Influence of the properties of 7 micro-grain activated carbons on organic micropollutants removal from wastewater effluent

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Authors

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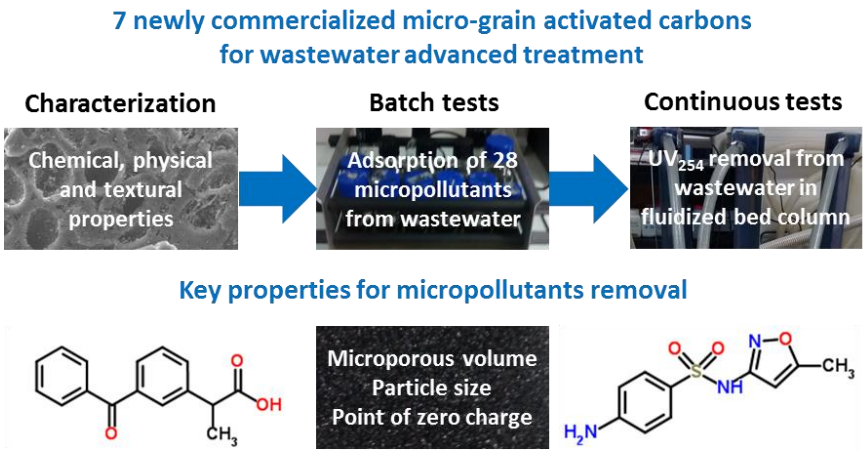
Highlights

- 7 commercial µGACs were characterized and tested with real wastewater
- A percentage of microporous volume higher than 65% reduced OMPs adsorption
- DOM reduced the adsorption of negatively-charged OMPs more than positive ones
- OMPs charge, hydrophobicity and minimal projection area influenced their adsorption
- The µGACs particle size had an impact on UV_{254} removal in continuous column tests

Graphical abstract



Abstract

Most studies dedicated to organic micropollutants (OMPs) removal from wastewater effluents by adsorption onto activated carbon (AC) only consider a few conventional AC properties. The link between OMPs removal and these properties is often missing, which limits the understanding of the adsorption process and the interpretation of the results. The chemical, physical and textural properties of seven newly commercialized micro-grain activated carbons (µGACs) were determined to assess their influence on the removal of 28 OMPs. Conventional batch tests with wastewater effluent showed that a high percentage of microporous volume (> 65%) was detrimental for the removal of 10 OMPs, probably due to a higher blockage of micropores by dissolved organic matter (DOM). The removal of 5 OMPs was correlated with µGACs surface chemistry properties (i.e. charge) which were potentially modified by DOM adsorption or inorganic species, thus favoring the adsorption of positively-charge compounds. A combination of OMPs properties including their charge, hydrophobicity and minimal projection area could explain their removal. Correlations were found between the removal of several OMPs and UV_{254} and dissolved organic carbon, suggesting that DOM and OMPs interacted with each other or followed similar adsorption mechanisms. A decrease in µGACs particle size had a positive impact on UV_{254} removal under continuous-flow conditions in columns representative of a large-scale pilot due to better expansion.

Keywords

Wastewater advanced treatment; Organic micropollutants; Adsorption; Micro-grain activated carbon.

1. Introduction

Advanced processes from the drinking water industry have been increasingly transferred to wastewater treatment plants to find an adequate technology for organic micropollutants (OMPs) removal, and activated carbon (AC) adsorption is a promising solution as it is easy to use, flexible and doesn't produce byproducts as compared to oxidation processes (Bui et al., 2016). Two types of ACs are commonly employed for drinking water production and advanced wastewater treatment: powdered activated carbon (PAC) and granular activated carbon (GAC). PAC, with particle sizes smaller than 100 µm, can be used in conventional processes (Streicher et al., 2016) or in contact reactors followed by a separation step (i.e. membrane filtration or coagulation/flocculation) (Mailler et al., 2015; Margot et al., 2013). GAC, with particle sizes higher than 800 µm, is used in fixed bed filters (Benstoem et al., 2017; Ek et al., 2014; Paredes et al., 2016). Emerging types of ACs have been studied in recent years, such as micro-grain activated carbon (µGAC) with a particle size ranging from 100 to 800 µm (Alves et al., 2018; Guillossou et al., 2019; Mailler et al., 2016a). µGACs have the advantages of being regenerable like GACs and easily fluidized like PACs but without the need of a separation step. The properties of µGACs are however poorly documented, especially in conjunction with their performances in terms of OMPs removal.

The adsorption of OMPs onto AC is a complex process that depends on many factors, including the chemical, physical and textural characteristics of the AC. These characteristics include particle density and size, surface area, pores sizes, pore volume distribution (micro-, meso- or macropores) and the presence of surface functional groups. Raposo et al. (2009) studied the adsorption of methylene blue on 3 GACs with 5 different particle sizes and found a decrease in methylene blue adsorption with an increase in particle size. The decrease in particle size allows, for an identical activated carbon mass, an increase of the available external surface area and thus facilitates the access to adsorption sites for OMPs. The particle size also influences AC expansion in fluidized bed reactors. An excessive expansion can lead to mass loss whereas an insufficient expansion increases the energy consumption and decreases the mass transfer (Bello et al., 2017).

The adsorption capacity depends on both textural and chemical characteristics of the AC. Mailler et al. (2016b) observed that the efficiency of 4 PACs was linked to their specific surface (Brunauer-Emmett-Teller, BET) which could be estimated from bulk density measurement. Contrarily, Benstoem and Pinnekamp (2017) showed that the BET surface was not correlated with the removal of 3 OMPs by 5 GACs. The iodine number and the methylene blue number were not correlated with the removal of OMPs, but a good correlation was

observed with the apparent density. Moreover, Zietzschmann et al. (2014a) found that the BET surface and the iodine number of 8 PACs were not correlated with the removal of 7 OMPs. The pore size and the pore volume distributions of the AC also have an impact since the adsorption energy value is related to the pore size relatively to the size of the adsorbate (Hsieh and Teng, 2000). OMPs are preferentially adsorbed onto high-energy adsorption sites which are primarily located in the smallest pores accessible (Quinlivan et al., 2005). The average micropore size is a key parameter for OMPs removal because the largest OMPs can be subjected to size exclusion from the narrowest micropores (Li et al., 2002; Yu et al., 2012). Alves et al. (2018) studied the removal of 23 pharmaceuticals onto 6 µGACs and found that their textural properties played the most important role in the adsorption process in ultrapure water. The mesoporous volume was better correlated with OMPs removal than the microporous volume. Some authors observed that a low mesoporous volume is problematic for OMPs adsorption because of a possible pore blockage in the presence of DOM which is preferentially adsorbed onto mesopores and large micropores (Li et al., 2003; Newcombe et al., 2002b). Mesopores play a key role by adsorbing DOM and preventing micropores blockage which would further limit OMPs removal.

The surface chemistry of ACs (i.e. the presence of heteroatoms) leads to the presence of acidic and/or basic functional groups which may influence OMPs adsorption (Karanfil et al., 1996; Li et al., 2002). The AC surface can be charged due to protonation or deprotonation of these functional groups, and the point of zero charge (pH_{pzc}) is defined as the pH value of the solution required to give a zero net surface charge. It is an important parameter controlling the electrostatic interactions between DOM, OMPs and the AC (Newcombe, 1994; Yu et al., 2012). Alves et al. (2018) observed that in the presence of wastewater effluent, the surface chemistry of µGACs had more influence than textural properties due to the adsorption of DOM which modified µGACs surface chemistry. The presence of acidic functional groups (e.g. carboxylic acids, phenols, lactones) can also lead to the formation of water molecule clusters that can cause pore blockage and consequently prevent OMPs removal (Delgado et al., 2014; Li et al., 2002; Quinlivan et al., 2005).

Many studies have been carried out about the characterization of AC and the influence of their characteristics on the adsorption of OMPs, but most of the time only a limited number of OMPs were studied (Delgado et al., 2014; Yu et al., 2008), or experimental conditions were far from those of wastewater treatment facilities (e.g. in deionized/ultra-pure water) (Li et al., 2002; Yu et al., 2008). On the other hand, studies have been conducted

in advanced wastewater treatment facilities or in laboratory with real wastewater effluents, but AC characteristics are often lacking which limits the interpretation of the results (Benstoem et al., 2017; Margot et al., 2013).

The aim of this study was to fully characterize seven newly commercialized µGACs and to assess the influence of their properties on OMPs adsorption. First, a large diversity of chemical, physical and textural properties of the µGACs were determined. Then, conventional batch tests were conducted to determine the removal of 28 OMPs from a real wastewater effluent. A statistical analysis was assessed to explore possible correlations existing between the chemical, physical and textural properties of the µGACs and OMPs removal. The properties of OMPs (e.g. charge, hydrophobicity and minimal projection area) were also considered to understand their removal. Finally, column tests were conducted in the laboratory under operative conditions that can be considered as representative of a large-scale pilot (i.e. continuous-flow mode, fluidized bed and similar carbon/flow ratio) to estimate bed expansion and optimal ascending velocity. Breakthrough curves of UV absorbance at 254 nm (UV_{254}) were obtained for each µGAC to assess whether simple column tests carried out under operative conditions could be complementary to batch tests as an operational tool.

2. Material and methods

2.1. µGACs

The seven µGACs were activated or reactivated by steam. Three µGACs were regenerated: ReSorb MC (RS, Jacobi) regenerated from AquaSorb 630 (AS-6, from aggregated mineral base, Jacobi), Norit REACT 2442 (NR, Cabot) regenerated from Norit GAC 2442 (NG, from re-aggregated coal, Cabot) and CycleCarb 305 (CC, from bituminous coal, Calgon Carbon) also produced from a regenerated AC. The other µGACs studied were PC 1000 300 (PC, from vegetal material, DaCarb) and AquaSorb 2000 (AS-2, from bituminous coal, Jacobi). µGACs were dried for 24 h at 105 °C prior to each experiment.

2.2. µGACs chemical, physical and textural characterization

The physical, textural and chemical properties commonly described in the literature for AC and determined in this study are listed in Table S1 along with the method used and the theory or model applied for calculations.

Nitrogen at 77.4 K adsorption – desorption isotherms were obtained to examine textural properties. Tube tests measurements and helium pycnometry were performed to determine the apparent density and the density, respectively. Elemental analysis was performed to evaluate the carbon, hydrogen, nitrogen, sulfur, oxygen and ash contents. Mass titration was used to measure pH_{pzc}, and Boehm titration allowed the quantification of total basic and total acidic groups. SEM-EDX analyses were performed to determine the mineral impurities on µGACs surface. The particle size distribution was determined using a sieve shaker (AS 200 digit, Retsch) with 8 sieves (800, 630, 500, 400, 315, 160, 100 and < 100 µm). 100 g of µGAC sample were shaken for 10 min and the mass retained by each sieve was weighed and the intercept for 50% of the cumulative mass (d_{50}) was calculated. More information about the methods and experimental details are available in the supplementary information (Text S1).

The methylene blue number, defined as the amount of methylene blue (MB) adsorbed on a porous material, is a common indicator to evaluate the adsorptive capacity of an AC for OMPs with a close molecular size (Lussier et al., 1994; Raposo et al., 2009). 0.5 L of 400 mg/L MB solution (VWR) was placed in a beaker with 0.625 g of activated carbon at room temperature and under controlled stirring on a jar test bench. The experiment was stopped when the adsorption equilibrium was reached for each µGAC (UV_{254} removal variation < 1%) and the samples were then filtered on a 0.45 µm PVDF filter before analysis. A second experiment was conducted with similar operational conditions and the same particle size for all µGACs (crushed and sieved between 50 and 63 µm) to overcome the influence of particle size and evaluate the effect of other characteristics. The contact time was reduced to 30 min (similar contact time to batch tests performed with OMPs) since adsorption kinetics are much faster for PAC than for µGAC. Residual MB concentrations were determined with UV absorbance at 254 nm (Genesys 10S UV-VIS spectrophotometer, Thermo Scientific) based on a calibration range (0-400 mg/L).

2.3. Batch tests

Prior to the batch tests, µGACs were crushed and sieved between 50 and 63 µm to ensure proper adsorption after 30 min and to avoid the influence of particle size which would have masked the influence of other properties. Nitrified water (secondary wastewater effluent, pH = 7.2, temperature = 19 °C) was sampled before the denitrification stage from the Seine Centre WWTP (Colombes, France) (Text S2). 1.5 L of the nitrified

water was placed in a glass bottle with 15 mg of activated carbon (dose of 10 mg/L) at room temperature and under strong stirring (300 rotation per minute) on a stirring table during 30 min. At the end of the experiment, appropriate volumes of samples were homogenized and filtered on 0.7 µm GF/F glass filters (Whatman) prior to analyses. Multiple tests have shown that for an identical activated carbon dose (10 mg/L, CycleCarb 305) and a similar water quality, the removal of micropollutants is not very variable (< 10%, Figure S1) and negligible compared to the variability observed here between coals. As a result, experiments with other AC were carried out only once. Dissolved organic carbon (DOC) was analyzed by the certified SIAAP laboratory (NF EN 1484, limit of quantification = 0.3 mgC/L). 28 OMPs (21 pharmaceuticals, 6 pesticides and 1 perfluorinated acid) were analyzed within 48 h at the Institute of Analytical Sciences (ISA – Villeurbanne, France) by liquid chromatography coupled to tandem mass spectroscopy (Vulliet et al., 2011). Information about OMPs physico-chemical characteristics and the analytical procedures used are provided in the supporting information (Table S2). OMPs removal was calculated following the approach of Choubert et al. (2017), which stated that the uncertainty on OMP concentrations in wastewater generally ranges from 30% to 100% when the measured value is lower than 2.5 to 10 times the limit of quantification (LOQ) of the compound. Therefore, when a compound was quantified at levels above 5 times the LOQ in the nitrified water and above the LOQ after adsorption, the removal was conventionally calculated. When a compound concentration was above 5 times the LOQ in the nitrified water but below the LOQ after adsorption, the removal was estimated using LOQ/2. Removals were not calculated when concentrations in both the nitrified water and after adsorption ranged between the LOQ and 5 times the LOQ. UV_{254} was measured directly after sampling and filtration on 0.45 µm polyvinylidene fluoride filters (Milex®, Merck) in a 1 cm quartz cuvette using a spectrophotometer (Genesys 10S UV-Vis, Thermo Scientific).

2.4. Column tests

Continuous-flow column tests were performed at the Seine Centre WWTP. The nitrified water was pumped at a controlled ascending flow (14 L/h) in polyvinyl chloride columns operated in parallel (height = 100 cm, diameter = 4.2 cm, cross section = 13.8 cm^2, volume = 1380 cm^3) (Figure S2). 115 g of µGAC were introduced to get the same mass per volume of water as in the large-scale pilot studied in previous researches (83.7 kg/m^3, CarboPlus®, Saur) (Mailler et al., 2016a). The fluidized carbon bed height was measured for various ascending water velocities (ranging from 0 to 20 m/h) to determine µGACs bed expansion. Due to excessive expansion

in the case of PC µGAC, the ascending water velocity was limited to 10 m/h to avoid carbon mass loss. The results reported in literature show that UV_{254} removal can provide a good estimation of organic matter adsorption and can be used to monitor OMPs removal (Altmann et al., 2016; Mailler et al., 2016a; Zietzschmann et al., 2014; Ziska et al., 2016). Therefore, the adsorption performances of the 7 µGACs under operative conditions close to those of a full-scale application were evaluated by measuring UV_{254} at the entrance and at the exit of the columns. UV_{254} was first measured every hour (0-8h) then twice a day until the bed equilibrium was reached (UV_{254} removal variation < 1%).

2.5. Statistical analysis

Data were treated with the R software (R Core Team, 2007) with the *Hmisc* package (E Harrel Jr, 2017) and the *rcorr* function in order to explore for possible correlations between µGACs properties, OMPs removal and column tests results.

3. Results

3.1. µGACs characterization

3.1.1. µGACs physical, textural and chemical properties

The properties of the 7 µGACs are summarized in Table 1. The values obtained for the BET surface were lower for CC, RS and NR (748, 527 and 885 m^2/g, respectively) which are regenerated µGACs, showing as expected that reactivation had a substantial negative impact on ACs textural properties (Han et al., 2014). The BET surface was positively correlated with both the total porous volume ($r_{Pearson}$ = 0.85, p-value = 0.014), the microporous volume ($r_{Pearson}$ = 0.99, p-value < 0.001), the percentage of microporous volume ($r_{Pearson}$ = 0.96, p-value < 0.001) and negatively correlated with the average pore size ($r_{Pearson}$ = -0.95, p-value = 0.001). As expected, the decrease of the average pore size induces the increase of both the BET surface and the microporous volume value and percentage. As indicated by the shape of the hysteresis loops from nitrogen adsorption-desorption isotherms (Figure S3), these micro-mesoporous carbons (i.e. microporous + mesoporous volume > 75%) exhibited different pore volume distributions. The microporous, mesoporous and macroporous volumes were similarly distributed for CC, AS-2, NG and NR. On the contrary, PC and AS-2

exhibited a higher microporous and macroporous volume but a lower mesoporous volume. Finally, RS exhibited the lowest microporous volume and the highest macroporous volume.

The ash content ranged from 4.4 to 18.5% and its variation among µGACs may be due to differences in the nature of the raw materials used, as well as for mineral impurities on µGACs surface (Table S3). The pH_{pzc} for the studied µGACs ranged from 8.4 to 11.2. Consequently, the surface of the µGACs should be globally positively charged at the pH of conventional WWTP effluents (i.e. pH ~ 7 to 8) and electrostatic interactions are thus expected between µGACs surface, OMPs and DOM, the latter one being negatively charged in those pH conditions (Margot et al., 2013; Yu et al., 2012). According to the measured pH_{pzc} values, µGACs exhibited higher concentrations of basic groups than acidic groups (except for AS-2). The pH_{pzc} values of µGACs were positively correlated with their basic group concentrations ($r_{Pearson}$ = 0.81, p-value = 0.027) and negatively correlated with their acidic group concentrations ($r_{Pearson}$ = -0.84, p-value = 0.018).

µGACs apparent density was in the range 0.43-0.47 g/cm^3 (except for AS-2 with 0.53 g/cm^3), close to a value reported for a widely used GAC (FiltraSorb 400, 0.43 g/cm^3, Al-Degs et al. (2000)), and their density was in the range 2.19-2.33 g/cm^3. Sieving showed that the studied µGACs have a particle size distribution ranging from 250 to 600 µm except PC (100 to 400 µm) and AS-2 (500 to > 800 µm) (Figure S4).

3.1.2. Methylene blue number

MB adsorption was fast until 18 h, then slowed down and reached equilibrium after 160 h with final values (i.e. MB numbers) ranging from 200 to 320 mg/g (Figure 1), similar to those obtained at pH = 5.0 after 160 h from commercial GACs prepared with similar raw material (Wang et al., 2005) or with different raw materials (Rafatullah et al., 2010), and from non-commercial GACs after 48 h (Raposo et al., 2009). The MB number was negatively correlated with the particle size (d_{50}, $r_{Pearson}$ = 0.93, p-value = 0.003), confirming that MB and by extension OMPs adsorption kinetics are controlled by particle size (Delgado et al., 2012; Raposo et al., 2009; Shi et al., 2014). The MB number was also negatively correlated with the ash content ($r_{Pearson}$ = -0.77, p-value = 0.041). Similar observations were reported for the adsorption of bisphenol A which was more important when the mineral content decreased (Bautista-Toledo et al., 2005). According to the authors, the decrease of the mineral content increased the hydrophobicity of the AC which increased the adsorption of bisphenol A.

Table 1. Properties of the seven µGACs. CC = CycleCarb 305, PC = PC 1000 300, AS-2 = AquaSorb 2000, AS-6 = AquaSorb 630, RS = ReSorb MC, NG = Norit GAC 2442 and NR = Norit REACT 2442. *: MB adsorption after 30 min and an identical particle size for all µGACs (50-63 µm).

Properties	Micro-grain activated carbon						
	CC	PC	AS-2	AS-6	RS	NG	NR
BET surface (m^2/g)	748	1255	1006	954	527	1012	885
Total porous volume (cm^3/g)	0.33	0.38	0.32	0.37	0.25	0.35	0.33
Microporous volume (cm^3/g)	0.18	0.29	0.24	0.23	0.12	0.25	0.22
Mesoporous volume (cm^3/g)	0.15	0.05	0.03	0.11	0.08	0.09	0.11
Macroporous volume (cm^3/g)	< 0.01	0.03	0.05	0.03	0.06	0.02	< 0.01
Microporous volume (%)	53	79	73	61	46	69	66
Mesoporous volume (%)	46	12	10	30	31	25	34
Macroporous volume (%)	1	9	17	9	23	6	0
Average pore size (nm)	2.8	1.9	2.0	2.4	3.0	2.2	2.3
Average micropore size (nm)	0.8	0.8	0.9	0.8	0.8	0.8	0.8
Average mesopore size (nm)	6.7	6.6	6.6	8.1	6.9	8.1	7.2
Ash content (%)	18.5	4.4	16.2	13.5	12.4	12.0	9.2
C content (%)	78.6	91.4	82.0	84.8	83.3	85.5	88.5
H content (%)	0.3	0.5	0.4	0.5	0.5	0.3	0.4
N content (%)	0.3	0.4	0.4	0.3	0.5	0.4	0.4
S content (%)	1.2	0.1	0.6	0.1	0.4	0.5	0.4
O content (%)	1.1	3.2	0.4	0.8	3.0	1.3	1.1
pH_{pzc}	10.9	9.8	9.3	10.5	11.2	8.4	9.4
Basic groups (µmol/g)	512	436	66	400	558	236	209
Acid groups (µmol/g)	62	88	71	45	59	156	96
d_{50} (µm)	517	198	689	362	357	439	439
Apparent density (g/cm^3)	0.47	0.44	0.53	0.43	0.46	0.45	0.47
Density (g/cm^3)	2.27	2.31	2.25	2.25	2.19	2.33	2.30
MB number (mg/g)	234	320	206	285	266	288	254
MB adsorption* (mg/g)	126	225	157	151	155	194	164

A second experiment was performed in the same operational conditions but using a similar particle size for all µGACs (crushed and sieved between 50 and 63 µm) to overcome the influence of the particle size. MB adsorption after 30 min was negatively correlated with the ash content ($r_{Pearson}$ = -0.86, p-value = 0.013) but positively correlated with the carbon content ($r_{Pearson}$ = 0.85, p-value = 0.017). Those results confirmed that the presence of mineral elements impaired MB adsorption. MB adsorption was correlated to a lesser extent with the BET surface ($r_{Pearson}$ = 0.73, p-value = 0.063) which indicates that MB adsorption can only be used to compare the adsorption capacity of AC with a similar particle size.

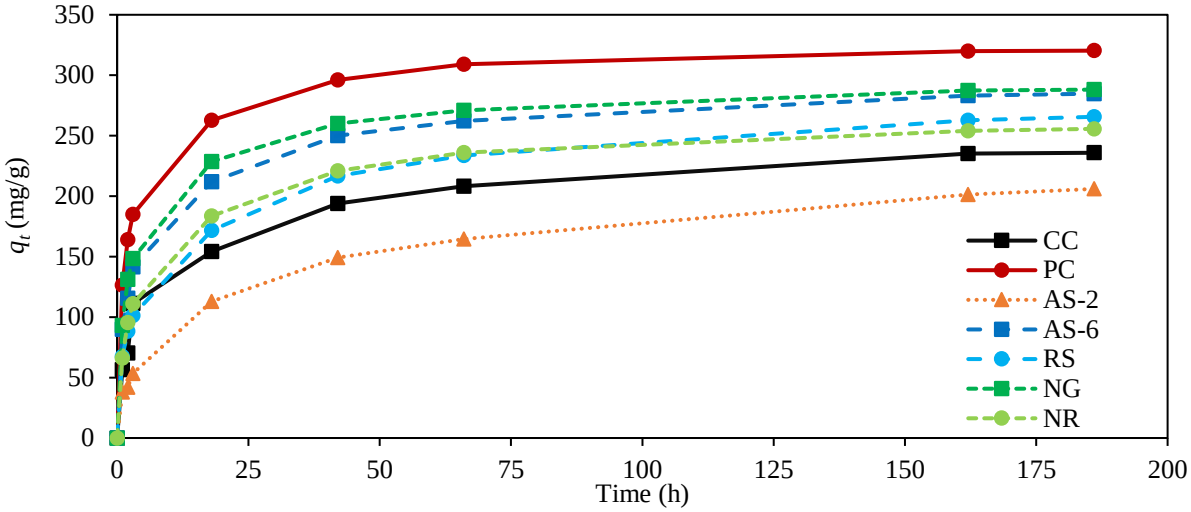


Figure 1. Evolution of the quantity of MB adsorbed (q_t, mg of methylene blue per g of µGAC) on the seven µGACs in batch tests during 186 h (initial MB concentration = 400 mg/L, activated carbon concentration = 0.625 g/L).

3.1.3. Expansion test

Bed expansion was measured in continuous-flow column experiments to determine the behavior of each µGAC in conditions similar to those applied to a full-scale CarboPlus® process (i.e. continuous flow with up to 15 m/h fluid velocity). Bed expansion started to increase linearly above a fluid velocity of 4-6 m/h, except for PC (2 m/h) and AS-2 (10 m/h) (Figure S5), and it was negatively correlated with the particle size (d_{50}, $r_{Pearson}$ = -0.97, p -value < 0.001) as expected from the Ergun equation which is used for describing fluidized bed expansion (Ergun and Orning, 1949). The particles density can also exert an influence on expansion, with dense particles requiring high up-flow velocity to achieve expansion (Bello et al., 2017). However, the density was not the main parameter controlling bed expansion in our experiments because all µGACs had similar density. AS-2 exhibited a limited expansion (i.e. bed expansion of only ~ 10-20% at 15 m/h), which would lead to insufficient particle mixing, heat and mass transfers in a reactor at the industrial scale and therefore to reduced adsorption performances (Bello et al., 2017). On the other hand, PC exhibited excessive expansion leading to mass loss at fluid velocities higher than 10 m/h, which would be detrimental for a use at the pilot scale (e.g. in the CarboPlus® process).

3.2. OMPs adsorption test

Out of the 28 OMP monitored, 7 OMPs (acetamiprid, clothianidin, estrone, ibuprofen, imidacloprid, thiacloprid and thiamethoxam) were not detected in the secondary wastewater effluent. The OMPs

concentration ranged from 8 ng/L for PFOS to 805 ng/L for sulfamethoxazole (Table S2). Ciprofloxacin, norfloxacin and tetracycline were quantified in the wastewater but their removal was not calculated (values close to their respective LOQ). The OMPs, UV_{254}, DOC removals and average OMPs removal for each µGAG are illustrated in Figure 2.

Among the 18 OMPs considered, the highest OMPs removals were obtained for RS (average removal ± standard deviation = 38 ± 16%), NR (34 ± 16%), AS-6 (35 ± 15%) followed by CC (27 ± 7%) and NG (27 ± 14%), while the lowest average removals were obtained for PC (22 ± 6%) and AS-2 (23 ± 10%) (Figure 2). These results could be surprising since PC showed the highest values of BET surface (1 255 m^2/g), total porous volume (0.376 cm^3/g) and microporous volume (0.295 cm^3/g), while RS had the lowest values of BET surface (527 m^2/g), total porous volume (0.252 cm^3/g) and microporous volume (0.117 cm^3/g). There was actually a negative correlation between the average OMPs removal and the BET surface ($r_{Spearman}$ = -0.79, p-value = 0.033), as well as with the microporous volume ($r_{Spearman}$ = -0.79, p-value = 0.033) and the percentage of microporous volume ($r_{Spearman}$ = -0.81, p-value = 0.027, Figure 3). As previously mentioned (part 3.1.1.), these 4 properties are all linked, which means that the correlations observed with the average removal may reflect a single phenomenon. The average removal decreased for µGACs with microporous volumes above 65% (Figure 3), despite the fact that OMPs are generally considered to be preferentially adsorbed into micropores unlike DOM (Li et al., 2002; Quinlivan et al., 2005). An increase in the percentage of microporous volume leads to a decrease in macro- and mesoporous volumes, which play a key role in OMPs removal by adsorbing the DOM also present in the bulk water (Newcombe et al., 2002a). Therefore, for the same amount of DOM adsorbed, the surface coverage of DOM on AC is globally lower with an increase in the percentage of the microporous volume but is higher in macro- and mesopores (Li et al., 2003). An increase of the AC surface coverage by DOM in macro- and mesopores was demonstrated to exert a negative impact on OMPs surface diffusion, and the pore blockage it caused was higher for AC showing a higher percentage of micropores (Li et al., 2003).

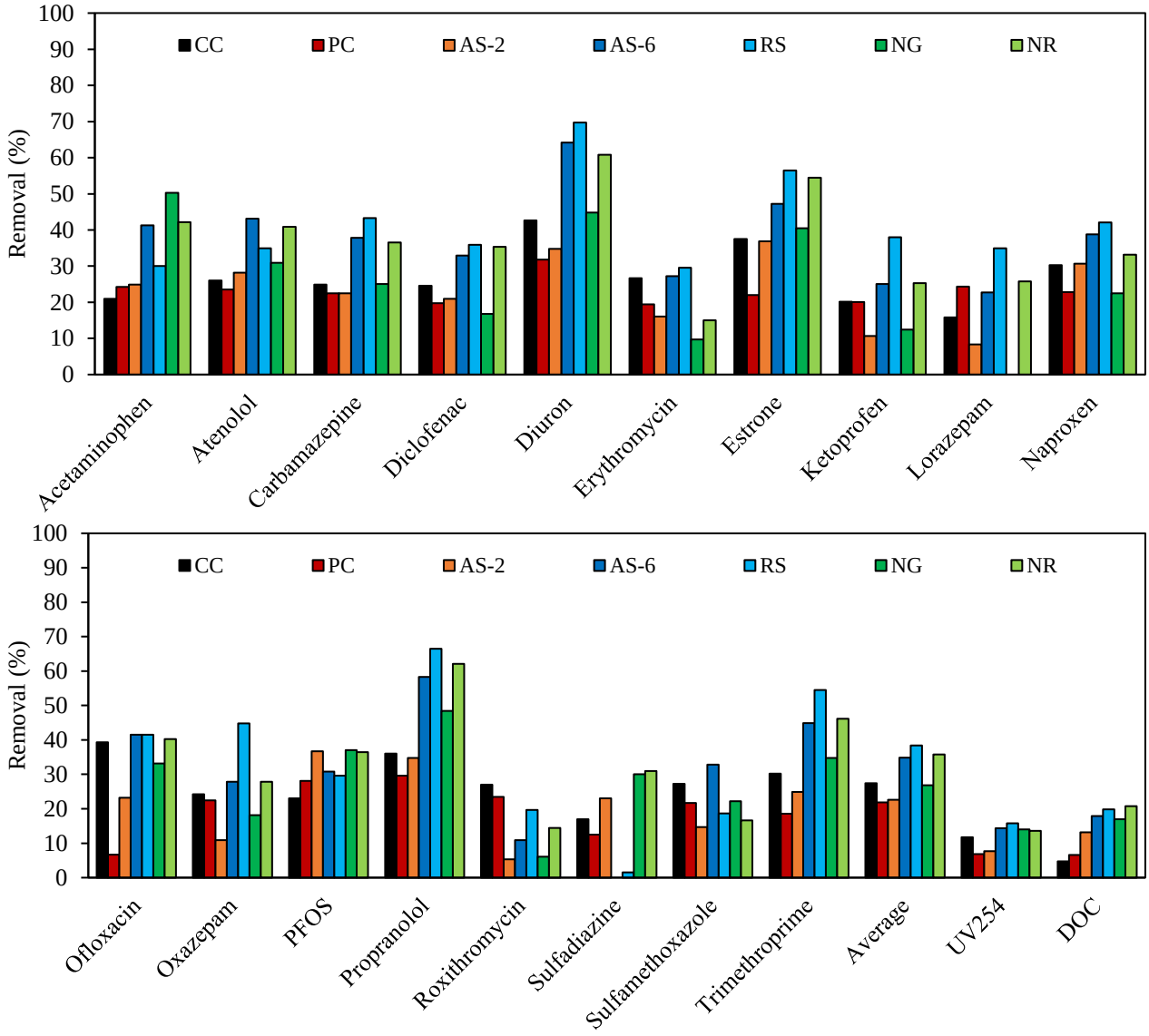


Figure 2. OMPs, UV_{254}, DOC removals and average OMPs removal for the 7 µGACs studied (10 mg/L, crushed and sieved at 50-63 µm, initial UV_{254} = 0.204 1/cm and initial DOC = 10.6 mgC/L) after 30 min of contact time with nitrified water.

A positive correlation was observed between the average removal and the average pore size ($r_{Spearman}$ = 0.81, p-value = 0.027), but no correlation was found with MB adsorption for a similar particle size. Several molecules (carbamazepine, diuron, ofloxacine and oxazepam) exhibited a negative correlation between their removal and the percentage of micropores ($r_{Spearman}$ = -0.78, -0.79, -0.87 and -0.78 and p-value < 0.05, respectively) (Figure 3). The percentage of microporous volume should not exceed 65 % to ensure DOM adsorption in macro- and mesopores and to avoid micropores blockage.

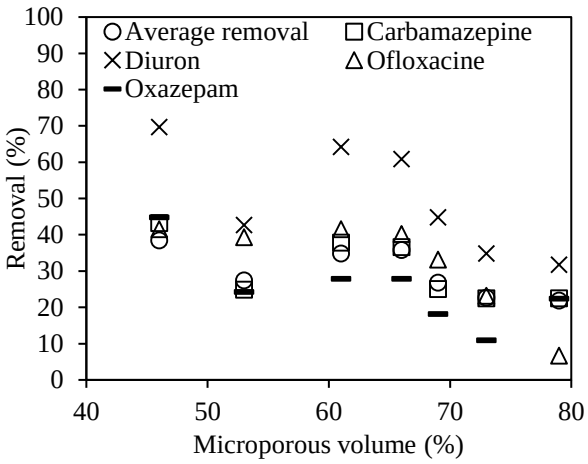


Figure 3. Removal of selected OMPs and the average removal of the 18 OMPs according to the percentage of microporous volume for the 7 µGACs studied (10 mg/L, crushed and sieved at 50-63 µm) after 30 min of contact time with nitrified water.

µGACs surface chemistry also had an impact on OMPs adsorption. A positive correlation was observed between the pH_{pzc} and the removal of erythromycin ($r_{Spearnan}$ = 0.93, p-value = 0.007) while a negative correlation was found for PFOS ($r_{Spearnan}$ = -0.82, p-value = 0.034). The increase of the point of zero charge, thus the positive charges on the activated carbon surface, improved the adsorption of the DOM which was negatively charged at the pH of the effluent. Moreover, DOM adsorption can modify the net charge of the activated carbon surface to negative values and consequently increase the adsorption of erythromycin (positively charged) and decrease the adsorption of PFOS (negatively charged). In the same way, a positive correlation was also found between the quantity of basic groups and roxithromycine ($r_{Spearnan}$ = -0.79, p-value = 0.048) which is positively charged, while a positive correlation was observed between the quantity of acidic groups and sulfadiazine ($r_{Spearnan}$ = -0.86, p-value = 0.024) which is mostly negatively charged. The absence of correlation for other positively (atenolol, propranolol and trimethoprim) and negatively charged compounds (diclofenac, ketoprofen, naproxen, ofloxacin and sulfamethoxazole) indicated that other phenomena influenced their adsorption. These phenomena could include hydrophobic interactions and hydrogen bonds. The study of these interactions, whom study requires specific experiments (e.g. modification of activated carbon surface chemistry, Mahajan et al., 1980) or analytical techniques (e.g. FTIR, Tran et al., 2017a), is more complex than that of electrostatic interactions, and the presence of dissolved organic matter also complicates the interpretations.

The mineral composition of the nitrified water was not determined during the study (except nitrogenous and phosphorous species), but the concentrations of most minerals were available for the WWTP treated water

and are presented in Table S4. The chemical composition (in terms of nutrients) of the nitrified is also available in the supplementary material (Table S5). Inorganic ions could influence the electrostatic interactions between activated carbon, dissolved organic matter and micropollutants as observed at the surface of membranes used in filtration processes. The formation of cation bridges was indeed reported between the membrane surface and DOM in the presence of calcium ions (Bellona et al., 2004). The confirmation of such an impact of inorganic species on the adsorption of OMPs and DOM would require additional experiments.

No correlation was found between any specific OMPs property and the removal on each µGAC. Adsorption is a complex process resulting from the influence of several OMPs properties such as the charge, the size, the hydrophobicity or the presence of specific groups. The obtained removals can be explained by analyzing the physico-chemical properties of each targeted compound and their link with µGACs characteristics. For some OMPs, limiting and/or strongly drifting factors can be highlighted. Erythromycin and roxithromycin are large compounds (molar mass > 700 g/mol) with a minimal projection area of 55 and 69 $Å^2$, respectively. The average micropore size of most µGACs was 8 Å, which gave an opening area of 50 $Å^2$ based on the assumption that micropores are cylindrical. These two OMPs were therefore too large to access most micropores, which explained their reduced adsorption capacity and thus their low removal (i.e. the average removal for the 7 µGACs was 21% for erythromycin and 15% for roxithromycin). Moreover, they may have been subject to steric hindrance with the DOM during diffusion from the water to the activated carbon pores, as well as competition for adsorption sites on larger micropores and mesopores.

The positively charged compounds atenolol, propranolol and trimethoprim were among the best removed OMPs (average removal for the 7 µGACs of 33, 48 and 36%, respectively). However, no correlation was observed between their removal and pH_{pzc} values This difference from other OMPs was attributed to the presence of DOM, which modified the surface chemistry and thus inhibited the effect of the pH_{pzc} of µGACs (Newcombe, 1994; Yu et al., 2012). Adsorption of the positively charged compounds was therefore favored by attractive electrostatic interactions with the negatively charged DOM adsorbed onto the activated carbon. Propranolol exhibited the highest removal, probably because its minimal projection area was lower (32 $Å^2$ compared to 42 $Å^2$ for atenolol and 38 $Å^2$ for trimethoprim), thus it was less subjected to steric hindrance with DOM and could access to smaller micropores.

The negatively charged compounds diclofenac, ketoprofen, sulfadiazine and sulfamethoxazole were less removed than other OMPs (average removal between the 7 µGACs ranging from 16 to 27%). This can be explained by the repulsive electrostatic interactions existing with the negatively charged DOM adsorbed onto the activated carbon surface. However, other negatively charged compounds (naproxen, ofloxacin and PFOS) were better removed (31-32%), which suggests that other properties played a role in their adsorption. Naproxen and ofloxacin have linked aromatic rings which may have created π-π interactions with µGACs aromatic rings. PFOS is a fluorosurfactant with a hydrophilic sulfonate group and a hydrophobic fluorinated chain which may have favored its presence at the water/solid interface and thus its adsorption.

Various removals were obtained for neutral compounds: an important adsorption was observed for diuron and estrone (average removals for the 7 µGACs were 50 and 42%, respectively), a medium adsorption for acetaminophen and carbamazepine (average removals of 33 and 30%, respectively) and a low removal for lorazepam and oxazepam (average removal of 19 and 25%, respectively). Carbamazepine, lorazepam and oxazepam (minimal projection area > 33 A^2) are larger than acetaminophen, diuron and estrone (< 28 A^2) and thus were probably subjected to a higher steric hindrance with DOM and could access to smaller micropores. Acetaminophen was less adsorbed and is less hydrophobic (log D = 0.91 at pH 8) than diuron and estrone (log D = 2.53 and 4.31 at pH 8, respectively), which suggests that the hydrophobicity could also play a role for the adsorption of neutral compounds.

3.3. UV_{254} and DOC removal

3.3.1. Batch tests

UV_{254} (initial value = 0.204 mgC/L) and DOC (initial value = 10.6 mgC/L) were measured in the batch experiments to study the adsorption of DOM in conjunction with OMPs. The highest UV_{254} removals were obtained for AS-6, RS, NG and NR (14-15%), then CC (12%) and last PC and AS-2 (7-8%). The UV_{254} removal was negatively correlated with the percentage of microporous volume ($r_{Pearson}$ = -0.75, p-value = 0.052), which confirmed that a higher proportion of both meso- and macroporous volumes favored the adsorption of DOM. AS-6, RS, NG and NR were also the most efficient at removing DOC (17-21%), followed by AS-2 (13%), CC (5%) and PC (7%).

There was a strong positive correlation between the UV_{254} removal and the OMPs average removal ($r_{Pearson}$ = 0.88, p-value = 0.010), carbamazepine ($r_{Pearson}$ = 0.80, p-value = 0.032), diuron ($r_{Pearson}$ = 0.89, p-value = 0.008), estrone ($r_{Pearson}$ = 0.88, p-value = 0.010), ofloxacine ($r_{Pearson}$ = 0.90, p-value = 0.006), propranolol ($r_{Pearson}$ = 0.90, p-value = 0.006) and trimethoprim ($r_{Pearson}$ = 0.93, p-value = 0.003) (Figure 4). Those molecules were among the most removed, which suggested that UV_{254} could only be used to predict the removal of OMPs that were well adsorbed. Correlations were also obtained between the DOC removal and the average OMPs removal ($r_{Pearson}$ = 0.76, p-value = 0.046) (Figure 4), atenolol ($r_{Pearson}$ = 0.83, p-value = 0.020), diuron ($r_{Pearson}$ = 0.77, p-value = 0.046), estrone ($r_{Pearson}$ = 0.020, p-value = 0.83), propranolol ($r_{Pearson}$ = 0.89, p-value = 0.007) and trimethoprim ($r_{Pearson}$ = 0.81, p-value = 0.027).

These correlations suggested that DOM and OMPs followed similar adsorption mechanisms onto activated carbon or that they interacted (e.g. electrostatic interactions) and were adsorbed together as suggested by several studies (Aristilde and Sposito, 2013; Aschermann et al., 2019; Liu et al., 2014). Correlations between OMPs removal and UV_{254} were also observed in other studies (Anumol et al., 2015; Mailler et al., 2016a; Zietzschmann et al., 2014), which confirmed the relevance of UV_{254} as a surrogate for the monitoring of µGACs performances regarding OMPs adsorption.

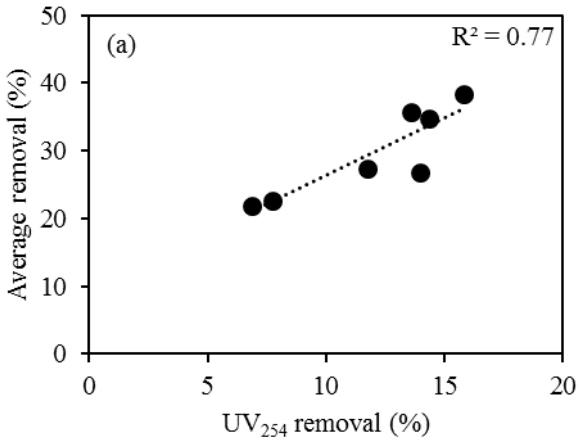


Figure 4. Average OMPs removal (%) versus UV_{254} removal (%)after 30 min of contact with nitrified water (10 mg/L of activated carbon, crushed and sieved at 50-63 µm, initial value for UV_{254} = 0.204 1/cm).

3.3.2. Column tests

UV_{254} removal was investigated in continuous-flow column tests in order to compare the performances of µGACs between batch experiments and operative conditions closer to full-scale application, and to obtain

supplementary information on the influence of µGACs properties on UV_{254} removal. For each µGAC, the UV_{254} removal decreased rapidly during the first 20 hours and stabilized after 200 hours between 10 and 20% except for AS-2 (4%) for which it started to stabilize after only 7 hours (Figure 5). This plateau indicated that adsorption still took place in the columns even if the system reached the equilibrium. It could be due to slow diffusion in pores or to the development of a biological activity on µGACs which degraded the adsorbed DOM and thus liberated some pores for further adsorption. At the end of the experiment, the UV_{254} removal was the highest for AS-6, RS, NG and NR (17-20%), then PC (15%), CC (11%) and last AS-2 (4%). This classification of µGACs is different from batch tests where the highest UV_{254} removals were obtained for AS-6, RS, NG and NR, then CC and last PC and AS-2. No correlations were found with µGACs characteristics.

The low performances of AS-2 were attributed to its limited expansion which reduced the mass transfer from the effluent to the AC surface. Its high percentage of micropores may have also impaired DOM adsorption. Despite higher expansion, surface area and total volume, PC exhibited a UV_{254} removal similar to those obtained with other µGACs. This could be due to its relatively high ratio microporous volume/mesoporous volume which limited its ability to adsorb all DOM fractions and thus increased competition between OMPs and DOM and the pore blockage effect. In contrast to AS-2, the smaller particles size of PC allowed it to compensate the negative impact of its high percentage of microporous volume by a higher expansion and probably faster adsorption kinetics. The particles size is, as expected, an important characteristic to be considered when selecting an activated carbon for an industrial application in the case of a process in fluidized bed.

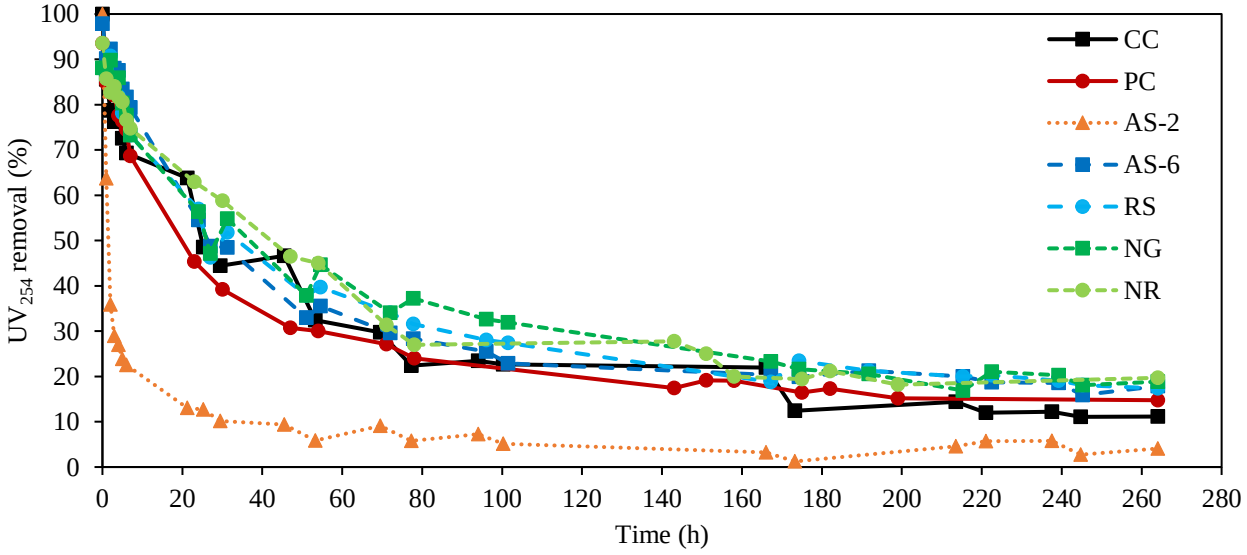


Figure 5. UV_{254} breakthrough curves for the seven µGACs in continuous-flow columns (115 g per column) with nitrified water (233 mL/min) for 11 days.

4. Conclusions

The physical, textural and chemical characterization of the 7 µGACs and the batch tests performed with secondary wastewater effluent revealed the influence of several µGACs properties on OMPs adsorption. An increase in the percentage of microporous volume leads to a decrease in the percentages of macro- and mesoporous volumes which play a key role in OMPs removal by adsorbing DOM and thus reducing micropores blockage. As a recommendation, the percentage of microporous volume should not be higher than 65 % to ensure DOM adsorption in macro- and mesopores and hence to limit micropores blockage. The adsorption of DOM onto µGACs modified their surface charge from positive to negative. This modification promoted the adsorption of positively charged OMPs in contrast to negatively charged OMPs.

In agreement with the literature, OMPs adsorption did not depend on a single specific OMPs property and their removal could rather be explained by a combination of their properties. The minimal projection area was a key property that conditioned the access of OMPs into micropores and influenced their diffusion into µGACs due to steric hindrance and pore blockage with the adsorbed DOM. As a result, the largest molecules (i.e. erythromycin and roxithromycin) were subject to size exclusion and exhibited low removals. The highest removals were obtained with the neutral compounds that showed the highest hydrophobicity values (i.e. log D). Charge was then another parameter influencing OMPs adsorption through electrostatic interactions with DOM, positively charged OMPs being more retained on µGACs covered with DOM than negatively charged OMPs. Other properties (e.g. the presence of hydrophobic functional groups) may explain the various removals obtained for negatively charged OMPs.

A different classification of µGACs for UV_{254} removal was obtained between batch tests and column tests under operative conditions representative of those of a large-scale process. The particle size appeared to be a key parameter controlling µGACs expansion which had an impact on UV_{254} and consequently on OMPs removal for µGACs. It is therefore recommended, before an application on a full-scale installation, to perform column tests in order to anticipate these behaviors which cannot be observed in batch.

The observed trends between OMPs, UV_{254} and DOC removals suggested that DOM and OMPs followed similar adsorption mechanisms on µGACs or interacted and were adsorbed together. The important role of DOM in OMPs adsorption and the various mechanisms involved (i.e. pore blockage, co-adsorption) will be further investigated (e.g. by using fluorescence spectroscopy or size exclusion chromatography) to improve the understanding of the adsorption process.

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