

Integrating granular activated carbon in the post-treatment of membrane and settler effluents to improve organic micropollutants removal

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Highlights

The application of GAC filters was evaluated to treat effluents of different quality

The GAC breakthrough was quicker for diclofenac than for carbamazepine and diazepam

The high TSS content in settler effluent strongly limited the lifespan of GAC filters

The 2 types of GAC tested exhibited very similar technical performance in OMP removal

Economical and environmental criteria were included to select the most suitable GAC

Integrating granular activated carbon in the post-treatment of membrane and settler effluents to improve organic micropollutants removal

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Abstract

Granular activated carbon (GAC) is applied as post-treatment technology in wastewater treatment plants (WWTPs) in order to increase the elimination of organic micropollutants (OMPs). However, the efficiency and life-time of GAC depend on several parameters, such as the quality of the effluent to be treated or the type of GAC. In the present paper, two types of GAC, based on bituminous carbon (BC-GAC) and coconut shell (CS-GAC), were assessed from a technical, economic and environmental point of view to further remove OMPs present in two secondary effluents, coming from integrated biological systems with a membrane or a settler, respectively. Although all GAC filters were efficient in removing selected OMPs, the quality of the secondary effluent had a strong influence on the lifespan of adsorbent material and the technical operability of the filtration systems. While GAC filters treating membrane effluent were highly effective to remove recalcitrant compounds, such as carbamazepine and diazepam (> 80%), even after 430 d of operation (> 30,800 BV), the efficiency of GAC filters treating settler effluent quickly lowered to 50% after 100 d of operation (< 7,200 BV). Both types of GAC showed similar adsorption capacities and only slight differences were found in terms of costs (2.4 €/kg vs 2.7 €/kg). However, CS-GAC has a lower carbon footprint than BC-GAC, mainly due to the more environmentally friendly production process of CS-GAC.

Keywords: granular activated carbon; holistic assessment; membrane effluent; pharmaceuticals; settler effluent

1. Introduction

The appearance of new challenges in wastewater policy concerning organic micropollutants (OMPs), such as the inclusion of four pharmaceuticals and three hormones in the watch list defined by European Commission (Decision 2015/495/EU), have promoted that some countries, such as Switzerland, have already established OMPs discharge thresholds in WWTP effluents [1]. Others, such as Austria, Germany and The Netherlands, are considering some initiatives to increase the removal of OMPs during wastewater treatment (overall elimination of 80%) [2]. A potential solution to achieve these challenges is the application of post-treatment technologies in order to increase the removal of OMPs in WWTPs and, consequently, to enhance the quality of treated effluents before their discharge into the environment. Adsorption on activated carbon and ozonation are the most applied tertiary treatment technologies in WWTPs since both were proven as effective to reduce the concentration of different OMPs [2-4] and are economically viable [5]. Despite its high capacity for OMPs abatement, the possible appearance of toxic by-products during the ozonation stage compromises its sole application as final treatment unit in WWTPs [6]. Activated carbon can be used as granular activated carbon (GAC) or powdered activated carbon (PAC) in wastewater treatment. PAC is normally applied in combination with biological treatment [7] whereas GAC is used as post-treatment system with the additional advantage that can be regenerated once its adsorption capacity has been exhausted [2, 8]. The application of GAC filters to remove OMPs from WWTP effluent was widely studied in literature [2, 9-10]. The properties of activated carbon, the empty bed contact time (EBCT) and the composition of the effluent to be treated were identified as key parameters affecting the process efficiency [8-9, 11].

Different types of activated carbon exist in the market, being their properties (specific surface area, pore size and composition) dependent on the raw material used as precursor and the production process [12]. The selection of the raw material together with the method employed for its activation (physical or chemical) also affects the market price and the carbon footprint [13]. Previous studies evaluated the application of GAC and PAC with different origin (hard coal, coconut shell, wood and peat), observing a strong link between the efficiency of activated carbon to remove OMPs and its specific surface area [14, 15]. The pore size is also a key factor controlling the effectiveness of the adsorbent material for a given OMP [16].

The influence of EBCT on the efficiency of GAC filters to remove OMPs was extensively studied [9, 11, 17], being the typical values employed in WWTPs between 10 and 30 min [2]. EBCT mainly affects the adsorption kinetics of OMPs on the adsorbent material and the size of the filtration system.

Most studies found in literature are based on the post-treatment of secondary effluents coming from conventional activated sludge (CAS) systems and few information is available about the lifespan of these technologies treating effluents from membrane bioreactors (MBR) [2, 18]. While the effect of dissolved organic matter on the saturation of GAC filters is unquestionable [9, 10], the influence of total suspended solids (TSS) (either colloids and/or sedimentable solids) on the adsorption capacity of filters is not clear. Even though a negative effect is expected on the adsorption process, because TSS can block the pores of the adsorbent material hampering the arrival of OMPs to the surface of GAC, other factors, such as the frequency of backwash cycles and the development of a biofilm on the surface of GAC should be also considered [19, 20]. This unclear effect was evidenced in literature since Bornemann et al. [21] observed higher removals for carbamazepine and sulfamethoxazole in

GAC filters preceded by a sand filter where TSS were separated. In contrast, Benstoem et al. [22] could not demonstrate that the sand prefiltration extended the lifespan of GAC.

The main objective of this work was to assess the application of GAC filters to remove OMPs from two secondary wastewater effluents of different quality (from a membrane and a settler, respectively). Moreover, the influence of the type of GAC was assessed not only in terms of technical performance but also under an economic and environmental perspective. This would allow us to directly relate the results since the comparison among different studies is hampered by the application of filters of varying sizes and the use of various types of GAC and wastewaters with different composition.

2. Materials and methods

2.1. Target organic micropollutants

Three antiphlogistics (ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF)), four antibiotics (erythromycin (ERY), roxithromycin (ROX), sulfamethoxazole (SMX) and trimethoprim (TMP)), an antidepressant (fluoxetine (FLX)), an antiepileptic (carbamazepine (CBZ)), a tranquillizer (diazepam (DZP)), three musk fragrances (galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI)) and five endocrine disruptor compounds (estrone (E1), 17 β -estradiol (E2), 17 α -ethinylestradiol (EE2), bisphenol A (BPA) and triclosan (TCS)), were selected in this work.

2.2. Selected secondary effluents

Two different secondary effluents were selected to assess the influence of effluent quality on the efficiency of GAC filters to remove OMPs. The effluents were produced in two biological systems treating the same urban wastewater composed of anaerobic treatment followed by anoxic/aerobic chambers (Figure S1). The difference between both systems is the technology employed to separate the biomass from the treated effluent: one system

employed a settler (Figure S1A), whereas an ultrafiltration membrane was used in the second system (Figure S1B) [23]. The physicochemical characterization and the concentrations of target OMPs detected in membrane and settler effluents are shown in Tables 1 and 2, respectively. It can be observed that the method employed to retain the biomass not only affects the concentration of suspended solids detected in the effluents (Table 1) but also the biological activity developed in the integrated system due to the effect of the recirculation between anoxic and aerobic chambers (nitrification was complete in membrane system, but only partial in settler system, Table 1). Consequently, the concentrations of OMPs detected in membrane and settler effluents were slightly different (Table 2).

2.3. Characterization of granular activated carbons

Two different types of granular activated carbon were tested: one based on bituminous carbon (BC-GAC) (MG 1050, ChiemiVall) and the second produced from coconut shell (CS-GAC) (CG 1000, ChiemiVall). These adsorbent materials were selected in order to evaluate and compare from a technical, environmental and economic point of view the application of two GAC with different origin for OMPs abatement: BC-GAC produced from a resource and CS-GAC produced from a waste. The chemical composition of both activated carbons was determined by elemental analysis whereas the physical characterization (structure, specific surface area and pore size distribution) was determined by Scanning Electron Microscope (SEM), the application of BET isotherm and high-pressure mercury porosimetry, respectively. Batch experiments were conducted to determine the adsorption capacity of both activated carbons to remove selected OMPs. Adsorption assays were performed with 600 mL glass bottles in a shaker (150 rpm and 25°C) during 48 h to achieve adsorption equilibrium. Phosphate buffer (pH 7) and initial OMPs concentrations ranging between 1 and 20 µg/L (1

$\mu\text{g/L}$ for hormones, $20 \mu\text{g/L}$ for musk fragrances and $10 \mu\text{g/L}$ for the rest of compounds) were employed. The experiments were conducted in duplicate using different concentrations of adsorbent material (0, 50, 100, 250 and 500 mg/L). After 48 h, samples were filtered to remove suspended GAC particles before the analysis of OMPs in liquid phase. Freundlich isotherm (Eq [1]), the recommended model to study the adsorption of compounds present in wastewater at low concentrations [19], was selected to fit the experimental data.

$$\ln(q) = \ln(K_f) + (1/n) \cdot \ln(C_e) \quad [1]$$

where q is the adsorption capacity (μg of adsorbate/ mg of adsorbent), C_e is the final equilibrium concentration of OMPs in the liquid phase ($\mu\text{g/L}$), K_f and $1/n$ are the Freundlich parameters. The K_f constant characterizes the adsorption capacity whereas $1/n$ is related to the intensity of the adsorption force between the activated carbon surface and the adsorbate.

2.4. GAC filters

Two column reactors (0.7 L of bed volume, Figure S2), one with BC-GAC and the other with CS-GAC as adsorbent materials, were coupled in parallel to each biological system as post-treatment. Both activated carbons were sieved using a 1 mm mesh to obtain a particle size distribution between 1 and 2 mm in the bed. GAC filters were operated with a constant empty bed contact time (EBCT) of 20 min during 430 d (corresponding to a treated effluent volume per GAC volume (BV) of around $31,000 \text{ m}^3 / \text{m}^3$) in the case of membrane effluent and 300 d (around 21,600 BV) in the case of settler effluent. Filters were operated in up-flow mode using a peristaltic pump for the feeding being the final effluent obtained from the top by liquid displacement. This plug flow reactor model minimizes the appearance of dead zones. Four periodical cleanings were only applied in GAC filters treating settler effluent to

remove the excessive content of suspended solids accumulated when they obstructed the filter inlet (at 8,000 BV; 12,000 BV; 15,500 BV and 19,000 BV). More frequent cleanings were not done due to two reasons: 1) to compare the performance of GAC filters operated under the same conditions but using effluents of different quality (no periodical cleanings in filters treating membrane effluent), and 2) to enable biofilm development and test its effect on OMPs elimination.

During the whole operating period, samples of influent and effluent of the four filtration systems were taken every week for pH, ammonium (N-NH_4^+), nitrite (N-NO_2^-), nitrate (N-NO_3^-), dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}) and, volatile and total suspended solids (VSS and TSS) determinations. The OMPs monitoring was conducted more or less once per month through the determination of the soluble concentrations of OMPs in the influent and effluent of each filter.

2.5. Analytical methods

Physicochemical parameters (TSS and VSS, N-NH_4^+ , N-NO_3^- and N-NO_2^-) were determined according to Standard Methods [24]. Total, inorganic and organic carbon (TC, IC and DOC) were determined by a Shimadzu analyser (TOC-5000). UV absorbance was measured at 254 nm employing a spectrophotometer (Shimadzu UV-1603, UV-visible) and pH was monitored using a selective electrode pH meter GLP 22 (Crison).

To determine soluble OMP concentrations, solid phase extraction (SPE) was used as preconcentration technique prior to quantification using an Agilent G1312A liquid chromatograph with binary pump and automatic injector HTC-PAI (CTC Analytics) coupled with a mass spectrometer API 4000 triple quadrupole (Applied Biosystems) or a gas chromatograph (Varian CP-3900) coupled with an ion trap mass spectrometer (Varian GC-

2100), depending on the compound. The analytical procedure was described in detail by Fernandez-Fontaina et al. [25].

3. Results and discussion

3.1. Characterization of granular activated carbons

The chemical composition, expressed in percentage, for BC-GAC and CS-GAC was 86.4 (C), 2.2 (H), 0.0 (N) and 0.0 (S) and, 94.0 (C), 0.6 (H), 0.0 (N) and 0.0 (S), respectively. CS-GAC exhibited a slightly higher content in carbon than BC-GAC whereas the content in nitrogen and sulphur was null in both cases. Despite the different origin, the specific surface area exhibited by both activated carbons was very similar, around 900 m²/g (the average BET multipoints were 895 m²/g and 902 m²/g for BC-GAC and CS-GAC, respectively). A structure with high presence of macropores was observed for BC-GAC (Figures 1A and 1B). In the case of CS-GAC, the porous structure was not clearly visible in SEM images (Figures 1C and 1D). Consequently, pores with smaller size than BC-GAC were assumed. The application of the high-pressure mercury porosimetry confirmed that the porous texture of CS-GAC was based on the presence of pores with a diameter smaller than 0.1 μm (representing 52% of the total volume of pores). In contrast, the porous texture of BC-GAC was mainly attributed to the presence of pores with a diameter larger than 0.1 μm (18% and 41% of the total volume for pores larger than 10 μm and between 0.1-10 μm, respectively). This observation is in accordance with Ello et al. [26] who observed that the activated carbon produced from coconut shell has a porous structure based on micropores.

The adsorption capacity of BC-GAC and CS-GAC was determined through the Freundlich isotherm (Table S1). The coefficients of determination indicate that, in general, the adsorption of all selected OMPs on CS-GAC ($R^2 > 0.88$) and BC-GAC ($R^2 > 0.85$) follows the Freundlich model, being 17α-ethynilestradiol, roxithromycin and fluoxetine the compounds

that exhibited the worst fit for BC-GAC. Although there are small differences between the application of BC-GAC and CS-GAC in terms of a specific pollutant adsorption (Figure 2), in general, both activated carbons exhibited very high adsorption capacity for triclosan, carbamazepine and musk fragrances (K_f were higher than 0.048 and 0.038 for BC-GAC and CS-GAC, respectively) and low adsorption capacity for the three hormones (E1, E2 and EE2), sulfamethoxazole and ibuprofen ($K_f < 0.020$). In all cases, the $1/n$ parameter was lower than 1 indicating that the adsorption was favourable and relatively strong unions were formed between the micropollutant and the adsorbent material [27]. The results obtained are in accordance with those previously reported in bibliography since, regardless the type of GAC used, carbamazepine exhibits higher adsorbability on GAC than diclofenac and diazepam [18, 28], whereas the adsorption capacity for sulfamethoxazole and ibuprofen is significantly lower [28, 29]. This higher affinity of activated carbon for carbamazepine and diclofenac compared to sulfamethoxazole was also demonstrated by Ruhl et al. [30] during the evaluation of eight PAC from different source materials. Additionally, these authors also demonstrated that the adsorption capacity does not depend on the origin of activated carbon since two types of PAC produced from charcoal coal and coconut shell showed similar adsorption capacity for diclofenac, probably explained by their similar surface area (around 1,050 m²/g).

3.2. Influence of effluent quality on the operation of GAC filters in terms of macropollutant removal

As expected, the application of GAC filters as post-treatment system allowed to improve the quality of membrane and settler effluents in terms of physicochemical parameters, regardless the type of GAC used (BC-GAC and CS-GAC). The removal of dissolved organic matter was detected through the monitorization of DOC and UV₂₅₄ absorbance (Figure 3).

While a correlation between the removal of adsorptive UV_{254} substances and the volume of treated secondary effluent per bed volume was observed, describing the breakthrough curves represented in Figures 3A and 3C, DOC removal was very variable during whole operation of the four filtration systems (removal efficiencies between 0-100%) and a connection between the efficiency of filters for DOC abatement and the treated bed volumes was not found due to this erratic behaviour (Figures 3B and 3D). Consequently, DOC monitoring did not allow to predict the saturation of the adsorbent materials. This is in agreement with previous studies, which demonstrated that UV absorbance measured at 254 nm can be used as indicator to monitor and control the removal of OMPs in activated carbon systems [31, 32] whereas the monitoring of DOC is not an accurate indicator since the breakthrough of GAC is faster for DOC than for OMPs [2].

The higher content in dissolved organic matter affected the performance of GAC filters treating settler effluent. After a gradual growth during the first 100 d (< 7,200 BV), UV_{254} absorbance was only reduced around 10% after 280 d of operation (> 20,000 BV). On the contrary, GAC filters treating membrane effluent were still able to reduce it around 20% after 360 d of operation (> 25,500 BV).

Since the concentration of nitrate measured in both influent and filter effluents was very similar (Figures S4C and S5), the adsorption of nitrate on both types of GAC was discarded (regardless the origin of secondary effluent) even though the capacity of BC-GAC to adsorb this compound has been demonstrated in a previous study [11]. Although ammonium and nitrite were also detected in settler effluent (Table 1), GAC filters were only able to remove a little fraction of nitrite (from 0.37 ± 0.23 to 0.18 ± 0.13 mg N- NO_2 /L) under the operating conditions employed in this study (Figure S4). This observation could be explained taking into account the anoxic conditions under which the filters were operated (< 0.7 mg O_2 /L),

favouring the denitrification, which is limited by the low levels of dissolved organic matter detected in settler effluent (Table 1). As expected, the capacity of GAC filters to remove suspended solids during the post-treatment of settler effluent was evidenced, obtaining removal efficiencies of TSS up to 80% (data not shown).

3.3. Technical assessment of GAC filters in terms of OMP removal

The breakthrough profiles obtained for carbamazepine, diazepam and diclofenac in both BC-GAC and CS-GAC filters treating membrane and settler effluent are displayed in Figure 4. These three compounds were selected as indicators considering that they were the OMPs detected in the highest concentrations in both membrane and settler effluents (Table 2) and they exhibit low removal during conventional wastewater treatment [33]. Moreover, carbamazepine and diclofenac are considered key compounds to evaluate the efficiency of post-treatment technologies in WWTPs [2]. The results corresponding to the hydrophobic compounds detected in the highest concentrations in both secondary effluents (musk fragrances and fluoxetine) are displayed in Figure S3 whereas the results obtained for the rest of compounds are summarized in Tables S2 and S3.

No influence of the type of GAC was detected regardless the composition of the effluent and the OMP studied (Figure 4), since, in general, the breakthrough curves obtained with BC-GAC and CS-GAC filters merged together during the whole operation of both filters treating the same secondary effluent. These findings are in accordance with the results obtained in the batch experiments since both types of GAC exhibited very similar adsorption capacities for selected OMPs (Figure 2). This observation demonstrates that the raw material employed during the production process is not determining the adsorption capacity of the adsorbent for the removal of OMPs, although it should be said that the properties of the two activated carbons (specific surface area, particle size, etc.) used in this study are comparable. On the

other hand, the application of GAC based on coconut shell resulted to be highly effective to retain selected OMPs and comparable to the use of GAC based on bituminous carbon even though CS-GAC is not recommendable for wastewater treatment due to its surface area is based on the majority presence of micropores [14, 34].

The breakthrough profiles for carbamazepine, diazepam and diclofenac represented in Figures 4A, 4B and 4C indicate the slow saturation of the adsorbent materials (BC-GAC and CS-GAC) treating membrane effluent, since removal efficiencies higher than 94% were observed even after 13,000 BV (around 180 d). In the case of settler effluent (Figures 4D, 4E and 4F), the obtained breakthrough curves do not follow the normal S-shaped breakthrough curves described in other studies [10]. This different behaviour was not only associated to the sorption competence between organic matter and OMPs [9], but also to the influence of the periodical cleanings on the performance of the adsorbent material. During the first period of operation (< 13,000 BV), after the periodical cleanings, an increase in the removal efficiency was observed for carbamazepine and diazepam: from 50% to 87% after the first cleaning (around 8,000 BV) and from 60% to 85% after the second one (around 12,000 BV). However, this effect was not detected for diclofenac since similar or lower removal efficiencies were observed after both cleanings. During the second period (> 13,000 BV), the adsorption capacities of BC-GAC and CS-GAC were not modified after the periodical cleanings (at 15,500 BV and 19,000 BV), indicating that the effectiveness of these cleanings depend on the volume of treated wastewater per adsorbent volume. The behaviour observed after the first two cleanings could be attributed to the disappearance of preferential pathways, promoting the uniform displacement of the secondary effluent through the filtering material. Nevertheless, during the second period, although the excessive amount of solids accumulated in the inlet of filters was removed during the

cleanings, the blockage of pores and the growth of the biofilm thickness increased over operation time, which limited the diffusion of OMPs from liquid phase to the surface of GAC. Other studies, such as Katsigiannis et al. [35], attributed the changes observed in the shape of breakthrough curves to the biological activity developed in GAC filters. Although these authors identified the biotransformation as the main mechanism involved in the removal of some compounds in GAC filters after seven days of operation, such as bisphenol A, ibuprofen and triclosan, the role of biotransformation was not evidenced in the present study, thus discarding its contribution in the shape of breakthrough curves obtained in GAC filters treating settler effluent even for highly biotransformable compounds (Figure S3).

The influence of the quality of secondary effluent on the adsorption capacity of GAC filters was evidenced (Figure 4). In general, filters treating membrane effluent exhibited higher adsorption capacities for selected OMPs during whole operation, being still efficient to remove carbamazepine and diazepam above 84% and diclofenac (> 75%) after 30,800 BV. In contrast, the quick breakthrough of both GAC during the first 100 d of operation (< 7,200 BV) with settler effluent with removal efficiencies below 50% for these three compounds before the first cleaning points out a clear effluent matrix effect. Despite different periodical cleanings were applied during the 300 d of operation of these two filtration systems in order to favour their technical operability, the lifespan of both CS-GAC and BC-GAC was strongly reduced, with removal efficiencies lower than 40% for carbamazepine and diazepam and lower than 17% for diclofenac at 21,000 BV. This reduction in the adsorption capacity of filters treating settler effluent (also observed for the rest of selected OMPs (Figure S3 and Tables S2 and S3)) is likely associated to its higher content in dissolved organic matter (8.6 ± 4.9 vs 3.5 ± 2.7 mg DOC/L) and the presence of TSS (attributable to colloids and small sedimentable solids) in comparison with membrane effluent. Although the competence

between organic matter and OMPs has been previously identified as one of the main factors affecting to the adsorption process on activated carbon [9, 10], the high presence of suspended solids could have a higher influence in this case since the blockage of the pores not only hampered the arrival of OMPs from the liquid phase to the internal surface of activated carbon but also promoted the appearance of preferential ways. This observation is in accordance with previous works which identified the difficulty of applying GAC with grain distributions of 8 x30 ASTM-mesh (0.6-2.4 mm) to treat secondary effluents with a content in TSS > 10 mg/L [2].

In contrast to the behaviour observed in batch experiments where both GAC exhibited very similar adsorption capacities for diclofenac and diazepam (around $0.043 \text{ (mg/g)} \cdot (\text{L}/\mu\text{g})^{1/n}$), the breakthrough of the adsorbent material was quicker for diclofenac than for carbamazepine and diazepam (Figure 4), being this pharmaceutical identified as the compound limiting the lifespan of the adsorbent material, regardless the composition of secondary effluent and the type of activated carbon. This fact confirms that the adsorption process of OMPs on GAC not only depends on the hydrophobic character of the compounds but also on their charge [18, 36]. Even though diclofenac shows a higher octanol-water partition coefficient ($\log K_{ow}$: 4.5) than carbamazepine and diazepam ($\log K_{ow}$: 2.4 and 2.8, respectively), its adsorption kinetics was mainly dominated by the charge (diclofenac is negatively charged at pH 8 whereas carbamazepine and diazepam are neutral). This affirmation is consistent with the results obtained by other authors who observed that the progressive saturation of activated carbon is quicker for negatively charged compounds [7, 11, 18].

According to literature, the potential of other post-treatment technologies applied at large scale for the abatement of OMPs, such as ozonation and the addition of PAC into a separate

unit after biological treatment, is also strongly linked to the quality of secondary effluents. In this sense, lower ozone doses were required to achieve a high reduction of persistent OMPs during the post-treatment of MBR permeates [37-39] compared to the studies focused on the application of this technology to treat settler effluents [3, 36]. This fact is mainly attributed to the presence of higher concentrations of dissolved organic matter and solid particles which can compete with OMPs in the reaction with ozone, increasing the required ozone dose to reduce the concentration of OMPs [40, 41]. Regarding PAC addition after biological treatment, lower OMPs removal efficiencies were generally observed during the treatment of effluents coming from secondary settlers compared to those obtained treating MBR effluents. For instance, Kovalova et al. [38] observed removals higher than 96% for carbamazepine and diclofenac during the post-treatment of MBR permeate employing an average dosage of 8 mg PAC/L, whereas these compounds showed lower elimination (68-90%) during the post-treatment of secondary effluents generated in biological systems with settler and applying PAC doses between 10-20 mg/L [36, 42]. Moreover, similarly to GAC, the lifespan of the PAC was strongly set by the content of dissolved organic matter in the secondary effluent, observing a faster reduction in the adsorption efficiency of PAC with increasing DOC [42, 43].

3.4. Selection of GAC based on economic and environmental indicators

Considering that both BC-GAC and CS-GAC exhibited very similar technical performance, the economic and the environmental burdens should be considered to select the most suitable GAC in post-treatment systems.

3.4.1. Economic indicator

The market price of granular activated carbon ranges from 0.3-19 €/kg based on the review published by Alhashimi et al. [13]. The country of production, the precursor material, the

type of activation employed during the production process and the physicochemical properties of the adsorbent material obtained (surface area, particle size, porosity...) were identified as decisive to establish this price. Different market prices for GAC based on bituminous carbon and coconut shell were observed in literature [13, 14], ranging from 1.2 to 18 €/kg and 0.3 and 7.9 €/kg for BC-GAC and CS-GAC, respectively.

Both GAC used in this study were manufactured by the company ChiemiVall, located in Catalonia (Spain), being the market price in 2017, 2.4 €/kg for BC-GAC and 2.7 €/kg for CS-GAC. The difference is just explained by the precursor material since the production process (physical activation) and the final properties (surface area, particle size) are identical. Although a priori the prices seem very similar, the high amount of GAC employed in full-scale filtration systems (in the order of tons) and the need of replacing the activated carbon once its adsorption capacity has been exhausted results in a net cost difference of several thousand euros per year. For example, considering a GAC filter designed to treat 250 m³/h of secondary effluent operated with an EBCT of 14 min, the amount of activated carbon required is 28 tons (assuming that both BC-GAC and CS-GAC exhibited an apparent density around 480 kg/m³). Considering this information, the investment cost of the filter employing CS-GAC would be 8,400 € more expensive than for BC-GAC. In addition, taking into account the shorter lifespan of GAC filters treating settler effluent compared to membrane effluent, the operational costs associated with GAC replacement would be higher due to the need of replacing the adsorbent material more frequently. Assuming 20% of breakthrough of the adsorbent ($C/C_0=0.2$) for the recalcitrant compounds (carbamazepine and diazepam) as replacement criteria according to the thresholds defined by some European countries, the replacement cost of the CS-GAC treating membrane effluent (replacement after 31,000 BV)

and settler effluent (replacement after 15,050 BV) would increase up to 7,200 €/year and 14,700 €/year, respectively, in comparison with the application of BC-GAC.

3.4.2. Environmental indicator

The relevance of carrying out the environmental assessment of GAC filters for advanced wastewater treatment was shown in previous studies [44, 45], which demonstrated that the application of GAC based on bituminous carbon filters involved much lower environmental impacts than other advanced alternatives such as ozonation or UV disinfection. However, there are no studies comparing directly the environmental profile of different types of GAC. In the present work, a literature review was conducted to compare the BC-GAC and CS-GAC from an environmental point of view considering data related to the production of both activated carbons. While the production of GAC based on bituminous carbon was widely studied [13, 44, 46], few studies have been performed dealing with the environmental assessment of GAC with coconut shell origin, being the inventory related to GAC production from vegetal sources not intensely developed.

For BC-GAC, the environmental assessment conducted by Muñoz [44] was based on the inventory data reported by Meier [47]. The carbon footprint (CF) related to conventional processes to produce GAC from bituminous carbon ranged from 10.33 to 19.60 kg CO₂ eq per kg of GAC, according to inventories made by Bayer et al. [46] and Meier [47], respectively. Regarding CS-GAC, the works of Remy et al. [48] and Arena et al. [49], who considered a modern process in which most off-gases were re-used for heating purpose, were considered. The advantage of using streams from the process instead of external fuels to produce heat was demonstrated with a CF of 1.07 kg CO₂ eq per kg of GAC produced [49], much lower than the value obtained (7.00 kg CO₂ eq per kg GAC) when a more conventional process was applied [48].

Even though the CF are not directly comparable since they come from different inventories and production processes, a priori, the results evidence that the environmental burden attributed to CS-GAC is lower than for BC-GAC. Moreover, this environmental profile would be enhanced because coconut shell is a waste and its impact is null whereas bituminous carbon is a resource with environmental impacts associated to its extraction.

4. Conclusions

This study demonstrates that GAC filters are versatile technologies with capacity to remove selected OMPs during the treatment of secondary effluents of different quality. However, the composition of secondary effluent, especially the TSS content, not only affects the lifespan of the adsorbent material but also the technical operability of these filtration systems. Out of three recalcitrant OMPs monitored (carbamazepine, diazepam and diclofenac), diclofenac was identified as the compound limiting the lifespan of GAC. This is very relevant as this compound is included in the watch list defined by European Union. Several types of GAC are available and the selection of the most suitable GAC should be based on a holistic approach considering technical, economic and environmental indicators. This study provides interesting results about the technical applicability of GAC filters and the aspects to be considered before their installation as post-treatment in WWTPs.

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Table 1. Characterization of secondary effluents from membrane (n=50) and settler (n=28). n represents the number of samples considered to calculate the average value and the standard deviation for each parameter.

	Membrane effluent	Settler effluent
pH	8.1±0.3	8.0±0.3
DOC (mg/L)	3.5±2.7	8.6±4.9
Transmittance at 254 nm (%)	93.1±2.6	89.0±2.4
N-NH ₄ ⁺ (mg/L)	n.d.	12.0±7.2
N-NO ₂ ⁻ (mg/L)	n.d.	0.4±0.2
N-NO ₃ ⁻ (mg/L)	41.9±12.0	19.0±4.7
TSS (mg/L)	n.d.	32.0±15.3

*n.d.: not detected

Table 2. Concentrations of OMPs ($\mu\text{g/L}$) detected in membrane (n=10) and settler (n=12) effluents during whole operation of GAC filters. n represents the number of samples considered to calculate the average value and the standard deviation for each parameter.

	Membrane effluent	Settler effluent
CBZ	12.46 \pm 4.78	14.00 \pm 2.88
DZP	8.22 \pm 2.91	9.29 \pm 2.56
DCF	3.17 \pm 1.38	5.73 \pm 3.74
ADBI	3.99 \pm 1.27	2.86 \pm 0.66
HHCB	3.67 \pm 0.94	2.33 \pm 0.65
AHTN	2.90 \pm 0.57	1.96 \pm 0.42
FLX	1.24 \pm 0.40	2.03 \pm 0.28
NPX	0.55 \pm 0.21	0.49 \pm 0.20
ROX	0.25 \pm 0.25	1.45 \pm 0.99
BPA	0.38 \pm 0.14	0.73 \pm 0.38
IBP	0.28 \pm 0.17	0.69 \pm 0.30
TCS	0.29 \pm 0.22	0.59 \pm 0.22
ERY	0.04 \pm 0.04	0.62 \pm 0.54
SMX	0.005 \pm 0.003	0.53 \pm 0.53
TMP	0.01 \pm 0.00	0.02 \pm 0.00
EE2	0.07 \pm 0.02	0.18 \pm 0.02
E2	0.02 \pm 0.01	0.02 \pm 0.01
E1	0.02 \pm 0.00	0.03 \pm 0.02

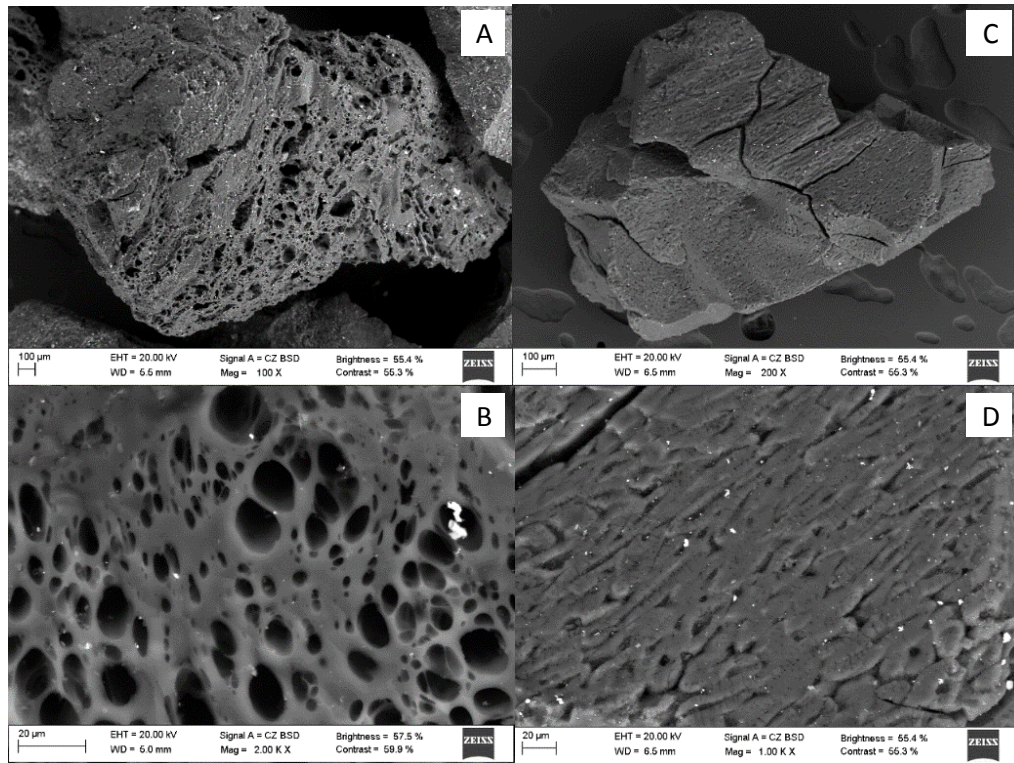


Figure 1. SEM images obtained for GAC based on bituminous carbon (A, B) and GAC based on coconut shell (C, D).

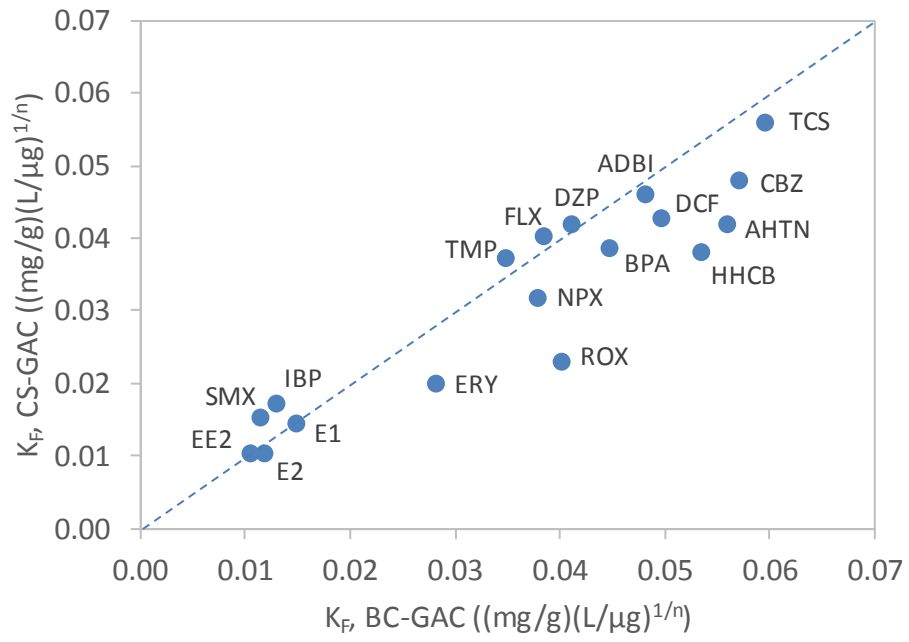


Figure 2. Freundlich isotherm constants (K_f) obtained during the adsorption experiments of selected OMPs on BC-GAC and CS-GAC.

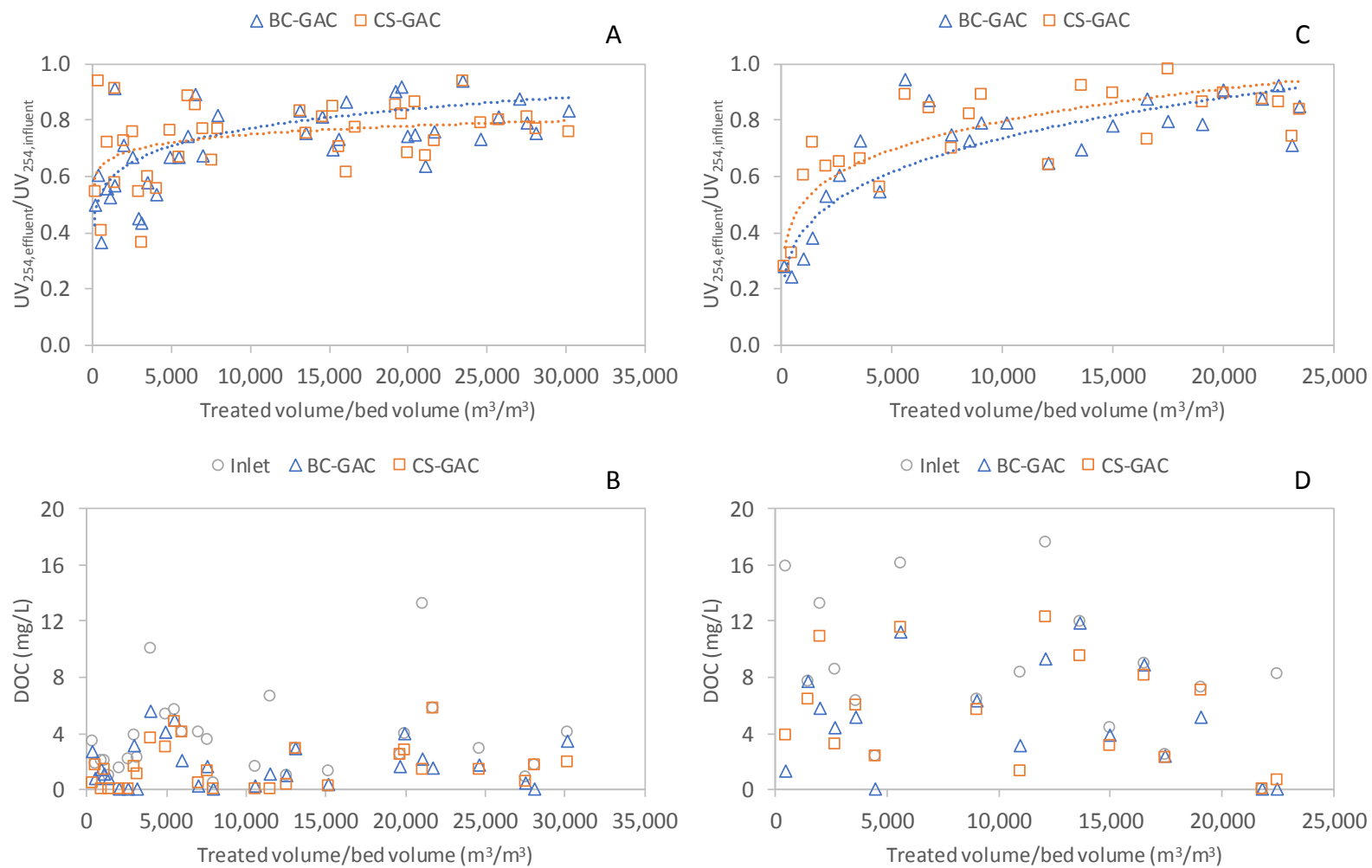


Figure 3. UV absorbance at 254 nm and DOC detected in BC-GAC and CS-GAC filters treating membrane (A, B) and settler (C, D) effluents. Dash lines represent the trend line of the points throughout the operation.

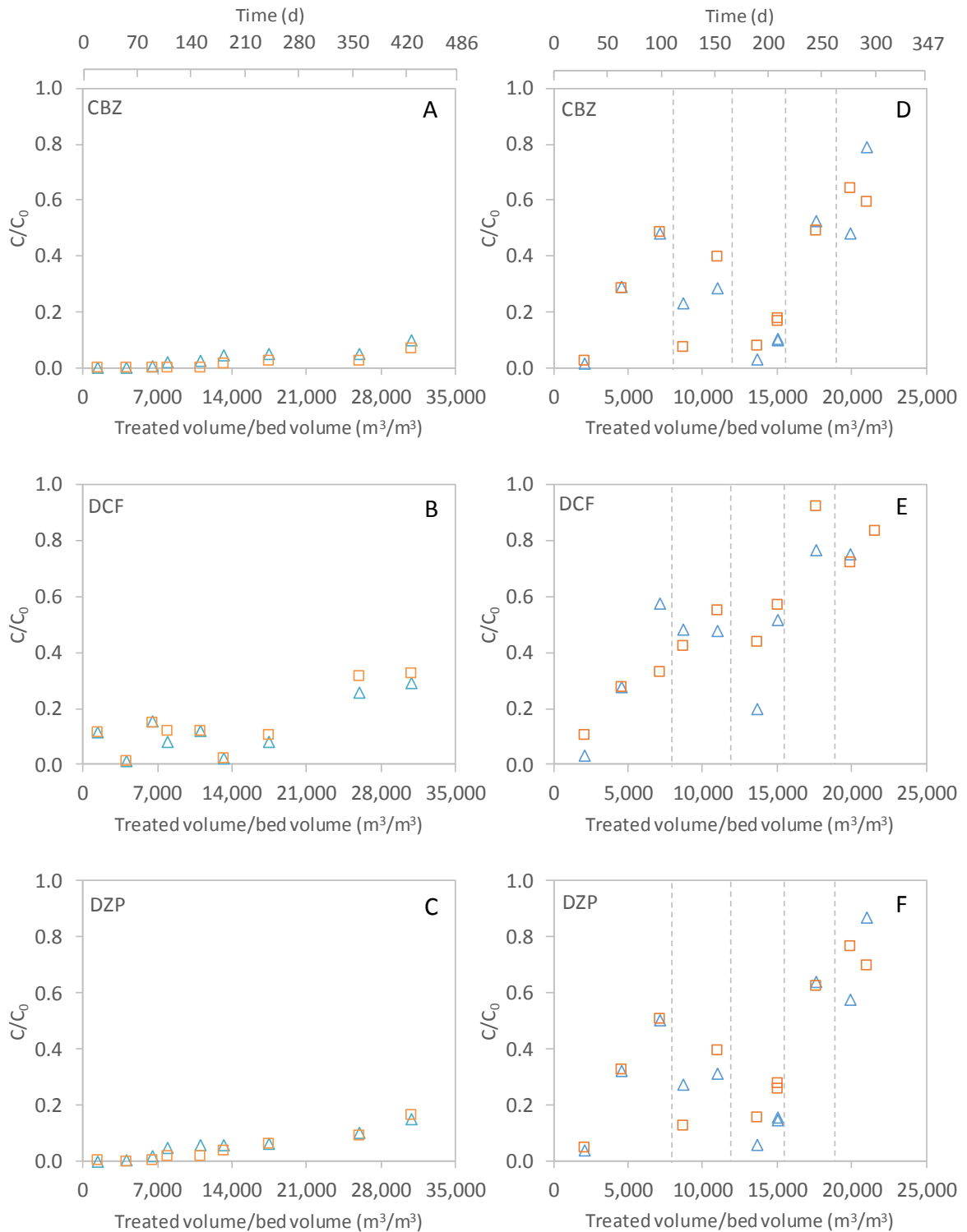


Figure 4. Breakthrough profiles obtained for carbamazepine, diclofenac and diazepam in BC-GAC (triangle) and CS-GAC (square) filters treating membrane (A, B and C) and settler (D, E and F) effluents. Dash lines represent the periodical cleanings.