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**Optimizing microwave-assisted production of waste-based activated carbons for
the removal of antibiotics from water**

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Abstract

This work aimed at the microwave-assisted production of activated carbon (AC) from primary paper mill sludge (PS) for the adsorption of antibiotics from water. Production conditions, namely pyrolysis temperature, pyrolysis time and activating agent (KOH):PS ratio, were optimized as a function of product yield, specific surface area (S_{BET}), total organic carbon (TOC) content and adsorptive removal percentage of two target antibiotics (amoxicillin (AMX) and sulfamethoxazole (SMX)). Under the optimized conditions (pyrolysis at 800 °C during 20 min and a KOH:PS ratio of 1:5), a microporous AC (MW800-20-1:5, with $S_{\text{BET}} = 1196 \text{ m}^2 \text{ g}^{-1}$, TOC = 56.2 % and removal of AMX and SMX = 85 % and 72 %, respectively) was produced and selected for further kinetic and equilibrium adsorption studies. The obtained results were properly described by the Elovich reaction-based kinetic model and the Langmuir equilibrium isotherm, with maximum adsorption capacities of $204 \pm 5 \text{ mg g}^{-1}$ and $217 \pm 8 \text{ mg g}^{-1}$ for AMX and SMX, respectively. Considering the satisfactory comparison of these results with the performance of commercial and alternative AC produced by conventional pyrolysis, this work demonstrated the feasibility of the microwave-assisted production of environmentally and energetically sustainable waste-based AC to be applied in the efficient removal of antibiotics from water.

Keywords: Water treatment; pharmaceuticals; cellulose-derived waste; pyrolysis; carbon adsorbents; chemical activation.

1. INTRODUCTION

Antibiotics belong to a large group of pharmaceutical compounds which are used worldwide for human and veterinary treatment (Ahmed, 2017; Bharagava and Chowdhary, 2019) aiming to control infectious diseases and increase average life expectancy (Karkman et al., 2018; Xu et al., 2016). Due to the high consumption of antibiotics, they are ubiquitous in the environment (Michael et al., 2013) and can be found in aquatic ecosystems at concentration levels ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ (Hernández et al., 2019; Saitoh et al., 2017). Although these concentrations might not be deemed harmful to humans, they can induce the development of bacterial resistance, which certainly involves serious risks to human health (Michael et al., 2013). For that reason, the occurrence of antibiotics in the environment can be considered as an emerging issue and has raised particular attention. In this sense, the European Union (EU) has recently included two antibiotics (amoxicillin and ciprofloxacin) as substances that should be monitored by EU member states due to the risks to the aquatic environment (Decision 2018/840/EU).

After consumption, antibiotics are not fully metabolized by humans and animals, so part of them are excreted into wastewater through urine (Michael et al., 2013). Then, in wastewater treatment plants (WWTPs), the removal of antibiotics by conventional processes is generally incomplete due to the relatively low biodegradability of these compounds (Adams et al., 2002). Therefore, WWTPs are known to be among the main sources of antibiotics' release into various compartments of the environment worldwide (Michael et al., 2013). Hence, the development of effective and sustainable treatments for the removal of antibiotics from contaminated waters is both emerging and urgent, in order to mitigate their entry into the environment

and reduce the impact of their presence on water quality and in human and animal health (Mezzelani et al., 2018).

Several technologies, such as coagulation, flocculation and advanced oxidation processes (AOP), have been tested for the removal of organic micropollutants that are often recalcitrant to WWTPs' conventional processes (Kanakaraju et al., 2018; Tokumura et al., 2016). However, these advanced solutions still have numerous disadvantages, namely low removal rates for a large number of pharmaceuticals and/or the formation of by-products, causing a potential risk of contamination for treated waters (Iwuozor, 2019). Amongst advanced treatment options, adsorption is an effective and versatile process with no by-product formation. In this context, activated carbon (AC) is considered a highly efficient adsorbent due to its high surface area (S_{BET}) and interesting surface chemistry properties, showing high pharmaceutical removal rates (Kovalakova et al., 2020; Mansour et al., 2018). Still, the implementation of an advanced treatment using AC produced from non-renewable fossil precursors may be unaffordable for many WWTPs due to its relatively high cost. Alternatively, the use of agricultural or industrial wastes as AC precursors contributes to the sustainability of these materials and improves the valorisation of such wastes, enhancing circular economy (Silva et al., 2018). AC production can be accomplished by physical or chemical activation of a precursor along with thermal decomposition by pyrolysis (Alslaibi et al., 2013; Wong et al., 2018). Physical activation uses carbon dioxide or steam as activating agents, while chemical activation is performed using chemical agents (e.g. H_3PO_4 , KOH , ZnCl_2 , NaOH , FeCl_3) (Keey et al., 2018). The main advantages of chemical activation over the physical processes are the lower costs of production and the higher S_{BET} usually attained (Ao et al., 2018). Typically, AC materials are prepared under conventional heating in pyrolysis reactors (Akbar Babar et

al., 2019; Krithiga et al., 2017; Vighnesha et al., 2018), but in recent years, microwave irradiation has attracted considerable attention and has been used as an alternative heating method (Keey et al., 2018; Liew et al., 2019). When compared to conventional heating, the use of microwave radiation is promising for thermochemical treatment due to it is rapid, uniform, and volumetric heating, with lower energy consumption and higher production yields (Ao et al., 2018; Mansour et al., 2018). Recent studies have explored the use of microwave heating in the production of ACs to be applied in water treatment for removal of pharmaceuticals, including antibiotics, using precursors such as bamboo waste, cocoa shell and giant reed (Reza et al., 2014; Saucier et al., 2015; Ahmed and Theydan, 2013a, 2013b; Chayid and Ahmed, 2015). Some of these works reported the production of ACs with high S_{BET} , which allowed for the efficient adsorption of these contaminants (Cheng et al., 2016; Zbair et al., 2018).

Paper mill sludge is the solid waste generated from wastewater treatment at pulp and paper mills. Around 50 kg of dry sludge (of which approximately 70 % is primary sludge (PS) and 30 % is secondary sludge (SS)) result from the production of a tonne of paper, which makes evident the necessity for a cost-effective and environmentally friendly management options. Among them, and in line with the Circular Economy principles, is the conversion of such sludge into added-value products such as carbon adsorbents (Calisto et al., 2014). Conventional pyrolysis of paper mill sludge has already been used to produce biochars and ACs with remarkable efficiency in the adsorptive removal of pharmaceuticals from water (Calisto et al., 2015; Coimbra et al., 2019; Jaria et al., 2015; Pereira et al., 2019; Pereira et al., 2020; Silva et al., 2019). Still, the microwave-assisted production of AC has only been tested for mixed PS-SS (Namazi et al., 2015) without any studies on the adsorptive application of the resulting material.

In the above described context, this manuscript aimed, for the very first time, at using PS as precursor for the microwave-assisted production of efficient AC for the removal of antibiotics from water. Amoxicillin (AMX) and sulfamethoxazole (SMX) were chosen as target antibiotics since they are amongst the most widely consumed and resistant to conventional treatments, having been detected in surface waters around the world (Kovalakova et al., 2020) and even in drinking water (Praveena et al., 2019). A main novelty of this work was the optimization of AC production conditions, which was carried out considering three variables, namely, temperature of pyrolysis, pyrolysis time (dwell), and activating agent: PS ratio and evaluating their impact on the product yield, S_{BET} , total organic carbon (TOC) and adsorptive removal (%) of AMX and SMX from water. After production optimization, the selected AC was further characterized and used for kinetic and equilibrium studies on the adsorption of AMX and SMX from ultra-pure water.

2. MATERIALS AND METHODS

2.1 Chemicals

Amoxicillin (AMX, $\geq 98\%$, TCI) and sulfamethoxazole (SMX, 99 %, TCI) were the pharmaceuticals selected for the adsorption tests. Potassium hydroxide (KOH, $\geq 86\%$, BCHM) was used as chemical activating agent and hydrochloric acid (HCl, 37 %, Honeywell FLUKA) was used for washing the pyrolyzed materials. For the analytical determination of pharmaceuticals in water, Micellar Electrokinetic Chromatography (MEKC) was applied as described in section 2.6 and the separation buffer consisted of sodium tetraborate (borax, Riedel-de Haën), sodium dodecyl sulphate (SDS, 99 %, Sigma Aldrich); ethylvanillin (99 %, Sigma Aldrich) was used as internal standard. For capillary coating in MEKC, solutions of 0.5 % (w/v) hexadimethrine bromide (polybrene, $\geq 95\%$, Sigma–Aldrich) in sodium chloride (NaCl,

$\geq 99.5\%$, Fluka) and sodium hydroxide (NaOH, 99.3 %, José Manuel Gomes dos Santos) were used. All the solutions were prepared in ultra-pure water obtained from a PURELAB Flex 4 system (Elga, Veolia).

2.2 Microwave-assisted production of carbon materials

AC was produced by chemical activation and microwave pyrolysis of primary sludge (PS) resulting from the wastewater treatment in a pulp and paper industry. Proximate and ultimate analyses of this precursor were determined in a previous work (Jaria et al., 2019) and are depicted in Table S1, as Supplementary Material (SM1). After collection, PS was dried at room temperature for several days, followed by 24 h at 105 °C in an oven. Subsequently, it was ground with a blade mill, impregnated with the activating agent (KOH), sonicated for 1 h in an ultrasonic bath and then dried at room temperature. Then, impregnated materials were pyrolyzed using a Phoenix TM AirWave CEM industrial microwave furnace (dimensions 46.15 x 65.40 x 49.78 cm (w x d x h)), which was heated at a rate of 15 °C min⁻¹ up to the desired temperature. The microwave furnace is equipped with a temperature sensor and a programmable temperature controller that allows to define the required heating ramp time in order to attain the referred heating rate.

Alkaline KOH was used in this work as activating agent due to its ability to produce AC with high surface area and narrow pore size distribution as well as its lower environmental contamination, corrosive ability and cost (Foo et al., 2011; Ukanwa et al., 2019), when compared with other commonly used activated agents. The improved porosity resulting from activation with KOH can be attributed to potassium interaction and the stretching of carbon and it is known to be highly effective when using biomass as precursor (Ukanwa et al., 2019), including PS (Jaria et al., 2019). Moreover, KOH

has been pointed out as appropriate activating agent for microwave-assisted production of activated carbon (Ukanwa et al., 2019), also when using mixed primary and secondary paper mill sludge as precursor (Namazi et al., 2015). Firstly, an activating agent: precursor (KOH:PS) ratio of 1:1 (w/w) was tested at three different pyrolysis temperatures (600, 700 and 800 °C) and three pyrolysis residence times (10, 15 and 20 min) at each of these temperatures. The production condition at 800 °C for 20 min was selected for the evaluation of the effect of different KOH:PS ratios and thus four extra ratios were tested: 1:0.5, 1:2, 1:5, and 1:10 (w/w). For the different impregnation ratios a specific volume of an aqueous solution of the activating agent was added to PS. Accordingly, solutions with KOH concentrations of 0.60 g mL⁻¹, 0.30 g mL⁻¹, 0.15 g mL⁻¹, 0.06 g mL⁻¹, and 0.03 g mL⁻¹ were used for achieving KOH:PS ratios of 1:0.5, 1:1, 1:2, 1:5, and 1:10 (w/w), respectively. For comparative purposes, biochar was also produced through pyrolysis of PS without any activating agent, to evaluate the impact of using chemical activation on the resulting material. The considered variables and the designation of the respective obtained materials are described in Table 1.

Globally, thirteen AC and one biochar were obtained. All materials were subjected to a washing step with 1 M HCl for 1 h to remove ashes, followed by a washing with distilled water, and were dried overnight. Additionally, the synthesis of some materials, namely MW700-10-1:1, MW800-15-1:1 and MW800-20-1:5, was repeated to assess the repeatability of the production procedure under different conditions.

The product yield (%), as described in Eq. 1, was determined for all the produced materials.

$$Yield (\%) = \frac{W_f}{W_0} \times 100 \quad (1)$$

where $W_f(g)$ is the final mass of AC or biochar (after pyrolysis, washing and drying) and $W_0(g)$ is the mass of precursor.

2.3 Optimization of the microwave-assisted production of AC for the adsorption of AMX and SMX

The produced materials (Table 1) were characterized for their textural properties and TOC, and subsequently tested for the adsorption of the target antibiotics (AMX and SMX). In order to optimize the microwave-assisted production of AC, the impact of pyrolysis temperature, dwell and KOH:PS ratio on the product yield, S_{BET} , TOC and antibiotics adsorptive removal (%) was evaluated so to determine the optimum conditions and to select the corresponding material for further characterization and adsorption studies.

2.3.1 Textural properties and TOC

The textural properties of all the materials were obtained using a Micromeritics Instrument, Gemini VII 2380 at 77 K. The samples were degassed at 120 °C. Nitrogen adsorption-desorption experiments were then carried out using liquid nitrogen at -196 °C. The adsorption isotherm obtained was used to calculate S_{BET} and estimate the total pore volume (V_p) at a relative pressure of 0.99. S_{BET} was calculated from Brunauer-Emmett-Teller equation (Brunauer et al., 1938) in a relative pressure range between 0.001 and 0.1. Microporosity (W_0) was determined by Dubinin-Astakov equation (Dubinin, 1975) to the lower relative pressure zone of the nitrogen adsorption isotherm.

TOC was determined through a TOC analyser (TOC-VCPH Shimadzu, solid sample module SSM-5000A). TOC was calculated by determination of inorganic carbon (IC) and total carbon (TC). All the analyses were performed in triplicate.

2.3.2 Adsorptive percentage removal of AMX and SMX

In a first approach, preliminary batch adsorption experiments were performed to determine the adsorptive percentage removal of the selected pharmaceuticals with a specific dose of each of the fourteen produced carbon materials. All these materials consisted of at least 90 % by mass (% w/w) of particles with a size less than 0.5 mm (35 US Mesh), as corresponding to powder activated carbon (Council Regulation (EC) No 649/2008 of 8 July 2008). AMX and SMX solutions with an initial concentration of 5 mg L⁻¹ were prepared separately in ultra-pure water. These solutions were not buffered, or pH adjusted; their pH was of approximately 6.8 for AMX and 5.6 for SMX. Each pharmaceutical solution was put in contact with 25 mg L⁻¹ of each material in 50 mL polypropylene tubes and stirred overnight on an overhead shaker (Heidolph, Reax 2) at 80 rpm under controlled temperature (25.0 °C ± 0.1 °C). Then, solutions were filtered through 0.22 µm PVDF filters (Whatman) and immediately analysed for the remaining concentration of antibiotic by MEKC, as described in section 2.6. In addition, control experiments consisting of pharmaceutical solutions without adsorbent were performed simultaneously and used as reference for the calculation of adsorption percentages, using Eq. (2):

$$\text{Adsorption (\%)} = 100 \times \frac{C_c - C_f}{C_c} \quad (2)$$

where C_f (mg L⁻¹) is the final antibiotic concentration after stirring and C_c (mg L⁻¹) is the antibiotic concentration in the control. The experiments were performed in triplicate.

2.3.3 Principal component analysis

To gain insights on the preliminary batch adsorption tests and to correlate the obtained data with some of the intrinsic properties of the materials (TOC, S_{BET} and

product yield), a principal component analysis (PCA) was applied to group the produced materials (Table 1). Such analysis will be used as a basis to select the most interesting material to be further characterized and used in adsorption studies. The software MATLAB was used to carry out the PCA analysis.

2.4 Characterization of selected AC

Based on the results obtained in section 2.3, an AC was selected and subjected to further characterization, namely scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

SEM images were obtained at magnifications of 500x, 3 000x, 10 000x, 20 000x and 50 000x using a Hitachi SU-70 microscope. Prior to the analysis, the samples were coated with a thin film of amorphous carbon.

The determination of the surface chemistry of the material was achieved by XPS. XPS spectra were obtained in an Ultra High Vacuum (UHV) system with a basic pressure of 2×10^{-10} mbar and equipped with a hemispheric electronic energy analyser (SPECS Phoibos 150), with a delay line detector and an X-ray source monochromatic $\text{AlK}\alpha$ (1486.74 eV). The high-resolution spectra were recorded at the normal emission take-off angle and with a 20 eV pass-through energy, which provides an overall instrumental peak increase of 0.5 eV.

2.5 AMX and SMX adsorption kinetics and equilibrium

2.5.1 Kinetic experiments and modelling

In order to determine the time needed to attain the adsorption equilibrium, 5 mg L⁻¹ solutions of SMX or AMX were shaken with the selected AC, during increasing time intervals (from 5 to 240 min and from 5 to 900 min, respectively), using an

adsorbent dose of 15 mg L⁻¹ in 150 mL polypropylene tubes, under the experimental conditions described in section 2.3.2. The remaining concentration of referred pharmaceuticals in solution after each contact time was then determined by MEKC (section 2.6). The amount of the target pharmaceutical adsorbed onto the selected AC at a certain time, q_t (mg L⁻¹), was calculated by Eq. (3).

$$q_t = \frac{(C_c - C_t)V}{m} \quad (3)$$

where C_c (mg L⁻¹) is the pharmaceutical concentration in the control, C_t is the pharmaceutical concentration after shaking during a time t (min), V is the volume of the solution (L) and m is the mass (mg) of adsorbent.

For the description of the experimental data obtained for the adsorption kinetics of AMX and SMX onto the selected AC, different theoretical (reaction and diffusion) models were considered.

Considering reaction-based models, the following were used: pseudo-first order (Eq. 3) (Lagergren, 1898), pseudo-second order (Eq. 5) (Y.SHo and G.McKay, 1999) and Elovich (Eq. 6) (Chien and Clayton, 1980) models.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

$$q_t = \frac{1}{\beta} \ln(\alpha \beta t) \quad (6)$$

where, t (min) is the contact time between the adsorbent and solution; q_t (mg g⁻¹) is the amount of pharmaceutical adsorbed per mass unit of the adsorbent at time t ; q_e represents the amount of pharmaceutical adsorbed at equilibrium (mg g⁻¹); k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the pseudo-first and pseudo-second order rate constants, respectively; α (mg g⁻¹ min⁻¹) and β (g mg⁻¹) are the initial adsorption rate and desorption constant, respectively, related to the extent of surface coverage and

activation energy constant for chemisorption. Fittings to the described kinetic models were obtained by non-linear regression analysis using GraphPad Prism version 5.03.

As for the diffusion-based models, Webber's intraparticle diffusion (Eq. 7) (Weber & Morris, 1963) and Boyd's film diffusion models (Eq's. 8 and 9) (Boyd et al., 1947) were considered to describe the experimental kinetic data:

$$q_t = k_{id} t^{1/2} \quad (7)$$

$$Bt = -0.4977 - \ln(1 - F), \text{ for } F \text{ values } > 0.85 \quad (8)$$

$$Bt = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F}{3}} \right)^2, \text{ for } F \text{ values } < 0.85 \quad (9)$$

The diffusion modelling analysis was conducted by piecewise linear regression methodology (PLR) and using a Microsoft Excel™ worksheet developed by Malash and El-Khaiary (2010).

2.5.2 Equilibrium experiments and modelling

The equilibrium experiments were carried out in 150 mL polypropylene tubes containing 5 mg L⁻¹ solutions of each pharmaceutical together with different doses of the selected AC (between 12.5 and 50.0 mg L⁻¹), which were shaken during enough time to guarantee equilibrium conditions, as determined in the kinetic experiments. More detailed adsorption experimental conditions are described in section 2.3.2.

Subsequently, the concentration of each pharmaceutical in the aqueous phase at the equilibrium C_e (mg L⁻¹) was determined and the amount of pharmaceutical adsorbed at equilibrium q_e (mg g⁻¹) was calculated similarly to q_t (mg g⁻¹) in Eq. 3, but replacing C_t (mg L⁻¹) by C_e (mg L⁻¹). Equilibrium data were described using the non-linear

models of Langmuir (1918) and Freundlich (1907) isotherms, respectively represented by Eq. (10) and (11):

$$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \quad (10)$$

$$q_e = K_F \times C_e^{1/n} \quad (11)$$

where q_m is the maximum adsorbed concentration of adsorbate at the equilibrium (mg g^{-1}), K_L is the Langmuir equilibrium constant (L mg^{-1}), $1/n$ is the exponent of non-linearity of Freundlich isotherm and K_F is the Freundlich equilibrium constant ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$). GraphPad Prism version 5.03 was used to perform the non-linear regression analysis and to determine the fitted equilibrium parameters for the considered models.

2.6 Pharmaceuticals quantification

The quantification of AMX and SMX in the aqueous phase was carried out by Micellar Electrokinetic Chromatography (MEKC) using a Beckman P/ACE MDQ (Fullerton, CA, USA) instrument, equipped with a UV/visible detection system and operated with the software 32 Karat 8.0. A bare silica capillary with 40 cm length (30 cm length to the detector), and 75 μm of internal diameter was coated with 0.5 % (w/v) of hexadimethrine bromide in 0.5 M sodium chloride after a previous treatment with sodium hydroxide 1 M. Samples and standard solutions were injected for 4 seconds at 0.5 psi and the electrophoretic separation was performed in direct polarity mode with a positive power supply of 25 kV during 5 min runs at 25 °C. The separation buffer consisted of 15 mM of sodium tetraborate and 30 mM of sodium dodecyl sulphate. Ethylvanillin was used as the internal standard; an ethylvanillin solution was prepared by dissolution in acetonitrile/water (10/90, v/v); such solution was added to all samples and standards to a rigorous final concentration of 3.3 mg L^{-1} . Capillary washing

between runs consisted of 1 min of ultra-pure water followed by 2 min of separation buffer. AMX and SMX concentrations were determined by calibration with seven standard solutions in the linear range of 0.25 to 5.0 mg L⁻¹. All samples and standard solutions were analysed in quadruplicate.

3. RESULTS AND DISCUSSION

3.1 Product yield of microwave-assisted production of carbon materials

The product yield (Eq. 1) was determined for the fourteen materials depicted in Table 1 and the results indicate that similar yields, ranging between 3.2 % and 4.4 %, were obtained for the materials produced using a KOH:PS ratio of 1:1 and pyrolysis temperatures of 600 and 700 °C. However, when increasing the pyrolysis temperature to 800 °C, a decrease was observed in the product yield, with values varying between 1.9 % and 2.8 %. These relatively low yields must be related to the high mass fraction of elemental carbon (46.69%) but small fixed carbon content (only 8.30 %) as well as large volatiles and ashes of PS (Table S1). In fact, similar yields to those obtained in this work were also reported by Jaria et al. (2019) when using the same precursor, namely PS, for the production of AC under conventional pyrolysis. These authors also observed a decrease of yield with increasing temperature (Jaria et al., 2019), which is due to a more complete carbonization (Zhao et al., 2017). Decreasing the KOH:PS ratio from 1:0.5 to 1:10 and maintaining the pyrolysis temperature at 800 °C, a variation in the product yield from 1.2 % to 19.7 % was observed. Liew et al. (2019) also verified that smaller impregnation ratios with NaOH-KOH (mixture activated agent) led to larger yields in the production of AC by microwave pyrolysis, which was associated to a reduction in the release of volatile carbon components such as CH₄, CO₂, or CO. The lower yields obtained when using larger activating agent quantities and higher pyrolysis temperatures, are indicative of the greatest decomposition/release of volatiles of PS due

to the reaction with the activating agent. For the biochar material (PS800-20), the product yield (21.6 %) was larger than for any of the produced AC.

3.2 Optimization of the microwave-assisted production of AC for the adsorption of AMX and SMX

3.2.1 Textural properties and TOC

The textural properties and TOC of the produced materials are depicted in Table 2. Carbonization of the KOH-impregnated PS occurred along with pyrolysis, so the resulting biochar and AC materials had high TOC contents, with values ranging between 55 % and 61 %, except for MW800-20-1:10, which presented a lower value (31 %). The relatively low TOC in MW800-20-1:10 must be related to the lower activating agent impregnation ratio (1:10), which might have caused a reduced carbonization. On the other hand, the produced materials presented an IC content below 3 % (data not shown), and these low values suggest that the acid washing step was effective in the elimination of both ashes produced in microwave pyrolysis and inorganic matter of the precursor itself.

Regarding the textural properties of the produced materials, the obtained results evidenced that S_{BET} values (Table 2) increased with the pyrolysis temperature. The materials produced at 600 °C presented S_{BET} from 654 to 740 $\text{m}^2 \text{g}^{-1}$, and these values increased up to 1208 $\text{m}^2 \text{g}^{-1}$ for the materials produced at 800 °C. Moreover, an increase in V_p and W_0 with pyrolysis temperature (within 600 and 800 °C) can be also observed in Table 2. Indeed, along with increasing pyrolysis temperature, an increase of S_{BET} and pore volume of resulting materials has been verified and related with a more extensive carbonization (Zhao et al., 2017). As for the pyrolysis time, within the interval of 10 to 20 min, no effects on the S_{BET} values or on the other textural properties were

observed. Furthermore, results in Table 2 showed that, under pyrolysis at 800 °C during 20 min, S_{BET} barely varied when increasing the KOH:PS ratio from 1:5 to 1:0.5. Thus, complete carbonization may have been attained under these conditions, and therefore, increasing pyrolysis time or KOH:PS ratio do not have evident effects on porosity. Nevertheless, this is as long as the ratio fairly ensures carbonization, since under pyrolysis at 800 °C during 20 min, for the KOH:PS ratio of 1:10 (MW800-20-1:10), a significant decrease in S_{BET} was clearly observed. The obtained S_{BET} was closer to that of the biochar material (PS800-20), indicating that the amount of activating agent was not enough to promote porosity development. The repeatability of the S_{BET} values of materials from different production batches was evaluated through the production of a second batch for the materials MW700-10-1:1, MW800-15-1:1 and MW800-20-1:5, which presented S_{BET} of 914, 1209 and 1084 $\text{m}^2 \text{g}^{-1}$, respectively. The similarity of such values with the ones presented in Table 2 for the first batch of the referred materials, constitutes a clear indication of the repeatability of the production procedure.

The obtained results highlighted that the pyrolysis temperature was the main parameter affecting the surface area of the produced materials, and that, within 600 and 800 °C, higher temperatures favour the production of AC with higher S_{BET} values. An increase of S_{BET} with pyrolysis temperature was also observed by Jaria et al. (2019) when using PS to produce AC by conventional pyrolysis at 650 and 800 °C. Likewise, these authors (Jaria et al., 2019) pointed out that, when using KOH and K_2CO_3 as activating agents, the 1:1 activating agent: PS ratio favoured porosity development and the production of AC with higher S_{BET} values as compared with the 1:10 ratio. Also, according with Calisto et al. (2014) the temperature of conventional pyrolysis was a key parameter in the development of porosity in biochar materials produced from primary and biological paper mill sludge, and, within 315 and 800 °C, the higher the temperature

the higher the S_{BET} . On the other hand, a residence time of 150 min under pyrolysis at 800 °C led to an increase of biochar S_{BET} as compared with 10 min (Calisto et al., 2014). However, using longer residence times (60 and 150 min), no effects were verified on the S_{BET} of AC produced from PS by Jaria et al. (2019) under conventional pyrolysis. . Therefore, as it was observed in this work, and also under conventional pyrolysis, temperature is the operational parameter that most affects porosity of AC produced from PS, with the residence time and the activating agent:precursor ratio having no remarkable effects as long as minimum requirements are fulfilled. However, it must be highlighted that such minimum requirements are lower under microwave-assisted pyrolysis, which needs significantly shorter residence times and activating agent:precursor ratios to ensure complete carbonization, in comparison to conventional pyrolysis. This is due to the microwave pyrolysis heat transfer mechanism, namely by the fact that heat is generated within the core of the target material by the interaction with microwaves and then evenly distributed (Foong et al., 2020).

3.2.2 Adsorptive percentage removal of AMX and SMX

Results from preliminary adsorption tests on the removal of AMX and SMX by the produced materials (Table 1) are depicted in Fig. 1. The biochar (PS800-20) revealed very low adsorption percentages, between 5 and 10 %, which is in agreement with the very low S_{BET} obtained for this material. On the other hand, the material was superior in S_{BET} values when compared to the biochar produced by conventional pyrolysis (Calisto et al., 2015). Concerning the performance of the materials produced at 600 °C, they presented adsorption percentages between 39 % and 45 % for AMX and between 21 % and 37 % for SMX. As for the materials produced at 700 °C, an increase in the adsorbed percentage of AMX and SMX was observed and the values obtained

ranged from 50 % to 72 %. The largest adsorption percentages were achieved with materials produced at 800 °C and using a KOH:PS ratio of 1:1, which provided removals ranging from 79 % to 87 % for AMX and from 66 % to 79 % for SMX. Furthermore, AC produced under a pyrolysis temperature of 800 °C during 20 min and with KOH:PS ratios of 1:0.5, 1:2 and 1:5 resulted in adsorptive removals between 85 % and 94 % for AMX and between 72 % and 80 % for SMX. Under pyrolysis at 800 °C, MW800-20-1:10 was the material presenting the poorest removals, which must be related, at least partially, with its relatively low S_{BET} ($432 \text{ m}^2 \text{ g}^{-1}$). Regarding the performance of a second batch (obtained under the same conditions) of MW700-10-1:1, MW800-15-1:1 and MW800-20-1:5 in the removal of SMX and AMX, it must be highlighted that the repeatability was quite satisfactory. The SMX adsorption percentage onto the second batch of MW700-10-1:1, MW800-15-1:1 and MW800-20-1:5 was 56.0, 70.1 and 84.6 %, respectively, while the AMX adsorption was 50.0, 80.0 and 75.6 %, respectively. These results compare very favourably with the ones presented for the first batch of referred materials in Fig. 1.

3.2.3 Principal component analysis

The PCA depicted in Fig. 2 showed that the AC produced at 800 °C and with different ratios of activating agent can be grouped since they showed similar responses regarding S_{BET} , TOC and percentage of adsorbed AMX and SMX. The only exception in this set of materials produced at 800 °C is MW800-20-1:10, which was beyond from the centre along with the biochar PS800-20, as they both present comparatively lower S_{BET} and SMX adsorption. These two materials occupy opposite positions in the PCA biplot, showing a strong correlation with the product yield, since they present the highest values (as described in section 3.1). On the other hand, materials produced at

600 °C can be also gathered in a group as they present relatively low S_{BET} values, removal percentages for both AMX and SMX and product yield. As for the materials produced using a pyrolysis temperature of 700 °C, they can be gathered together and classified as a group of materials showing intermediate values for the five analysed responses (TOC, S_{BET} , product yield, % of adsorption of AMX and SMX).

It can be inferred from the PCA graph (Fig. 2) that MW800-20-1:0.5, MW800-20-1:1, MW800-20-1:2 and MW800-20-1:5 presented the largest S_{BET} values and satisfactory removal percentages for both AMX and SMX. Based on this and considering that the preparation of MW800-20-1:5 requires much lower amounts of activating agent, which has a direct influence in the production cost and environmental impact, this material was selected for further studies. It must be also highlighted, that the activating agent: precursor ratios reported in the literature for the preparation of AC materials by conventional pyrolysis, are typically up to 1:0.2 (Alcañiz-Monge and Illán-Gómez, 2008; Lillo-Ródenas et al., 2007; Zuo et al., 2016), which are higher than the ratios used in the present work (Table 1).

3.3 Characterization of selected AC

SEM images obtained for the selected AC, namely MW800-20-1:5, are depicted in Fig. 3, together with images of the biochar (PS-800-20), which were obtained for comparison purposes. As it is possible to observe, using an activating agent (KOH) largely favoured the development of microporosity in MW800-20-1:5 (Fig. 3b), when compared with PS-800-20 (Fig. 3a). The material MW800-20-1:5 presented a relatively large pore diameter (D), i.e. 1.43 nm (Table 2), with different shapes and sizes. The morphologic features of this AC corroborate the higher values obtained for the total pore volume (V_p), i.e. $0.85 \text{ cm}^3 \text{ g}^{-1}$, when compared with that of $0.33 \text{ cm}^3 \text{ g}^{-1}$

(Table 2) for the biochar PS800-20. Also, AC has a microporous volume (W_0) larger than biochar, providing a higher surface area ($1196 \text{ m}^2 \text{ g}^{-1}$).

The analysis of surface functional groups of MW800-20-1:5 was performed using XPS survey and peak deconvolution for C 1s and O 1s. The corresponding peak assignments and binding energies are depicted in Table 3. Analysing the overall XPS spectra (Fig. S1) and the relative atomic contents, it was possible to verify that the surface of material was mainly composed by carbon (77%) and oxygen (20%).

The deconvolution of the XPS high resolution C1s spectrum resulted in five peaks with binding energies ranging between 284.4 eV and 290.6 eV. These binding energies were assigned to the graphitic Csp^2 (peak 1) (Nielsen et al., 2014; Velo-Gala et al., 2014), the C-Csp^3 bond of the edge of the graphite layer and phenolic, alcoholic and etheric carbon (peak 2), the C-O single bond in ether and alcohol groups (peak 3), the C=O bond of carbonyl, quinones and ketones (peak 4) and the $\pi-\pi^*$ transition in C (peak 5).

Concerning O 1s spectra, peak 1 with an energy binding of 532.7 eV is assigned to C=O in quinones and peak 2 at 532.6 eV is ascribed to C-O-H groups (Abd-El-Aziz et al., 2008). Two additional peaks were verified at 533.8 eV (peak 3) that can be attributed to oxygen atoms in carboxyl groups ($-\text{COOH}$ or COOR) and at 535.3 eV (peak 4) which might be attributed to physisorbed water (Velo-Gala et al., 2014).

3.4 AMX and SMX adsorption kinetics and equilibrium

3.4.1 Kinetic experiments and modelling

The study of AMX and SMX adsorption kinetics q_t (mg g^{-1}) vs t (min), allowed for the determination of the corresponding parameters and the assessment of the equilibrium time, which is an essential information for the practical application of the

produced material. In order to find the kinetic model that best described the adsorption of AMX and SMX onto MW800-20-1:5, fittings to the kinetic models of pseudo-first order, pseudo-second order and Elovich were determined (Fig. 4a). Furthermore, in order to evaluate the mechanism and rate-controlling steps affecting the sorption process, fittings to the Boyd's film diffusion (Fig. 4b) and Webber's intraparticle diffusion (Fig. 4c) models were used and piecewise linear regression (PLR) was applied to the experimental data. The fitted parameters for each of the considered models are listed in Table 4.

As it may be seen in Fig. 4a, results of q_t vs time are better explained by the Elovich model than by the pseudo-first or pseudo-second kinetic order models both for the adsorption of AMX and SMX. The determined kinetic parameters, depicted in Table 4, confirmed that fittings of experimental data to the pseudo-first and pseudo-second order models presented lower correlation coefficients (R^2) and higher standard deviation of the residuals ($S_{y/x}$) than the ones of Elovich model (the mathematical expressions of the error functions are described in SM). On the other hand, the Elovich model, which is known to describe well chemisorption processes, provided a very good fitting with correlation coefficients R^2 above 0.99 and with the lowest $S_{y/x}$, for both systems. The fitted values obtained for the initial adsorption rate constant α were $23 \pm 4 \text{ mg g}^{-1} \text{ min}^{-1}$ for AMX and $267 \pm 121 \text{ mg g}^{-1} \text{ min}^{-1}$ for SMX, suggesting that the adsorption surface reaction was faster in SMX. Besides that, the equilibrium was more quickly attained in SMX adsorption ($t \sim 120 \text{ min}$), while for AMX longer times were needed ($t \sim 400 \text{ min}$). Under comparable experimental conditions to this work, similar equilibrium times were determined for the adsorption of SMX onto AC produced from the same precursor (PS) (Silva et al., 2019) and also onto AC obtained from bleached and raw pulp derived from the paper production process (Oliveira et al., 2018). However, faster SMX adsorption (t

~30 min) was verified to occur onto biochar produced from PS (Calisto et al., 2015). Yet, conventional pyrolysis was used for the production of the materials of the above referred studies and, differently from this work, the obtained kinetic results on the adsorption of SMX reasonably fitted the pseudo-first and the pseudo-second kinetic order models (Calisto et al., 2015; Oliveira et al., 2018; Silva et al., 2019). To the best of authors' knowledge, there are no published results on the adsorption of AMX onto carbon materials produced using wastes from the paper industry as precursors. For microwave prepared AC from giant reed, using the same activating agent as in this work (KOH), faster AMX adsorption kinetics ($t \sim 120$ min) than the one verified in this work, with results fitted by the pseudo-second kinetic model, were determined by Chavid and Ahmed (2015). However, faster kinetics may be related, at least to some extent, to the higher experimental temperatures (30 °C), initial AMX concentrations (50 to 450 mg L⁻¹) and adsorbent dosage (500 mg L⁻¹) that were used by these authors (Chavid and Ahmed, 2015).

Regarding the diffusion-based models, the Boyd's plots (Bt vs t) (Fig. 4b) show good fittings ($R^2 \geq 0.983$), with a linear segment in the initial stage of the adsorption process for both AMX and SMX. The intercept values obtained for these antibiotics (Table 4) are significantly different from zero (with 95% confidence limits), suggesting that film diffusion is the rate controlling mechanism in the beginning (*ca.* 480 min for AMX and 60 min for SMX) of the adsorptive removal. For the Webber's plots (q_t vs $t^{1/2}$) obtained for both AMX and SMX (Fig. 4c), the inexistence of a straight line passing through the origin, is indicative that the intraparticle diffusion is not the only mechanism controlling the kinetic process. According to the PLR, two operational stages were defined for both AMX and SMX and each linear segment is an indication of multiple mechanisms controlling the adsorption process. The first linear stage, which

corresponds to the steep-sloped portion of q_t vs $t^{1/2}$ plot, reasonably described the results ($R^2 \geq 0.915$) and comprises t between 0 and 100 min for AMX and between 0 and 120 min for SMX. As it may be seen, this is a relatively fast initial stage involving the film diffusion and binding of AMX and SMX on the active sites distributed on the outer surface of MW800-20-1:5. Poorer fittings ($R^2 \leq 0.875$) were obtained for the second stage, which is slower and comprises the intra-particle diffusion of the target antibiotics on the porous structure of MW800-20-1:5, as the systems approaches equilibrium. Furthermore, the similar K_{id} fitted value obtained for AMX and SMX, in both stages, suggests that the molecular diffusion from the external surface into the pores of MW800-20-1:5 is similar for both pharmaceuticals. Overall, it may be said that both film diffusion and intraparticle diffusion mechanisms have an important role in the adsorption process of AMX and SMX onto MW800-20-1:5.

3.4.2 Equilibrium experiments and modelling

The adsorption isotherms, represented as the amount of each pharmaceutical adsorbed onto MW800-20-1:5 at equilibrium (q_e , mg g⁻¹) vs the amount of pharmaceutical remaining in solution (C_e , mg L⁻¹), are shown in Fig. 5, together with fittings to the models of Freundlich and Langmuir. For each of these models, the corresponding fitted parameters are depicted in Table 5.

As it may be seen in Fig. 5, equilibrium results on the adsorption of AMX and SMX onto MW800-20-1:5 are satisfactorily described by both the Langmuir and the Freundlich models, which is confirmed by the corresponding R^2 and $S_{y/x}$ depicted in Table 5. However, considering that Langmuir isotherm provided more satisfactory R^2 (≥ 0.98) and $S_{y/x}$ (< 10.5), the corresponding fitting parameters were selected for the subsequent discussion. In this sense, maximum adsorption capacities (q_m) achieved by

MW800-20-1:5 were 204 ± 5 mg g⁻¹ for AMX and to 217 ± 8 mg g⁻¹ for SMX. As for the K_L , which is related to binding energy and affinity (Kumar et al., 2019), the higher value determined for the adsorption of SMX (*ca.* two times) points to a stronger binding and a greater affinity of MW800-20-1:5 for SMX, when compared with AMX.

The q_m (mg g⁻¹) of MW800-20-1:5 towards AMX and SMX was compared with values determined for alternative waste-based and commercial AC recently reported in the literature regarding the adsorption of these pharmaceuticals (Table 6).

As it may be seen in Table 6, the here produced MW800-20-1:5 compared well with the alternative and commercial AC used for the adsorption of AMX and SMX in the literature, and displayed q_m that, in most of the cases, were similar or even higher. It should be highlighted that the adsorption capacities of MW800-20-1:5 for both AMX and SMX are larger than published values for the adsorption of these antibiotics by commercial activated carbons (Franco et al. 2017; Çalışkan and Göktürk, 2010; Silva et al., 2019). On the other hand, the q_m determined for the adsorption of AMX onto the AC produced from guava seeds by conventional pyrolysis (Pezoti et al., 2016) and for the adsorption of SMX onto the AC produced from almond shell by microwave pyrolysis (Zbair et al., 2018) stand out from the presented set of studies. However, it must be taken into account that these values were determined at the optimum pH (4 and 5, respectively, which are not common values for effluents from WWTPs), and studies on the adsorption of AMX and SMX onto MW800-20-1:5 were carried out at unadjusted. It is noteworthy that none of the alternative AC used for AMX adsorption (Table 6) is produced from industrial wastes. In the case of SMX adsorption, the AC produced by Silva et al. (2019) and Oliveira et al. (2018), who applied conventional pyrolysis using PS and bleached paper pulp, respectively, as precursors, displayed lower q_m for SMX than MW800-20-1:5 under the same experimental conditions.

Regarding the S_{BET} values, MW800-20-1:5 shows far superior values than all commercial ACs in Table 6. This is especially remarkable considering that MW800-20-1:5 was produced by microwave heating, which allows for shorter production times and energy savings and, consequently, lower energy costs relatively to conventional heating. Overall, it was here demonstrated the feasibility of producing efficient AC in the removal of antibiotics by microwave pyrolysis of industrial wastes such as PS.

CONCLUSIONS

Microwave-assisted pyrolysis of primary pulp and paper mill sludge was tested to produce carbon adsorbents and their adsorptive performance was evaluated towards the removal of AMX and SMX from aqueous solution. Chemical activation with KOH revealed to be determinant in the development of porosity and the pyrolysis temperature was essential to increase the specific surface area (S_{BET}) of the produced materials. The AC obtained under pyrolysis at 800 °C during 20 min and applying KOH:precursor ratio of 1:5 exhibited a microporous structure (as evidenced by the SEM images) and S_{BET} of 1196 m² g⁻¹. Therefore, the procedure developed in this work not only avoided the use of longer pyrolysis times, that can be extended to several hours in conventional furnaces, but also the use of higher proportions of activating agent typically used in the production of AC. The kinetic experimental data were adequately described by the Elovich reaction-based model. As for the diffusion-based models, both film and intraparticle diffusion mechanisms were involved in the adsorption process of AMX and SMX onto MW800-20-1:5. The equilibrium isotherms were adequately described by the Langmuir models, with maximum monolayer adsorption capacities of 204 mg g⁻¹ and 217 mg g⁻¹ for AMX and SMX, respectively, which point to comparable or better performances than commercial and waste-based AC in the literature.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The corresponding author, on the behalf of all the authors

Vânia Glist

Figure Captions

Fig. 1. Adsorption percentage of amoxicillin (AMX) and sulfamethoxazole (SMX) obtained for one biochar and thirteen AC materials. Experimental conditions: 5 mg L⁻¹ of AMX and SMX (single solutions), material dose of 25 mg L⁻¹, stirring overnight (80 rpm) at 25.0 °C ± 0.1 °C. Note: Error bars stand for standard deviations, n = 3.

Fig. 2. Biplot of PCA - PC1 and PC2 account, respectively, for 67.6 % and 23.6 % of the variability. Note that, for simplicity and to allow a better visualization of the PCA groups, the materials nomenclature was simplified (the prefix MW was eliminated).

Fig. 3. SEM images of a) PS800-20 and b) MW800-20-1:5 at magnifications of 3 000x, 10 000x and 50 000x.

Fig. 4. Kinetic modeling of the experimental data on the adsorption of AMX and SMX onto MW800-20-1:5 using reaction-based models, namely pseudo-first order, pseudo-second order and Elovich models (a) and diffusion-based models, namely Boyd's film diffusion (b) and Weber's intraparticle diffusion (c) models. For simplicity, the standard deviation was omitted (RSD <10%) in Boyd's film diffusion. Note that x and y-axis scales are not the same in all graphs to allow a better visualization of the results. Experimental conditions: 5 mg L⁻¹ of AMX and SMX (single solutions), material dose of 15 mg L⁻¹, stirring (80 rpm) at 25.0 °C ± 0.1 °C. Note: Error bars stand for standard deviations, n = 3.

Fig. 5. Equilibrium experimental data and fittings to Langmuir and Freundlich models from ultra-pure water. Experimental conditions: 5 mg L⁻¹ of AMX and SMX (single

solutions), material doses between 12.5 and 50 mg L⁻¹, stirring (80 rpm) at 25.0 °C ± 0.1

°C. Note: Error bars stand for standard deviations, n = 3.

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Table 1. Experimental conditions tested to produce carbon materials and corresponding nomenclature.

Carbon Materials	Variables		
	Temperature (°C)	Residence time (min)	KOH:PS (w/w)
MW600-10-1:1	600	10	1:1
MW600-15-1:1	600	15	1:1
MW600-20-1:1	600	20	1:1
MW700-10-1:1	700	10	1:1
MW700-15-1:1	700	15	1:1
MW700-20-1:1	700	20	1:1
MW800-10-1:1	800	10	1:1
MW800-15-1:1	800	15	1:1
MW800-20-1:0.5	800	20	1:0.5
MW800-20-1:1	800	20	1:1
MW800-20-1:2	800	20	1:2
MW800-20-1:5	800	20	1:5
MW800-20-1:10	800	20	1:10
PS800-20 (biochar)	800	20	-

Table 2. Total organic carbon (TOC), specific surface area (S_{BET}) and textural properties (V_p – total pore volume; W_0 – micropore volume; L – average micropore width; D – average pore diameter) of the produced carbon materials.

Carbon materials	TOC (%)	N ₂ Adsorption at -196 °C				
		S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	D (nm)	Dubinin–Astakhov	
					W ₀ (cm ³ g ⁻¹)	L (nm)
MW600-10-1:1	60.7 ± 0.6	727	0.54	1.48	0.32	1.59
MW600-15-1:1	58.7 ± 0.2	790	0.57	1.45	0.36	1.57
MW600-20-1:1	56 ± 1	654	0.47	1.43	0.28	1.56
MW700-10-1:1	58 ± 1	1006	0.68	1.36	0.46	1.56
MW700-15-1:1	59.6 ± 0.6	1040	0.70	1.35	0.48	1.60
MW700-20-1:1	56 ± 1	1028	0.69	1.34	0.48	1.59
MW800-10-1:1	58 ± 0.3	1208	0.83	1.38	0.57	1.63
MW800-15-1:1	61.2 ± 0.7	1191	0.83	1.39	0.56	1.62
MW800-20-1:0.5	55 ± 3	1159	0.81	1.39	0.55	1.68
MW800-20-1:1	60.9 ± 0.1	1133	0.79	1.39	0.53	1.63
MW800-20-1:2	59 ± 2	1284	0.83	1.29	0.61	1.67
MW800-20-1:5	56 ± 2	1196	0.85	1.43	0.57	1.69
MW800-20-1:10	31.4 ± 0.4	432	0.37	1.26	0.20	1.57
PS800-20	60 ± 3	238	0.33	2.80	0.11	1.72

Table 3. X-ray photoelectron spectroscopy (XPS) results.

	Peak	Binding Energy (eV)	%	Possible bond assignment
C 1s	1	284.4	58.1	C sp ² , graphitic carbon
	2	285.2	15.7	C–C sp ³ , C–(O, N, H): phenolic, alcoholic, etheric carbon
	3	286.5	12.5	C–O single bond, ether, and alcohol groups
	4	287.5	13.8	C=O: carbonyl, quinones and ketones
	5	290.6	5.8	π–π* transition in C
O 1s	1	532.7	72.4	C=O, quinones
	2	532.5	17.3	C–O–H
	3	533.8	9.1	Oxygen, –COOH or COOR
	4	535.5	1.0	Physiosorbed water

Table 4. Fitting parameters of reaction-based models (pseudo-first order, pseudo-second order and Elovich) and diffusion-based models (Boyd's film diffusion and Webber's intraparticle diffusion).

	Reaction models			Diffusion models	
	<i>Pseudo-1st order</i>	<i>Pseudo-2nd order</i>	<i>Elovich</i>	<i>Boyd's film diffusion</i>	<i>Webber's intraparticle diffusion</i>
AMX	k_1 (min ⁻¹) 0.025±0.005	k_2 (g mg ⁻¹ min ⁻¹) 0.00019±0.00003	α (mg g ⁻¹ min ⁻¹) 23±4	Intercept (mg g ⁻¹) 0.1627	1 st Stage k_{id} (mg g ⁻¹ min ^{-1/2}) 12.3
	q_e (mg g ⁻¹) 171±8	q_e (mg g ⁻¹) 186±6	β (g mg ⁻¹) 0.033±0.001	Interval of Intercept (mg g ⁻¹)	R ² 0.9149
	R ² 0.9128	R ² 0.9691	R ² 0.9945	[0.0100; 0.3086] *	2 nd Stage k_{id} (mg g ⁻¹ min ^{-1/2}) 2.86
	$S_{y/x}$ 19.52	$S_{y/x}$ 11.61	$S_{y/x}$ 4.88	R ² 0.9825	R ² 0.8733
SMX	k_1 (min ⁻¹) 0.10±0.04	k_2 (g mg ⁻¹ min ⁻¹) 0.0007±0.0002	α (mg g ⁻¹ min ⁻¹) 2.67±1.21	Intercept (mg g ⁻¹) 0.2995	1 st Stage k_{id} (mg g ⁻¹ min ^{-1/2}) 11.4
	q_e (mg g ⁻¹) 210±14	q_e (mg g ⁻¹) 227±12	β (g mg ⁻¹) 0.32±0.003	Interval of Intercept (mg g ⁻¹)	R ² 0.9971
	R ² 0.8649	R ² 0.9413	R ² 0.9889	[0.1698; 0.4292] *	2 nd Stage k_{id} (mg g ⁻¹ min ^{-1/2}) 2.28
	$S_{y/x}$ 30.94	$S_{y/x}$ 20.39	$S_{y/x}$ 8.5	R ² 0.9936	R ² 0.7914

* 95 % confidence interval

Table 5. Fitting parameters corresponding to the equilibrium isotherm Langmuir and Freundlich models for the adsorption of AMX and SMX onto MW800-20-1:5.

Isotherm models		
	<i>Langmuir</i>	<i>Freundlich</i>
AMX	q_m (mg g ⁻¹) 204±5	K_F (mg g ⁻¹ (mg L ⁻¹) ^{1/n}) 137±4
	K_L (L mg ⁻¹) 2.4±0.2	n 3.5±0.4
	R ² 0.9909	R ² 0.9610
	$S_{y/x}$ 5.41	$S_{y/x}$ 11.21
SMX	q_m (mg g ⁻¹) 217±8	K_F (mg g ⁻¹ (mg L ⁻¹) ^{1/n}) 172±2
	K_L (L mg ⁻¹) 4.9±0.9	n 4.6±0.5
	R ² 0.9772	R ² 0.945
	$S_{y/x}$ 10.41	$S_{y/x}$ 5.13

Table 6. Comparison of the adsorption capacities and SBET of MW800-20-1:5 and other waste-based and commercial AC for the adsorptive removal of AMX and SMX from water. Maximum adsorption capacities (q_m (mg g⁻¹)) determined by the Langmuir model.

Pharmaceutical	Material	Pyrolysis type	Experimental adsorption conditions (material dose; temperature; pH)	Pharmaceuticals initial concentration (mg L ⁻¹)	q_m (mg g ⁻¹)	S_{BE} (m ² g ⁻¹)	Reference	
AMX	AC from guava seeds	Conventional	1 g L ⁻¹ ; 25 °C; pH 4	50-800	570	257	(Pezoti et al., 2016)	
	AC from vinewood		0.4 g L ⁻¹ ; 25 °C; pH 2	20-200	2.6	13	(Pouretedal and Sadegh, 2014)	
	AC from olive stone		1 g L ⁻¹ ; 25 °C; pH not adjusted	12.5-100	57	117	(Limousy et al., 2017)	
	AC from marine alga		0.60 g L ⁻¹ ; 25 °C; pH 7	25-200	265	484	(Balarak et al., 2017)	
	AC from date pits	Microwave	1 g L ⁻¹ ; 22 °C; pH not adjusted	20-700	319	106	(Belhache mi and Djelaila, 2017)	
	AC from giant reed		0.1 g L ⁻¹ ; 29 °C; pH 7	50-450	249.3	106	(Chayid and Ahmed, 2015)	
	Biochar from giant reed		0.1 g L ⁻¹ ; 29 °C; pH 7	50-450	92	106	(Chayid and Ahmed, 2015)	
	AC from paper mill sludge (MW800-20-1:5)		0.0125-0.05 g L ⁻¹ ; 25 °C; pH not adjusted	5	204	119	This study	
	Commercial granular AC		-	12.5 g L ⁻¹ ; 25 °C; pH 7	10-1000	3.1	462	(Franco et al., 2017)
	SMX		AC from primary paper mill sludge	Conventional	0.008-0.050 g L ⁻¹ ; 25 °C; pH not adjusted	5	194	162
AC from bleached paper pulp		0.035-0.30 g L ⁻¹ ; 25 °C; pH not adjusted	5		110	965	(Oliveira et al., 2018)	
Functionalized biochar		0.010 g L ⁻¹ ; 21 °C; pH not adjusted	0.5-50		81	1.1	(Ahmed et al., 2017)	
AC from walnut shell		Microwave	0.010 g L ⁻¹ ; 30 °C; pH 5.5	0.5-40	93	934	(Teixeira et al., 2019)	
AC from almond shell			0.01 g L ⁻¹ ; 25 °C; pH 5	5-100	345	127	(Zbair et al., 2018)	
AC from			0.0125-0.05	5	217	119	This study	

	paper mill sludge (MW800- 20-1:5)		g L ⁻¹ ; 25 °C; pH not adjusted			6	
	Commercial AC	-	0.02-0.8 g L ⁻¹ ; 25 °C; pH not adjusted	20	185	851	(Çalışkan and Göktürk, 2010)
	Commercial AC	-	0.008-0.050 g L ⁻¹ ; 25 °C; pH not adjusted	5	118	996	(Silva et al., 2019)

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HIGHLIGHTS

- Microwave-assisted production of activated carbons (ACs) was optimized
- Amoxicillin (AMX) and sulfamethoxazole (SMX) adsorption by produced ACs was tested
- Optimized conditions were 20 min pyrolysis at 800 °C and KOH:precursor ratio of 1:5
- Kinetic and equilibrium studies were done for the selected AC ($S_{BET} = 1196 \text{ m}^2 \text{ g}^{-1}$)
- Maximum adsorption capacities of 204 mg g^{-1} (AMX) and 217 mg g^{-1} (SMX) were attained