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Turning Waste into Treatment: Sugarcane Bagasse Biochar for Sustainable Removal of Pharmaceuticals and Illicit Drugs from Wastewater

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Abstract

This study evaluates the bioadsorption efficiency of sugarcane bagasse (SCB) for removing pharmaceuticals and illicit drugs—such as acetaminophen, atenolol, caffeine, carbamazepine, diclofenac, orphenadrine, losartan, enalapril, citalopram, cocaine, and benzoylecgonine—from wastewater effluents. In Brazil, where 46% of the population lacks access to sewage systems, and over 5.3 billion pharmaceutical packages are consumed annually, untreated discharges contribute significantly to aquatic contamination. Results show that applying SCB biochar at a 1% (m/v) ratio removes up to 99.8% of these compounds at total concentrations of 140 ng mL^{-1}, reducing the ecological risk from high to low for caffeine and losartan. SCB offers several advantages as a bioadsorbent: it is abundant, non-toxic, inexpensive, easy to handle, and exhibits high adsorption capacity and rapid kinetics across a wide range of chemical polarities. These findings highlight SCB's potential as a sustainable and efficient material for wastewater treatment applications.

Keywords: sugarcane bagasse biochar; pharmaceutical pollutants; illicit drugs; wastewater treatment; bioadsorption; environmental risk reduction

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1. Introduction

The emerging contaminants (EC) are defined strictly as "*any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment, but has the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects*" [1]. Thus, the term "*emerging*" refers not only to the contaminants themselves but also to the growing concern regarding their presence and potential impacts on the environment and human health. As such, emerging contaminants are often referred to as '*chemicals of emerging concern*' or '*contaminants of emerging concern*' [2]. The EC are typically divided into the following categories: pharmaceuticals and personal care products (PPCPs), surfactants, plasticizers, pesticides, and flame retardants [3]. This work is focused on PPCPs, mainly prescription pharmaceuticals, and the illicit drug cocaine and its main metabolite, benzoylecgonine. These chemical compounds enter the environment and drinking water supplies following their discharge from sewage treatment plants, which are often unable to remove them using conventional treatment techniques such as activated sludge, flocculation, and aerobic processes [4]. Rasheed [5] published a review reporting the occurrence of PPCPs in tap water, surface water, and groundwater across various countries.

The study also highlighted key issues related to water source contamination, analytical methods for detection and quantification, and treatment strategies [5].

In Brazil, 54% of the population—approximately 114.6 million people—have access to sewage collection and treatment in their homes, whereas 46% of the population, around 98 million people, are not connected to the sanitary sewer system [6]. In addition, drug consumption in Brazil is very high; in 2019, approximately 5.3 billion packages of 5897 pharmaceutical products—corresponding to 1935 active ingredients and their combinations—were commercialized. Considering the country's population of approximately 213 million inhabitants, this corresponds to an estimated 24.7 packages of medicines sold per person [7]. These data highlight a significant environmental concern with serious implications for aquatic life and ecosystem health, as most PPCPs are discharged—directly or indirectly—into water bodies in large quantities on a daily basis.

Indeed, several Brazilian research groups, as well as international studies, have reported the presence of PPCPs and illicit drugs in surface waters and seawater [8–12]. Roveri [13] analyzed seawater samples collected around the Sao Paulo state coastal submarine sewage outfall, and they reported the presence of PPCPs and cocaine in those samples. Furthermore, the study indicated that sewage treatment plants are largely inefficient at removing PPCPs, as well as cocaine and its metabolite benzoylecgonine, resulting in their continuous and frequent discharge into the marine environment [13]. The presence of PPCPs in water sources can pose significant risks to aquatic ecosystems, and these compounds have also been detected in various aquatic organisms [14,15]. As clear evidence of environmental contamination, Ortega [16] have highlighted the occurrence and potential ecological risks of pharmaceuticals and illicit drugs (PhID) in the Santos–São Vicente Estuarine System (SSVES), a densely populated coastal region in the state of São Paulo, Brazil. The results revealed the widespread presence of caffeine (72.1 ng L^{-1}) > losartan (29.6 ng L^{-1}) > orphenadrine (25.9 ng L^{-1}) > benzoylecgonine (18.6 ng L^{-1}) > carbamazepine (7.4 ng L^{-1}), and cocaine (3.6 ng L^{-1}) in surface water. The study also examined the presence of these compounds in sediments and oyster tissues, and the overall results, based on ecological risk assessment, indicated a significant environmental concern, particularly for algae, crustaceans, and fish species [16].

Unfortunately, there are currently no regulations established by Brazilian environmental or health agencies—at the federal, state, or municipal level—to control the concentrations of PhID in either water sources or wastewater, including the specification of Maximum Residue Levels (MRLs). The European Medicines Agency (EMEA) suggested the maximum Measured Environmental Concentration (MEC) should be 10 ng L^{-1} (0.01 ng mL^{-1}) for the EC. If the MEC exceeds this concentration, an ecological risk assessment is recommended [17]. The situation is further exacerbated by the absence of scientific studies or monitoring programmes to evaluate the efficiency of sewage, industrial, and hospital treatment plants in removing PhID and other EC.

The selected PPCPs are among the most widely consumed pharmaceuticals in Brazil (2019 data) and are frequently detected in water sources, including rivers, seas, and wastewater: losartan (antihypertensive) is the best-selling prescription pharmaceutical (approximate 200 mi packages/year), with a production and consumption of 300 tons/year; acetaminophen (analgesic) is in the 11^{th} position out of the top 20 (approximately 75 mi packages/year), with 1.1 tons/year; atenolol (antihypertensive) is in the 13^{th} position (approximately 75 mi packages/year), with 200 tons/year; enalapril (antihypertensive) is in the 18^{th} position (approximately 37 mi packages/year), with 16.6 tons/year; diclofenac (anti-inflammatory) achieved a consumption of 68 tons, and 33 tons of caffeine (stimulant) was consumed, both are in 20^{th} ranked position (approximately 25 to 50 mi packages/year) [7]. Caffeine, present in coffee beans and beverages, serves as a marker of

anthropogenic environmental pollution. In Brazil, per capita coffee consumption reached 4.84 kg in 2021, corresponding to a total ingestion of approximately 7700 tons of caffeine that year [18]. The sale of antidepressants and mood stabilizers, such as carbamazepine (anxiolytic) and citalopram (antidepressant), has increased considerably in Brazil in recent years. The data indicate that nearly 100 million boxes of these drugs were sold in 2020, representing a 17% increase compared to the previous year. In 2021, sales continued to rise, with antidepressant medications showing an additional 14% growth [19]. Orphenadrine (anticholinergic), which is formulated together with sodium dipyrone and caffeine, is indicated as an analgesic and muscle relaxant. In 2021, sales of this medication generated over BRL 638 million in revenue. This drug sold, in 2018, 55 tablets/second, and, extrapolating, the sale or consumption of this asset, reached 165 kg/day and 59 tons/year [20,21]. Last but not least is cocaine, considered an abused or illicit drug. According to the 2nd Brazilian Drug Report, published in 2021 by the Ministry of Justice and Public Security (National Secretariat for Drug Policies and Asset Management), Brazil is the second largest country in population of cocaine consumers, with 2.8 million people, and is positioned behind to the USA, with 4 million consumers, followed by 65 other South American countries (2.4 mi), the UK (1.1 mi), Spain (0.8 mi), and Canada (0.5 mi), according to data cited in this study and surveyed among the population between 2001 and 2005. It is estimated that several tons of this central nervous system stimulant are produced, trafficked, and consumed in Brazil [22]. Cocaine is metabolized by human liver enzymes into benzoylecgonine, which is subsequently excreted in urine and feces.

Considering the presence of PhID in wastewater treatment plant (WWTP) effluents at an average total concentration of 100 μg L^{-1}, a typical system flow rate of 16 m^3 s^{-1}, and assuming no removal efficiency, it is estimated that approximately 140 kg of these emerging contaminants are released into water bodies on a daily basis.

Sarker [23] published a comprehensive review detailing the adsorption properties of sugarcane bagasse (SCB), a lignocellulosic material capable of trapping both inorganic and organic chemical compounds [23]. This review showed SCB's capability to remove metals, dyes, phenolic compounds, herbicides, and pesticides from aqueous solution [24–27]. Sugarcane bagasse (SCB) is a promising low-cost bioadsorbent for the removal of pharmaceutical and illicit drugs (PhID) from wastewater due to its abundant availability as an agro-industrial residue. SCB is generated during sugarcane juice extraction, which is rich in sugars that are subsequently converted into bioethanol, liquor, and refined sugar through enzymatic processes. Utilizing SCB as a bioadsorbent not only provides an environmentally sustainable strategy for waste valorisation but also offers an economically attractive alternative to conventional wastewater treatment materials. The majority of sugarcane bagasse (SCB) is combusted to generate energy in sugarcane mills, while the remaining fraction is treated as waste residue. In São Paulo State, Brazil, approximately 60 million tons of SCB are produced annually, alongside 50 billion liters of biofuel.

The increasing concern over environmental contamination by PhID has highlighted adsorption as an effective remediation strategy. This approach offers several advantages: it is low-cost, it is easily implemented in developing countries where advanced technologies, skilled personnel, and capital are limited, and it represents a broadly feasible method for pharmaceutical removal that can be readily integrated into WWTPs. Another advantage is the flexibility of SCB biadsorbent material, as it can be used in different forms: *in natura* (raw), as chemically modified activated carbon, biochar, clay minerals, and nano-materials. The biochar SCB form has already applied, with high efficiency, to remove ibuprofen (analgesic) and sulfamethoxazole (antibiotic) from wastewater [28,29]. Lebre [30] published a scientific article describing the use of SCB as a solid-phase extraction (SPE) material sorbent to retain synthetic hormones (ethynylestradiol, drospirenone, and levonorgestrel)

from industrial pharmaceutical plant effluent samples prior to LC−MS/MS quantitative analysis. The hormones' affinity to SCB was higher than 99%, and this finding was the scientific pathway to produce data for the PhID [30].

Herein, we evaluated the bioadsorption capabilities of sugarcane bagasse (SCB) for the efficient removal of the PhID from both aqueous solutions and effluent samples collected from the four largest wastewater treatment plants (WWTPs) in São Paulo State: São Caetano do Sul, Barueri, Suzano, and São Miguel. Caffeine was selected as a model compound to investigate the adsorption capabilities of SCB in both its raw (*in natura*) and biochar forms. Concentrations of PhID in WWTP samples were determined using the gold-standard LC–MS/MS technique, chosen for its high selectivity and sensitivity.

We expect that this study will contribute to advancing the large-scale application of sugarcane bagasse (SCB) for the removal of emerging contaminants from wastewater, while also promoting the valorisation of SCB residues that are typically burned in sugarcane mills and released as CO_2 emissions into the atmosphere.

2. Materials and Methods

2.1. Chemicals and Reagents

The chemical standards of acetaminophen (>99%), atenolol (99%), caffeine (99% purity), carbamazepine (>99% purity), diclofenac sodium salt (>99% purity), orphenadrine citrate salt (>99%), and losartan potassium were purchased from a local sales representative from Sigma-Aldrich (St. Louis, MO, USA), and enalapril melanate and citalopram were acquired from the local pharmaceutical industry (São Paulo, Brazil) and chemically consider as a secondary standard. Each pharmaceutical compound was prepared separately as stock solutions at a concentration of 1 mg mL^{-1} and 10 mg mL^{-1} in methanol. Cocaine and benzoylecgonine at a concentration of 1 mg mL^{-1} in methanol (Cerilliant, Round Rock, TX, USA) were acquired from local Sigma-Aldrich. LC-MS grade acetonitrile was purchased from Supelco (Darmstadt, Germany), formic acid (<98%) for mass spectrometry was procured from Sigma-Aldrich (St. Louis, MO, USA), and HPLC grade methanol was purchased from Supelco (Darmstadt, Germany). Lastly, Na_2HPO_4 salt was purchased from local Sigma-Aldrich (São Paulo, Brazil).

2.2. Sugarcane Bagasse (SCB) Sorbent Preparation (Raw)

The peeled triturate sugarcane stalks were collected from a local sugarcane juice market and washed with ultrapure water 18.2 mΩ (Integral 3, Millipore, Guyancourt, France) to remove the juice residues and impurities. Then, the stalks were dried for 48 h at 50 °C inside the Fanem Orion 515 drying oven (Fanem, São Paulo, Brazil). Approximately 250 g of the dried stalk was ground into small pieces using a semi-industrial blender. A total of 15 g of the material was ground again for 24 h in a laboratory ball mill apparatus (Retsch, GmbH, Haan, Germany) to create a fine SCB powder. The SCB powder was filtered using molecular sieves of 2 mm, 1 mm, and ultimately 75 µm. This material was kept at room temperature in a laboratory desiccator chamber containing silica balls [30].

2.3. Sugarcane Bagasse (SCB) Sorbent Preparation (Biochar)

After the same procedure described above, 250 g (weight in a ceramic vessel) of the raw SCB material at 1 mm particle size was burned at 550 °C in a ceramic oven for approximately 10 to 15 min, or until it became charcoal. The remaining material, representing approximately 10% of the initial mass (≈25 g), was ground in a mortar to a fine powder and prepared for use in the adsorption study.

2.4. Caffeine Solutions for Adsorption Tests

The caffeine was prepared in phosphate saline buffer solution (Na_2HPO_4) at 1 mM (pH 7.4) in the following concentrations: 0 (Blank), 1, 5, 10, 25, 50, 100, 250, 500, and 750 μg mL^{-1}. These solutions were used to build the adsorption curves in batch assays for SCB raw (50 mg) and SCB biochar (20 mg) materials.

2.5. Pharmaceuticals, Cocaine, and Benzoylecgonine Solutions for Adsorption Tests

A total of 100 mL of the compound mixture in ultrapure water (18.2 mΩ) was prepared in the following concentrations: acetaminophen: 100 μg mL^{-1}; atenolol: 50 μg mL^{-1}; caffeine: 10 μg mL^{-1}; carbamazepine: 100 μg mL^{-1}; citalopram: 20 μg mL^{-1}; diclofenac: 50 μg mL^{-1}; enalapril: 35 μg mL^{-1}; losartan: 50 μg mL^{-1}; orphenadrine: 10 μg mL^{-1}; cocaine: 5 μg mL^{-1}; and benzoylecgonine: 5 μg mL^{-1}. It is important to keep the solvent (methanol) concentration of this solution below 5% (v/v), and therefore, some of the pharmaceutical compounds were weighed and dissolved straight from the standard powder or the pill formulation. This solution was applied in adsorption batch assays for SCB raw (50 mg) and SCB biochar (20 mg) material.

2.6. Effluent Samples from WWTP

Four effluent samples were collected from four sewage treatment plants located in the Sao Paulo metropolitan region. Table 1 describes the samples collected in August 2024. The samples were maintained at freezing temperatures, −18 °C, until they were used for the laboratory tests.

Table 1. Wastewater sample information.

Effluent	Location (City)	nº of Inhabitants Served (mi)	Treatment Flow (m^3 s^{-1})	pH
WWTP 1	São Caetano do Sul	2.8	3.0	7.8
WWTP 2	Barueri	7.7	16	7.9
WWTP 3	Suzano	0.3	1.5	8.3
WWTP 4	São Miguel	1.8	6.0	8.9

2.7. SCB (Raw) Procedure for Batch Assay

A total of 50 mg of the bioadsorbent material was weighed in an appropriate 1.5 mL Eppendorf tube and washed two times with 1 mL of ultrapure water (18.2 mΩ); in between the washes, it was centrifuged at 14,000× g rpm for 2 min, and the supernatant was discharged. A 1 mL aliquot of the adsorption solution or wastewater sample was mixed for 10 min using a vortex mixer set at its maximum speed (10 arbitrary units). After the adsorption step, the tube was centrifuged at 14,000× g rpm for 3 min, and the eluate (supernatant) was diluted when needed and analyzed by LC-MS/MS for compound quantitation.

2.8. SCB Biochar Procedure for Batch Assay

A total of 20 mg of the bioadsorbent material was weighed in an appropriate 1.5 mL Eppendorf tube, and 1 mL load volume of the adsorption solutions or the wastewater samples was added and mixed for 10 min in a vortex apparatus. After the adsorption step, the tube was centrifuged at 14,000× g rpm for 6 min, and the eluate (supernatant) was filtered in 0.22 μm (hydrophilic filter disc), prior to dilution when needed, and it was analyzed by LC-MS/MS for compound quantitation.

2.9. LC-MS/MS Analysis

The HPLC system (binary pump and degasser) with a refrigerator autosampler and column oven, model series 1260 from Agilent Technologies (Santa Clara, CA, USA) equipped with a reversed-phase C18 analytical column of 50 mm × 4.6 mm, and a 1.8 µm particle size (XDB-C18, Agilent Technologies, Santa Clara, CA, USA) was used, coupled with the mass spectrometer analyzer. The temperature of the column was maintained at 25 °C. The injected sample volume was 10 µL (autosampler temperature 10 °C). Mobile phases A and B were water with 0.1% formic acid (v/v) and acetonitrile with 0.1% formic acid (v/v), respectively. The optimized chromatographic method maintained the initial mobile phase composition (5% B) constant for 0.5 min, followed by a linear gradient to 95% B in 5.0 min and holding at this concentration for 1.0 min, and then back to the initial composition (5% B) for 2 min. The chromatographic run time was 8 min, plus 1.0 min for initial conditional equilibration, keeping the LC flow rate of 0.7 mL min^{-1}. A hybrid triple quadrupole linear ion trap mass spectrometer (QqLIT), model 3200 QTRAP (Sciex, Concord, ON, Canada), was utilized to quantify the compounds. The compounds were ionized using an electrospray (ESI) TurboV® source operated in the positive mode at the following parameters: ESI (IS) voltage, 5.2 kV; temperature, 550 °C; nebulizer gas (GS1), 50 psi; heater gas (GS2), 55 psi; and curtain gas (CUR), 20 psi (with interface heater on). The multiple reaction monitoring (MRM) mode was employed to quantitatively analyse the target compounds using a triple quadrupole mass spectrometer, with the optimal signal transition conditions specified in Table 2. The dwell time for each MRM transition was set to 12 msec, and the collision cell was filled with the CID gas "high" (arbitrary unit). The results were processed by Analyst software version 1.5.2 (Sciex, Concord, ON, Canada).

Table 2. Multiple reaction monitoring (MRM) transitions for PhID.

Compound	MRM (*m*/*z*)	DP (V)	EP (V)	CEP (V)	CE (eV)	CXP (V)
Acetaminophen	152 > 93	26	9.0	12	29	4
	152 > 110				19	4
Caffeine	195 > 110	36	5.5	15	29	4
	195 > 138				25	4
Carbamazepine	**237 > 179**	36	9.5	16	43	4
	237 > 194				25	4
Atenolol	**267 > 145**	41	8.0	20	25	4
	265 > 195				19	4
Orphenadrine	270 > 167	16	6.0	24	53	4
	270 > 181				19	4
Benzoylecgonine	290 > 105	31	5.0	14	37	4
	290 > 168				25	4
Diclofenac	**296 > 214**	21	6.5	14	39	4
	296 > 250				19	4
Cocaine	304 > 105	36	5.0	14	39	4
	304 > 182				27	4
Citalopram	**325 > 109**	41	6.0	24	35	4
	325 > 262				27	4

Table 2. *Cont.*

Compound	MRM (*m*/*z*)	DP (V)	EP (V)	CEP (V)	CE (eV)	CXP (V)
Enalapril	**366 > 234**	36	6.5	16	27	4
	366 > 377				25	4
Losartan	**423 > 207**	21	6.0	18	31	4
	423 > 405				17	4

Note: The bold font highlights the MRM quantitation transitions followed by the confirmation. Declustering Potential (DP), Entrance Potential (EP), Collision Entrance Potential (CEP), Collision Energy (CE), and Collision Exit Potential (CXP).

3. Results and Discussion

3.1. Caffeine Adsorption Curve

Prior to the application of SCB material to remove the PhID in wastewater, it was necessary to understand the bioadsorbent capabilities. Adsorption is a mass transfer operation that studies the ability of certain solids to concentrate certain substances existing in liquid or gaseous fluids on their surface, enabling the separation of the components of these fluids. Since the adsorbed components are concentrated on the external surface, the larger this external surface is per unit of solid mass, the more favourable the adsorption will be. Therefore, adsorbents are generally solids with porous particles. The species that accumulates at the material interface is normally called an adsorbate, and the solid surface on which the adsorbate accumulates is the adsorbent [31]. The adsorption process depends on several parameters: surface area, physical–chemical surface properties, temperature, solvent, and the pH of the adsorption process; and also, the nature of adsorbent compounds includes polarity, molecular mass, water solubility, and acid and basic chemical properties, which all have an influence on the adsorption capabilities [32].

To evaluate the adsorption capacities of both raw and biochar forms of sugarcane bagasse (SCB), adsorption isotherms at room temperature were obtained using caffeine as a model compound. The results are presented in Tables 3 and 4 and illustrated in Figures 1 and 2. Adsorption isotherm experiments were conducted by adding a fixed mass of adsorbent to a known volume of solution (V_0 = 1 mL) containing different initial solute concentrations (C_0). After adsorption equilibrium was reached, the equilibrium concentration in solution (C_e) and the adsorption capacity of the adsorbent (q_e, expressed as mass of solute per unit mass of adsorbent) were determined. The adsorption isotherms were constructed by plotting q_e as a function of C_e. To determine C_e, the adsorbent was separated from the solution by centrifugation, and the supernatant was analyzed by LC–MS/MS to quantify the residual solute concentration.

Table 3. Adsorption isotherm results for caffeine using SCB raw (50 mg) and load (C_0) volume of 1 mL.

C_0 (μg mL^{-1})	m_0 (μg)	C_e (μg mL^{-1})	m_r (μg)	q_e (μg mg^{-1})	Removal (%)
1	1	0.640	0.360	0.007	36.0
5	5	2.93	2.07	0.041	41.4
10	10	6.64	3.36	0.067	33.6
25	25	16.1	8.90	0.178	35.6
50	50	30.4	19.6	0.392	39.2
100	100	65.2	34.8	0.696	34.8

Note: C_0 (initial/load concentration); C_e (eluate concentration); m_0 (initial adsorbate mass); m_r (retained mass); and q_e (adsorption capacity in equilibrium).

Table 4. Adsorption isotherm results for caffeine using SCB biochar (20 mg) and load (C_0) volume of 1 mL.

C_0 (µg mL^{-1})	m_0 (µg)	C_e (µg mL^{-1})	m_r (µg)	q_e (µg mg^{-1})	Removal (%)
1	1	0.0030	0.997	0.050	99.7
5	5	0.0043	5.00	0.25	99.9
10	10	0.0066	10.0	0.50	99.9
25	25	0.0331	25.0	1.25	99.9
50	50	0.136	49.9	2.49	99.7
100	100	0.794	99.2	4.96	99.2
250 *	250	27.8	222	11.1	88.9
500	500	127	373	18.7	74.6
750	750	376	374	18.7	49.9

Note: (*) breakthrough concentration.

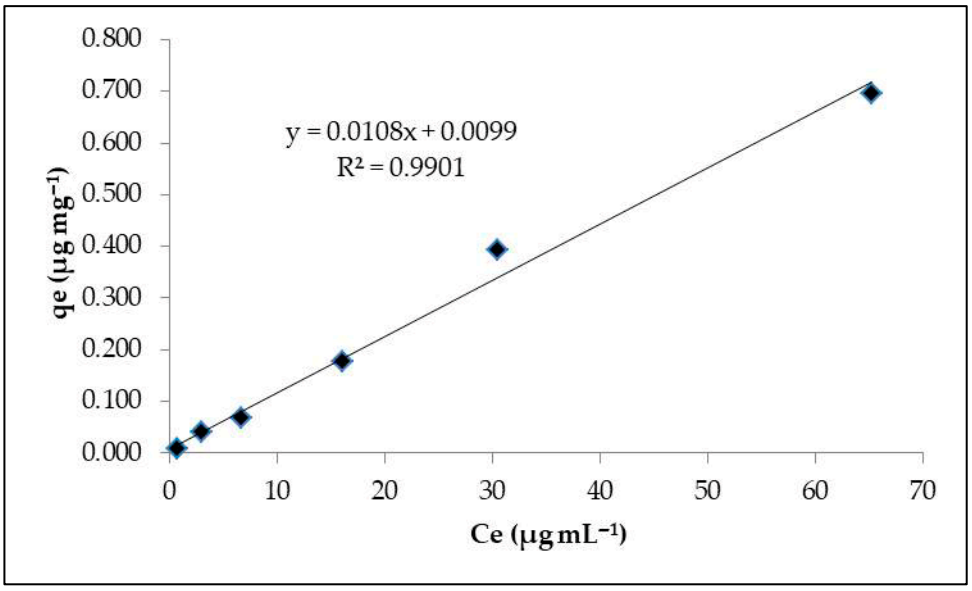

Figure 1. Adsorption isotherm curve for caffeine—SCB raw material (50 mg).

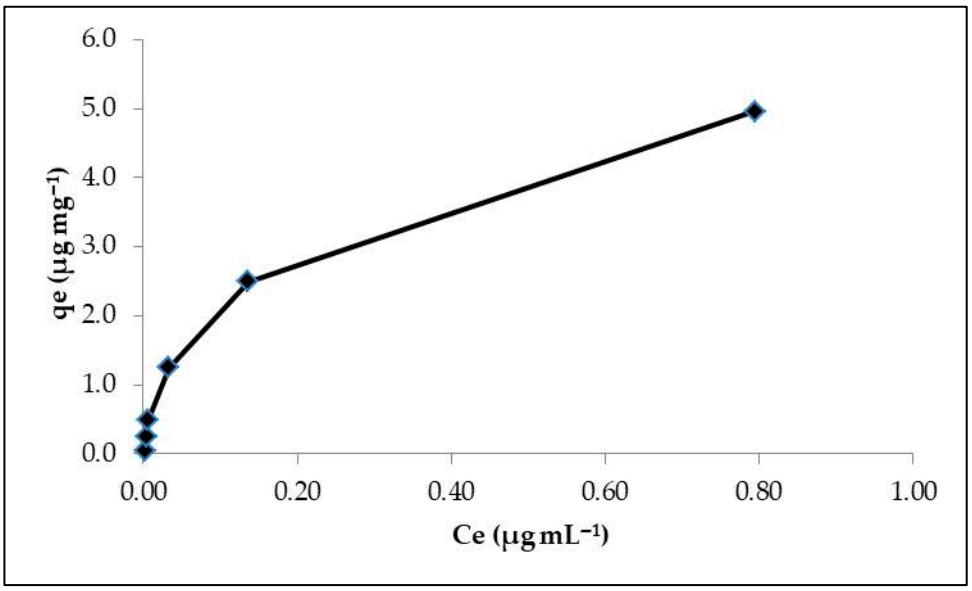

Figure 2. Adsorption isotherm curve for caffeine—SCB biochar material (20 mg).

Caffeine (adsorbate) was selected as the model adsorbate due to its relevance as an anthropogenic pollution marker and its physicochemical properties, including high water solubility (11.3 g L^{-1}), hydrophilic character (log P = −0.50), and Lewis base behaviour (pK_a = 14). These characteristics make caffeine a challenging compound for interaction with adsorbent materials.

The obtained results showed some differences in the adsorption process for SCB raw versus SCB biochar material. The percentage average of adsorption or removal of caffeine using the SCB raw adsorbent was 36.8%, while the SCB biochar revealed better efficiency with 99.7%, considering the concentration (C_0) range in solution from 1 to 100 μg mL^{-1} (1.0 to 100 μg in mass). The breakthrough of SCB biochar material occurs at 250 μg in caffeine mass, where the adsorption efficiency decreases (88.9%). By analyzing the two isotherm curves, we obtained extremely relevant information about the adsorption process. The linear isotherm form ($r^2 > 0.99$) for SCB raw material, shown in Figure 1, revealed that the mass of adsorbate (caffeine) retained per unit mass of the adsorbent is proportional to the equilibrium concentration of the adsorbate in the liquid phase. The favourable isotherm form obtained by SCB biochar, Figure 2, revealed that the mass of the adsorbate (caffeine) retained per unit mass of the adsorbent is high for a low equilibrium concentration of the adsorbate in the liquid phase. The SCB biochar material presented better adsorption results for caffeine and fits the Langmuir isotherm model, as shown in Figure 3, which represents the graphic C_e/q versus C_e and fits the linear model from 1.0 to 750 μg mL^{-1} (1 to 750 μg in mass) of the range of caffeine concentration (C_0).

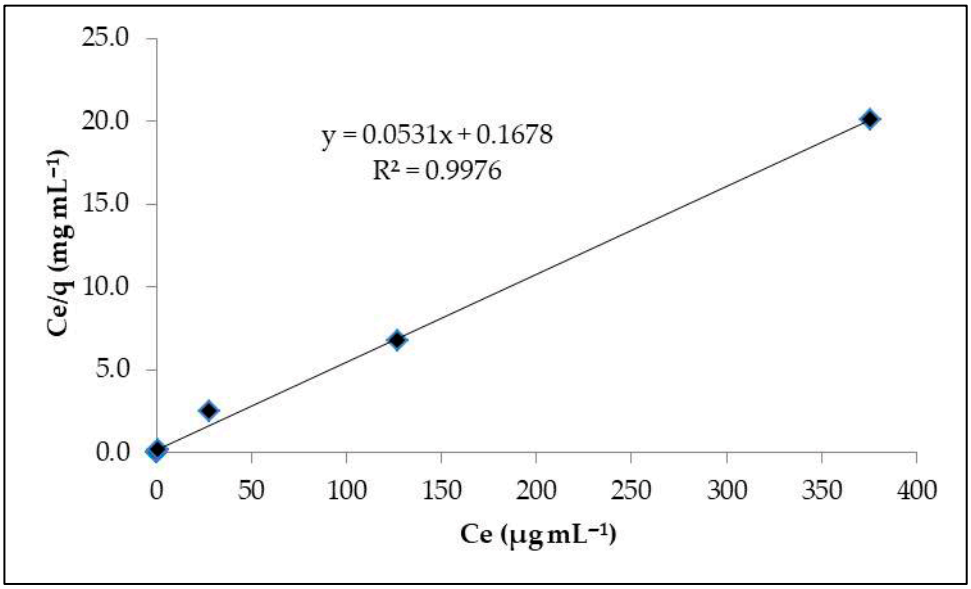

Figure 3. Langmuir isotherm curve for caffeine—SCB biochar material (20 mg).

The Langmuir isotherm equation curve obtained for caffeine and SCB biochar allowed the calculation of the following parameters: the maximum adsorption capacity (q_{max}) of 18.3 μg mg^{-1} and the constant of interaction adsorbate/adsorbent (KL) equal to 0.317 mL mg^{-1}. The separation factor (RL) was calculated for the caffeine concentration (C_0) range from 1 to 750 μg mL^{-1}, resulting in 0.004–0.760 values, that is, between 0 and 1, conferring the adsorbate preference to the solid phase instead of the liquid phase, and therefore, it is denominated as favourable adsorption [33].

The pronounced differences in textural properties between raw sugarcane bagasse (SCB) and SCB-derived biochar had a direct impact on adsorption kinetics and equilibrium behaviour. Raw SCB, characterized by a low specific surface area (3.51 m^2 g^{-1}) and larger pore sizes (<100 Å), exhibited slower adsorption rates and lower equilibrium uptake. In

contrast, the SCB-derived biochar, with a substantially higher surface area (427 m^2 g^{-1}) and a narrower pore size distribution (<5.1 Å), showed faster adsorption kinetics, indicating improved accessibility of active sites and enhanced mass transfer. Furthermore, equilibrium data fit well to the Langmuir isotherm, indicating monolayer adsorption on a homogeneous surface, which is consistent with the well-developed microporous structure of the biochar. These results demonstrate that the pyrolysis-induced structural modifications of SCB play a key role in improving adsorption performance toward PhDIs.

3.2. Performance of SCB Bioadosorbent—PhDIs

Before the direct application of the SCB materials in the wastewater effluent, a solution prepared with ultrapure water containing the PhID compounds at a concentration range from 5 to 100 μg mL^{-1} was tested to verify the adsorption/removal efficiency. Tables 5 and 6 summarize the results for SCB raw and biochar materials, respectively.

Table 5. Adsorption isotherm results for PhDIs using SCB raw (50 mg) and load (C_0) volume of 1 mL.

Compound	C_0 (μg mL^{-1})	m_0 (μg)	C_e (μg mL^{-1})	m_r (μg)	q_e (μg mg^{-1})	Removal (%)
Acetaminophen	100	100	53.0	47.0	0.94	47.0
Atenolol	50	50.0	22.9	27.1	0.54	54.2
Benzoylecgonine	5.0	5.0	3.88	1.12	0.02	22.4
Caffeine	10	10.0	7.84	2.16	0.04	21.6
Carbamazepine	100	100.0	26.9	73.1	1.46	73.1
Citalopram	20	20.0	0.87	19.1	0.38	95.7
Cocaine	5.0	5.0	0.35	4.65	0.09	93.1
Diclofenac	50	50.0	33.8	16.2	0.32	32.4
Enalapril	35	35.0	27.6	7.40	0.15	21.1
Losartan	50	50.0	19.4	30.6	0.61	61.2
Orphenadrine	10	10.0	0.78	9.22	0.18	92.2
Total	435	435	197	238	4.75	54.6 *

* Average.

Table 6. Adsorption isotherm results for PhDIs using SCB biochar (20 mg) and load (C0) volume of 1 mL.

Compound	C_0 (μg mL^{-1})	m_0 (μg)	C_e (μg mL^{-1})	m_r (μg)	q_e (μg mg^{-1})	Removal (%)
Acetaminophen	100	100	3.99	96.0	4.80	96.0
Atenololol	50	50.0	1.31	48.7	2.43	97.4
Benzoylecgonine	5.0	5.0	0.021	4.98	0.249	99.6
Caffeine	10	10.0	0.490	9.51	0.476	95.1
Carbamazepine	100	100	4.46	95.5	4.78	95.5
Citalopram	20	20.0	0.005	20.0	1.00	100
Cocaine	5.0	5.0	0.013	4.99	0.249	99.7
Diclofenac	50	50.0	12.0	38.0	1.90	76.0
Enalapril	35	35.0	12.7	22.3	1.12	63.7
Losartan	50	50.0	5.10	44.9	2.25	89.8
Orphenadrine	10	10.0	0.013	9.99	0.499	99.9
Total	435	435	40.1	395	19.7	90.8 *

* Average.

The results observed in Table 5 confirm the trend of SCB raw material affinity (retention > 90%) to compounds with lower water solubility and higher lipophilicity, such as citalopram, orphenadrine, and cocaine (slightly soluble in water). Lebre et al. (2022) reported similar results with synthetic hormones (ethynylestardiol, drosperinone, and levonorgestrel), indicating a higher SCB raw material affinity for those compounds [30].

Table 6 shows the results using the SCB biochar material, and it is notable to observe the removal improvement of higher than 90% for all tested compounds, regardless of the water solubility and lipophilic properties. It seems to be a trend that the compound affinity decreases with the increase in its acidity, such as with enalapril, diclofenac, and losartan, with pK_a 3.8, 4.1, and 5.5, respectively.

Overall, the SCB biochar material showed better adsorption capacity (q_e = 19.7 μg mg^{-1}) and removal efficiency (<90%) than SCB raw material for all tested compounds. It is important to emphasize that the concentration of compounds in the water solution assayed in this experiment is approximately 3000× above the concentration found in sewage effluent, as determined and shown in the next section.

3.3. Application of SCB Biochar in WWTP Effluents

Before the application of the SCB biochar material to remove the PhID from the sewage effluent (WWTP), their concentrations (C_0) were determined via LC-MS/MS by direct injection (after filtration), using the procedure described in the experimental section. Table 7 shows the compound concentration found for each effluent sample. It does not consider the concentrations below the limit of detection (LOD), and they were reported as not detected (n.d.). Table 7 also presents the LOD (signal-to-noise ratio = 3) for each compound analyzed by LC-MS/MS via direct injection.

Table 7. Concentrations of PhID measured in WWTP effluent samples.

Compound	Effluent Concentration (ng mL^{-1})				
	WWTP 1	**WWTP 2**	**WWTP 3**	**WWTP 4**	**LOD (ng mL^{-1})**
Acetominiophen	34.9	34.1	11.8	4.48	1.69
Atenolol	2.43	2.35	2.50	1.49	0.789
Benzoylecgonine	6.20	6.50	3.27	2.46	0.271
Caffeine	63.3	56.4	114	43.0	2.73
Carbamazepine	0.438	0.498	0.343	0.589	0.053
Citalopram	0.167	n.d.	n.d.	n.d.	0.059
Cocaine	0.679	0.57	0.187	0.140	0.033
Diclofenac	n.d.	n.d.	n.d.	n.d.	1.47
Enalapril	0.345	n.d.	n.d.	n.d.	0.204
Losartan	5.26	4.29	4.13	3.68	0.289
Orphenadrine	0.257	0.164	2.42	0.161	0.054
Total C_0 (ng mL^{-1})	114	105	139	56.0	-

These results can be analyzed in detail, and the presence of PhID in WWTP are determined by six factors: (i) human population size and distribution along with age distribution (demography); (ii) accessibility of health facilities (usage and consumption patterns and price regulations); (iii) the manufacturing sector's presence and size; (iv) sewage treatment systems and their connectivity; (v) the environment in which effluents are received; and (vi) the availability and effectiveness of regulation guidelines [34]. The discussion of the consequences of environmental pollution caused by the inefficiency of WWTPs to remove these compounds it is beyond our goals, although a glimpse of the problem can be simply estimated by multiplying the treatment system flow by the total concentration found, as mentioned before: 105 ng mL^{-1} (μg L^{-1}) is the total PhID found in WWTP 2 (Barueri municipality, SP) sample and 16,000 L s^{-1} is the WWTP flow capacity. Assuming there is no removal of these compounds by WWTP 2, 145 kg (1.68 g s^{-1}) are released into the Tiete River (the most important and longest river that crosses Sao Paulo, city and state) on a daily basis.

The application of the SCB biochar, as described in the experimental section, using 20 mg of the adsorbent material and a load effluent volume (V_0) of 1 mL, none of the PhID compounds were detected by LC-MS/MS in the eluate (C_e) solution, after 10 min agitation (excepted for cocaine in sample WWTP 1 = 0.061 ng mL^{-1}). Table 8 summarizes the PhID' removal efficiency for each WWTP effluent sample.

Table 8. Removal efficiency of PhID using 20 mg of SCB biochar and 1 mL (V_0) of WWTP effluent sample.

Compound	Estimate of Removal Efficiency (%)			
	WWTP 1	**WWTP 2**	**WWTP 3**	**WWTP 4**
Acetaminophen	>98.3	>98.3	>98.3	>98.3
Atenolol	>99.2	>99.2	>99.2	>99.2
Benzoylecgonine	>99.7	>99.7	>99.7	>99.7
Caffeine	>97.3	>97.3	>97.3	>97.3
Carbamazepine	>99.9	>99.9	>99.9	>99.9
Citalopram	>99.9	n.d.	n.d.	n.d.
Cocaine	91.1	>99.9	>99.9	>99.9
Diclofenac	n.d.	n.d.	n.d.	n.d.
Enalapril	>99.8	n.d.	n.d.	n.d.
Losartan	>99.7	>99.7	>99.7	>99.7
Orphenadrine	>99.9	>99.9	>99.9	>99.9

In order to prove the veracity of the obtained results using the SCB biochar to remove the PhID from the WWTP samples, two assays were performed with the WWTP 3 sample, which contains the highest PhID concentration levels (C_0 = 139 ng mL^{-1}).

In the first assay, the quantity of SCB biochar was kept at 20 mg, and the load effluent volume (V_0) was varied from 1 to 100 mL (the PhID mass was increased from 139 ng to 13,900 µg). Table 9 shows that a breakthrough occurred at 2 mL sample volume. Therefore, 20 mg of SCB biochar per 2 mL of effluent is the minimum, and is necessary to remove 278 ng of all tested compounds from the WWTP 3 sample. This assay verified that 1% (*w*/*v*) of SCB biochar per total sample volume is sufficient to remove the PhID from the tested effluent.

Table 9. Removal efficiency of PhID using a fixed SCB biochar mass of 20 mg with varying volumes (V_0) of WWTP effluent.

Compound	C_e WWTP 3 Concentration (ng mL^{-1})						
	1 mL	**2 mL**	**5 mL**	**10 mL**	**50 mL**	**100 mL**	**C_0 (ng mL^{-1})**
Acetaminophen	n.d.	n.d.	n.d.	n.d.	3.99	6.93	11.8
Atenolol	n.d.	n.d.	n.d.	n.d.	n.d.	1.09	2.50
Benzoylecgonine	n.d.	n.d.	0.373	1.15	2.50	3.25	3.27
Caffeine	n.d.	n.d.	4.60	14.9	112	125	114
Carbamazepine	n.d.	n.d.	n.d.	n.d.	0.232	0.311	0.343
Citalopram	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cocaine	n.d.	n.d.	n.d.	n.d.	n.d.	0.115	0.187
Diclofenac	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Enalapril	n.d.	n.d.	n.d.	n.d.	n.d.	0.157	n.d.
Losartan	n.d.	n.d.	n.d.	1.02	3.15	2.80	4.13
Orphenadrine	n.d.	n.d.	n.d.	n.d.	0.108	0.432	2.42
Total (ng mL^{-1})	n.d.	n.d.	4.98	17.0	122	140	139
Average Total Removal %	>99.0%	>99.0%	96.4	87.7	12.3	0.00	-

Note: n.d. ≤ LOD.

In the second assay, 1 g of SCB biochar was used to adsorb 100 mL of WWTP 3 effluent volume (V_0). The eluate (C_e) was concentrated 500× via the solid-phase extraction (SPE) technique prior to the LC-MS/MS analysis in order to decrease the limit of detection and quantify the compounds in pg mL^{-1} scale (part per trillion). The SPE analytical method used was developed and validated by Shihomatsu [8]. After the adsorption process (10 min agitation), the eluate solution (Ce) was filtered using a 0.45 µm porous membrane, and 90 mL was submitted to the SPE procedure. The final SPE residue was dissolved in 0.180 mL of 80% water/20% acetonitrile (*v*/*v*) solution and injected into the LC-MS/MS system. The C_e solution was quantified, and the results are shown in Table 10 below, as well as the removal efficiency and other relevant information.

Table 10. Adsorption results for PhID using SCB biochar (1 g) and load of WWTP 3 effluent sample with a volume of 100 mL (V_0).

Compound	C_0 (ng mL^{-1})	m_0 (ng)	C_e (ng mL^{-1})	m_r (ng)	q_e (ng mg^{-1})	Removal (%)
Acetaminophen	11.8	1181	0.0038	1181	1.18	99.97
Atenolol	2.50	250	0.184	232	0.232	92.65
Benzoylecgonine	3.27	327	0.0030	327	0.327	99.91
Caffeine	114	11,395	0.124	11,383	11.38	99.89
Carbamazepine	0.343	34.3	0.0004	34.2	0.03	99.88
Citalopram	n.d.	n.d.	0.0007	n.d.	n.d.	n.d.
Cocaine	0.187	18.7	0.0007	18.7	0.019	99.65
Diclofenac	n.d.	n.d.	0.0024	n.d.	n.d.	n.d.
Enalapril	0.121	12.1	0.0009	12.0	0.012	99.22
Losartan	4.13	413	0.0036	412	0.412	99.91
Orphenadrine	2.42	242	0.0020	242	0.242	99.92
Total	139	13,874	0.325	13,842	13.8	99.77

Using the SPE technique allied with LC-MS/MS analytical instrumentation, it was possible to quantify all the PhID in the WWTP 3 eluate solution (C_e), i.e., due to the LOD improvement factor by 500×. The obtained results indicated a 99.8% removal efficiency for the total mass charge (m_0) of 13.9 ug of the compounds present in 100 mL of WWTP 3 sample.

It was also observed that the concentrations of the majority of compounds quantified in the eluate (C_e) were below 0.01 ng mL^{-1}. This value corresponds to the action limit for Predicted Environmental Concentration (PEC) recommended by the European Medicines Agency (EMA) guidelines, which calculates PEC based on the predicted percentage of the population using a given drug (market penetration) and the drug's maximum daily dose, providing a conservative estimate of environmental exposure. If the concentration of Emerging Contaminants (EC) in environmental samples, referred to as the Measured Environmental Concentration (MEC), is below the action limit of 0.01 µg L^{-1}, no further assessment is required, and no ecological risk is considered. However, if this limit is exceeded, a subsequent "Phase 2" assessment is conducted, which evaluates potential toxicity and environmental interactions based on standardized laboratory studies and compares the results to regulatory thresholds [14,16,17,35].

The concentration of atenolol in the effluent eluate from WWTP 3 was 0.184 ng mL^{-1} (184 ng L^{-1}), exceeding the recommended PEC level of 0.01 ng mL^{-1}. However, according to an Environmental Risk Report published by AstraZeneca in 2023 [36], the PEC value for atenolol is 0.49 ng mL^{-1} (490 ng L^{-1}). This report showed the Predicted No Effect Concentration (PNEC), which comprises the long-term test undertaken with *Daphnia magna* (crustacean species), and considering a NOEC value of 1480 ng mL^{-1} and an assessment factor of 10, the resulting calculated PNEC value was 148 ng mL^{-1}(148,000 ng L^{-1}) [36].

Using the measured atenolol concentration found in the WWTP 3 (C_0) and its eluate (Ce), considering the PNEC value, it was possible to estimate the Risk Quotient (RQ) described elsewhere by Ortega [16]. The RQ was obtained by dividing the maximum MEC, in this case C_0 and Ce, by the PNEC (RQ = MEC/PNEC), both expressed in ng L^{-1}. For caffeine, the rationale was the same, since the PNEC reported by Moore [37] was 5 ng mL^{-1} (5000 ng L^{-1}) for *Daphnia dubia* species [37]. Table 11 summarizes the results of the RQs obtained for atenolol, caffeine, and all PhID before and after the adsorption process.

Table 11. Estimated results of the ecological Risk Quotient (RQ)—before and after the application of SCB biochar in the WWTP 3 effluent.

Compound	C_0 (ng L^{-1})	RQ (C_0)	(C_e) (ng L^{-1})	RQ (Ce)	PNEC (ng L^{-1})	Trophic Level	Organism/ Specie	References PNEC
Acetaminophen	1.18×10^4	0.338	3.78×10^0	0.000	3.50×10^4	Acute	Crustacean/ *Daphnia magna*	[38]
Atenolol	2.50×10^3	0.017	1.84×10^2	0.001	1.48×10^5	Acute	Crustacean/ *Daphnia magna*	[36]
Benzoylecgonine	3.27×10^3	0.000	3.00×10^0	0.000	3.14×10^8	Acute	Crustacean/ *Daphnia magna*	[16]
Caffeine	1.14×10^5	22.8	1.24×10^2	0.025	5.00×10^3	Acute	Crustacean/ *Daphnia dubia*	[37]
Carbamazepine	3.43×10^2	0.000	4.00×10^{-1}	0.000	1.00×10^8	Acute	Crustacean/ *Artemia salina*	[39]
Citalopram	n.d.	n.d.	6.54×10^{-1}	xxx	xxx	xxx	xxx	xxx
Cocaine	1.87×10^2	0.342	6.52×10^{-1}	0.001	5.48×10^2	Acute	Crustacean/ *Daphnia magna*	[16]
Diclofenac	n.d.	n.d.	2.45×10^0	0.061	4.00×10^1	EQS	EQS	[40]
Enalapril	n.d.	n.d.	9.48×10^{-1}	xxx	xxx	xxx	xxx	xxx
Losartan	4.13×10^3	125	3.56×10^0	0.108	3.31×10^1	Acute	Crustacean/ *Daphnia magna*	[41]
Orphenadrine	2.42×10^3	0.054	2.01×10^0	0.000	4.50×10^4	Acute	Crustacean/ *Artemia salina*	[42]

Note: n.d. = not detected; no obtained data = xxx; EQS (environmental quality standards for surface water bodies).

According to Ortega et al. (2025), the RQ for aquatic organisms was classified into four categories: **no** (RQ < 0.01; represented in grey), **low** (0.01 ≤ RQ < 0.1; represented in green), **moderate** (0.1 ≤ RQ < 1.0; represented in yellow), and **high** ecological risk (RQ ≥ 1.0; represented in red) [16].

Finally, it was observed that the effluent from WWTP 3, without treatment using SCB biochar, posed a high ecological risk (average RQ = 18.5), primarily due to the presence of losartan (RQ = 125) and caffeine (RQ = 22.8). After the application of the bioadsorbent material, the ecological risk was significantly reduced, with the average RQ dropping to 0.022, indicating a low-risk scenario.

4. Conclusions

This study provides scientific evidence that sugarcane bagasse (SCB) biochar can effectively remove pharmaceuticals and illicit drugs (PhID) from wastewater treatment plant effluents. The use of SCB as an adsorbent offers several advantages: it is an inexpensive and abundant biomass-derived material, and it is non-toxic, easy to handle, and exhibits high adsorption capacity and rapid adsorption rates. Moreover, SCB shows a broad affinity toward various chemical compounds, ranging from lipophilic to hydrophilic and from water-soluble to insoluble substances. In this work, adsorption experiments were conducted using caffeine—an anthropogenic marker of environmental contamination—to evaluate the adsorption performance and mechanisms of both *raw* SCB and SCB biochar.

This experimental approach can be extended to assess the adsorption behaviour of other emerging contaminants, including both organic and inorganic compounds.

In addition, we employed a "gold standard" analytical technique—Liquid Chromatography coupled with tandem Mass Spectrometry (LC-MS/MS)—to quantify PhID and assess the adsorption effectiveness under the developed batch experimental procedure using real wastewater effluent samples. Furthermore, this study proposes a workflow that can be applied to wastewater characterization and to model adsorption mechanisms for novel materials.

The batch adsorption experiments demonstrated that applying 1% (w/v) of SCB biochar relative to the total wastewater sample volume was sufficient to remove up to 99.8% of PhID at total concentrations of up to 140 ng mL^{-1}.

This methodology also enables the estimation of ecological risk (RQ) values for WWTP samples before and after the application of SCB biochar, providing a model that can be adapted and scaled to different WWTP types, including domestic, industrial, and hospital systems.

The main future challenges in using SCB as an adsorbent material in industrial-scale set-ups are tailored engineering projects for each wastewater treatment system with the goal to enhance the adsorption rate and reduce the reaction time, which can be solved by the development of composite nano-material adsorbents.

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