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Spinning Submerged Filter Adsorber versus Packed Bed Adsorber for the Continuous Removal of Antibiotics from Wastewater with Activated Carbon

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Abstract: The removal of antibiotics from wastewater is receiving considerable attention to fulfill water quality parameters required for reuse. This study compares a spinning submerged filter adsorber with a fixed bed adsorber for continuous antibiotic removal. Adsorbers were evaluated with micro granular activated carbon (μGAC: 508 μm), coarse powder activated carbon (cPAC: 197 μm), powder activated carbon (PAC: 77 μm), and a domestic wastewater effluent spiked with a mixture of amoxicillin, sulfamethoxazole, and levofloxacin with concentrations ranging from 10 to 50 mg/L. The fixed bed adsorber packed with cPAC was the most efficient adsorber running with wastewater spiked with 50 mg/L of each antibiotic and an empty bed contact time (EBCT) of 4.5 min. The spinning submerged filter adsorber configuration also provided high removal effectiveness using a 15 g/L concentration of PAC but with a lower hydraulic retention time (HRT) of 40 min. This adsorption unit can be filled with small PAC particles, unlike packed beds, and PAC concentrations can be increased up to 150 g/L if necessary. It combines adsorption and filtration with a completely mixed mode of operation in which the PAC concentration can be adapted to effluent micropollutant concentrations, making it an interesting alternative for adsorption processes.

Keywords: spinning submerged filter adsorber; fixed bed adsorber; antibiotics removal; wastewater

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1. Introduction

Antibiotics have received much attention in recent years as emerging aquatic contaminants due to their potential threats to population health and aquatic ecosystems. The presence of antibiotics in natural ecosystems develops antibiotic-resistant genes, which limits their use as drugs [1].

Antibiotics are detected in the influents of wastewater treatment plants (WWTPs), mainly from the discharges from pharmaceutical plants, hospitals, and farms. Some recalcitrant antibiotics are not removed; thus, they are continually discharged into the environment and can reach surface waters, groundwater, and sediments [2]. A revision of 78 publications from 2010 to 2019 regarding the presence of antibiotics in influents and effluents of worldwide convectional and hospital WWTPs showed that the most frequently detected were sulfonamides, macrolides, quinolones, and tetracyclines. Hospital wastewaters contain more drug metabolites and usually higher antibiotic concentrations than wastewaters of conventional WWTPs [3]. Average influent antibiotics concentrations found in full-scale WWTPs on a global scale were 400 ng/L for β-lactams, 232 ng/L for quinolones, 208 ng/L for macrolides, 117 ng/L for tetracyclines, and 103 ng/L for sulfonamides [4]. India is a world leader in pharmaceutical production and consumption, and the antibiotics detected at higher concentrations in their conventional WWTPs were ciprofloxacin, sulfamethoxazole, amoxicillin, norfloxacin, and ofloxacin [5].

Strict water regulations for antibiotic levels in treated wastewater are on the horizon. As an example, the European Commission has a surface water watch list with antibiotics like ciprofloxacin, sulfamethoxazole, amoxicillin, and trimethoprim. In the future, concentrations of antibiotics in WWTPs effluents will be controlled in compliance with water quality laws for water reuse [6].

Conventional WWTPs remove antibiotics mainly by sorption and biodegradation during biological wastewater treatment processes. Despite major advancements, they are moderately effective, and efficiency ranges between 53% and 78%, lower than for organic pollutants at 80–95% [7,8]. Thus, these plants must implement tertiary treatment technologies, such as adsorption, advanced chemical oxidation methods like Fenton-like oxidation, ozonation, sulfate radical-based oxidation, ionizing radiation, electrochemical oxidation, or hybrid treatments [9–12].

Adsorption is a good choice for the high-scale removal of antibiotics in WWTPs because of its high efficiency, low operating cost, simplicity of operation, and absence of toxic by-products [13]. Although there is a high number of potential adsorbents available for antibiotics like biochar, waste-derived adsorbents, clays, zeolitic materials, biopolymers, and covalent-organic or metal-organic frameworks, high-scale applications typically use activated carbon [14–17]. Classic adsorption units are fixed bed columns packed with activated carbon that can be effectively applied as an economically viable tertiary treatment technology in WWTPs [18,19]. Columns are packed with granular activated carbon (GAC) of particle size diameters ranging from 1.2 to 1.6 mm; because powder activated carbon (PAC) particles are much smaller, they could cause bed compaction. An important parameter influencing the efficiency of the adsorption process is the empty bed contact time (EBCT). Typical values employed in WWTPs range from 10 to 40 min. The total suspended solids composition of the wastewater to be treated can negatively affect the adsorption process as the columns can be clogged. So full-scale WWTPs sometimes use a preceding sand filter or, periodically, columns must be flushed backward with clean water to solve this problem [10,20]. An option used in WWTPs that avoid clogging is a fluidized bed of micro granular activated carbon (μGAC) that is continuously renewed by equivalent addition and extraction of adsorbent. This adsorption unit, operating with a 20 min hydraulic retention time (HRT) and an activated carbon addition of 10 mg/L, revealed that all micropollutants were effectively removed (>60%), except azithromycin (28%) and sulfamethoxazole (18%) [21].

New challenges for continuous antibiotic removal use technologies that couple the dosing of small particle adsorbents with high adsorption capacities and membrane technologies for its retention. Different options are available depending on the place of adsorbent addition, the mixture, and the separation process [22]. A municipal WWTP running with a hydraulic retention time of 30 min can achieve a target-oriented reduction of trace substances by dosing 30 mg/L of fine PAC particles of 10 μm directly to the wastewater. Dosage into the post-treated wastewater is more effective than into the biological treatment unit [23]. Recently a spinning submerged filter adsorber has been proposed to remove wastewater contaminants that combines the use of adsorbents and filtration, works with small particle size adsorbents under complete mixing conditions, and can operate with particulate matter. An easy continuous adsorbent addition/removal is also possible [24].

This work compares the applicability of a novel spinning submerged filter adsorber configuration with the classic fixed bed technology to be used as a tertiary treatment for continuous removal of antibiotics from WWTPs wastewater with activated carbon. In this study, three antibiotics were selected, one from each group of the most frequent antibiotics in WWTPs influents. The sulfonamide sulfamethoxazole (SMX), the β-lactam amoxicillin (AMX), and the fluoroquinolone levofloxacin (LVX). The first two antibiotics are included in the substance watch list together with ciprofloxacin in the context of the European Water Framework Directive. We have preferred levofloxacin instead of ciprofloxacin as nowadays it is used on a large scale, and levofloxacin and moxifloxacin represent >40% of quinolone consumption in southern EU countries [25]. These three antibiotics were spiked in domestic

wastewater from a local domestic WWTP. The spinning submerged filter adsorber worked with commercial activated carbon located outside of the filter to maximize the adsorbent concentration in the adsorption unit and to facilitate the operation mode. The particle size of activated carbon stands out as a key factor influencing the operating conditions and adsorption capacity of adsorbers; thus, different activated carbon (AC) particle sizes, granular (GAC), micro granular (μGAC), coarse powder (cPAC), powder (PAC), and small powder (sPAC), were studied. Breakthrough curves for fixed bed and spinning submerged filter adsorbers were performed at a laboratory scale with the typical values of retention times employed in WWTPs. Antibiotic removal capacity was also evaluated with different inlet antibiotic concentrations. The studied inlet antibiotics concentrations were in the range of 10 to 50 mg/L to saturate the activated carbon present in the adsorber units. These high antibiotic concentrations were necessary to evaluate and compare the breakthrough curves of the adsorption units at the lab-scale.

2. Materials and Methods

2.1. Materials

Extra pure granular activated carbon (GAC) with a 1.5 mm particle diameter was from MERCK (ref. 102514, Darmstadt, Germany). Sulfamethoxazole (ref: S7507), amoxicillin (ref: A8523), levofloxacin (ref: 28266), hydrochloric acid (37%), and sodium hydroxide were from Sigma-Aldrich (Madrid, Spain). Phosphoric acid (85%) and acetonitrile HPLC grade were from Panreac AppliChem (ITW Reagents, Barcelona, Spain).

2.2. Obtention and Physicochemical Properties Determination of Activated Carbons

Commercial granular activated carbon (GAC) of 1.5 mm particle size was milled three times with a GVX242 Krups grinder (SEB Group, Barcelona, Spain) and fractionated using stainless steel sieves (FiltraVibración S.L, Barcelona, Spain). Fraction 0.85–0.25 mm was labeled as μGAC (micro Granular Activated Carbon), fraction 0.250–0.100 mm was labeled as cPAC (coarse Powder Activated Carbon), fraction 0.100–0.050 mm was labeled as PAC (Powder Activated Carbon), and fraction <0.05 mm was labeled as sPAC (Small Powder Activated Carbon). Particle size and particle size distribution curves were measured by laser diffraction using a Mastersizer 2000 S equipped with a "Hydro 2000G" unit (Malvern Instruments Ltd., Malvern, UK). All samples were measured in triplicate.

Specific surface areas of the activated carbons were obtained using adsorption-desorption isotherms of N_2 at 77 K with an Autosorb iQ XR-2 automated gas sorption analyzer (Quantachrome Instruments, Boynton Beach, Florida). Total surface areas were determined using the multipoint Brunauer–Emmett–Teller (BET) method, a total pore volume of P/P_0 0.95, and micropore volume (<2 nm) with Dubinin-Radushkevic model [26]. The true density of dry activated carbon was measured by an automated helium pycnometer (Ultrapyc 1200e, Quantachrome Instruments, Boynton Beach, FL, USA). pHs at the point zero charge (pH_{PZC}) were obtained, as explained in previous work [24].

The morphology of activated carbon was studied with a focused gallium ion beam field emission scanning electron microscope (FIB-FESEM) from Zeiss (Zeiss, Jena, Germany). Images were obtained with a secondary electron detector, at 10 kV and a working distance of 5.2 mm, with different magnifications. Elemental analyses of activated carbon surface were performed by energy dispersive X-ray spectroscopy (EDX, Oxford Instruments, Abingdon, UK).

2.3. Chemical Analyses of Wastewater and Antibiotics

Wastewater was collected from a domestic wastewater treatment plant located in the La Manga Golf Resort of Cartagena, Spain (37.60264435104736, −0.7946262855084706) after preliminary treatment, primary physicochemical treatment, conventional secondary treatment with activated sludge, and before final filtration and disinfection. The wastewater is used for irrigation. It was chemically characterized by pH (pHmeter Crison Basic 20, Crison Instruments, Barcelona, Spain), conductivity (Laqua PC1100-S, Horiba Advanced Techno,

Co., Ltd., Kyoto, Japan), ions (ion chromatography, Metrohm, Madrid, Spain), total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC), total nitrogen (Multi N/C 3100 Analytik Jena GmbH, Jena, Germany), DBO5 (OxiTop IS6, VWR International, Radnor, PA, USA), and turbidity (turbidimeter 2100AN, Hach Company, Loveland, CO, USA).

Standard dissolutions of antibiotics were prepared at 200 mg/L for sulfamethoxazole and 400 mg/L for amoxicillin and levofloxacin, adjusting the pH with NaOH to 5, 7, or 9. Antibiotic concentrations were determined by HPLC UV-Vis (Agilent 1290 Infinity II LC, Agilent Technologies, Santa Clara, CA, USA). The chromatography column was a Zorbax SB-C18 (3.5 µm, 150 mm × 4.6 mm) from Agilent Technologies (Santa Clara, CA, USA). The flow rate was 1 mL/min, and the injection volume was 5 µL. Samples were filtered with disposable cellulose regenerated Captiva syringe filters from Agilent (Santa Clara, CA, USA). The HPLC method uses phosphoric acid 0.1% as mobile phase A and acetonitrile as mobile phase B. Gradient elution was as follows: time 0 min-9% B, time 4 min-9% B, time 12 min-40% B, time 13 min-9% B, and time 15 min-9% B. The method was a modification of Ašperger et al. [27]. Retention times were 3.1 min for amoxicillin, 8.4 min for levofloxacin, and 11.5 min for sulfamethoxazole. The spectra of antibiotics, a typical chromatogram, and the HPLC calibration curves are shown as supplementary material (Figure S1).

2.4. Adsorption Isotherm Batch Studies

The adsorption isotherms of antibiotics in activated carbon were studied in amber glass bottles filled with 50 mL of a 50 mg/L antibiotic concentration adjusted to pH 7 and added weights ranging from 5 to 35 mg of the correspondent activated carbon µGAC, cPAC, or PAC. Bottles were introduced in a thermostated rotatory shaker fixed at 25 °C and 200× *g* rpm and left to stand for 48 h. Then, samples were withdrawn in Eppendorf tubes of 2 mL, centrifuged for 2 min at 13,400× *g* rpm (Minispin Centrifuge, Eppendorf, Hamburg, Germany), and the supernatant was analyzed for the antibiotic concentration by HPLC. The amount of antibiotic adsorbed per mass of adsorbent (mg/g) was quantified by:

$$q_e = (C_0 - C_e)\, V/W \quad (1)$$

C_0 is the initial concentration of the antibiotic (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of the solution (L), and W is the weight of the adsorbent used (g).

The data of q_e versus C_e were adjusted to the adsorption isotherms models of Langmuir and Freundlich (Equations (2) and (3)) by non-linear regression with EXCEL and solver function. The error function was used for minimization ($R^2 = 1$) [24].

$$\text{Langmuir model } q_e = q_{max} \frac{K_L}{1 + K_L\, C_e} \quad (2)$$

$$\text{Freundlich model } q_e = K_F\, C_e^{1/n_F} \quad (3)$$

where the parameters of the Langmuir model are K_L and q_{max}, and the parameters of the Freunlich model are K_F and n_F.

2.5. Adsorption Kinetics Batch Studies

The kinetic adsorption of antibiotics was studied in a jacketed glass beaker of 150 mL total volume and thermostated at 25 °C by a circulating water bath (Lauda, Königshofen, Germany). Powder activated carbon was added at concentrations ranging from 0.25 to 1.5 g/L into 100 mL of antibiotic solutions of different concentrations (25–100 mg/L) and pHs (5,7,9). PAC was mixed at 200 rpm with an overhead stirrer RW 16 Basic (IKA-Werke GmbH & Co., Staufen, Germany) equipped with a fixed blade stirrer. Samples were withdrawn, centrifuged for 2 min at 13,400× *g* rpm (Minispin Centrifuge, Eppendorf, Hamburg, Germany), and the antibiotic concentration was analyzed by HPLC.

The antibiotic adsorbed per mass of adsorbent (mg/g) was quantified by:

$$q_t = (C_0 - C_t)\, V/W \quad (4)$$

C_0 is the initial concentration of antibiotics (mg/L), C_t is the concentration at time t, V is the solution volume (L), and W is the weight of adsorbent added (g).

The data of q_t versus time were adjusted to equations of pseudo-first-order (Equation (5)) and pseudo-second-order (Equation (6)) by non-linear regression analyses with EXCEL and solver using the coefficient of determination (R^2 =1) as the error function. The initial adsorption rate with the pseudo-second-order kinetic model is calculated as $k_2\, q_t^2$ (mg/g min) [24].

$$\text{Pseudo-first-order } q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (5)$$

$$\text{Pseudo-second-order } q_e = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

where the kinetic constant of the pseudo-first-order is k_1, and the kinetic constant of the pseudo-second-order is k_2.

2.6. Continuous Operation of Fixed Bed and Spinning Submerged Filter Adsorbers

The fixed bed adsorber used was a liquid chromatography column 8 mL (I.D. × L, 1.0 cm × 10 cm) (Sigma-Aldrich, Madrid, Spain) filled with activated carbon and operated down flow or up flow with an Äkta Prime Plus liquid chromatography system (GE Healthcare Bio-Sciences AB, Uppsala, Sweden). Äkta Prime Plus equipment allows for the fixation of the required influent flow rate and monitors pressure (Figure S2).

The spinning submerged filter adsorber was a jacketed glass beaker of 150 mL total volume and thermostated at 25 °C by a circulating water bath (Lauda, Königshofen, Germany). Inside the glass beaker, the spinning submerged filter was located, and four equally spaced baffles were positioned to minimize the rotational vortex. The filter was a rectangular prismatic basket joined to a metallic tube that rotated at 200 rpm with an overhead stirrer RW 16 Basic (IKA-Werke GmbH & Co., Staufen, Germany). The filter was placed at the height of one-third of the beaker diameter from the bottom. The structure of the filter was made of plastic ABS plus using a rapid Prototyping 3D printer (Dimension BST 1200es, Stratasys, Eden Prairie, MN, USA). The 3D solid model was generated with a CAD system. The filter was built with a plastic structure covered by a stainless-steel woven wire mesh glued with cyanoacrylate adhesive. The stainless-steel woven wire was 500 mesh (27 µm mesh hole size) from Amazon, Spain. The filter volume was 12 mL (3 cm × 2 cm × 2 cm). The activated carbon used for each experiment was weighed and added to the beaker. The continuous flow was kept with two peristaltic pumps (Dinko Instruments, Barcelona, Spain). The influent flow rate was fixed at the desired value, while the filtrate flow rate was adjusted to maintain a constant volume. A scheme of the experimental adsorption units is shown in Figure 1.

The breakthrough curves of the adsorption units were studied at different HRT and antibiotic concentrations. The adsorber units were run with deionized water or domestic wastewater spiked with amoxicillin, levofloxacin, and sulfamethoxazole concentrations ranging from 10 to 50 mg/L. A constant pH of 7 and a temperature of 25 °C were used during experimentation. The adsorption process was monitored, collecting samples of effluents during the experimental time. The samples were filtered with 0.45 µm disposable syringe filters and analyzed for the antibiotic concentration by HPLC. HRT (min) was calculated as the ratio between the liquid volume of the adsorber unit (mL) and the influent volumetric flow rate (mL/min). In the case of the fixed bed, HRT was defined as the Empty Bed Contact Time (EBCT), where liquid volume is empty bed volume. Breakthrough times were calculated as the time when the effluent antibiotic concentration reached 5% of the influent antibiotic concentration.

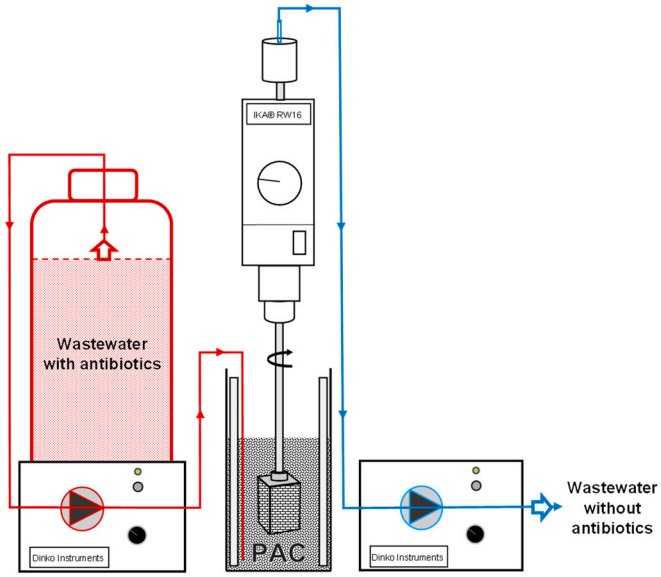

Figure 1. Experimental set-up of the studied spinning submerged filter adsorber.

The breakthrough curves of the fixed bed adsorbers were modeled with simplified mathematical models of Bohart-Adams (Equation (7)), Thomas (Equation (8)), Yoon-Nelson (Equation (9)), and Yan or the modified dose-response (Equation (10)) [28,29] that describe the experimental data satisfactorily:

$$\text{Bohart-Adams model } \frac{C}{C_0} = \frac{1}{1 + \exp\left(K_{BA} q_m \frac{H}{u} - K_{BA} C_0 t\right)} \quad (7)$$

$$\text{Thomas model } \frac{C}{C_0} = \frac{1}{1 + \exp\left(K_T q_o \frac{M}{Q} - K_T C_0 t\right)} \quad (8)$$

$$\text{Yoon-Nelson model } \frac{C}{C_0} = \frac{1}{1 + \exp(K_{YN}\tau - K_{YN} t)} \quad (9)$$

$$\text{Yan or >modified dose-response model } \frac{C}{C_0} = \frac{1}{1 + \left(\frac{q_F m}{C_0 Q t}\right)^{\alpha'}} \quad (10)$$

where C_0 is the influent antibiotic concentration (mg/L), K_{BA} is the Bohart-Adams rate constant (cm^3/ mg min), q_m is the maximum adsorptive capacity per unit volume of bed (mg/cm^3), H is the bed height (cm), u is the surface velocity (cm/min), K_T is the Thomas rate constant (cm^3/ mg min), q_o is the solid loading per unit mass of adsorbent (mg/g), M is the mass of adsorbent (g), Q is the volumetric flow-rate (cm^3/min), K_{YN} is the Yoon-Nelson rate constant (h^{-1}), τ is the time required for 50% breakthrough (h), α' is the model parameter of the modified dose-response method, q_F is the adsorptive capacity in equilibrium (mg/g), Q is the flow rate (dm^3/min), and m is the mass of adsorbent (g). Linear regression analyses of Ln [(C_0/C) − 1] versus time (Equations (11)–(13)) were used to obtain the model parameters of Bohart-Adams (K_{BA}, q_m), Thomas (K_T, q_0), and Yoon-Nelson (K_{YN}, τ), and linear regression analyses of Ln [(C_0/C) − 1] versus Ln (C_0 Q t) (Equation (14)) were used for the modified dose-response model (α', q_F).

$$\text{Bohart-Adams model Ln}\left(\frac{C_0}{C} - 1\right) = K_{BA} q_m \frac{H}{u} - K_{BA} C_0 t \quad (11)$$

$$\text{Thomas model Ln}\left(\frac{C_0}{C} - 1\right) = K_T q_m \frac{M}{Q} - K_T C_0 t \quad (12)$$

$$\text{Yoon-Nelson model } \mathrm{Ln}\left(\frac{C_0}{C}-1\right) = K_{YN}\tau - K_{YN}t \quad (13)$$

$$\text{Yan or modified dose-response model } \mathrm{Ln}\left(\frac{C_0}{C}-1\right) = \alpha \mathrm{Ln}(q_F m) - \alpha \mathrm{Ln}(C_0 Q t) \quad (14)$$

3. Results and Discussion

3.1. Isotherm Adsorptions of Antibiotics in Activated Carbons

The antibiotics proposed in this study were amoxicillin, levofloxacin, and sulfamethoxazole. Their molecular structures and properties are shown in Table S1 of the supplementary material. Adsorbents were obtained by milling and sieving from commercial granular activated carbon (GAC) and labeled as micro granular activated carbon (µGAC), coarse powder activated carbon (cPAC), powder activated carbon (PAC), and small powder activated carbon (sPAC). µGAC, cPAC, and PAC showed low span and good uniform particle size distributions, with the particle size measured as a De Broucker diameter D [3,4] of 508, 197, and 77 µm, respectively (Figure S3, Table S2). Studies were focused on µGAC, cPAC, and PAC, while the sPAC of 19 µm was ignored because it cannot be completely retained by the filters used in this experimentation with a 27 µm mesh hole size. Particle morphology was irregular due to milling, as shown by scanning electron microscopy of the PAC (Figure S4). Activated carbon particles were mesoporous (2–50 nm) with a high micropore volume, as shown in the adsorption-desorption isotherms of nitrogen (Figure S5). Milling has an important effect in increasing the surface area and pore volume of activated carbon. Surface areas improved 32%, from 942 m^2/g for GAC to 1245 m^2/g for PAC. Micropore and mesopore volumes also increased when particle diameter decreased. The total pore volume increased by 41%, from 0.492 cm^3/g for GAC to 0.693 cm^3/g for PAC (Table S3).

Isotherm adsorption experiments were performed to evaluate the adsorption capacity of amoxicillin, levofloxacin, and sulfamethoxazole in activated carbons of different particle sizes: µGAC, cPAC, and PAC. The antibiotics were prepared individually with an initial concentration of 50 mg/L at pH 7.0 and 25 °C, and the concentration of activated carbon varied. Data of equilibrium concentrations achieved after two days were used to obtain the adsorption isotherm with Langmuir and Freundlich models. Results are shown in Table 1 and Figure S6.

Table 1. Modeling antibiotic adsorption isotherms at pH 7 with activated carbons of different particle sizes.

			Isotherm Model Parameters					
			Langmuir			**Freundlich**		
AC	**Antibiotic**	q_{max} **(mg/g)**	q_{max} **(mmol/g)**	K_L **(L/mg)**	R^2	K_F **($mg^{(n-1)/n}/g \cdot L^{1/n}$)**	n_F	R^2
µGAC	Amoxicillin	116	0.317	0.31	0.7685	47.51	4.12	0.9464
	Levofloxacin	150	0.415	10.20	0.8703	128.61	20.97	0.9424
	Sulfamethoxazole	193	0.762	0.08	0.9671	29.23	2.24	0.989
cPAC	Amoxicillin	171	0.468	0.24	0.9790	55.24	3.29	0.9823
	Levofloxacin	246	0.681	3.96	0.8125	171.42	8.96	0.9476
	Sulfamethoxazole	234	0.924	0.10	0.9823	44.21	2.48	0.9941
PAC	Amoxicillin	172	0.471	0.50	0.8081	71.27	3.71	0.9813
	Levofloxacin	299	0.827	3.57	0.8095	216.47	8.96	0.9476
	Sulfamethoxazole	225	0.888	0.25	0.8393	76.99	3.57	0.9636

The Freundlich model offered the best fits of adsorption isotherms for all antibiotics and activated carbons with R^2 values closer to 1. It described adsorption isotherms well,

while the Langmuir model gave poorer results. The n_F values of the Freundlich model were higher than 1 for all antibiotics and activated carbons studied, meaning that antibiotic adsorption is favorable ($0 > 1/n_F > 1$). The equilibrium is directed to adsorption even with low antibiotic concentrations. The high values of the Freundlich constant (K_F) indicated a high adsorption capacity. The adsorption capacity of the three antibiotics was higher when using PAC. According to q_{max} values of the Langmuir model, amoxicillin adsorption in PAC increased 32% in comparison to µGAC, levofloxacin increased 50%, and sulfamethoxazole increased 14%. Levofloxacin adsorption is especially high with PAC.

The maximum antibiotic adsorption capacities obtained with PAC and according to the Langmuir model were 172 mg/g for amoxicillin (0.471 mmol/g), 299 mg/g for levofloxacin (0.827 mmol/g), and 225 mg/g for sulfamethoxazole (0.888 mmol/g). These values are high and competitive for high-scale use when compared to previous works with carbon-based materials successfully applied for antibiotic adsorption [30,31]. The literature data of the maximum adsorption capacities of amoxicillin were 100 mg/g in $CoFe_2O_4$-modified biochar [32], 189.5 mg/g in GAC [33], or 261.8 mg/g in standard AC [34]. In the case of levofloxacin, the maximum adsorption capacities were 76.3 mg/g in vinasse waste biochar [35], 159 mg/g in $ZnCl_2$ modified pharmaceutical sludge biochar [36], 158 mg/g in swine manure biochar, and 164 mg/g in activated charcoal Darco [37]. Sulfamethoxazole adsorption capacities were 54.4 mg/g with bagasse biochar [38], 100.3 mg/g with ball-milled biochar [39], 232 mg/g in activated carbon [40], 274.5 mg/g for F-400 AC [41], or 450 mg/g with activated grape seed hydrochar [42].

The high surface area of PAC versus cPAC or µGAC and the high values of the mesopore and micropore volumes of activated carbon used in this experimentation are related to its high adsorption capacity. The high mesopore volume has a strong influence on the micropollutants removal in the absence of dissolved organic matter (DOC); however, in the presence of DOC, the effect of the mesopore volume might be outweighed by the effect of the chemical properties of the carbon [43,44]. Antibiotic adsorption is controlled by multiple mechanisms, including hydrophobic interaction, pi-pi interaction, hydrogen bonding, electrostatic interaction, and van der Waals forces [14,31]. Sulfamethoxazole and levofloxacin showed the highest adsorption capacity, mainly due to their higher aromaticity and hydrophobicity in comparison to amoxicillin. In addition, electrostatic interactions are also important because of the functional groups present in activated carbon and antibiotics.

3.2. Effect of pH in Antibiotic Adsorption Kinetics on Activated Carbon

The pH may affect the adsorption kinetics of antibiotics in activated carbon. Thus, adsorption kinetics were studied at pHs 5, 7, and 9, using 50 mg/L mixtures of the three studied antibiotics. PAC was selected as the adsorbent because it shows the highest antibiotic adsorption capacities. Its assay concentration was fixed at 0.35 mg/L. The experimental results obtained at 25 °C are shown in Figure 2.

The pH had no important effect on amoxicillin (Figure 2a) and levofloxacin (Figure 2c) adsorption kinetics, but the sulfamethoxazole adsorption rate is clearly affected by the pH (Figure 2e). A lower pH was related to a higher adsorption rate. The adsorption rate at pH 5 was faster for sulfamethoxazole, followed by levofloxacin and amoxicillin (Figure 2b), while faster at pH 7 (Figure 2d) and pH 9 (Figure 2f) for levofloxacin. Literature references also showed higher adsorption rates for amoxicillin (AMX) at pH 5 versus 7 [33] and a maximum adsorption rate at pH 6, with no major differences between pH 4 and 9 [34]. Thi:s effect of pH on the adsorption can be explained by considering the charge of the adsorbent and antibiotic at the different pH values investigated. The pH of zero charge PAC (pH_{PZC}) is 9.7 [24], so PAC is positively charged at the studied pHs between 5 and 9. AMX has pKa values of 2.4 (carboxyl), 7.4 (amine), and 9.6 (phenol); therefore, at pHs of 5–6, the AMX molecule is dissociated into carboxylate and favors electrostatic attraction between AMX (anionic) and the surface of the activated carbons (cationic). At pHs of 5–6, the AMX structure is zwitterionic (Figure S7). In the case of levofloxacin, the maximum adsorption was also found at pH 7 [37]. Levofloxacin (LVX) has two pKa values,

6.1 (carboxyl) and 8.1 (piperazine amine), so the higher adsorption at pH 7 can be attributed to carboxylate interaction of the LEV ions with cationic activated carbon sites, while pH 5 favors electronic repulsion between the positively charged LVX and the AC surface [37]. At pH 7, the levofloxacin structure is zwitterionic (Figure S7).

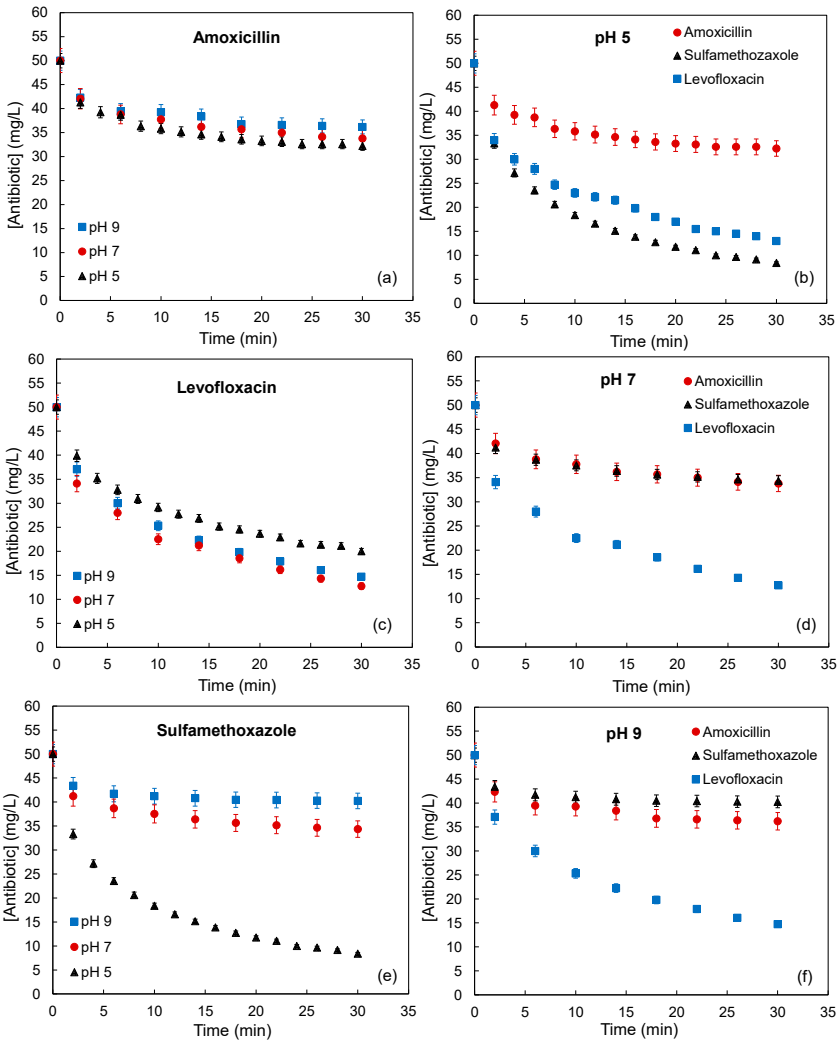

Figure 2. Effect of pH on adsorption kinetics of a 50 mg/L mixture of amoxicillin, levofloxacin, and sulfamethoxazole in PAC. Left hand figures shows effect of pH on adsorption kinetics for every antibiotic studied: amoxicillin (**a**), levofloxacin (**c**), and sulfamethoxazole (**e**), and right hand figures shows the adsorption kinetics for every pH value studied: pH 5 (**b**), pH 7 (**d**), and pH 9 (**f**).

Serna-Carrizales studied sulfamethoxazole (SMX) adsorption at pHs of 2, 6, and 10 and reported optimum adsorption also in the range between 4–6, but it decreased dramatically by increasing the pH to 10 when considering that at this pH, the surface of the GAC (pH_{PZC} = 9.43) and SMX is negatively charged, leading to the establishment of repulsive electrostatic interactions [40]. Sulfamethoxazole has two pKa values of 1.8 (amine) and 5.6 (sulfonamide) with no carboxylic groups. Sulfamethoxazole has a neutral pH between a pH of 1.7 and 5.6, so the adsorption mechanism is mainly governed by pi-pi interactions [40]. Moral-Rodriguez also found the maximum adsorption of sulfamethoxazole at a pH of 5 in GAC, decreasing both at lower and higher pH values [41]. In brief, the maximum adsorption of the studied antibiotics is achieved at their point of zero charge, as illustrated in Figure S7, and different pHs affect adsorption by electrostatic interactions.

Although the best antibiotic adsorption for amoxicillin and sulfamethoxazole was at pH 5, the pH was fixed to 7 for the following experiments because that is the pH of the

wastewater used. At pH 7, amoxicillin and sulfamethoxazole showed similar adsorption rates, while the levofloxacin adsorption rate was clearly higher.

3.3. Effect of PAC Concentration in Antibiotic Adsorption Kinetics on PAC

The PAC concentration plays an important role in adsorption kinetics. The initial kinetic studies were performed with antibiotics prepared individually with an initial concentration of 50 mg/L at pH 7.0 and 25 °C, and the concentration of PAC was varied in the range of 0.25 to 0.5 g/L. The results are shown in Table 2 and Figure S8. The data of adsorption kinetics were modeled according to the two models most widely used in the literature for the adsorption of organic compounds in activated carbon, which are the pseudo-first-order kinetic model and the pseudo-second-order kinetic model [30]. Data were better described by pseudo-second-order kinetics, as R^2 values were closer to 1 (Table 2).

Table 2. Modeling of antibiotic adsorption kinetic data using different PAC concentrations.

		Pseudo-First-Order Model Parameters			**Pseudo-Second-Order Model Parameters**				
Antibiotic	**[PAC] (g/L)**	**q_e (mg/g)**	**K_1 (min^{-1})**	**R^2**	**q_e (mg/g)**	**q_e (mmol/g)**	**K_2 (g/mg min)**	**$K_2\ q_e^2$ (mmol/g min)**	**R^2**
Amoxicillin	0.25	131.3	0.40961	0.975	147.6	0.404	0.00365	0.217	0.992
	0.35	118.7	0.45433	0.947	126.1	0.345	0.00547	0.238	0.989
	0.50	89.4	0.63766	0.984	95.8	0.262	0.01053	0.265	0.998
Levofloxacin	0.25	184.5	0.33143	0.972	205.6	0.568	0.00223	0.260	0.992
	0.35	136.5	0.47790	0.982	151.5	0.419	0.00427	0.271	0.983
	0.50	96.9	0.60975	0.986	104.9	0.290	0.00951	0.289	0.998
Sulfamethoxazole	0.25	175.7	0.16557	0.964	197.2	0.778	0.00113	0.173	0.989
	0.35	128.6	0.24814	0.861	138.7	0.547	0.00303	0.230	0.929
	0.50	92.5	0.55086	0.952	104.0	0.410	0.00606	0.259	0.994

Then, all kinetic studies were fitted with pseudo-second-order kinetics. The best experimental data the fits with the pseudo-second-order model obtained in this work were also found in other studies for amoxicillin [34], levofloxacin [37], or sulfamethoxazole [40] adsorption in activated carbons.

The antibiotic adsorption rate of the three antibiotics increased when a higher concentration of adsorbent was used, as found by other authors [30]. This means better availability of active sorption sites and less competition between adsorbate molecules. The highest values of the adsorption rate were measured with 0.5 g/L of PAC. The values were 0.289 mmol/g min for LVX, 0.265 mmol/g min for AMX, and 0.259 mmol/g min for SMX. Levofloxacin showed the highest adsorption rate followed by amoxicillin and sulfamethoxazole. It should me mentioned that although amoxicillin had faster initial adsorption rate than sulfamethoxazole, the later can reach a higher adsorption capacity.

3.4. Effect of Antibiotic Concentration in Antibiotic Adsorption Kinetics on PAC

The effect of antibiotic concentration on antibiotic adsorption kinetics was studied by assaying individual concentrations of antibiotics at 100, 50, and 25 mg/L at pH 7.0 and 25 °C, with a constant 0.5 g/L PAC concentration. Experimental data fit well with the pseudo-second-order kinetic model, and Table 3 offers the model parameters obtained. Figure S9 shows adsorption kinetics using different initial antibiotic concentrations.

Table 3. Modeling antibiotic adsorption kinetic data with the pseudo-second-order model using different antibiotic concentrations.

[Antibiotic] (mg/L)		q_e (mg/g)	q_e (mmol/g)	K_2 (g/mg min)	$K_2\ q_e^2$ (mmol/g min)	R^2
Amoxicillin	100	163.1	0.446	0.00088	0.064	0.988
	50	95.8	0.262	0.01053	0.264	0.998
	25	50.5	0.138	0.05905	0.412	0.996
Levofloxacin	100	211.4	0.585	0.00186	0.229	0.998
	50	104.9	0.290	0.00951	0.289	0.998
	25	50.6	0.140	0.15867	1.125	0.999
Sulfamethoxazole	100	142.5	0.562	0.00371	0.297	0.996
	50	104.0	0.410	0.00606	0.258	0.988
	25	50.5	0.199	0.06285	0.633	0.996

At the higher concentration assay of 100 mg/L, antibiotics showed the lowest adsorption rates. A high initial concentration of antibiotics in an assay means lower adsorption rates and a longer time to complete adsorption. This can be explained because of the competition between adsorbate molecules and the lower availability of active sorption sites of the adsorbent. For example, 100 mg/L of levofloxacin is fully adsorbed in more than 30 min, 50 mg/L takes about 14 min, and 25 mg/L needs only 6 min. Adsorption rates were higher with the lower values of the antibiotic concentrations assayed at 25 mg/L, independent of the antibiotic evaluated. At the antibiotic concentration of 25 mg/L, levofloxacin showed, again, the fastest adsorption rate kinetics versus sulfamethoxazole and amoxicillin with an equivalent PAC concentration of 0.5 g/L. Values were 1.125 mmol/g min for levofloxacin, 0.633 mmol/g for sulfamethoxazole, and 0.412 mmol/g min for amoxicillin.

Wastewaters do not have individual antibiotics but mixtures, so we studied the adsorption kinetics of a mixture of 50 mg/L of each antibiotic. This higher total antibiotic concentration of 150 mg/L needs a higher PAC concentration to achieve fast, complete adsorption. A PAC concentration of 1.5 g/L could fully adsorb the three antibiotics within 30 min (Figure S9). Levofloxacin showed, again, the fastest adsorption kinetics, followed by sulfamethoxazole and amoxicillin. This PAC concentration of 1.5 g/L was chosen for preliminary continuous experiments with the spinning submerged filter adsorber.

3.5. Fixed Bed Adsorber

3.5.1. Evaluation of Activated Carbon Particle Size on Fixed Bed Operation Conditions

GAC and μGAC filters are widely used in wastewater treatment plants, and the most important process parameter for the design of fixed bed adsorbers is the contact time, which can be measured as empty bed contact time (EBCT) [45]. EBCT values for water treatments are reported to be in the range of 10 to 50 min [45,46]. Thus, initial experiments were performed to estimate the range of EBCT that can be used to operate down flow or up flow a fixed bed adsorber packed with activated carbon of different particle sizes. Lab-scale columns were filled with the same weight of μGAC, cPAC, or PAC using a scalable ratio of bed height versus a column diameter of close to five. The column bed must avoid high compaction during downflow operation or high bed expansion during up flow operation. The evolution of bed compression/expansion and column pressure during down flow/up flow operation with water at different EBCTs is shown in Figure S10. Fixed bed adsorbers can run with μGAC and cPAC using an EBCT range from 1 to 45 min, as shown with minor bed compression or pressure increases. It should be noted that cPAC expands easier in comparison to μGAC, so when running up flow for decompaction or regeneration purposes, special care must be taken. This explains the preference of μGAC and GAC for high-scale operations [47]. PAC cannot be used as an adsorbent in a fixed bed as high bed compression (>25%), and overpressure occurs with down flow operation and a high bed expansion with up flow operation (>70%). Therefore, fixed bed adsorbers were studied with μGAC and cPAC.

3.5.2. Continuous Removal of Antibiotics with a Fixed Bed Packed with μGAC or cPAC

Fixed bed adsorbers were packed with μGAC or cPAC and run using the same adsorbent weight with the experimental setup described in Figure S2. The influent was a mixture of 50 mg/L of amoxicillin, levofloxacin, and sulfamethoxazole spiked in deionized water or wastewater at 25 °C and pH 7. The wastewater was from a local domestic wastewater treatment plant. It had a pH of 7 and a low organic load and conductivity, as shown in its analysis (Table S4).

Fixed bed adsorbers were run with an EBCT and bed height/diameter of 4 min and 5.1 for μGAC and 4.5 min and 5.7 for cPAC, respectively. Continuous experiments were required to obtain the breakthrough curves needed for the proper design and optimization of fixed-bed columns. The initial breakthrough curves were obtained using antibiotics spiked in deionized water (Figure 3).

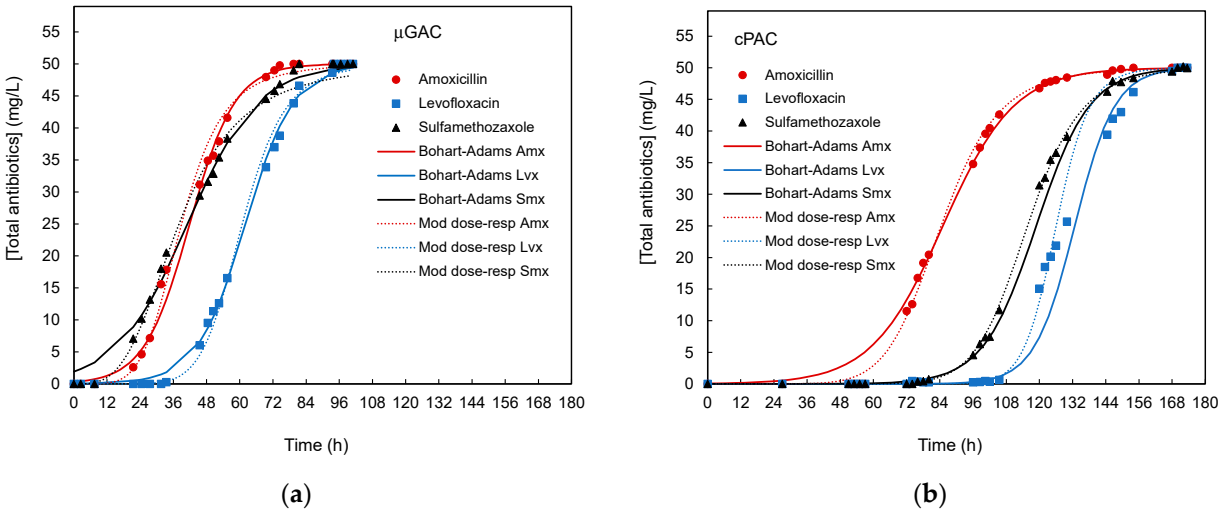

Figure 3. Breakthrough curves for fixed bed columns packed with (**a**) μGAC or (**b**) cPAC, running with an EBCT of 4 and 4.5 min, respectively, at pH 7, 25 °C. Antibiotics in deionized water.

Breakthrough curves were modeled with Bohart-Adams, Thomas, Yoon-Nelson, and dose-response models, and the values of model parameters are shown in Table S5. In the case of μGAC, the best fit was achieved with the Bohart-Adams model with R^2 values close to 1, while the dose-response model better fits the cPAC results. Bohart-Adams, Thomas, and Yoon-Nelson gave the same fit because they represent the logistic function from the mathematical perspective, which provides the same symmetric breakthrough curve [48]. Yoon-Nelson offered a good correlation of the dynamic adsorption of levofloxacin on GAC in fixed bed columns [49], and the dose-response model was also satisfactory to model amoxicillin adsorption on GAC [50] or sulfamethoxazole adsorption on biochar in fixed bed columns [39].

Results revealed that the column packed with cPAC gave breakthrough times much higher than μGAC for all antibiotics. The smaller particle size of cPAC versus μGAC favored antibiotic adsorption because of its higher adsorption capacity due to its higher adsorption surface area. The breakthrough curves of μGAC showed that, initially, amoxicillin was better retained than sulfamethoxazole, but after about 40 h, the opposite occurred. Amoxicillin and sulfamethoxazole compete for the adsorption sites of μGAC. However, in the case of cPAC, sulfamethoxazole was always adsorbed better than amoxicillin. Amoxicillin was the first antibiotic to elute, with the time required for 50% breakthrough being 85 h, followed by sulfamethoxazole and levofloxacin. In both cases, levofloxacin had breakthrough times higher than sulfamethoxazole and amoxicillin. The adsorption rates of antibiotics play an important role in determining the elution profiles of antibiotics, so levofloxacin was the last to elute as it showed the highest adsorption rate of the studied

antibiotics. The Thomas and dose-response models calculated similar maximum adsorption capacities with cPAC of 199.2/189.1, 178.3/173.6, and 127.7/126.7 mg/g for levofloxacin, sulfamethoxazole, and amoxicillin, respectively.

A final fixed bed adsorber packed with cPAC was run with wastewater as the influent with a mixture of 50 mg/L of each antibiotic at pH 7 and 25 °C. Figure 4 shows the breakthrough curves obtained with the Bohart-Adams and modified dose-response models. There were good correlations with both models, but R^2 was higher for the Bohart-Adams model (Figure 4a). The time required for 50% breakthrough of individual antibiotics with wastewater versus deionized water showed that levofloxacin elutes earlier at 124 h versus 133 h, sulfamethoxazole much earlier at 89 h versus 119 h, while amoxicillin elutes later at 108 h versus 85 h (Figure 4a). Antibiotics compete for cPAC adsorption sites, and wastewater components disserve levofloxacin and sulfamethoxazole adsorption, which favors amoxicillin adsorption.

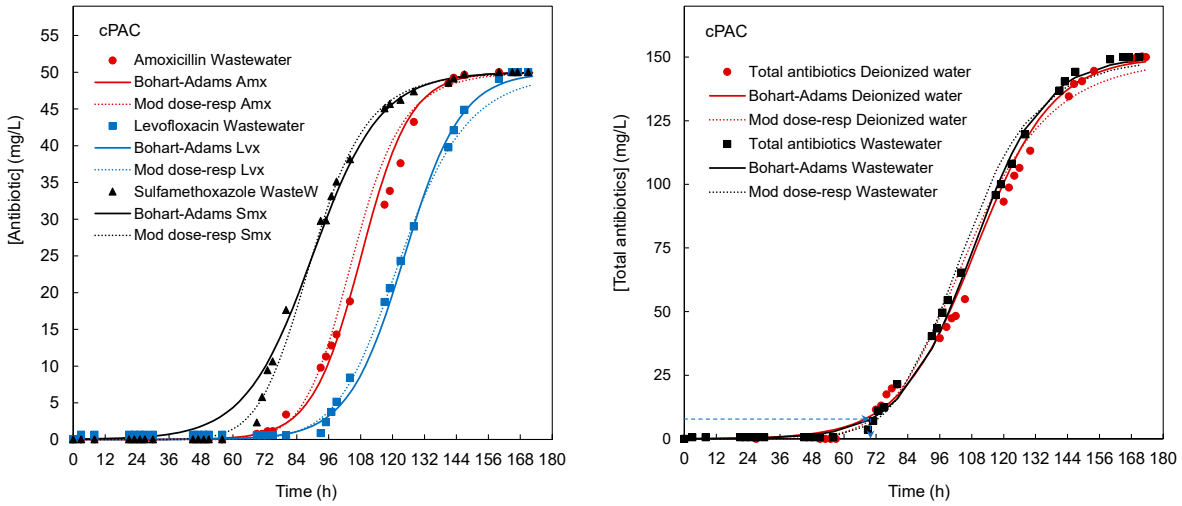

Figure 4. (**a**) Breakthrough curves of fixed bed columns packed with cPAC running with an EBCT of 4.5 min using 50 mg/L individual antibiotics concentrations in wastewater. (**b**) Comparison of wastewater and deionized water.

If we compare the breakthrough curves of the total antibiotics in deionized water and wastewater (Figure 4b), it can be concluded that antibiotics elute slightly earlier, and the effect of wastewater slightly reduces the total antibiotic adsorption. Wastewater composition affected the antibiotic elution profile but kept the total antibiotic removal capacity of the fixed bed adsorber. The total adsorption capacity of antibiotics calculated with the Thomas model decreased from 493.75 to 488.85 mg/g when using wastewater, obtaining similar breakthrough times close to 70 h in both cases (Table S6). These high values encourage the use of cPAC for antibiotic removal from wastewater. The small difference could be attributed to the presence of dissolved organic carbon (DOC) and the low molecular weight acid and neutral organics (LMWO) in wastewater, which induces adsorption competition and decrease the adsorption capacity of activated carbons [51].

3.6. Continuous Removal of Antibiotics with a Spinning Submerged Filter Adsorber with PAC

The novel spinning submerged filter adsorber proposed for antibiotic removal was operated continuously with PAC using a spinning submerged filter (Figure 1). The filter located inside the beaker was a rectangular prismatic basket covered with a stainless-steel mesh of 27 µm hole size that rotated at 200 rpm. The submerged filters completely retained PAC particles with an average diameter of 75 µm and allowed complete mixing inside the beaker. The effluent exited through the central tube using a pump. At the beginning of the experiment, the beaker was filled with antibiotic solution, and time zero was the

adsorbent addition and inlet pump connection. The spinning submerged filter adsorber was run initially with an HRT of 40 min using an influent mixture of 10, 25, or 50 mg/L of each antibiotic in deionized water at 25 °C and pH 7. Figure 5 shows that when using a low PAC concentration of 1.5 g/L, like that used in the batch adsorption kinetic experiments, antibiotics can be completely removed with influent concentrations of 10 and 25 mg/L (Figure 5a,b) but not with 50 mg/L (Figure 5c).

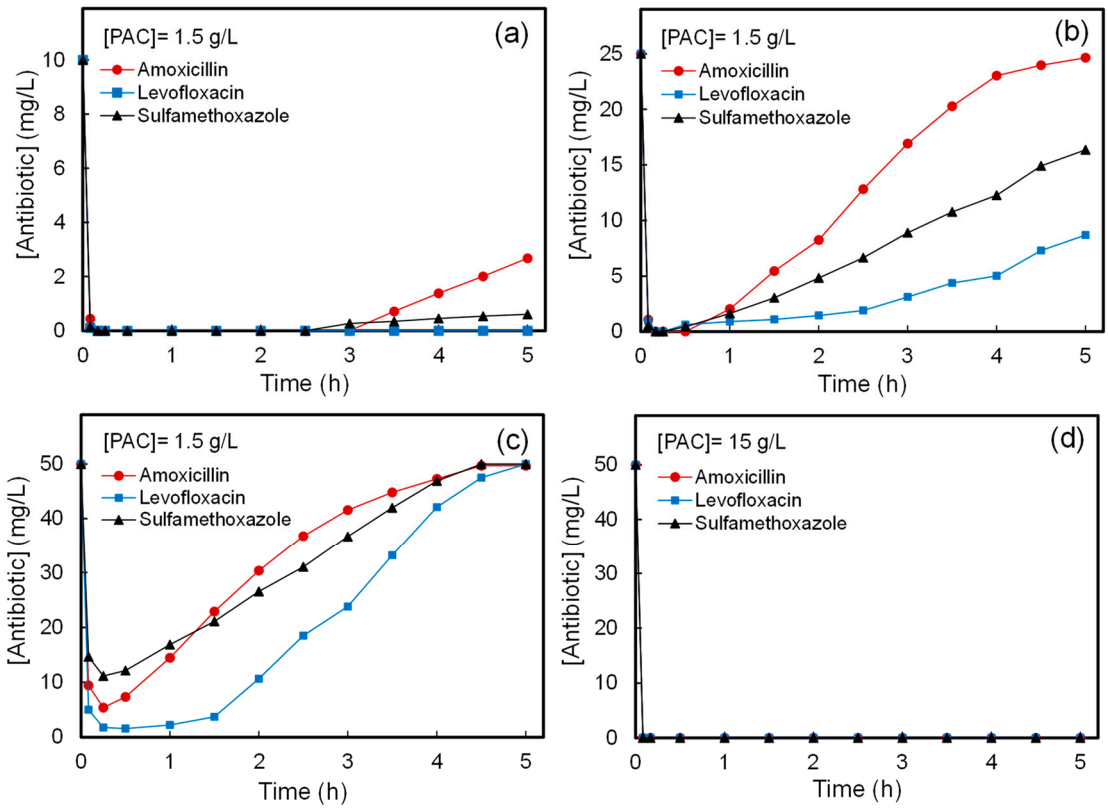

Figure 5. Effluent antibiotic concentrations of a spinning filter adsorber running with a PAC concentration of 1.5 g/L (**a**–**c**) or 15 g/L (**d**) at an HRT of 40 min. Individual influent antibiotics concentrations in deionized water at pH 7 were (**a**) 10 mg/L, (**b**) 25 mg/L, and (**c**,**d**) 50 mg/L.

Levofloxacin was always adsorbed preferentially followed by sulfamethoxazole and amoxicillin with 10 or 25 mg/L inlet concentrations, but with a 50 mg/L influent concentration, amoxicillin removal improved versus sulfamethoxazole. A higher antibiotic concentration favors the competition of amoxicillin and sulfamethoxazole for adsorption sites of PAC. To achieve complete antibiotic removal using a 50 mg/L influent concentration, a higher PAC concentration in the adsorber unit is needed. Complete antibiotic removal using an HRT of 40 min was achieved with a PAC concentration of 15 g/L (Figure 5d). This result indicates that the spinning submerged filter can be used successfully for antibiotics removal using PAC.

The last experiments were performed with a lower HRT of 10 min to evaluate the maximum adsorption capabilities using a PAC concentration of 15 g/L and 50 mg/L of antibiotics in deionized water and wastewater. As shown in Figure 6, it was possible to remove antibiotics but only during the initial hour with both deionized and wastewater influents. This means that higher PAC concentrations are needed to work with lower HRT.

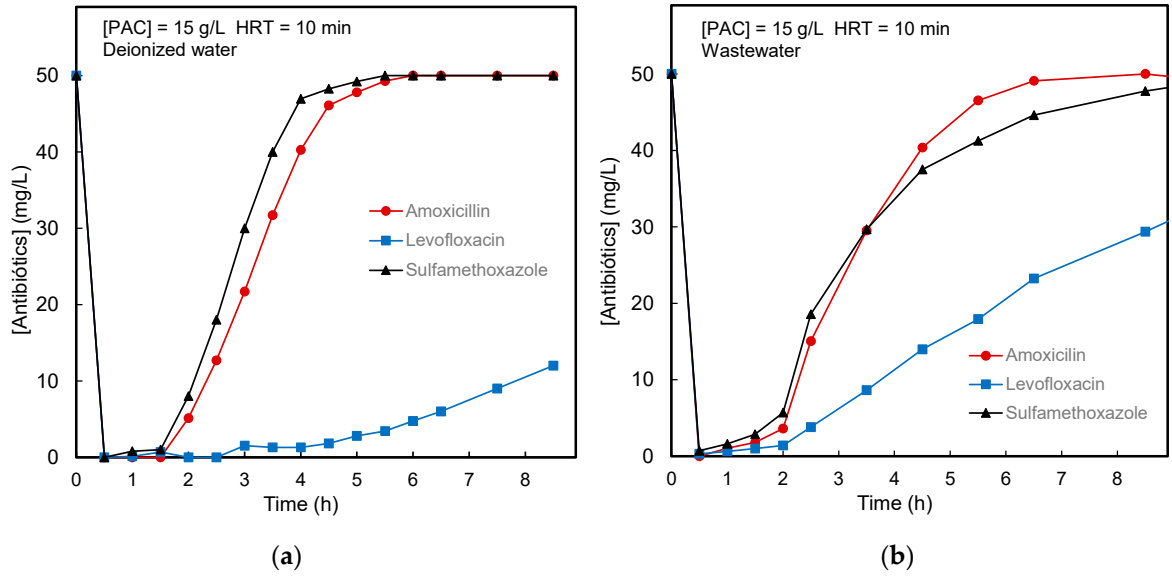

Figure 6. Continuous antibiotic adsorption with a spinning submerged filter adsorber with PAC, running with an HRT of 10 min at pH 7, 25 °C. Antibiotics in (**a**) deionized water or (**b**) wastewater.

The breakthrough curves of the total antibiotics showed no remarkable differences between deionized water and wastewater as the water matrix. The breakthrough curves of individual antibiotics showed, again, that levofloxacin had the best adsorption in comparison to amoxicillin and sulfamethoxazole. Wastewater components disserve levofloxacin adsorption and play an important role in the competition of amoxicillin and sulfamethoxazole for the active sites of PAC. It was argued that the adsorption rate of ternary mixtures is based on multiple interactions of antibiotics with themselves and the carbon surface, creating an antibiotic network in contact with the surface that enhanced the covered area of the carbon [40]. Finally, when the antibiotic mixture was fully adsorbed, a PAC particle was studied by elementary mapping analyses with energy-dispersive X-ray spectroscopy. The initial elementary composition of activated carbon was 0.4% sulfur, 0% fluor, and 0% nitrogen and increased after adsorption to 0.8% sulfur, 0.5% fluor, and 0.2% nitrogen. Enhancement of mapping signals of sulfur (AMX and SMX), fluor (LVX), and nitrogen (AMX, LVX, SMX) present in antibiotic molecules showed that adsorption occurs homogeneously, covering all PAC surfaces (Figure S11).

In WWTPs, PAC is typically added in a post-treatment stage after biological treatment with a dosing tank combined with an additional sedimentation basin with subsequent sand or membrane filtration. This post-treatment configuration needs low PAC addition, shows higher removal rates than direct dosage to activated sludge reactors (ASR), and PAC can be reused [52]. PAC dosage to an ASR has the advantages of ensuring PAC exhaustion and PAC separation with sludge, but the presence of organic matter competes for the adsorption active sites of PAC minimizing adsorption efficiency [53]. A pilot-scale study compared a post-treatment stage with a PAC dosing tank combined with separation units for PAC and fixed beds packed with GAC for the removal of 22 pharmaceuticals frequently occurring in municipal WWTPs from Sweden. The authors concluded that, in both cases, wastewater has an important effect on the adsorption of individual substances, suggesting the use of PAC if the specific task is the removal of pharmaceutical residues in uncharted wastewater, but no considerable differences regarding pharmaceutical removal were observed with the different configuration tested [54].

In this work, we have proposed as an alternative to fixed bed adsorbers for micropollutant removal an interesting, simple post-treatment unit that uses adsorption and filtration in a compact configuration with high antibiotic removal rates and is able to run with low HRT and PAC concentrations as high as 15 g/L.

4. Conclusions

This work suggests packing fixed bed adsorbers with cPAC of 197 μm average diameter particle size versus μGAC of 508 μm. A fixed bed packed with cPAC achieved a high breakthrough time of 70 h when run with an EBCT as low as 4.5 min using a mixture of 50 mg/L of amoxicillin, sulfamethoxazole, and levofloxacin spiked in domestic wastewater at pH 7 and 25 °C. The excellent effectiveness of the fixed bed adsorber relies on the high concentration of adsorbent inside the column, close to 500 g/L.

The small particle size adsorbent PAC of 77 μm offers higher adsorption capacities to remove antibiotics from wastewater versus cPAC or μGAC. Thus, a novel spinning submerged filter adsorber was proposed as an alternative to packed beds that cannot use PAC. The spinning submerged filter adsorber configuration achieved complete continuous antibiotic removal working with a higher HRT of 40 min using a mixture of 50 mg/L of amoxicillin, sulfamethoxazole, and levofloxacin spiked in domestic wastewater. The lower effectiveness can be explained because of the lower concentration of 15 g/L used in comparison with the fixed bed configuration.

The advantage of the fixed bed adsorber is its high efficiency, while its main disadvantage is the possibility of clogging due to the presence of particulate matter in the wastewater and channeling. The proposed spinning submerged filter adsorber is not as efficient as the fixed bed adsorber, but it has the advantages that it can operate with complete mixing facilitating pH control, the filter rotation that minimizes clogging, the PAC dosage can be adjusted to the concentration of micropollutants expected in the WWTP effluent, and it can be increased to reach final PAC concentrations as high as 150 g/l if necessary.

Pilot-scale studies using real antibiotic concentrations found in WWTPs are encouraged to evaluate the effectivity and applicability of the proposed spinning submerged filter adsorber configuration for micropollutant removal. The promising results obtained in this study allow us to suppose that the spinning submerged filter adsorber configuration running at typical HRT of WWTPs could remove antibiotic concentrations in the range of μg/L, as found in wastewater much lower than the concentration values studied.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15091726/s1, Figure S1: Spectra of antibiotics, a typical HPLC chromatogram, and HPLC quantification curves; Figure S2: Experimental set-up of the studied fixed bed adsorber; Figure S3: Particle size distribution curves of studied activated carbons; Figure S4: SEM images of PAC using different magnifications 100, 200, 1000 and 2000 (A, B, C, D); Figure S5: Adsorption-desorption isotherms of N2 at 77 K; Figure S6: Isothermal adsorption of individual antibiotics on μGAC, cPAC, and PAC, fitted with Freundlich model; Figure S7: Distribution of molecular species at different pHs of amoxicillin (AMX), levofloxacin (LVX), and sulfamethoxazole (SMX). Green are structures at the pH of best adsorption; Figure S8: Antibiotics adsorption kinetics at pH 7 with different PAC concentrations, fitted with second-order kinetic model; Figure S9: Adsorption kinetics at pH 7 with different individual antibiotic concentrations using 0.5 g/L PAC, and an antibiotic's mixture with 1.5 g/L PAC concentration. Data fitted with pseudo-second order model; Figure S10: Evaluation of operation conditions of fixed bed adsorbers packed with different activated carbons: μGAC, cPAC and PAC; Figure S11: Elemental analyses of a PAC particle determined by energy dispersive X-ray spectroscopy, before (A) and after (B) amoxicillin, levofloxacin, and sulfamethoxazole full adsorption; Table S1: Antibiotic properties; Table S2: Parameters of particle size distributions of studied activated carbons; Table S3: Specific surface area and pore volumes of obtained activated carbons; Table S4: Wastewater analysis; Table S5: Modelling breakthrough curves of fixed bed adsorbers packed with μGAC or cPAC using deionized water with 50 mg/L antibiotic concentrations as influent; Table S6: Modelling breakthrough curves of fixed bed adsorbers packed with cPAC using as influent wastewater with 50 mg/L antibiotic concentrations.

Author Contributions: J.M.O.: Writing—Original Draft, Writing—Reviewing and Editing, Conceptualization, Investigation, Methodology, Data curation. J.A.F.-L.: Supervision, Conceptualization, Formal analyses, Methodology, Resources. M.A.: Conceptualization, Methodology, Visualization. J.M.A.: Conceptualization, Investigation, Methodology, Data curation. All authors have read and agreed to the published version of the manuscript.

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