pharmaceuticals [9–11]. Table 1 summarizes the use of various wetland systems and their effectiveness in removing pharmaceuticals.

Table 1. Recent studies of pharmaceutical removal using CWs and hybrid treatment systems.

Treatment System	Support Medium Used	Reported Pharmaceutical Removal
V-CWs [12]	Mixture of gravel and sand	>75% for Ibuprofen and Paracetamol
Combined Anaerobic Digester, V-CWs and UV Photolysis [13]	Mixture of gravel and sand	100% removal of Ibuprofen, 98% for Paracetamol, and 87% for Caffeine
V-CWs [14]	Mixture of gravel, sand and biochar	79.93% removal of Ibuprofen, and 87.53% of caffeine
V-CWs [15]	Light expanded clay aggregates (LECA)	87–93% removal of Caffeine
V-CW with Microbial Fuel Cell (MFC) [16]	Gravel and granular activated carbon (GAC)	49–62% removal of Ibuprofen
Horizontal-CWs (HCWs) [17]	Gravel	94.03 average removal of Ibuprofen
HCWs and Stabilization Ponds [18]	Tezontle	Increased concentrations of Ibuprofen due to anoxic conditions.
Aerobic reactor and H-CWs [19]	Gravel, GAC, river sand, and potting soil	94% removal of paracetamol
V-CWs [20]	Biochar	Up to 99% removal of Ibuprofen

Recent research highlights the significance of substrate composition in enhancing CW performance. Biochar, a porous carbonaceous material obtained through the pyrolysis of organic biomass, has demonstrated a high adsorption capacity and excellent potential for supporting microbial growth, thereby facilitating both sorption and biodegradation of pharmaceutical contaminants [21]. Its incorporation into CWs has been shown to significantly enhance the removal of nutrients, organic matter, and pharmaceuticals, including acetaminophen [22,23]. Zeolite, a microporous aluminosilicate with high cation exchange capacity, further complements biochar by adsorbing a wide range of organic and inorganic contaminants. Studies have shown that zeolite-based wetlands achieve remarkable pharmaceutical removal efficiencies, in some cases achieving complete elimination [24].

As shown in Table 1, support media such as gravel and sand are the most commonly used support media in CWs. Support mediums such as biochar and LECA have been recently studied to enhance CW's performance. The combined use of biochar and zeolite in a vertical constructed wetland, however, remains underexplored, particularly in systems integrated with native wetland plants. Species such as *Typha dominguensis* are known to enhance phytoremediation and stimulate rhizospheric microbial activity [25], even promoting the removal of pharmaceuticals [26]. However, their performance in engineered biochar–zeolite systems has not been documented, as shown in Table 1. This represents a significant research gap in advancing sustainable wastewater treatment technologies.

Therefore, this study aims to evaluate the performance of vertical constructed wetlands under three configurations: traditional gravel–sand media with plants (V1), biochar and zeolite with plants (V2), and biochar and zeolite without plants (V3). The specific objective is to determine the efficiency of these systems in removing ibuprofen, paracetamol, and caffeine from wastewater. By addressing the combined role of engineered substrates and wetland vegetation, this work provides insights into the optimization of CWs for pharmaceutical removal. It offers a pathway toward safeguarding vulnerable aquifers such as those of the Yucatán Peninsula.

2. Materials and Methods

2.1. Reagents and Materials

The standards of caffeine (Ph Eur, anhydrous, ≥99.0%; Fluka Analytical, Buchs, Switzerland; Cat. No. 27602), ibuprofen (≥98%; Sigma-Aldrich, St. Louis, MO, USA; Cat. No. I4883), and paracetamol (acetaminophen, BioXtra, ≥99.0%; Sigma-Aldrich, St. Louis, MO, USA; Cat. No. A7085) were purchased for the laboratory analysis and spiking of the septic tank as described in Section 2.3. Gravel, zeolite, and sand were acquired from local material stores. Biochar was prepared using the method described in Section 2.2.

All the materials used for setting up the Vertical CWs and sampling were described in Sections 2.4 and 2.6.

2.2. Biochar Preparation

In this study, the biochar used was provided by Díaz Lara et. al. [27], who produced it using a Kon-Tiki open-pit kiln designed for flame curtain pyrolysis. The process involved layering dried biomass—sourced from gardening residues—into the kiln and igniting it from the top. As each layer underwent carbonization, fresh biomass was added, allowing the combustion gases to form a protective flame curtain that minimized oxidation of the underlying char.

Once the kiln was fully loaded and pyrolysis was complete, the hot biochar was quenched with water to halt combustion and stabilize the material. The resulting biochar was then dried, ground to a particle size below 2 mm, and stored in sealed containers until further use.

The characterization of the biochar was carried out based on its physical and chemical properties, including pH, electrical conductivity, moisture content, ash content, volatile matter, and fixed carbon. These parameters were determined following standardized procedures and were detailed by Díaz Lara et al. [27].

Figure 1 shows the methodological steps followed in this research.

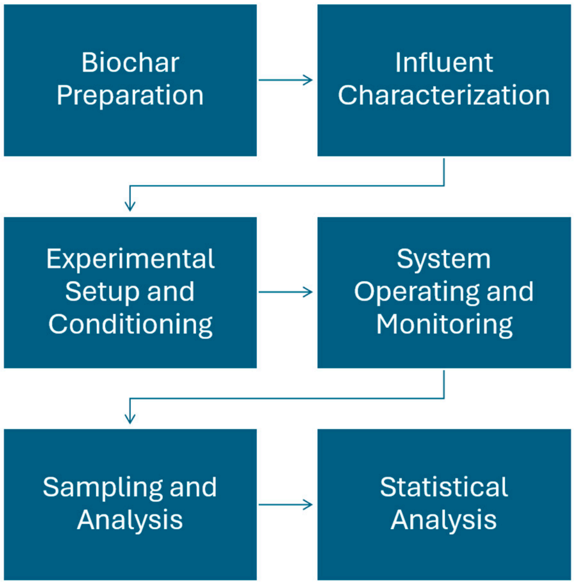

Figure 1. Block Flow Diagram of the Study's Methodology.

2.3. Influent Characterization and Fortification of the Septic Tank Water with Pharmaceuticals

Before starting the operation phase of the CWs, the influent wastewater from the WWTP was sampled to analyze the presence of the target pharmaceuticals. During a two-month monitoring campaign, three composite samples were obtained. Each composite consisted of individual samples collected every 4 h over a 12 h period. The analyses focused on Chemical Oxygen Demand (COD), Biochemical Oxygen Demand over 5 days (BOD_5), Total Suspended Solids (TSS), ibuprofen (IBU), paracetamol (PAR), and caffeine (CAF). The analytical methods are explained in Section 2.5.

During the initial sampling of raw wastewater, the detected concentrations of pharmaceuticals were too low to allow for a meaningful evaluation of their removal in constructed wetlands. To overcome this limitation, water stored in the septic tank was fortified to a concentration of 10 mg/L for each one of the compounds studied: paracetamol, ibuprofen, and caffeine. This experimental adjustment ensured that removal processes could be observed and quantified more clearly under controlled conditions.

In addition to facilitating the assessment of treatment performance, the spiking strategy provides valuable insights into the potential behavior of constructed wetlands under higher pharmaceutical loads than those currently encountered in domestic wastewater. That approach not only strengthens the understanding of removal mechanisms but also highlights the applicability of constructed wetlands for treating more contaminated effluents, such as hospital wastewater, where pharmaceutical concentrations are typically elevated.

2.4. Experimental Setup and Startup

The experimental system was constructed at the San Carlos wastewater treatment plant (WWTP) in the city of Mérida, Yucatán, Mexico. The WWTP is abandoned, but the sump pit still collects the neighborhood's wastewater to pump it to another WWTP.

The experimental setup was adapted from the design reported by Vega De Lille et al. [28]. It consisted of a polyethylene tank with a capacity of 1.1 m^3, which worked as a septic tank for pretreatment. The septic tank received the raw wastewater that was pumped from WWTP's sump pit. Then, the septic tank fed three vertical CWs (V-CWs). The V-CWs were made of 1 cm thick glass, with dimensions 0.6 m × 0.4 m × 0.7 m. The V-CWs were supported by tubular steel bases at a height of 0.6 m to ensure the system's stability.

PVC pipes and valves were used to connect the system and were located at the inlet and outlet of each stage, including the septic tank. To pump the wastewater from the septic tank to the V-CWs, a 1 HP submersible pump was used. A diagram of the Vertical CWs system is shown in Figure 2.

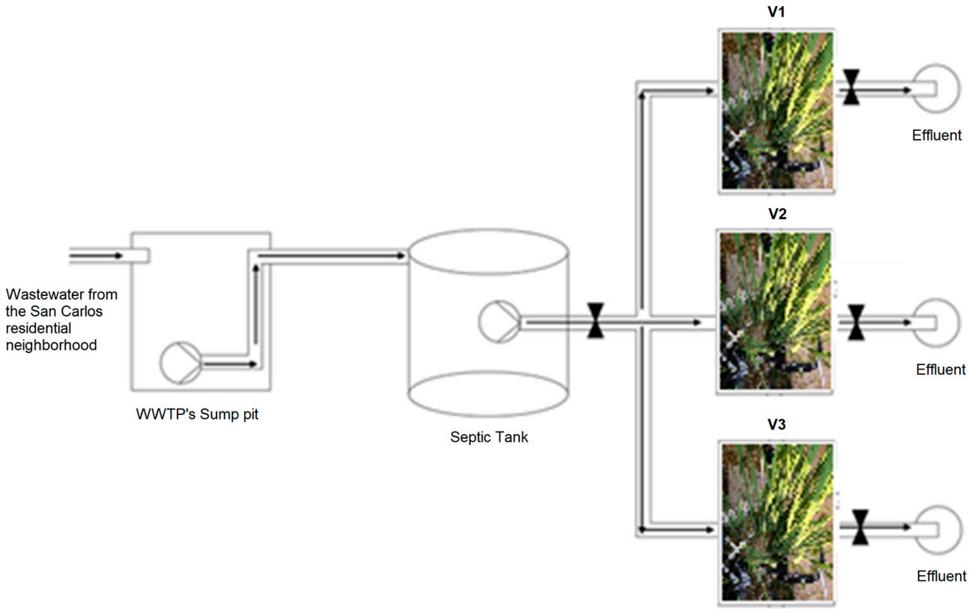

Figure 2. V-CWs system diagram. (V1: gravel/sand with *Typha dominguensis*, V2: biochar/zeolite with *Typha dominguensis*, V3: unplanted biochar/zeolite).

The variation for the three V-CWs was the substrate used as support media and the plants. For the first wetland (V1), a 15 cm layer of 20–40 mm gravel was placed at the bottom, while a 30 cm layer of 1–4 mm sand and a 15 cm layer of 5–10 mm gravel filled the middle and upper part, following the recommendations by Vega De Lille et al., 2021 [28]. For the second and third wetlands (V2 and V3), 15 cm layers of 5–20 mm zeolite were placed at the bottom and upper part of the V-CW, while a 35 cm layer of 0.5–2 mm biochar filled the middle. Zeolite, gravel, and sand were bought from local materials stores. Finally, the CWs walls were covered with plastic bags to avoid algae formation.

Typha dominguensis was the plant selected for this study because it has been widely used in previous research conducted in Yucatán [29], demonstrating high adaptability to local climatic and hydrological conditions. Its robust growth, tolerance to varying pollutant loads, and effectiveness in removing nutrients and contaminants make it a suitable macrophyte for constructed wetlands. The species were planted just in V1 and V2, dividing the wetlands area into 6 quadrants of 20 cm $\times$ 25 cm and allocating one plant per quadrant. V3 remained unplanted as a control wetland. The *Typha dominguensis* specimens were taken in their adult stage from the Temozon Norte waterhole, on the outskirts of Merida. Once planted in the CWs, an acclimatization plan was implemented. The system was operated in batch mode for 2 months, with a contact time of 3 d, following the method proposed by Vega De Lille et al., 2021 [28] to achieve the successful acclimatization of the plant species.

2.5. System Operation and Monitoring

The vertical CWs system was operated in a batch configuration (fill and draw), using a contact time of 4 d per cycle. At the beginning of each cycle, the septic tank was filled with wastewater collected from the WWTP sump and allowed to settle for at least 30 min. Subsequently, each V-CW was fed with the septic tank effluent at the start of the experiment (day 0). Once the V-CW units reached the 4 d retention period, the valves were opened, and the effluent was collected. In total, 12 cycles were completed.

During the operation phase, system performance was evaluated by collecting samples from the septic tank outlet before pumping and from the effluent of each V-CW unit once the designated contact time had elapsed. The analyzed parameters included COD, BOD_5, TSS, ibuprofen, paracetamol, and caffeine, as described in the methods outlined in this section. All parameters were measured in every cycle.

2.6. Sampling Procedure, Preparation, and Water Analysis

Effluent samples from each constructed wetland unit and the septic tank were collected using a simple grab sampling method. For each sampling event, a single sample was taken directly from the outlet of the respective unit at the end of the 4 d contact time. Samples were immediately stored in clean, amber glass bottles and kept at 4 °C. Physicochemical parameters (COD, BOD_5, TSS) were analyzed within 24 h, according to the procedures described in the Standard Methods for the Examination of Water and Wastewater [30], ensuring standardized and reproducible results.

The samples for pharmaceutical analysis (ibuprofen, paracetamol, and caffeine) were filtered through 0.45 μm membranes, acidified to a pH range of 2–3 with HCl, and stored at 4 °C until quantification by High-Performance Liquid Chromatography (HPLC).

Pharmaceutical compounds in the wastewater samples were extracted and pre-concentrated using a solid phase extraction (SPE) procedure prior to chromatographic analysis. The SPE cartridges (C18, reversed phase) were first conditioned sequentially with methanol and ultrapure water to activate the sorbent and ensure reproducible retention of the analytes. Subsequently, 100 mL of the wastewater sample was passed through the cartridge under vacuum at a constant flow rate to promote the adsorption of pharmaceutical compounds onto the stationary phase. After sample loading, the cartridges were rinsed with ultrapure water to remove matrix interferences and dried under vacuum to eliminate residual moisture. Elution of the retained pharmaceuticals was then achieved with a small volume of methanol, yielding a concentrated extract suitable for injection into the HPLC system.

In cases where preliminary estimations suggested that pharmaceutical concentrations in the spiked influent could be below the method's analytical capacity—specifically the limits of detection (LOD), limits of quantification (LOQ), and the validated linear range—an additional sample concentration step was performed through controlled evaporation of the eluates under a gentle nitrogen stream. This process allowed adjustment of the analyte concentration within the validated working range of the method, thereby ensuring reliable quantification and compliance with quality assurance requirements. When analyte concentrations in the spiked samples exceeded the validated linear range of the HPLC method, appropriate dilutions of the SPE eluates were performed with the initial mobile phase prior to injection.

The concentrations of ibuprofen, caffeine, and paracetamol in wastewater samples were determined using high-performance liquid chromatography (HPLC) with a UV detector. Standard solutions of each pharmaceutical (5 mg/L) were prepared in the selected mobile phase using 25 mL volumetric flasks. Chromatographic conditions were optimized to simultaneously quantify ibuprofen, caffeine, and paracetamol, achieving proper peak resolution. Separation was performed on a C18 Hypersil Gold column (Thermo Scientific, Waltham, MA, USA) with a mobile phase composed of 70:30 water: methanol, a flow rate of 1 mL/min, and a column temperature of 25 °C. The retention times were 4.18 min for ibuprofen, 5.02 min for paracetamol, and 7.80 min for caffeine, with detection wavelengths of 272 nm for ibuprofen and caffeine, and 254 nm for paracetamol. Each run lasted 12 min per sample.

The method was fully validated. Linearity was assessed by injecting standard solutions at different concentrations and integrating peak areas using Chromeleon 7.0. Calibration curves were obtained for each compound, showing linear responses with correlation coefficients (R) greater than 0.98 in the ranges of 0.5–5 mg/L for paracetamol and caffeine, and 1–5 mg/L for ibuprofen. Limits of detection (LOD) and quantification (LOQ) were determined, and accuracy was evaluated through recovery tests, yielding 97–103% for all three compounds. Precision, evaluated both intra- and inter-day, showed relative standard deviations of less than 2%. Selectivity was confirmed by calculating resolution factors (Rs) between ibuprofen–paracetamol, paracetamol–caffeine, and ibuprofen–caffeine, all of which indicated satisfactory separation. This validation ensured the method was reliable, accurate, precise, and selective for quantifying the target pharmaceuticals in wastewater samples.

2.7. Data and Statistical Analysis

The removal efficiency of ibuprofen, paracetamol, and caffeine in each constructed wetland unit was calculated based on the influent and effluent concentrations measured by HPLC. Removal (%) was determined using Equation (1):

$$\%R = \frac{C_{\text{influent}} - C_{\text{effluent}}}{C_{\text{influent}}} \times 100 \tag{1}$$

where %R is the removal efficiency (%), C_{influent} is the influent concentration (mg/L), and C_{effluent} is the effluent concentration (mg/L). The data were processed using Microsoft Excel 365, and statistical analyses were performed with R software (version 4.3.1). Mean removal efficiencies and standard deviations were calculated for each wetland configuration. A one-way ANOVA was performed to assess the effects of vegetation (*Typha domingensis* vs. no plants) and then another one for the substrate type (biochar/zeolite vs. gravel/sand) on removal efficiencies, including the interaction between these factors. Post hoc comparisons were conducted using Tukey's test at $p < 0.05$.

3. Results

3.1. Influent and Septic Tank Characterization

The results obtained in the influent characterization campaign are shown in Table 2. They exhibit both similarities and deviations when compared to the measurements from 2018 in the same WWTP [28] and the standard ranges established by Metcalf & Eddy Inc. [31]. For example, the COD concentration in raw domestic wastewater was 817.70 ± 71.83 mg/L, slightly lower than the 856.61 ± 279.67 mg/L reported in 2018, yet still within the typical range of 250–1000 mg/L cited by Metcalf & Eddy. Similarly, BOD_5 values in this study (365.76 ± 75.79 mg/L) are consistent with both the 2018 data (329.58 ± 40.53 mg/L) and the standard range of 110–400 mg/L. However, the TSS concentration (644.57 ± 118.19 mg/L) is notably higher than the average values reported in Metcalf & Eddy (150–350 mg/L), suggesting a possible increase in particulate matter, potentially due to changes in household practices or infrastructure aging.

Table 2. Raw domestic wastewater characterization and monitoring of the septic tank.

Parameter	Raw Domestic Water	Typical and Reported Concentrations in Domestic Wastewater [31]
COD (mg/L)	817.70 ± 71.83	250–1000
BOD5 (mg/L)	365.76 ± 75.79	230–560
TSS (mg/L)	644.57 ± 118.19	150–350
Ibuprofen (μg/L)	0.97 ± 0.12	1.05–1096
Paracetamol (μg/L)	4.21 ± 0.39	0.04–41.7
Caffeine (μg/L)	11.90 ± 0.44	9.05–89.5

The performance of the septic tank evaluated in this study (Table 3) showed variable removal efficiencies across different parameters, with the highest effectiveness observed in the removal of total suspended solids (TSS).

Table 3. Characterization and monitoring of the septic tank with removal efficiency.

Parameter	Septic Tank		Average Removal Efficiency
	Inlet Concentration	Outlet Concentration	
COD (mg/L)	817.70 ± 71.83	462.19 ± 57.66	43.47%
BOD5 (mg/L)	365.76 ± 75.79	286.39 ± 52.49	20.87%
TSS (mg/L)	644.57 ± 118.19	304.99 ± 68.66	52.68%
Ibuprofen (μg/L)	0.97 ± 0.12	0.89 ± 0.02	8.24%
Paracetamol (μg/L)	4.21 ± 0.39	4.06 ± 0.08	3.56%
Caffeine (μg/L)	11.90 ± 0.44	10.92 ± 0.34	8.23%

3.2. Removal of Organic Matter (COD and BOD5) and Suspended Solids (TSS) in V-CW

All three V-CW configurations—V1 (gravel/sand with vegetation), V2 (biochar/zeolite with vegetation), and V3 (biochar/zeolite without vegetation)—achieved high removal efficiencies for organic matter and suspended solids. The average COD removal efficiencies were 89.4 ± 2.7% for V1, 91.7 ± 1.4% for V2, and 91.4 ± 2.3% for V3. For BOD_5, the removal rates were 93.3 ± 2.9% (V1), 93.8 ± 1.1% (V2), and 93.7 ± 1.9% (V3). TSS removal was also consistently high across all systems, with V1 achieving 94.5 ± 3.5%, V2 96.0 ± 2.3%, and V3 96.6 ± 2.0%.

These results are summarized in Tables 4 and 5, which present the mean effluent concentrations, removal efficiencies, and standard deviations for each parameter and configuration.

Table 4. COD, BOD5, and TSS effluent concentration in V-CW units.

Parameters	Concentration in CW Units Effluent			
	Septic Tank	V1	V2	V3
COD (mg/L)	462.19 ± 57.66	49.38 ± 11.06	38.78 ± 7.33	40.69 ± 12.73
BOD5 (mg/L)	286.39 ± 52.49	19.71 ± 9.55	18.09 ± 3.65	18.39 ± 6.92
TSS (mg/L)	304.99 ± 68.66	18.14 ± 11.39	13.06 ± 7.67	11.16 ± 6.54

Table 5. COD, BOD5, and TSS removal efficiencies in V-CW units.

Parameters	Removal (%) in CW Units		
	V1	V2	V3
COD	89.4 ± 2.7	91.7 ± 1.4	91.4 ± 2.3
BOD_5	93.3 ± 2.9	93.8 ± 1.1	93.7 ± 1.9
TSS	94.5 ± 3.5	96.0 ± 2.3	96.6 ± 2.0

3.3. Pharmaceutical Removal (Ibuprofen, Paracetamol, Caffeine)

The removal of pharmaceutical compounds was evaluated for each V-CW configuration. Ibuprofen removal efficiencies were 81.8 ± 8.2% (V1), 91.5 ± 4.7% (V2), and 90.4 ± 4.9% (V3). Paracetamol removal was similarly high, with 90.0 ± 4.6% (V1), 94.2 ± 3.7% (V2), and 94.3 ± 3.5% (V3). Caffeine showed the highest removal rates among the pharmaceuticals, with 93.1 ± 2.3% (V1), 97.2 ± 2.1% (V2), and 96.5 ± 2.8% (V3).

Effluent concentrations and removal efficiencies for each compound are detailed in Tables 6 and 7.

Table 6. Ibuprofen, Paracetamol, and Caffeine effluent concentration in V-CW units.

Parameters	Concentrations in CW Units Effluent			
	Septic Tank	V1	V2	V3
Ibuprofen (μg/L)	9.54 ± 0.61	1.64 ± 0.73	0.77 ± 0.42	0.86 ± 0.44
Paracetamol (μg/L)	9.78 ± 0.34	0.97 ± 0.46	0.56 ± 0.36	0.55 ± 0.34
Caffeine (μg/L)	9.78 ± 0.29	0.66 ± 0.21	0.26 ± 0.19	0.33 ± 0.26

Table 7. Ibuprofen, Paracetamol, and Caffeine removal efficiencies (%) in V-CW units.

Parameters	Removal (%) in CW Units		
	V1	V2	V3
Ibuprofen	81.8 ± 8.2	91.5 ± 4.7	90.4 ± 4.9
Paracetamol	90.0 ± 4.6	94.2 ± 3.7	94.3 ± 3.5
Caffeine	93.1 ± 2.3	97.2 ± 2.1	96.5 ± 2.8

3.4. Statistical Analysis Results

To evaluate the influence of vegetation and substrate type on the removal efficiency of various water quality parameters, a one-way ANOVA was performed separately for each factor: vegetation presence (planted vs. unplanted) and substrate type (gravel/sand vs. biochar/zeolite). The results are summarized in terms of F-values and *p*-values for each parameter in Table 8.

Table 8. One-way ANOVA Results.

Parameter	Planted vs. Unplanted		Gravel/Sand vs. Biochar/Zeolite	
	F-Value	*p*-Value	F-Value	*p*-Value
COD	0.024	0.878	0.193	0.664
BOD5	0.001	0.973	0.009	0.924
TSS	0.433	0.517	0.813	0.377
Ibuprofen	1.310	0.266	10.720	0.003
Paracetamol	0.844	0.368	3.475	0.075
Caffeine	0.524	0.476	4.585	0.043

F-values and *p*-values in red indicate a significant difference.

The analysis revealed that substrate type had a statistically significant effect on the removal of ibuprofen ($p = 0.0035$) and caffeine ($p = 0.0436$). In contrast, vegetation presence did not show a statistically significant effect on the removal of any parameter, with all p-values exceeding 0.266.

The post hoc comparisons (Tukey Method with a 95% confidence) in Tables 9 and 10 revealed significant differences in caffeine and ibuprofen removals between the support medium used; the Biochar/Zeolite medium showed the highest removal for both compounds.

Table 9. Post Hoc Comparison for Ibuprofen in Gravel/Sand vs. Biochar/Zeolite CWs (Tukey Method and 95% Confidence).

Factor	*n*	Mean Removal (mg/L)	Grouping
Biochar/Zeolite	16	8.222	A
Gravel/Sand	8	7.397	B

Table 10. Post Hoc Comparison for Caffeine in Gravel/Sand vs. Biochar/Zeolite CWs (Tukey Method and 95% Confidence).

Factor	*n*	Mean Removal (mg/L)	Grouping
Biochar/Zeolite	16	9.241	A
Gravel/Sand	8	8.878	B

An additional One-way ANOVA (Table 11) was calculated to compare the removal efficiencies of planted and unplanted V-CWs that used biochar and zeolite. There were no statistically significant effects on the removal of any parameter or pharmaceutical. All p-values exceeded 0.698.

Table 11. One-way ANOVA Results to compare Planted vs. Unplanted Biochar/Zeolite CWs.

Parameter	Planted vs. Unplanted	
	F-Value	*p*-Value
COD	0.010	0.941
BOD5	0.000	0.987
TSS	0.070	0.800
Ibuprofen	0.160	0.698
Paracetamol	0.000	0.964
Caffeine	0.500	0.821

4. Discussion

4.1. Influent Characterization

The presence of pharmaceutical compounds such as ibuprofen, paracetamol, and caffeine in wastewater has been documented in various regions of Mexico, with concentrations ranging from 1.09 to 9.66 µg/L for ibuprofen [32–34], up to 34.3 µg/L for paracetamol, and up to 39.3 µg/L for caffeine [35]. In Yucatán, specifically, caffeine has been detected in coastal lagoons at concentrations up to 2.39 µg/L [36], indicating anthropogenic influence. However, data on ibuprofen and paracetamol in this region remain scarce. This study provides new insights into the concentrations of these pharmaceuticals in raw domestic wastewater in Yucatán, with measured values of 0.97 ± 0.12 µg/L for ibuprofen, 4.21 ± 0.39 µg/L for paracetamol, and 11.90 ± 0.44 µg/L for caffeine.

These results suggest that while the concentrations of ibuprofen and paracetamol in Yucatán's wastewater are within the lower range of national reports, caffeine levels appear comparatively elevated. This could reflect increased consumption patterns or differences in wastewater management practices [37].

4.2. Septic Tank Performance

The performance of the septic tank evaluated in this study (Table 3) showed variable removal efficiencies across different parameters, with the highest effectiveness observed in the removal of total suspended solids (TSS). The average TSS removal was 81.24%, confirming the primary function of the septic tank as a sedimentation unit, where particulate matter is efficiently retained. This result is consistent with the 2018 study [28], which reported a 71.62% reduction (from 674.83 to 191.55 mg/L), indicating stable performance in solids retention over time.

Regarding organic matter, the system achieved a 56.09% reduction in COD and 47.81% in BOD_5, which are slightly lower than the 2018 values of 73.16% and 69.49%, respectively. These differences may be attributed to changes in the characteristics of raw wastewater, potentially influenced by population growth, shifts in domestic consumption habits, and the use of household products between 2018 and 2022.

The presence of ibuprofen (0.89 ± 0.02 μg/L), paracetamol (4.06 ± 0.08 μg/L), and caffeine (10.92 ± 0.34 μg/L) was detected in the septic tank with low average removal efficiencies of 8.28%, 3.68%, and 8.25%, respectively. These low removal rates are expected, as septic tanks are not designed to remove pharmaceutical compounds, which are typically dissolved.

Overall, the results confirm that the septic tank effectively fulfills its primary role in removing solids and part of the organic load. However, it is limited in addressing emerging contaminants, highlighting the need for complementary treatment if higher effluent quality is desired.

4.3. Removal of Organic Matter (COD and BOD_5) and Suspended Solids (TSS)

The performance of the three vertical constructed wetlands (V-CWs)—V1 (gravel/sand with vegetation), V2 (biochar/zeolite with vegetation), and V3 (biochar/zeolite without vegetation)—was evaluated in terms of their ability to remove organic matter and suspended solids from fortified wastewater. The results revealed high removal efficiencies across all systems, yet some differences emerged when comparing their configurations.

In terms of chemical oxygen demand (COD), V2 achieved the highest removal efficiency at 91.73%, followed closely by V3 at 91.38% and V1 at 89.4%. Similarly, for biochemical oxygen demand (BOD_5), V2 and V3 reached 93.78% and 93.74%, respectively, while V1 attained 93.3%. These results suggest that the use of biochar and zeolite as support media significantly enhances organic matter removal, likely due to their high surface area, porosity, and ion-exchange capacity [21,38]. These properties facilitate both adsorption of organic compounds and microbial colonization, which in turn promote enzymatic degradation of complex pollutants [39–42].

The slightly superior performance of V2 compared to V3 indicates that vegetation, represented by *Typha dominguensis*, plays a complementary role. Plant roots contribute to rhizosphere oxygenation and release exudates that stimulate microbial activity, enhancing biodegradation processes [41]. However, the marginal difference between V2 and V3 suggests that substrate composition is the dominant factor influencing organic matter removal, while vegetation provides additional but limited benefits under the tested conditions.

V1, the conventional system using gravel and sand, demonstrated effective but comparatively lower removal rates. This configuration relies primarily on physical filtration and microbial processes supported by mineral substrates and vegetation [43]. Although it achieved substantial reductions in COD and BOD_5, its performance was outpaced by the engineered biochar–zeolite systems, highlighting the importance of substrate selection in optimizing wetland treatment.

Regarding total suspended solids (TSS), all three systems exhibited excellent removal capabilities. V3 achieved the highest efficiency at 96.61%, followed by V2 at 96.04% and V1 at 94.49%. The final effluent concentrations were 11.16 ± 6.54 mg/L for V3, 13.06 ± 7.67 mg/L for V2, and 18.14 ± 11.39 mg/L for V1. These results underscore the effectiveness of biochar and zeolite in physically capturing and retaining suspended particles. The superior performance of V3, despite the absence of vegetation, confirms that the physicochemical properties of the substrates alone are sufficient to achieve high TSS removal [44,45].

Interestingly, the minimal difference between V2 and V3 in TSS removal further supports the notion that vegetation has limited influence on this parameter. While *Typha dominguensis* may contribute to nutrient uptake and microbial stimulation, its role in suspended solids retention appears secondary compared to the filtration and adsorption capacity of the substrates [46,47].

The comparative analysis of V1, V2, and V3 demonstrated that biochar–zeolite systems (V2 and V3) outperform the traditional gravel–sand system (V1) in removing both organic matter and suspended solids. The results highlight the synergistic effects of biochar and zeolite, which combine strong adsorption potential with microbial support. These findings reinforce the value of engineered substrates in constructed wetlands and suggest that future designs should prioritize substrate composition to enhance treatment efficiency, particularly for emerging contaminants and multi-pollutant scenarios.

4.4. Pharmaceutical Removal

4.4.1. Ibuprofen

The removal of ibuprofen (IBU) in the vertical constructed wetlands (V-CWs) evaluated in this study provides valuable insights into the mechanisms governing the elimination of pharmaceuticals in nature-based treatment systems. The three configurations tested—V1 (gravel–sand with vegetation), V2 (biochar–zeolite with vegetation), and V3 (biochar–zeolite without vegetation)—achieved removal efficiencies of 81.84%, 91.51%, and 90.44%, respectively. These results confirm that the combination of biochar and zeolite significantly enhances IBU removal compared to conventional mineral substrates.

The statistical analysis revealed that substrate type had a significant effect on IBU removal ($p = 0.003$), while vegetation presence did not ($p > 0.266$). This indicates that the physicochemical properties of biochar and zeolite are the primary drivers of removal, rather than plant-mediated processes. The negligible difference between V2 and V3 further supports this conclusion.

Biochar, produced via pyrolysis, possesses a high surface area, abundant micropores, and diverse functional groups [48]. These characteristics facilitate adsorption through multiple mechanisms, including π–π stacking, hydrogen bonding, and pore filling [49–51]. Literature reports maximum adsorption capacities for modified biochars ranging from 200.73 mg/g (grass jelly tree waste) to over 1000 mg/g (ZnAl/biochar composites) [52,53]. Zeolite complements biochar by providing ion exchange capacity and structural stability, and its adsorption performance is influenced by its SiO_2/Al_2O_3 ratio and surface modifications [54].

In acidic conditions (pH < 6.3), the biochar surface becomes positively charged, enhancing electrostatic attraction with the negatively charged ibuprofen molecules. This pH-dependent behavior has been confirmed in multiple studies, where lower pH values consistently improve adsorption efficiency [48,49,55]. Although pH was not controlled in this study, the high removal rates observed suggest that favorable conditions for adsorption were present.

While the experimental design did not include kinetic modeling or isotherm studies, the observed removal trends align with mechanisms described in the literature. Adsorption of IBU onto biochar typically follows Langmuir isotherm behavior, indicating monolayer coverage on homogeneous surfaces [56,57]. Kinetic studies often fit pseudo-second-order or Elovich models, suggesting chemisorption and surface diffusion as dominant processes [56–59].

The absence of direct kinetic and equilibrium data in this study limits the ability to quantify adsorption parameters such as rate constants, equilibrium capacities, and thermodynamic behavior. Therefore, the mechanistic interpretation is based on comparative performance and supported by external evidence. Future work should incorporate batch adsorption experiments and modeling to validate these mechanisms and optimize system design.

In addition to adsorption, biodegradation plays a crucial role in IBU removal, particularly in systems with sufficient oxygen availability, such as V-CWs [60]. Aerobic microbial degradation is widely recognized as the primary biological pathway, with identified intermediates such as carboxy-ibuprofen and hydroxy-ibuprofen, indicating a stepwise transformation. Both metabolic and cometabolic pathways are involved, with some bacteria capable of directly degrading IBU, while others contribute through the production of enzymes [61,62].

Constructed wetlands provide a conducive environment for microbial activity, especially when substrates such as biochar and zeolite support colonization [14,63]. Although vegetation can enhance microbial processes through rhizosphere oxygenation and root exudates [64–66], the minimal difference between V2 and V3 (p = 0.698) suggests that substrate-driven microbial activity was sufficient under the tested conditions.

Reported removal efficiencies in planted and aerated systems range from 70% to 99%, depending on hydraulic retention time (HRT), substrate type, and plant species [67,68]. In this study, the batch operation with a 4-day contact time likely provided adequate conditions for microbial degradation, complementing the adsorption processes.

The high removal efficiencies observed in V2 and V3 reflect the synergistic interaction between adsorption and biodegradation. Adsorption serves as the initial capture mechanism, concentrating IBU on the substrate surface and reducing its mobility. This facilitates subsequent microbial degradation, particularly in biofilms formed on biochar and zeolite particles. The dual functionality of these substrates—physical adsorption and biological support—makes them ideal for pharmaceutical removal in constructed wetlands.

Zeolite may also enhance the bioavailability of nutrients for microbial activity. Its porous structure and ion exchange properties create microenvironments that favor microbial colonization and nutrient retention [69,70].

4.4.2. Paracetamol

The removal of paracetamol (PCM) in the three vertical constructed wetland (V-CW) configurations evaluated in this study—V1 (gravel–sand with vegetation), V2 (biochar–zeolite with vegetation), and V3 (biochar–zeolite without vegetation)—demonstrated consistently high efficiencies, with recorded values of 90.03%, 94.2%, and 94.3%, respectively. Although the statistical analysis did not confirm a significant difference between configurations (p = 0.0757), the trend suggests that substrate composition, particularly the inclusion of biochar and zeolite, plays a more influential role than vegetation in enhancing PCM removal.

The elevated removal efficiencies observed in V2 and V3 are consistent with the known adsorption capacities of biochar and zeolite. Biochar, especially when produced under optimized pyrolysis conditions, exhibits high surface area, porosity, and functional groups (e.g., hydroxyl, carboxyl, carbonyl) that facilitate adsorption through hydrogen bonding, π–π stacking, and van der Waals interactions. Reported adsorption capacities for biochar range from 20 to 286 mg/g, depending on feedstock and activation method [71,72]. Zeolite, particularly MFI-type structures, contributes through micropore confinement and electrostatic interactions, with capacities reaching up to 85 mg/g [73,74].

In this study, the lack of kinetic and isotherm modeling prevents a quantitative assessment of adsorption behavior. No Langmuir or Freundlich isotherms were fitted, and no pseudo-first or pseudo-second-order kinetic models were applied. As such, the interpretation of adsorption mechanisms is based on comparative performance and supported by literature rather than direct experimental evidence.

Beyond adsorption, biodegradation is a critical pathway for PCM removal in constructed wetlands. Aerobic microbial communities, particularly those dominated by Proteobacteria and Pseudomonas spp., are known to metabolize PCM through enzymatic pathways involving peroxidases and glutathione S-transferases [75–77]. As occurred with IBU, the minimal difference between V2 and V3 suggests that substrate-supported microbial activity was sufficient to drive biodegradation, even in the absence of vegetation.

The batch operation with a 4-day hydraulic retention time (HRT) likely provided adequate contact for microbial transformation. Literature reports half-lives for PCM ranging from 5 to 10 h under aerobic conditions [78], indicating that the system design was appropriate for biological degradation.

Paracetamol adsorption and biodegradation are sensitive to environmental conditions, particularly pH and ionic strength [79]. Optimal adsorption typically occurs near neutral pH, with reduced efficiency under alkaline conditions due to electrostatic repulsion and desorption [79,80]. Ionic strength, especially in the presence of competing ions such as Na^+ or Cl^-, can negatively affect adsorption by shielding active sites and introducing competition [79,81].

In this study, pH and ionic strength were not measured or controlled, representing a limitation in interpreting the environmental influence on removal mechanisms. While the observed efficiencies suggest favorable conditions, future studies should include systematic monitoring of these parameters to better understand their role in the removal of PCM.

4.4.3. Caffeine Removal

The results obtained in this study confirm that vertical constructed wetlands (V-CWs) are highly effective for the removal of caffeine from wastewater. All three configurations—V1 (gravel–sand with vegetation), V2 (biochar–zeolite with vegetation), and V3 (biochar–zeolite without vegetation)—achieved removal efficiencies above 93%, with V2 reaching the highest at 97.23%. These findings are consistent with reported values in the literature, where V-CWs typically achieve caffeine removal rates between 70% and 97%, depending on the system design and operational conditions [82,83].

Caffeine's physicochemical properties—particularly its high solubility and low log Kow—limit its retention on inert substrates such as gravel and sand [84]. In contrast, biochar exhibits significantly higher adsorption capacities, ranging from 5 to 275 mg/g [85,86].

The adsorption of caffeine onto biochar is governed by a combination of electrostatic interactions, hydrogen bonding, and π–π stacking between caffeine molecules and surface functional groups, including hydroxyl, carboxyl, and carbonyl groups. These interactions are susceptible to environmental conditions [87,88]. Acidic pH (3–4.5) enhances electrostatic attraction, while elevated temperatures promote endothermic adsorption [87,89]. Ionic strength, particularly the presence of divalent cations like Ca^{2+} and Mg^{2+}, can reduce adsorption efficiency due to competition for active sites [89].

Zeolite contributes through ion exchange and physical confinement within its microporous structure. The Si/Al ratio of zeolite influences its surface charge and hydrophobicity, affecting both adsorption capacity and selectivity. Surface modifications, such as ceria decoration (cerium oxide, CeO_2) or iron impregnation, have been shown to enhance adsorption performance and regeneration potential [90].

Although this study did not experimentally evaluate adsorption kinetics or isotherms, the high caffeine removal efficiencies observed in V2 (97.23%) and V3 (96.55%) suggest that adsorption played a significant role alongside biodegradation. Literature reports suggest that chemisorption is the dominant mechanism, involving valence forces through the sharing or exchange of electrons between caffeine molecules and the adsorbent surface. For zeolite, both pseudo-first-order and pseudo-second-order models have been observed, depending on the degree of surface modification and Si/Al ratio.

Regarding equilibrium behavior, caffeine adsorption onto biochar and zeolite is well described by the Langmuir and Freundlich isotherm models. The Langmuir model suggests monolayer adsorption on a homogeneous surface, whereas the Freundlich model accounts for heterogeneous surface energies and multilayer adsorption [87,91]. The strong fit to these models in previous studies supports the hypothesis that the biochar–zeolite matrix in V2 and V3 provided favorable conditions for rapid and efficient caffeine adsorption, even in the absence of vegetation.

However, it is important to note that most kinetic and isotherm data are derived from controlled laboratory experiments using synthetic solutions [92]. Real wastewater contains competing organic matter and variable ionic strength, which can affect adsorption dynamics. Therefore, future studies should incorporate batch and column experiments using actual wastewater to validate these models and quantify adsorption parameters under realistic conditions.

Microbial degradation is an important mechanism for caffeine removal in V-CWs. The vertical flow design promotes aerobic conditions in the upper layers of the substrate, which are ideal for caffeine-degrading bacteria [82,83]. Key microbial taxa involved include *Pseudomonas putida*, *Alcaligenes*, and *Rhodococcus*, which utilize N-demethylation and oxidation pathways to break down caffeine into less toxic metabolites [93,94].

The presence of vegetation, although not statistically significant in this study, may enhance microbial diversity and activity through the release of root exudates and oxygen [14,82,83]. However, the comparable performance of V2 and V3 suggests that the biochar–zeolite matrix alone provides sufficient support for microbial colonization and activity.

The vertical stratification of redox zones in V-CWs allows for both aerobic and anaerobic degradation processes. Aerobic zones facilitate the rapid breakdown of caffeine, while deeper anoxic layers may support methanogenic and sulfate-reducing bacteria that contribute to complete mineralization [83,95]. The 4-day hydraulic retention time used in this study likely provided adequate contact for both adsorption equilibrium and microbial transformation.

The high removal efficiencies observed in V2 and V3 reflect the synergistic interaction between adsorption and biodegradation. Adsorption serves as an initial capture mechanism, concentrating caffeine on the substrate surface and reducing its mobility. This facilitates subsequent microbial degradation, particularly within biofilms formed on biochar and zeolite particles. The dual functionality of these substrates—physical adsorption and biological support—makes them ideal for caffeine removal in constructed wetlands.

4.4.4. Pharmaceutical Removal Inhibition by Other Compounds

The removal efficiency of pharmaceuticals such as caffeine, ibuprofen, and paracetamol in CWs is significantly influenced by the presence of co-contaminants. Inhibition phenomena are primarily driven by complex interactions between pharmaceuticals and other pollutants, including heavy metals, surfactants, and microplastics. These co-contaminants exert toxic effects on microbial communities, disrupt enzymatic degradation pathways, and compete for sorption sites, thereby reducing the overall removal efficiency of target compounds [96,97].

Heavy metals (e.g., Cu, Zn, Cd, Pb) and surfactants, commonly found in industrial and hospital effluents, are particularly potent inhibitors. They interfere with microbial enzymatic activity and promote shifts in microbial community structure, often leading to reduced biodiversity and increased proliferation of resistance genes [96,97]. Microplastics further exacerbate inhibition by physically blocking substrate pores, altering microbial habitats, and serving as vectors for other contaminants [98].

Plant-microbe interactions also contribute to the complexity of inhibition. Root exudates can either stimulate microbial degradation or, under stress conditions, alter microbial activity and exacerbate inhibition [61,99]. The selection of plant species and management of root exudate profiles are therefore essential for maintaining system resilience.

Future research should focus on elucidating specific microbial and enzymatic pathways affected by co-contaminants and developing real-time monitoring tools to assess inhibition in operational systems dynamically.

5. Conclusions

This study demonstrates that vertical constructed wetlands (V-CWs) are highly effective in removing pharmaceutical contaminants, including ibuprofen, paracetamol, and caffeine, as well as conventional water quality parameters such as COD, BOD_5, and TSS. Configurations using biochar and zeolite (V2 and V3) consistently outperformed the traditional gravel–sand system (V1), particularly in the removal of ibuprofen and caffeine. Mean removal efficiencies reached up to 91.5% for ibuprofen, 94.3% for paracetamol, and 97.2% for caffeine.

Statistical analysis confirmed that substrate type significantly influenced pharmaceutical removal ($p = 0.003$ for ibuprofen, $p = 0.043$ for caffeine), while vegetation presence had no significant effect. The dominant removal mechanisms were adsorption—driven by the physicochemical properties of biochar and zeolite—and biodegradation, supported by microbial activity within the substrate. Vegetation contributed modestly to organic matter removal but did not significantly enhance pharmaceutical degradation under the tested conditions.

Future research should focus on optimizing biochar–zeolite ratios and substrate dosing, conducting adsorption isotherm and kinetic modeling, evaluating long-term substrate regeneration and stability, and performing cost-effectiveness analyses. Field-scale validation and multi-contaminant performance assessments are also recommended, particularly in regions with vulnerable aquifers such as the Yucatán Peninsula. These findings support the use of engineered substrates in nature-based solutions for decentralized wastewater treatment.

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Abbreviations

The following abbreviations are used in this manuscript:

APHA	American Public Health Association
AOPs	Advanced Oxidation Processes
BOD_5	Biochemical Oxygen Demand over 5 days
CAF	Caffeine
COD	Chemical Oxygen Demand
CW	Constructed Wetland
d	Days
HPLC	High-Performance Liquid Chromatography
HLR	Hydraulic Loading Rate
IBU	Ibuprofen
LOQ	Limit of Quantification
LOD	Limit of Detection
mg/L	Milligrams per Liter
PCM	Paracetamol
PPCP	Pharmaceuticals and Personal Care Products
Rs	Resolution Factor
SPE	Solid Phase Extraction
TSS	Total Suspended Solids
V1	Wetland with gravel/sand and vegetation
V2	Wetland with biochar/zeolite and vegetation
V3	Wetland with biochar/zeolite without vegetation
VFCW	Vertical Flow Constructed Wetland
WWTP	Wastewater Treatment Plant
μg/L	Micrograms per Liter

References

1. Tijani, J.O.; Fatoba, O.O.; Babajide, O.O.; Petrik, L.F. Pharmaceuticals, Endocrine Disruptors, Personal Care Products, Nanomaterials and Perfluorinated Pollutants: A Review. *Environ. Chem. Lett.* **2016**, *14*, 27–49. [CrossRef]
2. Malnes, D.; Ahrens, L.; Köhler, S.; Forsberg, M.; Golovko, O. Occurrence and Mass Flows of Contaminants of Emerging Concern (CECs) in Sweden's Three Largest Lakes and Associated Rivers. *Chemosphere* **2022**, *294*, 133825. [CrossRef] [PubMed]
3. Ripanda, A.S.; Rwiza, M.J.; Nyanza, E.C.; Njau, K.N.; Vuai, S.A.H.; Machunda, R.L. A Review on Contaminants of Emerging Concern in the Environment: A Focus on Active Chemicals in Sub-Saharan Africa. *Appl. Sci.* **2021**, *12*, 56. [CrossRef]
4. Eapen, J.V.; Thomas, S.; Antony, S.; George, P.; Antony, J. A Review of the Effects of Pharmaceutical Pollutants on Humans and Aquatic Ecosystem. *Explor. Drug Sci.* **2024**, *2*, 484–507. [CrossRef]
5. Ferreira, A.P. Caffeine as an Environmental Indicator for Assessing Urban Aquatic Ecosystems. *Cad. Saúde Pública* **2005**, *21*, 1884–1892. [CrossRef]

6. Moreno-Pérez, P.A.; Hernández-Téllez, M.; Bautista-Gálvez, A. In Danger One of the Largest Aquifers in the World, the Great Mayan Aquifer, Based on Monitoring the Cenotes of the Yucatan Peninsula. *Arch. Environ. Contam. Toxicol.* **2021**, *81*, 189–198. [CrossRef]
7. Matamoros, V.; Caselles-Osorio, A.; García, J.; Bayona, J.M. Behaviour of Pharmaceutical Products and Biodegradation Intermediates in Horizontal Subsurface Flow Constructed Wetland. A Microcosm Experiment. *Sci. Total Environ.* **2008**, *394*, 171–176. [CrossRef]
8. Mumtaj, Z.A.; Khan, A.R.; Alsubih, M.; Aleya, L.; Khan, R.A.; Khan, S. Removal of Pharmaceutical Contaminants from Hospital Wastewater Using Constructed Wetlands: A Review. *Environ. Sci. Pollut. Res.* **2024**, *31*, 12856–12870. [CrossRef]
9. Zou, J.; Guo, X.; Han, Y.; Liu, J.; Liang, H. Study of a Novel Vertical Flow Constructed Wetland System with Drop Aeration for Rural Wastewater Treatment. *Water Air Soil Pollut.* **2012**, *223*, 889–900. [CrossRef]
10. Kumar, M.; Singh, R. Assessment of Pollutant Removal Processes and Kinetic Modelling in Vertical Flow Constructed Wetlands at Elevated Pollutant Loading. *Environ. Sci. Pollut. Res.* **2019**, *26*, 18421–18433. [CrossRef]
11. Porras-Socias, P.; Tomasino, M.P.; Fernandes, J.P.; De Menezes, A.B.; Fernández, B.; Collins, G.; Alves, M.J.; Castro, R.; Gomes, C.R.; Almeida, C.M.R.; et al. Removal of Metals and Emergent Contaminants from Liquid Digestates in Constructed Wetlands for Agricultural Reuse. *Front. Microbiol.* **2024**, *15*, 1388895. [CrossRef] [PubMed]
12. Al Falahi, O.A.; Abdullah, S.R.S.; Hasan, H.A.; Othman, A.R.; Ewadh, H.M.; Ismail, N.I.; Imron, M.F.; Kurniawan, S.B. Removal of Ibuprofen and Paracetamol by Rhizobacteria from Roots of Scirpus Grossus Exposed to a Synthetic Mix in Constructed Wetlands. *Water* **2025**, *17*, 2396. [CrossRef]
13. Sánchez, M.; Fernández, M.I.; Ruiz, I.; Canle, M.; Soto, M. Combining Constructed Wetlands and UV Photolysis for the Advanced Removal of Organic Matter, Nitrogen, and Emerging Pollutants from Wastewater. *Environments* **2023**, *10*, 35. [CrossRef]
14. Chand, N.; Suthar, S.; Kumar, K.; Singh, V. Removal of Pharmaceuticals by Vertical Flow Constructed Wetland with Different Configurations: Effect of Inlet Load and Biochar Addition in the Substrate. *Chemosphere* **2022**, *307*, 135975. [CrossRef]
15. Almeida, A.; Oliveira, J.; Matias, F.; Ribeiro, C.; Silveira, D.; Tavares, J. Removal of Emergent Pollutants by a Vertical Flow Constructed Wetland with Vetiveria Zizanioides: A Case Study for Caffeine. *KnE Mater. Sci.* **2022**, 184–192. [CrossRef]
16. Youssef, Y.A.; Abuarab, M.E.; Mahrous, A.; Mahmoud, M. Enhanced Degradation of Ibuprofen in an Integrated Constructed Wetland-Microbial Fuel Cell: Treatment Efficiency, Electrochemical Characterization, and Microbial Community Dynamics. *RSC Adv.* **2023**, *13*, 29809–29818. [CrossRef]
17. Cobarrubias-Escamilla, D.L.; Saldarriaga-Noreña, H.A.; Vergara-Sánchez, J.; Murillo-Tovar, M.A.; Moeller-Chávez, G.E. Removal of Ibuprofen, Naproxen and 17-β-Estradiol in Water Using *L. octovalvis* Constructed Wetlands. *Int. J. Phytoremediat.* **2025**, *27*, 74–83. [CrossRef] [PubMed]
18. Gallegos-Castro, E.; Almeida-Naranjo, C.E.; Rivas, A.; Figueroa, N.; Montellano, L.; Villamar-Ayala, C.A. The Removal of Acidic Drugs from Domestic Wastewater Using an Innovative System of Constructed Wetlands/Stabilization Ponds in Series. *Water* **2025**, *17*, 1192. [CrossRef]
19. Kamilya, T.; Majumder, A.; Saidulu, D.; Tripathy, S.; Gupta, A.K. Optimization of a Continuous Hybrid Moving Bed Biofilm Reactor and Constructed Wetland System for the Treatment of Paracetamol-Spiked Domestic Wastewater. *Chem. Eng. J.* **2023**, *477*, 147139. [CrossRef]
20. Lei, Y.; Wagner, T.; Rijnaarts, H.; De Wilde, V.; Langenhoff, A. The Removal of Micropollutants from Treated Effluent by Batch-Operated Pilot-Scale Constructed Wetlands. *Water Res.* **2023**, *230*, 119494. [CrossRef] [PubMed]
21. Munir, R.; Muneer, A.; Sadia, B.; Younas, F.; Zahid, M.; Yaseen, M.; Noreen, S. Biochar Imparted Constructed Wetlands (CWs) for Enhanced Biodegradation of Organic and Inorganic Pollutants along with Its Limitation. *Environ. Monit. Assess.* **2024**, *196*, 425. [CrossRef]
22. Kang, Z.; Jia, X.; Zhang, Y.; Kang, X.; Ge, M.; Liu, D.; Wang, C.; He, Z. A Review on Application of Biochar in the Removal of Pharmaceutical Pollutants through Adsorption and Persulfate-Based AOPs. *Sustainability* **2022**, *14*, 10128. [CrossRef]
23. Panghal, V.; Singh, A.; Arora, D.; Kumar, S. Biochar-Modified Constructed Wetlands Using Eclipta Alba as a Plant for Sustainable Rural Wastewater Treatment. *Environ. Sci. Pollut. Res.* **2024**, *31*, 17299–17310. [CrossRef]
24. Al-Mashaqbeh, O.; Alsalhi, L.; Salaymeh, L.; Dotro, G.; Lyu, T. Treatment of Pharmaceutical Industry Wastewater for Water Reuse in Jordan Using Hybrid Constructed Wetlands. *Sci. Total Environ.* **2024**, *939*, 173634. [CrossRef]
25. Martínez-Martínez, J.G.; Rosales-Loredo, S.; Hernández-Morales, A.; Arvizu-Gómez, J.L.; Carranza-Álvarez, C.; Macías-Pérez, J.R.; Rolón-Cárdenas, G.A.; Pacheco-Aguilar, J.R. Bacterial Communities Associated with the Roots of Typha Spp. and Its Relationship in Phytoremediation Processes. *Microorganisms* **2023**, *11*, 1587. [CrossRef]
26. Duré, G.M.; Medina García, L.; Rodríguez Bonet, S.; Ferrreira, F.; Sezerino, P.H.; López Arias, T. Fitorremediación de Contaminantes Emergentes de Origen Farmacéutico En Humedales Flotantes. *Rep. Cient. FACEN* **2022**, *13*, 153–159. [CrossRef]
27. Díaz Lara, C.O.; Cabañas Vargas, D.; Sacramento Rivero, J.C.; Baz-Rodríguez, S.; Ruiz Espinoza, J.E.; Aguilera-Cauich, E.A.; Baas-López, J.M.; Pacheco-Catalán, D.E. Towards Circularity in Anaerobic Digestion: Methane Yield Enhancement Using Biochar from Co-Pyrolysis of Anaerobic Sludge and Residual Lignocellulosic Biomass. *Recycling* **2025**, *10*, 84. [CrossRef]

28. Vega De Lille, M.I.; Hernández Cardona, M.A.; Tzakum Xicum, Y.A.; Giácoman-Vallejos, G.; Quintal-Franco, C.A. Hybrid Constructed Wetlands System for Domestic Wastewater Treatment under Tropical Climate: Effect of Recirculation Strategies on Nitrogen Removal. *Ecol. Eng.* **2021**, *166*, 106243. [CrossRef]
29. González, F.; Vallejos, G.; Silveira, J.; Franco, C.; García, J.; Puigagut, J. Treatment of Swine Wastewater with Subsurface-Flow Constructed Wetlands in Yucatán, Mexico: Influence of Plant Species and Contact Time. *Water Sa* **2012**, *35*. [CrossRef]
30. American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater*, 21st ed.; APHA: Washington, DC, USA, 2005; ISBN 0-87553-235-7.
31. Metcald and Eddy, Inc. *Wastewater Engineering: Treatment and Reuse*, 4th ed.; McGraw-Hill Inc.: Boston, MA, USA, 2003.
32. Elorriaga, Y.; Marino, D.J.; Carriquiriborde, P.; Ronco, A.E. Screening of Pharmaceuticals in Surface Water Bodies of the Pampas Region of Argentina. *Int. J. Environ. Health* **2013**, *6*, 330. [CrossRef]
33. SanJuan-Reyes, N.; Gómez-Oliván, L.M.; Pérez-Pastén Borja, R.; Luja-Mondragón, M.; Orozco-Hernández, J.M.; Heredia-García, G.; Islas-Flores, H.; Galar-Martínez, M.; Escobar-Huérfano, F. Survival and Malformation Rate in Oocytes and Larvae of Cyprinus Carpio by Exposure to an Industrial Effluent. *Environ. Res.* **2020**, *182*, 108992. [CrossRef]
34. Siemens, J.; Huschek, G.; Siebe, C.; Kaupenjohann, M. Concentrations and Mobility of Human Pharmaceuticals in the World's Largest Wastewater Irrigation System, Mexico City–Mezquital Valley. *Water Res.* **2008**, *42*, 2124–2134. [CrossRef]
35. Luque-Espinar, J.A.; Navas, N.; Chica-Olmo, M.; Cantarero-Malagón, S.; Chica-Rivas, L. Seasonal Occurrence and Distribution of a Group of ECs in the Water Resources of Granada City Metropolitan Areas (South of Spain): Pollution of Raw Drinking Water. *J. Hydrol.* **2015**, *531*, 612–625. [CrossRef]
36. Martínez-Casales, Y.; León-Aguirre, K.; Lamas-Cosío, E.; Noreña-Barroso, E.; Herrera-Silveira, J.; Arcega-Cabrera, F. Caffeine and Paraxanthine as Tracers of Anthropogenic Wastewater in Coastal Lagoons in Yucatan, Mexico. *Bull. Environ. Contam. Toxicol.* **2022**, *108*, 182–189. [CrossRef]
37. Quadra, G.R.; Paranaíba, J.R.; Vilas-Boas, J.; Roland, F.; Amado, A.M.; Barros, N.; Dias, R.J.P.; Cardoso, S.J. A Global Trend of Caffeine Consumption over Time and Related-Environmental Impacts. *Environ. Pollut.* **2020**, *256*, 113343. [CrossRef]
38. Zhou, X.; Liang, C.; Jia, L.; Feng, L.; Wang, R.; Wu, H. An Innovative Biochar-Amended Substrate Vertical Flow Constructed Wetland for Low C/N Wastewater Treatment: Impact of Influent Strengths. *Bioresour. Technol.* **2018**, *247*, 844–850. [CrossRef]
39. Marchioro, L.G.; Baggiotto, C.; Decezaro, S.T.; Freo, G.R.; Houndedjihou, D.; de Aquino Berriel Arruda, F.; Ramírez, R.J.M.G.; dos Santos, K.S.; Wolff, D.B. Influence of Partial Saturation and Organic Loading on the Performance of Vertical Wetlands for Raw Wastewater Treatment. *Int. J. Environ. Sci. Technol.* **2025**, *22*, 6585–6594. [CrossRef]
40. Xu, Q.; Chen, S.; Huang, Z.; Cui, L.; Wang, X. Evaluation of Organic Matter Removal Efficiency and Microbial Enzyme Activity in Vertical-Flow Constructed Wetland Systems. *Environments* **2016**, *3*, 26. [CrossRef]
41. Benvenuti, T.; Hamerski, F.; Giacobbo, A.; Bernardes, A.M.; Zoppas-Ferreira, J.; Rodrigues, M.A.S. Constructed Floating Wetland for the Treatment of Domestic Sewage: A Real-Scale Study. *J. Environ. Chem. Eng.* **2018**, *6*, 5706–5711. [CrossRef]
42. You, Y.; Guo, J. VFCW-MFC for Simultaneous Decontamination and Electricity Production under Sulfadiazine Stress: Effects of Substrates and Analysis of Bacterial Community Structure. *Process Saf. Environ. Prot.* **2024**, *190*, 11–21. [CrossRef]
43. Soundaranayaki, K.; Gandhimathi, R. Enhancing the Nitrogen Removal of Vertical Flow Constructed Wetland by Using Organic Media. *Desalination Water Treat.* **2020**, *175*, 125–140. [CrossRef]
44. Akinbile, C.O.; Yusoff, M.S.; Ahmad Zuki, A.Z. Landfill Leachate Treatment Using Sub-Surface Flow Constructed Wetland by Cyperus Haspan. *Waste Manag.* **2012**, *32*, 1387–1393. [CrossRef]
45. Singh, R.P.; Fu, D.; Fu, D.; Juan, H. Pollutant Removal Efficiency of Vertical Sub-Surface Upward Flow Constructed Wetlands for Highway Runoff Treatment. *Arab. J. Sci. Eng.* **2014**, *39*, 3571–3578. [CrossRef]
46. Aylan, R.A.; Al-Abbawy, D.A.H.; Yaseen, D.A. Development of the Horizontal Flow Wetland Using Palm Waste Biochar for Greywater Reclamation. *J. Ecol. Eng.* **2023**, *24*, 236–249. [CrossRef] [PubMed]
47. Visiy, E.B.; Djousse, B.M.K.; Martin, L.; Zangue, C.N.; Sangodoyin, A.; Gbadegesin, A.S.; Fonkou, T. Effectiveness of Biochar Filters Vegetated with Echinochloa Pyramidalis in Domestic Wastewater Treatment. *Water Sci. Technol.* **2022**, *85*, 2613–2624. [CrossRef]
48. Rabbat, C.; Pinna, A.; Andres, Y.; Villot, A.; Awad, S. Adsorption of Ibuprofen from Aqueous Solution onto a Raw and Steam-Activated Biochar Derived from Recycled Textiles Insulation Panels at End-of-Life: Kinetic, Isotherm and Fixed-Bed Experiments. *J. Water Process Eng.* **2023**, *53*, 103830. [CrossRef]
49. Ocampo-Perez, R.; Padilla-Ortega, E.; Medellin-Castillo, N.A.; Coronado-Oyarvide, P.; Aguilar-Madera, C.G.; Segovia-Sandoval, S.J.; Flores-Ramírez, R.; Parra-Marfil, A. Synthesis of Biochar from Chili Seeds and Its Application to Remove Ibuprofen from Water. Equilibrium and 3D Modeling. *Sci. Total Environ.* **2019**, *655*, 1397–1408. [CrossRef]
50. Wang, K.; Wang, Y.; Zhang, S.; Chen, Y.; Wang, R.; Ho, S.-H. Tailoring a Novel Hierarchical Cheese-like Porous Biochar from Algae Residue to Boost Sulfathiazole Removal. *Environ. Sci. Ecotechnol.* **2022**, *10*, 100168. [CrossRef]
51. Hama Aziz, K.H.; Mustafa, F.S.; Hassan, M.A.; Omer, K.M.; Hama, S. Biochar as Green Adsorbents for Pharmaceutical Pollution in Aquatic Environments: A Review. *Desalination* **2024**, *583*, 117725. [CrossRef]

52. Chaiwong, C.; Laungphairojana, A.; Artnaseaw, A.; Supanchaiyamat, N.; Hunt, A.J.; Macquarrie, D.J.; Ngernyen, Y. Modified Biochar Derived from Grass Jelly Tree Waste as a Potential Adsorbent for Ibuprofen Adsorption from Water. *J. Jpn. Inst. Energy* **2025**, *104*, 54–62. [CrossRef]
53. Moreno-Pérez, J.; Pauletto, P.S.; Cunha, A.M.; Bonilla-Petriciolet, Á.; Salau, N.P.G.; Dotto, G.L. Three-Dimensional Mass Transport Modeling of Pharmaceuticals Adsorption inside ZnAl/Biochar Composite. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *614*, 126170. [CrossRef]
54. Ikhlaq, A.; Brown, D.R.; Kasprzyk-Hordern, B. Catalytic Ozonation for the Removal of Organic Contaminants in Water on ZSM-5 Zeolites. *Appl. Catal. B Environ.* **2014**, *154–155*, 110–122. [CrossRef]
55. Dixit, A.; Ahammed, M.M. Use of Modified Biochar for Removal of Endocrine Disrupting Compounds from Water and Wastewater: A Review. *Bioresour. Technol. Rep.* **2023**, *23*, 101519. [CrossRef]
56. Chakraborty, P.; Banerjee, S.; Kumar, S.; Sadhukhan, S.; Halder, G. Elucidation of Ibuprofen Uptake Capability of Raw and Steam Activated Biochar of Aegle Marmelos Shell: Isotherm, Kinetics, Thermodynamics and Cost Estimation. *Process Saf. Environ. Prot.* **2018**, *118*, 10–23. [CrossRef]
57. Lin, L.; Jiang, W.; Xu, P. Comparative Study on Pharmaceuticals Adsorption in Reclaimed Water Desalination Concentrate Using Biochar: Impact of Salts and Organic Matter. *Sci. Total Environ.* **2017**, *601–602*, 857–864. [CrossRef]
58. Siara, S.; Elvis, C.; Harishkumar, R.; Velayudhaperumal Chellam, P. ZnAl2O4 Supported on Lychee-Biochar Applied to Ibuprofen Photodegradation. *Mater. Res. Bull.* **2022**, *145*, 111530. [CrossRef]
59. Mondal, S.; Bobde, K.; Aikat, K.; Halder, G. Biosorptive Uptake of Ibuprofen by Steam Activated Biochar Derived from Mung Bean Husk: Equilibrium, Kinetics, Thermodynamics, Modeling and Eco-Toxicological Studies. *J. Environ. Manag.* **2016**, *182*, 581–594. [CrossRef]
60. Sun, L.; Cao, Z.; Jia, S.; Zhang, P.; Zhang, G. Micro-Aeration Strategies: Optimizing Nitrogen and Phosphorus Removal in Vertical Flow Constructed Wetlands for Rural Sewage Treatment. *J. Water Process Eng.* **2025**, *75*, 107931. [CrossRef]
61. Li, Y.; Lian, J.; Wu, B.; Zou, H.; Tan, S.K. Phytoremediation of Pharmaceutical-Contaminated Wastewater: Insights into Rhizobacterial Dynamics Related to Pollutant Degradation Mechanisms during Plant Life Cycle. *Chemosphere* **2020**, *253*, 126681. [CrossRef]
62. Matamoros, V.; Hijosa, M.; Bayona, J.M. Assessment of the Pharmaceutical Active Compounds Removal in Wastewater Treatment Systems at Enantiomeric Level. Ibuprofen and Naproxen. *Chemosphere* **2009**, *75*, 200–205. [CrossRef]
63. Mohapatra, S.; Tong, X.; Mukherjee, S.; Dubey, M.; Subhash, S.; Luhua, Y.; Van Der Hoek, J.P.; Gin, K.Y.-H. Comprehensive Insights on the Detection, Occurrence and Modelling of Pharmaceuticals in Surface Water, Groundwater, and Drinking Water Treatment Plants. *J. Hazard. Mater. Adv.* **2025**, *18*, 100707. [CrossRef]
64. Leiva, A.M.; Gutierrez, E.; Arias, C.A.; Vidal, G. Influence of Water Quality Parameters on the Removal of Triclosan and Ibuprofen in Vertical Subsurface Flow Constructed Wetlands Using Multivariate Analysis. *Environ. Technol. Innov.* **2021**, *24*, 101846. [CrossRef]
65. Zhang, D.; Luo, J.; Lee, Z.M.P.; Maspolim, Y.; Gersberg, R.M.; Liu, Y.; Tan, S.K.; Ng, W.J. Characterization of Bacterial Communities in Wetland Mesocosms Receiving Pharmaceutical-Enriched Wastewater. *Ecol. Eng.* **2016**, *90*, 215–224. [CrossRef]
66. Li, Y.; Zhu, G.; Ng, W.J.; Tan, S.K. A Review on Removing Pharmaceutical Contaminants from Wastewater by Constructed Wetlands: Design, Performance and Mechanism. *Sci. Total Environ.* **2014**, *468–469*, 908–932. [CrossRef]
67. Ávila, C.; Nivala, J.; Olsson, L.; Kassa, K.; Headley, T.; Mueller, R.A.; Bayona, J.M.; García, J. Emerging Organic Contaminants in Vertical Subsurface Flow Constructed Wetlands: Influence of Media Size, Loading Frequency and Use of Active Aeration. *Sci. Total Environ.* **2014**, *494–495*, 211–217. [CrossRef]
68. Zhang, L.; Lv, T.; Zhang, Y.; Stein, O.R.; Arias, C.A.; Brix, H.; Carvalho, P.N. Effects of Constructed Wetland Design on Ibuprofen Removal–A Mesocosm Scale Study. *Sci. Total Environ.* **2017**, *609*, 38–45. [CrossRef]
69. Bandura, L.; Białoszewska, M.; Malinowski, S.; Franus, W. Adsorptive Performance of Fly Ash-Derived Zeolite Modified by β-Cyclodextrin for Ibuprofen, Bisphenol A and Caffeine Removal from Aqueous Solutions–Equilibrium and Kinetic Study. *Appl. Surf. Sci.* **2021**, *562*, 150160. [CrossRef]
70. Smiljanić, D.; De Gennaro, B.; Daković, A.; Galzerano, B.; Germinario, C.; Izzo, F.; Rottinghaus, G.E.; Langella, A. Removal of Non-Steroidal Anti-Inflammatory Drugs from Water by Zeolite-Rich Composites: The Interference of Inorganic Anions on the Ibuprofen and Naproxen Adsorption. *J. Environ. Manag.* **2021**, *286*, 112168. [CrossRef]
71. Gezahegn, A.; Selassie, Y.G.; Agegnehu, G.; Addisu, S.; Asargew Mihretie, F.; Kohira, Y.; Sato, S. Pyrolysis Temperature Changes the Physicochemical Characteristics of Water Hyacinth-Based Biochar as a Potential Soil Amendment. *Biomass Convers. Biorefin.* **2025**, *15*, 3737–3752. [CrossRef]
72. Madariaga-Segovia, P.; Villamar-Ayala, C.A.; Ramos, N.; Sánchez-Domínguez, M.; Lavín, R. Influence of Pyrolysis Conditions on the Adsorbent Properties of Hazelnut Shell Biochar to Remove Paracetamol, Amoxicillin, and Triclosan. *Case Stud. Chem. Environ. Eng.* **2025**, *12*, 101251. [CrossRef]

73. Tortet, L.; Ligner, E.; Blanluet, W.; Noguez, P.; Marichal, C.; Schäf, O.; Paillaud, J.-L. Adsorptive Elimination of Paracetamol from Physiological Solutions: Interaction with MFI-Type Zeolite. *Microporous Mesoporous Mater.* **2017**, *252*, 188–196. [CrossRef]
74. Matějová, L.; Bednárek, J.; Tokarský, J.; Koutník, I.; Sokolová, B.; Cruz, G.J.F. Adsorption of the Most Common Non-Steroidal Analgesics from Aquatic Environment on Agricultural Wastes-Based Activated Carbons; Experimental Adsorption Study Supported by Molecular Modeling. *Appl. Surf. Sci.* **2022**, *605*, 154607. [CrossRef]
75. Palma, T.L.; Donaldben, M.N.; Costa, M.C.; Carlier, J.D. Putative Role of Flavobacterium, Dokdonella and Methylophilus Strains in Paracetamol Biodegradation. *Water Air Soil Pollut.* **2018**, *229*, 200. [CrossRef]
76. Park, S.; Oh, S. Activated Sludge-Degrading Analgesic Drug Acetaminophen: Acclimation, Microbial Community Dynamics, Degradation Characteristics, and Bioaugmentation Potential. *Water Res.* **2020**, *182*, 115957. [CrossRef]
77. Sosa Alderete, L.G.; Vezza, M.; Ibañez, S.G.; Schroeder, P.; Agostini, E.; Talano, M.A. Unraveling Paracetamol Metabolism and Its Circadian Regulation: Insights from Tobacco Hairy Roots as a Model System. *Plants* **2025**, *14*, 2812. [CrossRef] [PubMed]
78. Ranieri, E.; Verlicchi, P.; Young, T.M. Paracetamol Removal in Subsurface Flow Constructed Wetlands. *J. Hydrol.* **2011**, *404*, 130–135. [CrossRef]
79. Zhao, Y.; Yang, S.; Li, H.; Wang, D. Adsorption Behaviors of Acetaminophen onto Sediment in the Weihe River, Shaanxi, China. *Int. J. Sediment Res.* **2015**, *30*, 263–271. [CrossRef]
80. Bernal, V.; Erto, A.; Giraldo, L.; Moreno-Piraján, J. Effect of Solution pH on the Adsorption of Paracetamol on Chemically Modified Activated Carbons. *Molecules* **2017**, *22*, 1032. [CrossRef]
81. Pauletto, P.S.; Lütke, S.F.; Dotto, G.L.; Salau, N.P.G. Exploring the Simultaneous Mass Transport of Nimesulide and Paracetamol Adsorption on Activated Carbon: A PVSDM Approach. *Sep. Purif. Technol.* **2024**, *329*, 125148. [CrossRef]
82. Matamoros, V.; Arias, C.; Brix, H.; Bayona, J.M. Removal of Pharmaceuticals and Personal Care Products (PPCPs) from Urban Wastewater in a Pilot Vertical Flow Constructed Wetland and a Sand Filter. *Environ. Sci. Technol.* **2007**, *41*, 8171–8177. [CrossRef]
83. de Oliveira, M.; Atalla, A.A.; Frihling, B.E.F.; Cavalheri, P.S.; Migliolo, L.; Filho, F.J.C.M. Ibuprofen and Caffeine Removal in Vertical Flow and Free-Floating Macrophyte Constructed Wetlands with Heliconia Rostrata and Eichornia Crassipes. *Chem. Eng. J.* **2019**, *373*, 458–467. [CrossRef]
84. Zhang, L.; Wen, X.; Zhang, J.; Chen, A.; He, X. Adsorption/Desorption of Ammonium and Phosphorus on Four Substrates in Constructed Wetland. *Asian J. Chem.* **2015**, *27*, 2477–2481. [CrossRef]
85. Kozyatnyk, I.; Oesterle, P.; Wurzer, C.; Mašek, O.; Jansson, S. Removal of Contaminants of Emerging Concern from Multicomponent Systems Using Carbon Dioxide Activated Biochar from Lignocellulosic Feedstocks. *Bioresour. Technol.* **2021**, *340*, 125561. [CrossRef]
86. Mengesha, D.N.; Abebe, M.W.; Appiah-Ntiamoah, R.; Kim, H. Ground Coffee Waste-Derived Carbon for Adsorptive Removal of Caffeine: Effect of Surface Chemistry and Porous Structure. *Sci. Total Environ.* **2022**, *818*, 151669. [CrossRef] [PubMed]
87. Barbosa, A.G.; Magalhães, T.F.D.S.; Golin, R.; Sousa, H.M.; Fukumoto, A.A.F.; Vasconcelos, L.G.D.; Morais, E.B.D. Adsorption of Caffeine in Aqueous Solution by Biochar from Cotton Processing Residues. *NAT* **2024**, *12*, 474–481. [CrossRef]
88. Anastopoulos, I.; Katsouromalli, A.; Pashalidis, I. Oxidized Biochar Obtained from Pine Needles as a Novel Adsorbent to Remove Caffeine from Aqueous Solutions. *J. Mol. Liq.* **2020**, *304*, 112661. [CrossRef]
89. Anastopoulos, I.; Pashalidis, I. The Application of Oxidized Carbon Derived from Luffa Cylindrica for Caffeine Removal. Equilibrium, Thermodynamic, Kinetic and Mechanistic Analysis. *J. Mol. Liq.* **2019**, *296*, 112078. [CrossRef]
90. Samara, F.; Al Abdel Hamid, A.A.; Gopal, V.; Dronjak, L.; Feghaly, F.; Kanan, S. Modified Zeolites for the Removal of Emerging Bio-Resistive Pollutants in Water Resources. *Catalysts* **2025**, *15*, 138. [CrossRef]
91. Keerthanan, S.; Rajapaksha, S.M.; Trakal, L.; Vithanage, M. Caffeine Removal by Gliricidia Sepium Biochar: Influence of Pyrolysis Temperature and Physicochemical Properties. *Environ. Res.* **2020**, *189*, 109865. [CrossRef] [PubMed]
92. Quintero-Jaramillo, J.A.; Carrero-Mantilla, J.I.; Sanabria-González, N.R. A Review of Caffeine Adsorption Studies onto Various Types of Adsorbents. *Sci. World J.* **2021**, *2021*, 9998924. [CrossRef] [PubMed]
93. Dash, S.S.; Gummadi, S.N. Catabolic Pathways and Biotechnological Applications of Microbial Caffeine Degradation. *Biotechnol. Lett.* **2006**, *28*, 1993–2002. [CrossRef]
94. Summers, R.M.; Mohanty, S.K.; Gopishetty, S.; Subramanian, M. Genetic Characterization of Caffeine Degradation by Bacteria and Its Potential Applications. *Microb. Biotechnol.* **2015**, *8*, 369–378. [CrossRef]
95. Gutiérrez, J.; Leiva, A.M.; Gómez, G.; Vidal, G. Performance of Vertical Subsurface Flow Constructed Wetlands for Commercial Laundry Greywater Treatment: Effects of Design and Operational Parameters. *J. Water Process Eng.* **2025**, *75*, 107951. [CrossRef]
96. Wang, J.-F.; Zhu, C.-Y.; Weng, B.-S.; Mo, P.-W.; Xu, Z.-J.; Tian, P.; Cui, B.-S.; Bai, J.-H. Regulation of Heavy Metals Accumulated by Acorus Calamus L. in Constructed Wetland through Different Nitrogen Forms. *Chemosphere* **2021**, *281*, 130773. [CrossRef] [PubMed]
97. Batkhuyag, N.; Matyakubov, B.; Mang, N.Z.L.; Lee, T. Additive Inhibitory Effects of Heavy Metals on Phenol-Utilizing Microorganism. *Environ. Eng. Res.* **2021**, *27*, 210342. [CrossRef]

98. Ma, Y.; Huang, J.; Li, R.; Chen, X.; Cao, M. Dissecting the Negative Influence Mechanisms of Microplastics on Plant and Microbial Mediated Nitrogen Removal in Constructed Wetlands. *Chem. Eng. J.* **2024**, *491*, 151910. [CrossRef]
99. Escolà Casas, M.; Matamoros, V. Novel Constructed Wetland Configurations for the Removal of Pharmaceuticals in Wastewater. In *Handbook of Environmental Chemistry*; Springer Science and Business Media Deutschland GmbH: Cham, Switzerland, 2021; Volume 108, pp. 163–190.