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Comparison between two forms of granular activated carbon for the removal of pharmaceuticals from different waters

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ABSTRACT

The aim of this study was to evaluate the performance of two forms of basic granular activated carbon (GAC), mineral (pH = 10.5) and vegetal (pH = 9), for the removal of three pharmaceuticals, as sulphamethoxazole (SMX), diclofenac (DCF) and 17β-estradiol (E2), from two different matrices: fortified distilled (2.4–3.0 mg L^{-1} and pH from 5.5 to 6.5) and natural (~1.0 mg L^{-1} and pH from 7.1 to 7.2) water in a bench scale. The Rapid Small-Scale Column Test used to assess the ability of mineral and vegetal GAC on removal of such pharmaceuticals led to removal capacities varying from 14.9 to 23.5 mg g^{-1} for E2, from 23.7 to 24.2 mg g^{-1} for DCF and from 20.5 to 20.6 mg g^{-1} for SMX. Removal efficiencies of 71%, 88% and 74% for DCF, SMX and E2, respectively, were obtained at breakthrough point when using mineral GAC, whereas for the vegetal GAC the figures were 76%, 77% and 65%, respectively. The carbon usage rate at the breakthrough point varied from 11.9 to 14.5 L g^{-1} for mineral GAC and from 8.8 to 14.8 L g^{-1} for vegetal GAC. Mineral CAG also exhibited the best performance when treating fortified natural water, since nearly complete removal was observed for all contaminants in the column operated for 22 h at a carbon usage rate of 2.9 L g^{-1}.

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Introduction

Negative environmental impacts caused mainly by incorrect disposal of waste in the aquatic environment result from the technological progress and from industrial growth, thus affecting both the biota and the quality of natural water that could be used for public supply. So, the challenge to obtain drinking water grows due to the deterioration of surface water sources and the progressively more restrictive drinking water standards. The solution frequently lies in the choice of water sources distant from the town centre, which increases considerably the water conveyance costs.

Under the prospective deterioration of water bodies, the discharge in the environment of pharmacologically active substances extensively used in the treatment of diseases in human beings and animals is worthy of mention. After the administration, a significant part of these compounds is excreted by human beings in the domestic wastewater. Several of these substances seem to be persistent in the environment and are not completely removed in the wastewater treatment plants.[1–3]

Antibiotics, like sulphamethoxazole, are a group of pharmaceuticals which require special attention, as their extensive use makes some microorganisms, usually bacteria, more resistant, from successive changes to their genetic material. In this sense, bacteria present in water bodies containing traces of antibiotics may become resistant to these substances, which compromises the public health.[4]

Diclofenac is one of the most used drugs in human medical care, and has been prescribed as an analgesic, antiarthritic and antirheumatic compound. In addition, it has been widely detected in aquatic environments throughout the globe[5] and the European Union Parliament has approved Directive 2013/39 which includes diclofenac in the first Watch List since the information available indicates it may pose a significant risk.[6]

Another large group to be emphasized is the hormones or endocrine disrupters, exogenous agents that interfere with the endocrine system, which is regarded as responsible for the maintenance of usual biological functions of the organisms by synthesis and secretion of hormones.[7] Sanderson et al.[8] have studied the toxicity of some substances and demonstrated that the sexual hormones are the most toxic for several aquatic organisms, such as cladocera, fish and algae. These

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synthetic hormones are compounds that perform their functions even in extremely low concentrations, being potentially dangerous to the aquatic biota of the locations where either treated or untreated wastewater is discharged. Besides that, there are no doubts that some endocrine disrupters, like estradiol, cause adverse effects on human beings, particularly on those with their endocrine system under development.[9]

Monitoring assessments have detected the presence of these organic contaminants in natural waters in several regions of the planet. The highest concentrations of pharmaceuticals have been found in Germany, as studied by Ternes et al.[10] and the presence of diclofenac and sulphamethoxazole has been detected at concentrations of 1200 and 480 ng L^{-1}, respectively. In France, these same pharmaceuticals have been detected at concentrations of 430, 41 and 133 ng L^{-1}, respectively.[10] A recent monitoring of 18 pharmaceuticals in 7 sampling points in one of the four largest rivers in the Malay Peninsula (Langat River) has identified concentrations of diclofenac close to 188 ng.L^{-1}, with detection frequency of 67%.[11] This pharmaceutical has been extensively used in several countries as a non-steroidal anti-inflammatory drug.

In Minas Gerais State (Brazil) the one-year monitoring period of three water sources showed that 4-nonylphenol was detected in all samples in a concentration range of 44–1918 ng L^{-1}, whilst the natural and synthetic estradiols were hardly detected (only in $\approx$ 15% of samples) and always in low concentrations (2–54 ng L^{-1}).[12]

A monitoring performed in the three water sources of the Metropolitan Region of Belo Horizonte, responsible for the water supply to 3.3 million people, showed the presence of estradiol in 15% of the samples at concentrations that varied from 1.5 to 50 ng.L^{-1}. [13,14]

Recognizing the limitations of the conventional water treatment process – usually consisting of coagulation, flocculation, sedimentation or flotation, filtration and disinfection units – for removal of organic contaminants has fostered the development of technologies specific for that purpose.[15] Membrane filtration, advanced oxidative processes and adsorption on activated carbon are worthy of mention. The construction and maintenance cost of the two first technologies tends to be favourable to the use of the adsorption, mainly in bigger treatment plants in which water sources are more compromised.[16]

The activated carbon can be used either powdered (PAC) or granular (GAC). PAC is usually used in the flocculation or rapid mix units, and GAC is used as post-treatment, preceding the final disinfection, fluoridation and pH correction. Removal by activated carbon is performed by the adsorption process, in which the adsorbate is accumulated on the surface of the adsorbent by means of physical and/or chemical forces of nature. Recently, carbon nanotubes have also been used as promising systems for a variety of applications, including as ‘filters’ for the removal of organic microcontaminants.[17]

GAC filters are rarely employed in water treatment plants in Brazil, despite their extensive use in residential and industrial water treatment units. However, the continuous presence of these organic contaminants and the fact that 69.5% of the flow rate of treated water distributed to the Brazilian population – approximately 510 $m^3 s^{-1}$ – comes from conventional treatment plants[18] reinforce the need for studies that evaluate the actual effectiveness of such technology. A recent work published by Meinel et al.[19] has shown that GAC filters were effective to remove pharmaceuticals, such as carbamazepine, diclofenac and 4-formylaminoantipyrine, and chemical pollutants such as benzotriazole and methylbenzotriazole, from contaminated water.

GAC filters may be used upstream of the water treatment plant, an alternative that – like the application of PAC in the water intake unit – will make the regeneration more frequent due to the adsorption of compounds liable to being removed in the coagulation. The second alternative, more usually employed in plants in developed countries, refers to the use of GAC filter as a polishing unit, implemented downstream of the filters. At last, another possibility would be the use of the so-called sandwich filters, in which a 40 cm GAC layer is inserted inside the filter medium, approximately 30 cm below the top.

In view of that, this work has aimed at evaluating the efficiency of two forms of GAC, vegetal and mineral, in the removal of sulphamethoxazole, diclofenac and 17β-estradiol from fortified (natural and distilled) water in bench scale. In order to explain which interactions might occur between the pharmaceuticals and the carbons, this study specially considered the pH of the water (from 5.5 to 6.5 for distilled water; and from 7.1 to 7.2 for natural water) and of the carbons (10.5 for mineral and 9.0 for vegetal) tested. Additionally, the influence of intrinsic characteristics of natural water was also analysed in relation to the efficiency of adsorption after its clarification with polyaluminum chloride (PAC) as primary coagulant.

Methodology

Characterization and quantification of the pharmaceuticals studied

Three pharmaceuticals – sulphamethoxazole, diclofenac and 17β-estradiol – belonging to miscellaneous classes and significantly present in surface waters, have been chosen in this study. Table 1 presents the physical-chemical characteristics of each compound studied.

Sulphamethoxazole (SMX), named 4-amino-N-(5-methyl-1,2-oxazol-3-yl) benzenesulphonamide by IUPAC, is a bacteriostatic antibiotic belonging to the sulphonamide group. This pharmaceutical is mainly applied to the treatment of infections by bacteria susceptible to its effect, like some species of *Streptococcus*, *Staphylococcus aureus*, *Escherichia coli* and *Haemophilus influenzae*. Diclofenac (DCF), traded as a salt and named sodium 2-[2-(2,6-dichloroanilino)] phenylacetate by IUPAC, represents the class of non-steroidal anti-inflammatory pharmaceuticals. This small, low-lipophilic molecule is largely used in the treatment of inflammations, rheumatic diseases and painful diseases of non-rheumatic origin. This pharmaceutical has been frequently detected in effluents from wastewater treatment plants.[20,21] 17β-estradiol (E2), named (8R,9S,13S,14S,17S)-13-methyl-6,7,8,9,11,12,14,15,16,17 decahydrocyclopenta[a] phenanthrene-3,17-diol by IUPAC, is the main estrogen produced by the ovaries, ordinarily known as the female sex hormone. This organic compound is produced at high levels during pregnancy and excreted at the rate of 2.4 µg day^{-1} by pregnant women.[22]

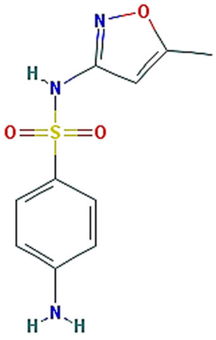
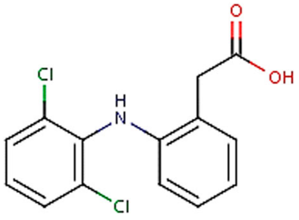
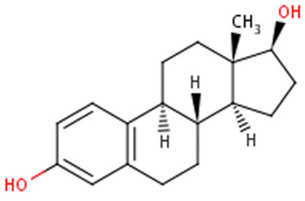
The organic contaminants used in this study have been quantified either by spectrophotometry (tests with distilled water) or by liquid chromatography coupled to mass spectrometry (tests with natural water). Solutions containing just one pharmaceutical (single component) were prepared in the tests with distilled water, and as the concentration was high (2.4–3.0 mg L^{-1}), the quantification could be performed in a BEL Photonics® UV–VIS spectrophotometer after the determination of the maximum adsorption wavelengths of each pharmaceutical (267 nm for SMX, 256 nm for DCF and 224 nm for E2).

In the tests with natural water, DCF, E2 and SMX were simultaneously added to the aqueous matrix so that the initial concentration of each pharmaceutical was 1.0 mg L^{-1}. The quantification has been performed in a liquid chromatography coupled to mass spectrometry apparatus (HPLC-MS); however, since the analyte concentrations were relatively high, it was not necessary to perform the analyte extraction step – which is usual in the preparation of environmental samples for chromatographic quantification. It is because the concentrations of influent and effluent contaminants range approximately from 50 to 1000 µg L^{-1}, thus allowing their analysis by direct injection (after sample filtration for solids removal) in the HPLC-MS equipment and thereby minimizing analytical errors.

The liquid chromatographer was fitted with a binary pump system (model LC-20AD Shimadzu) and an automatic sampler. The mass spectrometer (Shimadzu LC/IT/TOF) used ensured high sensitivity and resolution in the attainment of spectra. Two forms of ionization have been used in this study, the electrospray ionization (ESI) and the atmospheric pressure chemical ionization (APCI), and in both sources a voltage of − 3.5 kV was used in the negative and + 4.5 kV in the positive ionization mode.

The chromatographic separation was performed by the Kinetex C18 chromatographic column (50 × 3.0 mm; 2.6 µm – Phenomenex), with temperature of the oven at 40° C. The run time was 28 min and the volume of the injected sample was 10 µL. The aqueous phase was

Table 1. Physical-chemical characteristics of the organic contaminants assessed in the study.[23]

	Sulphamethoxazole	Diclofenac	17β-Estradiol
Molecular formula	$C_{10}H_{11}N_3O_3S$	$C_{14}H_{11}Cl_2NO_2$	$C_{18}H_{24}O_2$
Molecular structure			
C.A.S.	723–46–6	15307–86–5	50–28–2
M.M. (g mol^{-1})	253.277	296.150	272.382
Maximum length (Å)	12.259	10.841	11.518
pK_a	1.6 and 5.7	4.15	10.2
Log K_{ow}	0.89	4.51	4.01
K_{bio}	5.9–7.6	0.1	550–950
K_d	0.37–4.6	0.72	115.8

3.5 mM ammonia hydroxide solution and the organic phase was methanol, as per gradient optimized by Rodrigues et al.[14] Calibration curves were built with the standard solutions of each of the three organic contaminants and each curve had at least 8 points comprising the concentration range from 0.05 to 1.0 mg.L^{-1}. The resulting calibration curves presented coefficients of determination (R^2) of 0.9997 (SMX), 0.9987 (DCF) and 0.9973 (E2).

Characteristics of the waters and clarification tests

For each test in distilled water, concentrations ranging from 2.4 to 3.0 mg.L^{-1} of sulphamethoxazole standard (100%), of sodium diclofenac standard (99.9%) and of 17β-estradiol standard (98%) have been diluted, all of the Sigma-Aldrich® make. For distilled water, pharmaceuticals have been dissolved separately, for individual evaluation of the adsorption efficiency on GAC.

Natural water used in this study was obtained from a stream (Córrego do Maracujá, Rio das Velhas Basin) in the city of Ouro Preto, Minas Gerais, Brazil. This water has usually high turbidity (> 200 uT) in the rainy season and relatively low turbidity (< 10 uT) in the dry season. Furthermore, this water normally contains organic and inorganic matter (suspended and dissolved) such as fragments of clay, silt, plankton, microorganisms and by-products of microbiological degradation.

Concentrations of 1.0 mg L^{-1} of three pharmaceutical standards were simultaneously dissolved, aiming at prioritizing their removal by GAC adsorption. The adsorption tests have been preceded by clarification (coagulation, flocculation and sedimentation) by using polyaluminum chloride as primary coagulant. The characteristics of the natural water are presented in Table 2.

In the clarification treatment performed on jar test equipment, the conditions optimized by Lima et al. [15] were used for low-turbidity natural water. The acrylic jars were replaced by glass jars for all the clarification tests, thus minimizing the adsorption of the contaminants and the probability of errors during the tests.

The operational parameters of the clarification tests, presented in Table 3, have been defined according to the recommendations of the Brazilian Technical Standards Association, which establishes the conditions for design of water treatment plants. [24]

Table 2. Mean and standard deviation of the physical-chemical characteristics of the natural water used in the study ($n = 6$).

Parameter	Mean ± Standard deviation
Turbidity (ntu)	12.1 ± 1.3
Apparent colour (Hu)	41.2 ± 4.0
True colour (Hu)	35.5 ± 1.5
Conductivity (μS cm^{-1})	157.2 ± 1.4
Temperature (°C)	20.0 ± 0.5
pH	7.2 ± 0.1
Alkalinity (mg L^{-1} $CaCO_3$)	13.2 ± 2.7

The use of distilled water in the adsorption tests has been associated with the usual employment of the granular activated carbon filters as post-treatment, liable to be implemented in existing plants. As low-turbidity filtered water – usually lower than 0.5 ntu, in conformity with the Brazilian drinking water standard – will flow to these plants, the characteristics of the influent will become less different from those of the treated natural water.

Adsorption tests on GAC columns

The adsorption tests have been performed in the experimental apparatus shown in Figure 1 and the sampling points have been defined from the influent and effluent of both columns. The apparatus used the parallel configuration, containing two 1.0 cm internal diameter columns (50 mL capacity burette), one for each type of bed (mineral GAC and vegetal GAC). A 1.0 L amber flask was used for storage of the influent solution that was continuously stirred by a Fisatom® magnetic stirrer. New silicone hoses were used for connection of the system, which were replaced whenever a new test was started. The influent to the columns was delivered by a Milan® peristaltic pump, and the flow rate was controlled at least three times a day to avoid sudden changes that could compromise the reproducibility of the experiments. Samples were initially collected for analysis at the first 1.0 min and after that, every 240 min, until the exhaustion of each bed. Sterile beakers were used to collect samples, which were transferred to 1.5 mL vials and then frozen to be posteriorly analysed on HPLC-MS.

Temperature, pH, electric conductivity (Methrom® potentiometer) and the concentration of the targeted pharmaceuticals were determined in each sampling, as previously described.

Table 3. Operational parameters used for the clarification tests with natural water.

Coagulation		Flocculation		Sedimentation
Rapid mix time (s)	Rapid mix velocity gradient (s^{-1})	Flocculation time (min)	Flocculation velocity gradient (s^{-1})	Sedimentation rate (cm min^{-1})
15	600 ± 20	20	35 ± 5	2.0

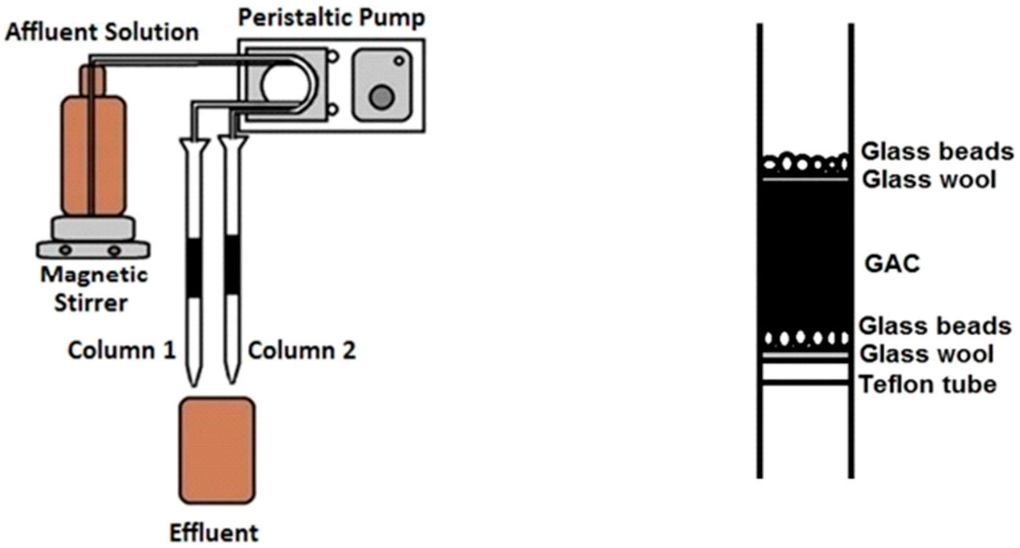


Figure 1. Schematic drawing of the experimental apparatus used in the adsorption tests.

Preparation of the activated carbon and assembly of the adsorption columns

With the purpose of considering the proportional diffusivity in the tests, both the mineral and the vegetal GAC, which originally had a 8 × 30 mesh grain size, were ground and screened in a 60 × 80 mesh, which resulted in grains with average diameter of 0.214 mm. Later on, the recommendations of the standards ASTM D6586-03 and ASTM D3922-89 were followed.[25,26]

A GAC sample (approximately 50 g) was carefully washed in ultrapure water, and after that it was screened in 60-mesh and 80-mesh screens. This washing process was repeated until the pH of the water was kept constant. After that, the GAC sample was dried in an oven at 150°C for 240 min. After drying, the sample was placed in a desiccator to have all the moisture removed, and after cooling it was appropriately stored in an amber flask. Prior to filling the columns with carbon, 40 mL of ultrapure water was added to the previously washed and weighed sample, followed by stirring. The system was led to vigorous boiling for 10 min to remove the air from the pores of the carbon. After that, the sample was left at rest until the room temperature was reached. This procedure was performed for both types of GAC, prior to their introduction in the columns.

A small Teflon tube was inserted in the burette to support the GAC bed and, after that, a thin glass wool layer (to prevent the adsorbent from passing through), some glass beads and, at last, the previously washed GAC bed were added. The GAC was carefully added in the column, with a water layer being always kept above the adsorbent during the transfer. At last, a thin glass wool layer was laid again, followed by some glass beads to prevent the adsorbing particles of the bed from floating and allow the uniform distribution of the influent. This scheme is seen in Figure 1(b).

After being built, the columns were fed upwards with ultrapure water, at the flow rate of approximately 2.0 mL min^{-1}, for the carbon particles to settle down and for removal of the air. After that, the experimental apparatus was assembled, and ultrapure water was then poured down flow at the desired flow rate, until the system was stabilized. After the stabilization, the columns were finally fed with the fortified solutions.

Dimensioning of the columns

The dimensioning parameters of the Rapid Small-Scale Column Test (RSSCT) columns (Table 4), identical for both the mineral and vegetal carbons, have been calculated from data from pilot adsorption systems by equations suggested in the literature.[27–30]

The column adsorption tests were based on the standard ASTM D6586-03 named RSSCT, using the EBCT – Empty Bed Contact Time and the hydraulic load to describe the adsorption process. The mean diameter of the carbon particle is used to dimension the column and estimate the performance of the adsorbent in a large scale. The main advantages of this method for estimation of GAC performance are: (i) the RSSCT system can be performed in a short time, when compared to the pilot column; (ii) it is not necessary to estimate mathematical models, as well as isotherms of longer

Table 4. Dimensioning parameters of the RSSCT columns for tests with GAC.

Parameter	Unity	Pilot Scale	GAC columns
Carbon granulometry	Mesh	8–30	60–80
	mm	0.59–2.38	0.177–0.250
Carbon mass	g	–	2.89 a 3.55
Average particle diameter	mm	1.485	0.214
Apparent density	g cm^{-3}	0.59	0.55
Empty bed contact time	min	5	0.720
Surface loading rate	m h^{-1}	5	5
	m^3 m^2 day^{-1}	120	120
Flow	mL min^{-1}	–	6.5
Reynolds number	–	3.61	0.55
Column diameter	cm	–	1.0
Carbon thickness	cm	–	3.6
Carbon volume	cm^3	–	4.71
Porosity of carbon	–	0.57	0.54

preparation or kinetic studies and (iii) a small water volume is required to perform the RSSCT, thus facilitating the conveyance of this water to the laboratory.[31]

Characterization of the carbons

The mineral GAC, made of bituminous material, and the vegetal GAC, made of coconut shell, were produced by Carbosolution LTDA, a Brazilian industry. They were characterized by determining the point of zero charge (PZC) and the main functional surface groups by spectrometry in the infrared region. The PZC was determined according to procedures detailed in Valdés et al.[32] For that purpose, six erlenmeyers containing different masses of GAC, with the initial pH adjusted to 3.0 with HNO3 0.1 M or NaOH 0.1 M, were submitted to constant stirring (130 rpm) at room temperature for 24 h, in order to ensure a balanced interaction with the water molecules. After that time, the pH was measured again and the data were used to prepare a chart relating the mass percentage of GAC to the final pH of the solution. This procedure was repeated by changing the initial pH to 7.0 and then to 11.0.

The infrared spectra (FTIR) were obtained in a Shimadzu IRAffnity-1 equipment fitted with a DLATGS (deuterated triglycine sulphate doped with l-Alanine) detector and a fixture for analysis by diffuse reflectance, as per procedures detailed in Teixeira et al.[33] The identification of the possible chemical bonds was made based on Nakanishi.[34]

Statistical analysis of the adsorption results

After the rupture curves for each test with distilled water have been obtained, the adsorption capacity was calculated by Equation 1.

$$q_R = \frac{V}{M}(C_0 - C_R), \tag{1}$$

in which q_R is the adsorption capacity at the point of rupture (mg g^{-1}); C_0 is the initial concentration of the adsorbate in aqueous phase (mg L^{-1}); C_R is the concentration of the adsorbate in aqueous phase at the point of rupture (mg L^{-1}); V is the volume of the solution (L); M is the mass of the adsorbent (g).

After calculation of the adsorption capacity, statistical analyses were made by using the software BioEstat 5.0, in order to evidence statistically significant differences between the removal efficiencies of the contaminants for both types of GAC. By the Shapiro–Wilk normality test, it was possible to observe if the results achieved followed a parametric (normal) or non-parametric (non-normal) distribution. When the preliminary tests indicated a normal distribution of the data, the analysis of variance (ANOVA) was performed, followed by the Tukey hypothesis test. On the other hand, for the non-normal distribution, the data were submitted to the Kruskal–Wallis ANOVA tests, by Student–Newman and Mann–Whitney. The comparisons were based on the *p*-values obtained. For a *p*-value $\leq .05$, the hypothesis of equality between the results compared was rejected at the confidence level of 95%.

Results and discussion

Characterization of the adsorbents and adsorbates

The mineral and vegetal GAC had manufacture information as shown in Table 5. The characteristics of the carbons listed in Table 5 meet the recommendations of the international[35] and national[36] standards for use in water treatment. Supplementing the information provided by the supplier, the activated carbon samples have been characterized as shown in Table 6.

For the specific surface area and distribution of porosity, it is observed in Table 6 that, despite the different average diameter values of the pores of the evaluated

Table 5. Characteristics of the activated carbons evaluated in the research.

Parameter	Mineral GAC/Vegetal GAC
Iodine number (mg g^{-1})	900
Apparent density (g cm^{-3})	0.45/0.55
Hardness (%)	95
Abrasion (%)	85
Ashes grade (%)	10
Granulometry (mesh)	8 × 30/12 × 40

carbons, both have presented values from 8 to 20 Å. This classifies both adsorbents as secondary microporous carbons, with micropore volume representing approximately 92–93% of the total volume of pores. These micropore values are within the range from 0.15 to 0.70 $cm^3 g^{-1}$ suggested by Bansal and Goyal[37] Additionally, both carbons have met the recommendations of the literature for all the parameters listed, except for the minimum value of specific surface area of 500 $m^2 g^{-1}$, which has not been met by the vegetal GAC.

The PZC can be understood as the pH at which the particle presents a null surface charge density, being the convergence value among the three pH curves. There is surely a net balance of negative charges above the pH taken as zero charge in the analysed material, while the positive charges prevail below this value. The PZC values of the mineral GAC and vegetal GAC have been determined as 10.5 and 9.0 (Figure 2), respectively, leading to the conclusion that the carbons studied are base-like materials. The pH of the solutions containing distilled water has ranged from 5.5 to 6.5, while the pH of the solutions containing natural water under the optimized conditions of the previous clarification has ranged from 7.1 to 7.2. These pH values are lower than the PZC value of the carbons, showing that the adsorbents presented excessive positive charges on their surfaces.

Another parameter characterized has been the infrared spectroscopy and, as shown in Figure 3, both types of carbon have presented similar spectra. The bands found in the analyses of infrared have provided information on the characteristic groups of the carbons. The vibrating band of approximately 3546 cm^{-1} indicates the presence of a phenol group, while the bands of approximately 3472 and 3412 cm^{-1} indicate stretching of pyridine or primary amide. Additionally, the bands at 1633 and 1612 cm^{-1} indicate a primary amine group, while the band at 615 cm^{-1} indicates a tertiary amine group. The presence of groups containing nitrogen is coherent with the fact that the PZC has indicated that such materials are basic.

Table 6. Additional specific characteristics of each carbon used in the study.

Parameter	Mineral GAC	Vegetal GAC
Specific mass (g cm^{-3})	1.629	1.607
BET specific surface ($m^2 g^{-1}$)	781.4	374.0
Microporous volume ($cm^3 g^{-1}$)	0.383	0.209
Microporous average size (Å)	12.74	14.20
Total volume of porous ($cm^3 g^{-1}$)	0.432	0.225
Porous maximum diameter (Å)	1458	754.0
Porous average diameter (Å)	11.06	18.21

For the organic contaminants studied, the pKa values were 4.15 (DCF), 10.2 (E2) and 1.6 and 5.7 (SMX). It means that DCF and SMX have negative charges in the pH of the distilled water solution used in the research, which suggests a significant driving force for the adsorption in the studied carbons, as it allows the occurrence of electrostatic interaction. On the other hand, no interaction of electrostatic nature with the carbon is expected for the adsorption of E2 due to the absence of charges of this pharmaceutical in the pH value of the influents.

It is also worth mentioning that the medium-size values of both carbons (12.74 Å for mineral GAC and 14.20 Å for vegetal GAC) are higher than the maximum length of all pharmaceuticals (Table 1), thus favouring the penetration of such contaminants in the pores of the adsorbent and their subsequent adsorption/removal.

Adsorption of the organic contaminants in distilled water

Three adsorption tests with pharmaceuticals solutions, prepared in distilled water, were performed until the point of exhaustion of the GAC bed (Figure 4). For all tests taking from 100 to 150 h, the flow rate of the system was kept at 6.5 mL min^{-1}, resulting in a surface loading rate of 120 $m^3 m^{-2} day^{-1}$. The characteristics of the solutions used are presented in Table 7, which shows that the temperature of the different tests was kept within a narrow range (22.5–24.5°C), as well as the initial concentration of pharmaceuticals, which ranged from 2.4 to 3.0 mg L^{-1}.

As there is no drinking water standards established in the literature for the pharmaceuticals studied, the point of rupture for each organic contaminant has been defined as the inflection point of the rupture curves, determined by the software Origin 6.0 from the calculation of the second-order derivative of the variation of the concentration in time. The total adsorbed mass to the point of rupture, the removal percentage and the adsorption capacity of the two GAC beds for the pharmaceuticals studied are presented in Table 8. The mineral GAC has presented a removal percentage of SMX slightly higher than that of the vegetal GAC. On the other hand, it got saturated 450 min prior to the vegetal GAC, with both adsorbing approximately 60 mg of SMX. Upon these evidences it seems that SMX adsorption capacity by both carbons has been the same, since both have

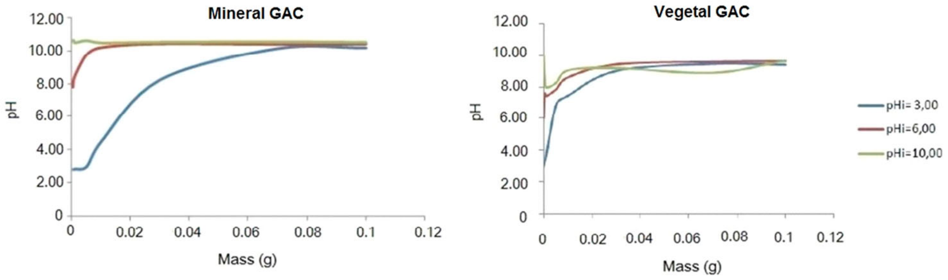


Figure 2. Determination of the PZC for the assessed carbons.

presented capacities of approximately 20 mg g^{-1}. Nevertheless, the statistical analyses have shown a significant statistical removal difference between both carbons ($p < .0001$; $\alpha = 0.05$).

Testing DCF adsorption on GAC, it was observed that the rupture point for the mineral GAC bed occurred in 7781 min (1.12 mg L^{-1}) with the test ending at 8400 min after reaching the bed exhaustion point. In contrast, the point of rupture for the vegetal GAC was 7456 min (1.92 mg L^{-1}) and the exhaustion point occurred by 7920 min (Figure 4). Once again, the vegetal bed got saturated before the mineral one, implying higher removal efficiency, larger adsorbed mass of DCF and, consequently, higher adsorption capacity for this compound. Therefore, it is inferred that the mineral carbon has presented a better performance in the removal of DCF when compared to the vegetal one. Statistical tests confirmed there was significant difference between the efficiencies of both carbons ($p < .0001$; $\alpha = 0.05$) for DCF removal.

From Figure 4, the points of rupture of E2 are identified in 5393 and 4630 min, for mineral carbon and vegetal carbon, associated with the concentrations of 1.82 and 2.04 mg.L^{-1}, respectively. According to Table 8, the mineral GAC presented larger adsorbed E2 mass and, consequently, higher adsorption capacity. The results have been significant, demonstrating the lower E2 removal capacity of the vegetal carbon evaluated when compared to the mineral carbon. The statistical tests have confirmed this statement by showing significant differences between both beds ($p = .0181$; $\alpha = 0.05$).

A removal similar to that obtained in this research has been demonstrated in an adsorption study performed by Corwin and Summers[38] by the RSSCT column method with bituminous (mineral) GAC, by testing the removal capacity of 17 organic contaminants in distilled water, including SMX and DCF. The results have shown that SMX was the first compound to saturate the GAC bed. The authors have also demonstrated that the removal was approximately 80% for SMX and 90% for DCF.

Among the three contaminants studied, DCF and E2 are hydrophobic compounds (Log Kow > 3.5) and SMX is a hydrophilic compound (Log Kow < 3.5). This way, the better performance in the adsorption of DCF can be explained by its hydrophobic nature, as well as by the conditions favourable to the electrostatic interaction ($pKa_{DCF} < pH_{adsorption} < PZC_{GAC}$), which would be a driving force for this pharmaceutical to approach the surface of the carbon.

SMX has a hydrophilic nature with two ionizable amine groups. As a result, in an aqueous solution, SMX may be present in the either neutral or negative forms, depending on pH of the solution. The removal observed for this compound can be explained by electrostatic

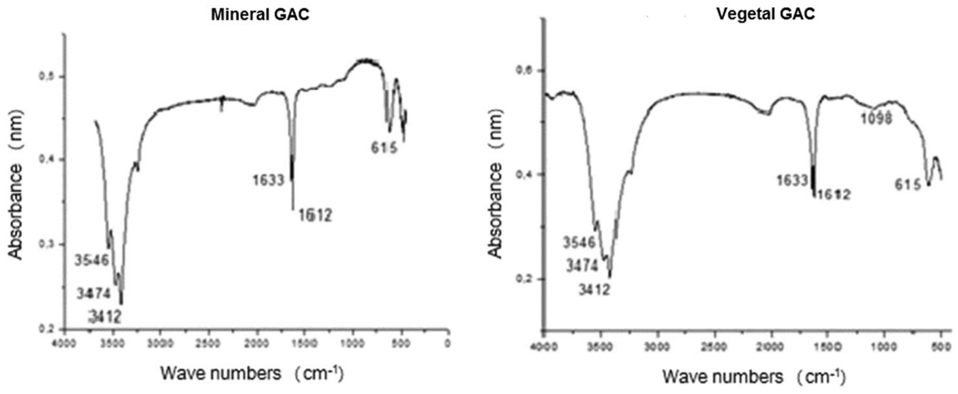


Figure 3. Infrared spectroscopy for mineral GAC and vegetal GAC.

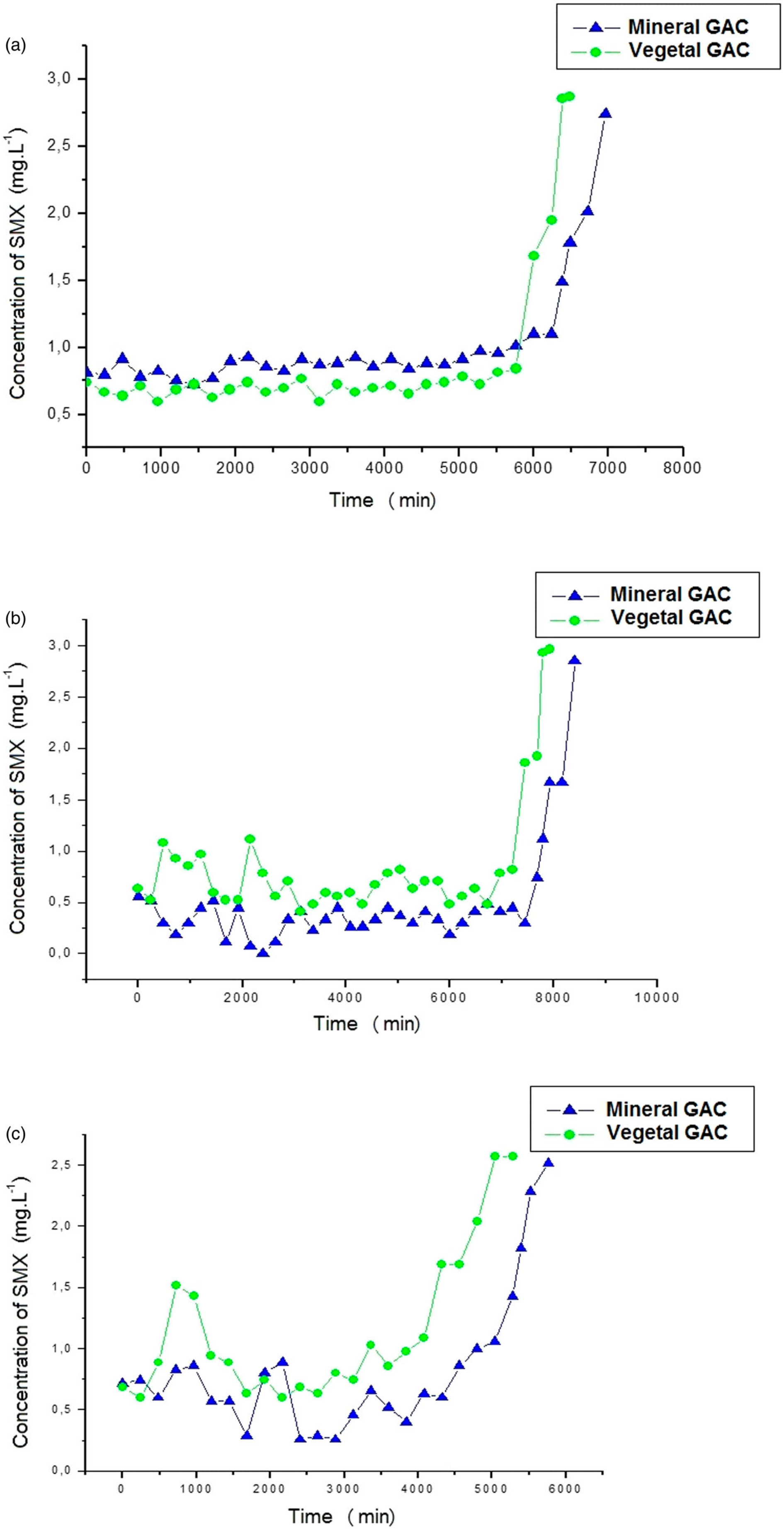


Figure 4. Rupture curves of the adsorbers for the pharmaceuticals SXM (a), DCF (b) and E2 (c).

Table 7. Characteristics of the contaminant solutions used in the adsorption tests.

Contaminant	Concentration (mg L^{-1})	pH	Temperature (°C)	Conductivity (µS.cm^{-1})
SMX	3.03	6.35	22.6	83.7
DCF	2.44	6.45	24.5	117.9
E2	2.55	5.9	22.5	144.9

interactions, since this compound was negatively charged, as the solution pH (6.35) was higher than the second pKa value (5.7). In this aspect, researchers have observed that hydrophilic compounds have lesser affinity for GAC, thus reducing their adsorption efficiency.[39] However, this condition can be suppressed, should there be interactions of other nature, like electrostatic ones.

Regarding the hormone E2, as its pKa value (10.2) is higher than the influent pH (5.91), there would not be electrostatic attraction as a driving force to keep this pharmaceutical close to the carbon surface. Therefore, it is hypothesized here that hydrophobic interactions, such as pi (π) stacking between the aromatic ring of the hormone and the graphene sheets of the carbon, were decisive for E2 adsorption.

Adsorption of organic contaminants in natural water

Taking into consideration the initial concentrations of the three contaminants measured right before the addition of the coagulant (SMX = 1.08 mg L^{-1}; DCF = 1.32 mg L^{-1}; E2 = 0.9 mg L^{-1}), the average removal efficiencies of SMX, DCF and E2 in the clarification process have been, respectively, 68%, 70% and 93%. These values are higher than those reported by Westerhoff et al.[2] and Lima et al.,[15] except for SMX, in the same range of pH of study (7.0–7.4). Westerhoff et al.[2] have observed removal values lower than 25% for some pharmaceuticals like DCF and of approximately 30% for some endocrine disrupters like E2.

Accordingly, Lima et al.[15] by using initial concentrations of contaminants close to 10 µg L^{-1}, have observed average removal values of DCF lower than 5% or 10%, when the coagulants were aluminium sulphate (AS) or polyaluminium chloride (PAC), respectively. For E2 hormone, the removal efficiencies in the clarification process ranged from 11% to 23% with AS and from 35% to 39% with PAC, while moderate efficiencies (66% to 71%) have been observed for SMX antibiotic for both coagulants.

Considering that the tests were conducted in concentrations of contaminants far from reality (mg L^{-1} instead of µg L^{-1} or ng L^{-1}), this work might be considered as a model for study of the kind of adsorbent material, as future trials should be conducted in concentrations of µg L^{-1} or ng L^{-1} of contaminants. So, the highest removal efficiencies observed in this study are probably due to the higher initial concentration of the contaminants used, which increases the probability of effective collisions between the particulate material and the microcontaminants and, in this case, a higher adsorption capacity on the aluminium hydroxide sludge formed. However, different results can be obtained at lower, and more usual, concentrations.

After the clarification performed in the conditions described in Table 3, the influent to the activated carbon columns had turbidity of 3.6 ntu, pH of 6.6, and the following average contaminants concentrations: SMX (0.34 mg L^{-1}), DCF (0.39 mg L^{-1}) and E2 (0.06 mg L^{-1}). After 1320 min (22 h) of GAC column operation, the removal efficiency of each contaminant was higher than 94% in the mineral GAC column, taking into consideration that their concentration was lower than their LC-MS detection limit (3.3–6.7 µg L^{-1}). On the other hand, the vegetal GAC presented lower removal efficiency, of 47% for SMX, 64% for DCF and 90% for E2. These removal efficiencies have been observed in a condition prior to the rupture of the column, when the rate of carbon usage was of 2.91 L g^{-1}.

The rupture curve could not be obtained for the tests with natural water because the concentrations influent to the GAC columns were lower than those of the tests with distilled water, since there was a considerable removal (68–93%) of the contaminants in the clarification step. In any way, it is probable that the usage rates of both carbons during the operation with fortified natural water

Table 8. Adsorption parameters of SMX, DCF and E2 in the GAC columns.

Contaminant	GAC	Breakthrough time (min)	Adsorbed mass (mg)	Removal (%)[a] ± SD[b]	q_e (mg.g^{-1})[a] ± SD	GAC usage rate (L g^{-1})[a] ± SD
SMX	Mineral	6450	60.6	70.8 ± 0.6	20.5 ± 0.2	14.2 ± 0.2
	Vegetal	6000	60.3	75.6 ± 1.9	20.6 ± 0.2	13.3 ± 0.2
DCF	Mineral	7920	86.0	88.0 ± 1.2	24.2 ± 0.1	14.5 ± 0.1
	Vegetal	7440	77.3	77.2 ± 1.9	23.7 ± 0.2	14.8 ± 0.1
E2	Mineral	5280	43.1	73.9 ± 0.6	14.9 ± 0.3	11.9 ± 0.2
	Vegetal	4320	34.8	64.6 ± 3.1	10.9 ± 0.3	8.8 ± 0.3

[a] Values calculated at the breakthrough point.
[b] Standard deviation.

Table 9. Results (*p*-value) of the hypothesis tests of average removal of the microcontaminants ($\alpha = 0.05$).

Comparison	SMX	DCF	E2
Mineral GAC × Vegetable GAC (distilled water)	<0.0001	<0.0001	0.0181
Mineral GAC × Vegetable GAC (natural water)	<0.0001	<0.0001	0.0005

are lower than those observed during the operation with distilled water. It happens because of the simultaneous presence of the three contaminants and other potential adsorbates in the fortified natural water.

At last, the *p*-values have been determined from statistical analyses to verify significant differences between the tests performed with the mineral and vegetal GAC in distilled water and in natural water, as presented in Table 9.

The results of the tests reject the hypothesis of equality among the samples and confirm the significant differences among the tests. Besides the favourable interactions between the contaminants and the activated carbon, a better performance of the mineral carbon has been observed compared to the vegetal carbon. It may be related to the fact that the mineral GAC presents a surface area and total volume of pores larger than those of the vegetal GAC (Table 7), resulting in more free spaces on the surface of the carbon, allowing a better settlement of the adsorbate molecules. In fact, studies about the removal of endocrine disrupters by adsorption on activated carbon have evidenced the relevance of the volume of the pores, as well as of the electrostatic interactions resulting from the charges on the surface and the pH of the solution.[40]

Conclusions

Adsorption of DCF and SMX on GAC seems to have been favoured by electrostatic interactions between these acid contaminants and the basic carbons, whereas E2 adsorption may be explained by hydrophobic interactions, such as pi stacking.

Experimental results with distilled water have shown that GAC columns (mineral and vegetal) were effective in the removal of SMX (70–75%), DCF (77–88%) and E2 (65–74%) from aqueous solutions, resulting in adsorption capacities of 20 mg g^{-1} for SMX and 24 mg g^{-1} for DCF in both kinds of GAC. For E2, the adsorption capacities were lower and varied from 11 to 15 mg g^{-1} for the vegetal and mineral GAC, respectively. GAC usage rates, calculated at the breakthrough point, ranged from 8.8 to 11.9 L g^{-1} for E2; from 14.5 to 14.8 L g^{-1} for DCF; and from 13.3 to 14.2 L g^{-1} for SMX; with the highest values being observed for the mineral GAC, except for DCF.

In the multicomponent adsorption tests (mixture of pharmaceutical concentrations of 0.34 mg L^{-1}, SMX; 0.39 mg L^{-1}, DCF and 0.06 mg L^{-1}, E2), the mineral GAC exhibited removal efficiencies higher than 94% by 22 h of column operation, while for the vegetal GAC the observed removal efficiencies were lower (47% for SMX; 64% for DCF and 90% for E2) for the same operation time. Therefore, the experimental results with both types of water evidenced the best performance of mineral GAC in all tests, which might be related to its larger surface area and volume of pores when compared to its vegetal counterpart.

As mentioned in Results and Discussion, the tests were conducted in concentrations far from those found in the real scenario. For that reason, results shown here should be considered as a model for study of the kind of adsorbent to removal organic contaminants. Thus, future studies should be made, in lower concentrations, in order to obtain more applicable results.

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Disclosure statement

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