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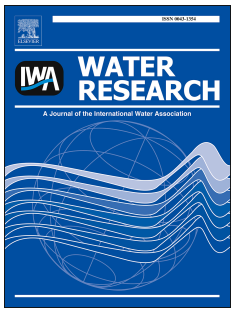

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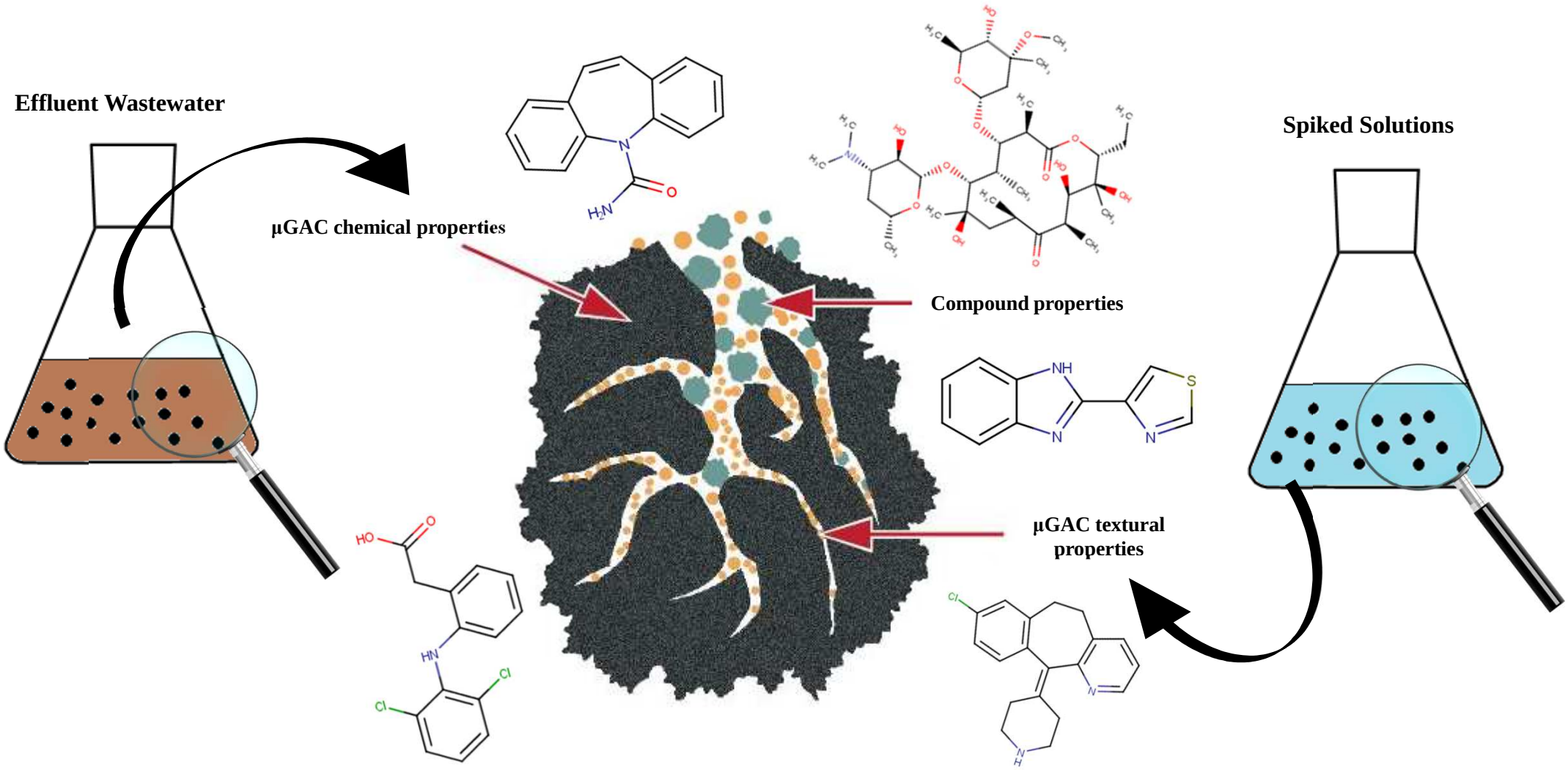

Influencing factors on the removal of pharmaceuticals from water with micro-grain activated carbon

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Abstract:

The removal efficiency of 6 micro-grain AC (μGAC) was examined for 23 selected pharmaceutical compounds, usually found at trace level in municipal wastewater treatment plant (WWTP) effluents. Two different sets of experiments were carried out using distilled water and a real WWTP secondary effluent in order to understand the adsorption mechanisms of pharmaceuticals, including the role of the presence of background organic matter. Physical and chemical properties of μGACs and target pollutants were checked for their potential to predict the pharmaceutical removal. Textural properties of μGACs, and especially the mesopore volume, seemed to play the most important role during the adsorption without background organic matter whereas the chemistry of the μGACs, such as the presence of surface oxygen groups and the point of zero charge, could have more influence in the experiments with WWTP effluent water. Positively charged molecules are better adsorbed due to the influence of the background organic matter and the presence of oxygenated groups in the surface of the μGACs. The UV_{254} removal correlated well with the pharmaceutical removal and it is confirmed as an indicator to control the performance of pharmaceuticals adsorption with μGACs in tertiary treatment.

Key-words: Adsorption; micropollutants; pharmaceuticals; wastewater; water reuse.

1. INTRODUCTION

Organic micropollutants (OMP) comprise a wide group of contaminants present in water at low concentration. They are an expanding class of anthropogenic substances, consisting mainly of active pharmaceutical compounds, personal care products, pesticides, endocrine disruptors and industrial products such as flame retardants and plasticizers (Petrie *et al.*, 2014). Pharmaceuticals, which are systematically discharged through wastewater, are attracting scientist's attention due to their ubiquitous presence in the environment, are constantly detected in the water bodies at trace and ultra-trace levels and mixed with high diversity of substances (Gros *et al.*, 2012). Some associated risks for the aquatic organisms exposed to pharmaceuticals are already known, such as cancer, infertility, fish feminization and bacterial resistance (Caliman and Gavrilescu, 2009).

Current conventional wastewater treatment plants (WWTP) are designed to remove macropollutants (chemical and biochemical oxygen demand and total suspended solids) and nutrients (phosphorous and nitrogen) through a primary and a secondary treatment, but are not efficient in the removal of pharmaceuticals (Meinel *et al*., 2016). Tertiary treatments are employed when high quality effluents are required and can increase removal rates of micropollutants, but are associated with higher costs (Luo *et al.*, 2014).

State of the art of tertiary treatments include advanced oxidation processes (AOP) (Knopp *et al*., 2016; Shu *et al*., 2016) and adsorption on activated carbon (AC). Through AOP, hazardous substances can be generated as oxidation byproducts (Fatta-Kassinos *et al*., 2011; García-Galán *et al*., 2016). In this sense, adsorption using powdered activated carbon (PAC) (Mailler *et al*., 2014; Meinel *et al*., 2016) or granular activated carbon (GAC) (Altmann *et al*., 2016; Benstoem *et al*., 2017; Kennedy *et al.*, 2015) is pointed out as a promising technique, since it can be adapted to any type of WWTP, it is less expensive than AOPs and competes with

ozonation in terms of treatment costs and it does not involve the formation of degradation by-products (Mailler *et al*., 2016).

Micro-grain AC (μGAC), characterized by having a particle size of 200–600 μm (between PAC (<100 μm) and GAC (>800 μm))(Mailler *et al*., 2016) has recently appeared as an interesting form of AC to be used in WWTP due to various operational advantages: μGAC is used in a fluidized bed reducing the solid waste to handle, non-necessity to inject a coagulant such as $FeCl_3$ to prevent AC leakages and overall higher operation simplicity for similar costs (Mailler *et al*., 2016).

Yet, the mechanisms and properties ruling the pharmaceuticals adsorption in AC are still not well-known, thus an accurate knowledge on these issues is required to optimize μGAC adsorption processes towards a better removal of pharmaceuticals. Porosity development and high surface area are generally sought to adsorb organic compounds from water (Fallou *et al.*, 2016). However, these features are not necessarily important when it concerns to pharmaceuticals adsorption from WWTP effluents due to their low occurrence levels in competition with the background organic matter of the water. Due to the large variety of AC produced from different materials and activated with different techniques, there is a wide range of properties conferred on the adsorbent, so it is important to determine which are the most relevant for each purpose.

In the literature few works have attempted to establish relationships between pharmaceuticals removal and AC properties. Zietzschmann *et al.* (2014) studied the influence of three physical PAC properties (BET surface area, iodine number and aniline number) on the removal of seven pharmaceuticals, concluding that these properties were too poor to predict the removal achieved. Accordingly, Benstoem and Pinnekamp, (2017) concluded that BET surface and methylene blue titre were not suitable markers for choosing an appropriate GAC product to eliminate pharmaceuticals from WWTP effluents. Contrarily, Mailler *et al*., (2016) studied the influence of two physical properties (BET surface area and bulk density) of four PACs on the adsorption of 15 pharmaceuticals and they concluded that removal efficiencies correlated well with BET surface area. Furthermore, Mailler *et al.* (2014) studied six physical-chemical

86 properties of 26 pharmaceuticals in a large scale PAC pilot plant using real wastewater, and
87 pointed out that the molecular charge of the pharmaceuticals was the most important property
88 influencing the adsorption. On the other hand, Mailler *et al*., (2016) found that the presence of
89 background organic matter was an important factor considering the competition for adsorption
90 with pharmaceuticals using PAC, but it was insufficient to explain the adsorption performance.
91 Therefore, the interactions between the properties of the AC and the pharmaceuticals are
92 still unclear, especially with μGAC, and further research is required to understand the
93 adsorption mechanisms for the removal of such compounds from WWTP effluents. In this
94 context, the present work studied the adsorption of 23 pharmaceuticals on six different μGAC
95 which were characterized in terms of textural and chemical properties. The pharmaceuticals
96 used were chosen to cover a wide range of therapeutic families with different physical-chemical
97 properties within the compounds usually found in WWTP effluents. The influence of the
98 presence of background organic matter was also assessed performing adsorption tests in both
99 spiked water and real WWTP effluent water.
100 Another issue of particular interest is the applicability of the UV_{254} absorbance to estimate
101 the pharmaceuticals removal (Mailler *et al*., 2016; Anumol et al., 2015; Zietzschmann *et al*.,
102 2014) during adsorption processes. In order to validate this technique in real cases, the
103 correlation of pharmaceuticals removal with the decrease in the UV_{254} was studied both for
104 spiked water and real WWTP effluent.
105

106 **2. MATERIAL AND METHODS**

107 **2.1 Pharmaceuticals as contaminant models**

108 23 pharmaceuticals typically found in the WWTP effluents (Collado *et al*., 2014) were
109 selected as target compounds based on their physical-chemical properties, shown in Table 1,
110 aiming to comprehend the broadest range of molecular weight (MW), log K_{ow}, log D at working
111 pH (pH=8), and the dominant charge at this pH. Partition coefficients, log K_{ow} and log D, can
112 indicate whether the compounds are likely to adhere to solids, incorporate oils and organic

matter, or be soluble in water. The molecular weight of the target compounds ranged between 236.3 and 791.1 g mol^{-1}; log K_{ow} ranged between -0.72 and 5.74; log D ranged between -1.87 and 4.48. 30% of the selected compounds were mostly charged positively, 39% negatively, 22% neutral, and 9% zwitterionic. The chemical structures of the pharmaceuticals considered are shown in Table S1 of the Supporting Information. All the target compounds were purchased from Sigma-Aldrich® with a purity higher than 99%.

2.2 Activated carbons

To perform pharmaceutical adsorption tests, a set of six commercial ACs generated with different precursors and activation processes were selected (see Table 2): Two chemically activated samples were supplied by MeadWestvaco (MWV; U.S.A.), and four steam activated ACs were supplied by Desotec (DST; Belgium), Chemviron Carbon (CMV; Belgium), Calgon (CLG; U.S.A.), and Norit (NRT; U.S.A.). All the ACs tested were exhaustively characterized in our previous works (Cabrera-codony *et al*., 2015; Cabrera-Codony *et al*., 2014) in order to determine the BET surface area (S_{BET}), the total pore volume (V_t), the volume of mesopores with diameter between 2-50 nm (V_{meso}), the volume of micropores with diameter <2 nm (VDR_{N2}) and the volume of micropores narrower than 0.7 nm (VDR_{CO2}) by N_2 and CO_2 adsorption/desorption isotherms. The chemistry of the outermost layers (spectra of the O (1s) and C (1s) was determined by X-ray photoelectron spectroscopy (XPS), and the quantification of the oxygen-containing groups by thermal programed desorption (TPD) of CO and CO_2. The different contributions of oxygen containing groups were obtained by the deconvolution of the XPS and TPD curves in previous work (Cabrera-Codony *et al*., 2014). The pH-point of zero charge ($pH_{(pzc)}$) measurements were carried out following the "pH drift" procedure (Yang *et al*., 2004). The ACs samples were grounded and sieved to obtain μGAC with a similar particle size range between 200 and 400 μm. Previously to their use, the μGAC samples were washed with DI water in order to remove fines, dried at 105 ºC overnight and stored in desiccators until their

use. The main physical and chemical surface properties of the six selected AC are summarized in Table 2.

2.3 Experimental adsorption set up

Adsorption experiments were performed in two sets of experiments following the methodology described by Zietzschmann *et al.* (2014). The first set was carried out with distilled water spiked with pharmaceuticals (spiked) and the second set was with a real secondary effluent (effluent) from a conventional WWTP with the objective of understanding the role of the background organic matter in realistic conditions.

The spiked water was prepared to obtain a final concentration of ca. 20 μg L^{-1} of each contaminant of Table 1 from an initial stock solution of 500 μg L^{-1}. μGAC suspensions of 2 g L^{-1} were prepared in a buffered ammoniun acetate/ammoniun solution (pH 8) to keep the pH constant and stored overnight for full wetting of the μGAC. Experiments were buffered in order to rule out any variation of some pharmaceutical characteristics such as molecule charge and partition coefficients because of pH changes. pH 8 was selected according to the mobile phase pH of the analytical methodology (see section 2.4) and the pH of the wastewater effluent (pH=7.4).

The experiments with spiked water were performed preparing 6 different suspensions of each μGAC (5, 20, 50, 100, 200 and 300 mg L^{-1}). The suspensions were mixed at 25 ºC during 48 hours following the methodology of Zietzschmann *et al.*, 2014. After that, the μGAC was removed using 0.45 μm membrane filters (PTFE, Macherey-Nagel, Germany) and the concentration of pharmaceuticals was analyzed. Theoretical AC doses for 80% of pharmaceutical removal (D80) were calculated in order to obtain comparable data points for the

tested carbons. This was accomplished by linear interpolation using the two data points, which were closest to the theoretical value of D80 (Zietzschmann *et al.*, 2014).

The second set of experiments were carried out adding µGAC to real effluent water samples to obtain a µGAC concentration of 20 mg L^{-1}, according to the typical doses of µGAC (Mailler *et al*., 2016) or PAC used in pilot plants (Altmann *et al*., 2014; De Ridder *et al*., 2011; Kårelid *et al*., 2017; Mailler *et al*., 2014; Margot *et al*., 2013; Ruhl *et al*., 2014; Streicher *et al*., 2016; Zietzschmann *et al*., 2014). Like in spiked water tests, the suspensions were buffered (pH=8) mixed at 25 ºC during 48 hours, filtered and analyzed to compare to the initial concentration of each pharmaceutical in the effluent sample.

2.4 Analytical methodology

Chemical analysis was performed following the methodology developed by Gros *et al.* (2012), using a Waters Acquity Ultra-Performance™ liquid chromatography (UPLC) system, equipped with two binary pumps system (Milford, MA, USA). An Acquity HSS T3 column (50 mm × 2.1 mm i.d., 1.8 µm particle) was used for the compounds analyzed in positive mode of electrospray ionization (PI) and an Acquity BEH C18 column (50 mm × 2.1 mm i.d., 1.7 µm) for the compounds analyzed in negative mode (NI). The solvents used in PI mode were: (A) Methanol and (B) formic acid/ammonium formiate 10 mM (pH 3.2) at flow of 0.5 mL min^{-1} whereas for the compounds analyzed in NI solvents (A) acetonitrile and (B) ammonium acetate/ammonium (pH 8) were used as solvents at 0.6 mL min^{-1} of flow. Sample volume injected was 5 µL. The UPLC instrument was coupled to a 5500 QTRAP hybrid triple quadrupole-linear ion trap mass spectrometer (Applied Biosystems, Foster City, CA, USA) with a turbo Ion Spray source.

Water samples from experiments with spiked waters were injected without further pretreatment in the UPLC-QTRAP, whereas wastewater samples from the second set of experiments with effluent water were pre-concentrated before their analysis. The extraction and clean-up of the WWTP effluent samples was performed following the methodology described in

192 Gros *et al.*, (2012) based on solid phase extraction (SPE) using Oasis HLB cartridges (Waters,
193 Milford, MA, USA). Briefly, an appropriate volume of a Na_2EDTA solution was added to water
194 samples to achieve a final concentration of 0.1% (g solute g solution^{-1}) without pH sample
195 adjustment. The SPE cartridges were conditioned with 5 mL methanol followed by 5 mL HPLC
196 grade water at a flow rate of 2 mL min^{-1}. 50 mL of wastewater were loaded onto the cartridges
197 at a flow rate of 1 mL min^{-1}. Analytes were eluted at a flow rate of 2 mL min^{-1}, using 6 mL of
198 pure methanol. Extracts were evaporated to dryness under a gentle nitrogen stream and
199 reconstituted with 1 mL of methanol/water (10:90, v/v). Finally, 10 µL of a 1 ng µL^{-1} standard
200 mixture containing all isotopically labeled standards were added in the extract as internal
201 standard. Further analysis of the extracts was performed using the above-mentioned
202 methodology based on UPLC-QTRAP. All the samples were analyzed by triplicate. The limits
203 of detection (LOD) and quantification (LOQ) for the analysis of spiked and wastewater samples
204 are gathered together in Tables S2 and S3 respectively. In those analysis that were below the
205 LOQ the concentration was considered 50% of the LOQ.

206 UV_{254} absorbance of filtered aqueous samples was measured in the two set of experiments
207 with spiked water and with WWTP effluent using an UV Vis Thermo Scientific Evolution 60
208 spectrophotometer at a wavelength of 254 nm. The measurements were carried out by triplicate.

209 Total organic carbon (TOC) of effluent sample was determined with a TOC-V CSH/CSN
210 analyzer from SHIMADZU.

211

212 **3. RESULTS**

213 **3.1 Adsorption of pharmaceuticals from spiked water**

214 *3.1.1 Determination of D80*

215 The competitive adsorption of 23 selected pharmaceuticals into 6 µGACs was studied at 6
216 different adsorbent doses ranging from 5 to 300 mg L^{-1}. As it can be observed in Figure S1, the
217 removal of pharmaceuticals depends on the type of µGAC and the concentration of adsorbent
218 used. Therefore, in order to compare the removal efficiency of different µGACs, the parameter

D80 (theoretical AC doses for 80% of pharmaceutical removal) was calculated for each compound following the approach described by Zietzschmann *et al*., (2014) (see section 2.3). Figure 1 shows the D80 values calculated for all the pharmaceuticals with each μGAC, which range from 5 mg L^{-1} of MWV-2 for fluoxetine, to 287 mg L^{-1} of NRT-2 for iopromide. The μGACs with the lowest average D80 (solid lines in Figure 1), and consequently with the highest adsorption capacity, were MWV-2 and MWV-1 with an average D80 (taking into account all the studied pharmaceuticals) of 17±11 mg L^{-1} and 27±23 mg L^{-1} respectively. The μGACs with the highest D80, i.e. with the lowest adsorption capacity, were NRT-2 and DST-2 that presented an average D80 of 144±52 mg L^{-1} and 134±66 mg L^{-1} respectively. MWV-2 and MWV-1 were μGACs produced from wood and activated chemically while NRT-2 and DST-2 are non-coal μGACs activated with steam.

Two pharmaceuticals, venlafaxine and metoprolol, and their two main respective metabolites, o-desmethylvenlafaxine and metoprolol acid, were selected to assess the adsorption of pharmaceutical metabolites compared to their parent compounds because the metabolites are found sometimes at concentrations even higher in the WWTP effluents (Aymerich et al., 2016). The D80 average value of venlafaxine for all the μGACs was 87±70 mg L^{-1} while for o-desmethylvenlafaxine was 115±103 mg L^{-1}. In the case of metoprolol, it presented an average D80 of 52±36 mg L^{-1} while metoprolol acid presented an average D80 of 56±39 mg L^{-1}.

3.1.2 Influence of the physical-chemical properties of the compounds on their adsorption

The influence of the molecular weight (Fig. 2A), hydrophobicity (Fig. 2B), and charge of the pharmaceuticals (Fig. 2C) on the average D80 for each μGAC was evaluated. There was not a strong influence of molecular weight and log D separately, denoted by the lack of linear correlations, however, pharmaceuticals with both low molecular weight and high log D presented lower D80 values. The compounds with the highest average D80 (D80>140 mg L^{-1}) were iopromide (D80 = 155 ± 123 mg L^{-1}) and valsartan (D80 = 150 ± 72 mg L^{-1}). These compounds have high molecular weight (MW>430 g mol^{-1}) and they are relatively hydrophilic (log D<1.5). On the contrary, the compounds that are more adsorbable, namely those with the

246 lowest average D80 (D80<30 mg L^{-1}), were loratidine (D80 = 27 ± 15 mg L^{-1}) and fluoxetine
247 (D80 = 29 ± 21 mg L^{-1}), both less hydrophilic (log D>1.5). In terms of the compound charge,
248 for the chemically activated μGACs , MWV-2 and MWV-1, the compounds with lower D80
249 were the cationic ones. This is due to the fact that these two μGACs have a negative surface
250 charge since the pH of the adsorption (pH = 8) was higher than their $pH_{(pzc)}$ (4.8 and 6.2 for
251 MWV-2 and MWV-1 respectively). In the rest of μGACs the differences were not so relevant.

252 *3.1.3 Influence of the physical-chemical properties of the μGAC on the pharmaceuticals*
253 *adsorption*

254 The relationship between the different textural properties of each μGAC and the average
255 D80 for the removal of the 23 studied pharmaceuticals was also analyzed. In general terms,
256 these physical properties correlated quite well with the average D80. The R^2 for the linear
257 correlation of D80 with V_t, VDR_{N2} and S_{BET} were 0.82, 0.76 and 0.74 respectively (see Figure
258 S2). In all cases the correlation was negative, so the D80 was lower with higher porous
259 development and surface area. As expected, there was not any correlation with the narrower
260 micropores volume (Figure S2) since the pharmaceuticals studied are too large (> 1 nm (Nielsen
261 *et al*., 2014)) to fit in pores < 0.7 nm. On the contrary, the best linear correlation (R^2=0.82) was
262 found with the mesopore volume, shown in Figure 3A. The mesoporosity development,
263 represented as % of mesoporous (V_{meso}/V_t), seems to play a key role on the adsorption of the
264 pharmaceuticals (Figure 3B), denoted by a correlation coefficient of R^2=0.95 between D80 and
265 the mesoporosity development. In this sense, the results pointed out to that mesopores were
266 more relevant than micropores in order to better accommodate these organic molecules in the
267 adsorbent. Accordingly, the microporous steam activated μGACs (DST-2, NRT-2, CLG-1 and
268 CMV-1) were the adsorbents which presented the highest D80 in this set of experiments with
269 spiked water.

270 The relationship between D80 and the oxygen containing groups of the μGACs surface
271 (determined by both XPS and TPD analysis) and the $pH_{(pzc)}$ was also studied. No clear lineal
272 tendencies were found (Figures S3 – S5): Correlations were below R^2<0.65 in all cases, much

lower than those found with textural properties, confirming that the most important parameter for pharmaceuticals adsorption was the mesoporosity of the μGACs in the spiked water experiments.

3.2 Adsorption of pharmaceuticals from WWTP effluent

3.2.1 Concentration of pharmaceuticals in the WWTP effluent

In order to validate the results obtained from the experiments with spiked water and to study the influence of the background organic matter on the adsorption of pharmaceuticals, similar experiments were performed using real secondary effluent from a conventional WWTP with activated sludge. The concentration of pharmaceuticals determined in the effluent sample is shown in Figure 4A (depicted as grey bars) and in Table S3: 2 compounds were not detected (atorvastatin and salbutamol) while 16 pharmaceuticals were found at concentrations ranging from ng L^{-1} to μg L^{-1}. Compounds of the class of anti-inflammatories (diclofenac and ketoprofen), antibiotics (azithromycin) and diuretics (furosemide) were the ones with the highest concentrations (>1 μg L^{-1}). The background organic matter, characterized by TOC analysis, was 13 ±1 mg L^{-1}.

3.2.2 Determination of adsorption removal of pharmaceuticals in WWTP effluent

Adsorption experiments were carried out with the selected μGAC concentration of 20 mg L^{-1}. In contrast to the results in the previous tests with spiked water, MWV-2, the most mesoporous μGAC, was not the best adsorbent, and only 30% of total removal of pharmaceuticals was obtained (solid lines in Figure 4A). The highest removal (54%) was obtained with MWV-1, the other chemical activated μGAC included in this study. Surprisingly, in this set of experiments the second best adsorbent was the steam activated μGAC DST-2, with

299 a total removal of 39%. DST-2 has a relative low surface area (933 m^2 g^{-1}) and mesopore
300 volume (0.08 cm^3 g^{-1}) comparing to the other adsorbents and showed low adsorption capacity in
301 the experiments with the spiked water. This result denotes that the adsorption behavior observed
302 in the spiked water tests cannot be extrapolated to the real effluent, since background organic
303 matter, can interfere the adsorption performance of some of the μGAC towards target
304 compounds.

305 The adsorption of each pharmaceutical varied depending on the μGAC used. For example,
306 with MWV-1 76% of carbamazepine and 76% of venlafaxine were removed, while with CMV-1
307 these compounds were not adsorbed. The compounds that were adsorbed in average more than
308 50% were the antibiotics, ciprofloxacin, azithromycin, ofloxacin and trimethoprim. The
309 compounds that were adsorbed in average less than 8% were bezafibrate, valsartan and
310 sulfamethoxazole. As observed in Figure 4B, the variability in the percentage of adsorption for
311 each μGAC was higher in the experiments with the effluent than in the experiments with spiked
312 water, probably due to the different initial concentration of each pharmaceutical and the
313 influence again of the background organic matter. In general, the presence of background
314 organic matter resulted in lower removal of pharmaceuticals in most of the cases.

315 *3.2.3 Influence of the physical-chemical properties of the pharmaceuticals on their*
316 *removals*

317 In terms of the compound charge, it can be observed in Figure S6 that the cationic
318 compounds were adsorbed with a higher percentage in all the μGACs except in DST-2 which
319 adsorb more or less the same percentage of cationic (42%) than anionic (39%) compounds. This
320 behavior of DST-2 can be explained by its $pH_{(pzc)}$ that is higher than the working pH, so it is
321 positively charged. However the surface charge of this material can be compensated by the
322 adsorption of background organic matter which is negatively charged. The materials with a
323 higher adsorption of cationic compounds were again MWV-1 (65%) and MWV-2 (61%).
324 MWV-1 and MWV-2 are adsorbents with a $pH_{(pzc)}$ lower than the adsorption pH what means
325 that they are negatively charged.

For negatively charged compounds, a slight positive relation of the adsorption with molecular weight was observed. Comparing gemfibrozil and valsartan, two negatively charged compounds with similar hydrophobicity (log $D_{gemfibrozil}$ = 1.00 and log $D_{valsartan}$ = 0.77) and initial concentration in the effluent ($C_{gemfibrozil,0}$ = 526 ng L^{-1} and $C_{valsartan,0}$ = 496 ng L^{-1}), it was observed that the compound with the lowest molecular weight was better adsorbed. The average removal of gemfibrozil (MW = 250 g mol^{-1}) was 29% while for valsartan (MW = 435 g mol^{-1}) was 3%. Hydrophobicity was not identified as enhancing the adsorption of the negatively charged compounds, in agreement with Mailler *et al*., (2014).

For neutral compounds, a slight positive relation of the adsorption with the hydrophobicity was observed. Comparing carbamazepine and trimethoprim, two neutral compounds with similar molecular weight ($MW_{carbamazepine}$ = 236 g mol^{-1} and $MW_{trimethoprim}$ = 290 g mol^{-1}) and initial concentration in the effluent ($C_{carbamazepine,0}$ = 38 ng L^{-1} and $C_{trimethoprim,0}$ = 28 ng L^{-1}), it was observed that the compound with the lowest log D was better adsorbed. The average removal of trimethoprim (log D = 0.99) was 52% while for carbamazepine (log D = 3.22) was 37%.

3.2.4 Influence of the physical-chemical properties of the μGAC on the pharmaceuticals removal

Poor linear correlations were found between the average pharmaceuticals removal achieved by each μGAC and their textural properties (Figure S7). All the correlations had an $R^2 < 0.18$. This can be explained by the presence of background organic matter in the water, which directly competes for the pores and surface area with the pharmaceuticals, at a concentration 10^3-10^6 times lower than the TOC (TOC = 13±1 mg L^{-1}). Typically, the TOC in secondary effluents can contain large organic molecules such as humic acids which can block the mesopores and even the entrance to the micropores (Hu *et al*., 2015). It is interesting to observe that DST-2, which has one of the lowest pore and surface area development (V_T = 0.38 cm^3 g^{-1} and S_{BET} = 933 m^2 g^{-1}) of the studied μGACs, was performing better than mesoporous adsorbents with pharmaceuticals. This result denotes that when the adsorption of micropollutants must be carried out in the presence of background organic matter, the importance of surface area and

353 porosity is not as relevant as in the case of experiments with cleaner matrices. Contrarily, the
354 surface chemistry of the μGACs, such as the presence of oxygen functional groups or the
355 surface charge, may play some role in the adsorption. Figure 5A shows the linear correlations
356 for carboxylic groups (R^2 = 0.38) obtained from XPS and lactone (R^2 = 0.59) and ether (R^2 =
357 0.43) groups obtained from TPD. It can be observed in general a positive trend that indicates
358 that a higher content of these oxygen surface groups in the μGACs can improve the
359 performance of the μGACs. The correlations of the average removal of pharmaceuticals with
360 other oxygenated surface groups of the μGACs (Figures S8 and S9) were worse (R^2 < 0.23). On
361 the other hand, the influence of the $pH_{(pzc)}$ on the removal of pharmaceuticals, shown in Figure
362 5B, must be discussed in two groups of carbons. The steam activated μGACs, which showed
363 $pH_{(pzc)}$ higher than the pH of the solution (pH=8), increased their average removal with the
364 $pH_{(pzc)}$, which consequently increases positively the surface charge. On the other hand, the
365 chemical activated μGACs (MWV-2 and MWV-1), were negatively charged ($pH>pH_{(pzc)}$) at the
366 working conditions. The most acidic, MWV-2, is thus the most negatively charged adsorbent,
367 which did not result of highest average removal.

368

369 **3.3 Correlation of UV_{254} removal with pharmaceuticals removal**

370 All the pharmaceuticals considered in this work have one or more aromatic rings on their
371 structures. Aromatic rings are known to absorb light at 254 nm (UV_{254}), therefore the decrease
372 of the pharmaceuticals concentration may cause a reduction in the UV_{254}, which is especially
373 relevant in the spiked water experiments. In this sense, Zietzschmann *et al.* (2014), working
374 with WWTP effluents, found a correlation between the reduction of the UV_{254} and the reduction
375 of some OMP such as diclofenac.

376 In this work, the UV_{254} of the aqueous samples was measured at the beginning and after
377 each adsorption test in order to calculate its reduction in both spiked water and WWTP effluent
378 samples. The results for each μGAC with the spiked water are shown in Figure S10 in the
379 supplementary information. All the points are depicted together in Figure 6 and, as also

observed by Zietzschmann *et al.* (2014), the higher the pharmaceutical removal, the higher the UV_{254} removal. After the adsorption, the remaining compounds were different for each μGAC, and moreover, each remaining compound contributes differently to the UV_{254}. For this reason, with spiked water, the intersection of the lineal correlation was far from the origin and the slope was far from the bisector.

In the case of effluent water, the removal of pharmaceuticals was translated into a lower reduction of the $UV_{254,}$ compared to what it was observed in spiked water, probably due to the presence of background organic matter that also absorb at this wavelength, at higher concentrations than pharmaceuticals. Despite of this, UV_{254} removal correlated slightly well with the total removal of pharmaceuticals.

4. DISCUSSION

Figure 7 shows the total removal of the 23 selected pharmaceuticals with different μGAC concentrations in spiked water. At these experimental conditions, the chemical activated μGACs, were the best performing adsorbents, obtaining 78.6 - 88.5% global removal with a 20 mg L^{-1} dose. The steam activated μGACs reached in general lower global removals (10.5 – 51.4% with 20 mg L^{-1} of μGAC). Almost all μGACs achieved a global removal over 88% using a dose higher than 200 mg L^{-1}. Therefore, the dose of AC required to remove the pharmaceuticals is clearly dependent on the adsorbent type. The chemical activated μGACs present two characteristics that, according to the results previously shown, are the most important in the adsorption of pharmaceuticals in the absence of background organic matter: a high pore volume and a higher distribution of this pore volume as mesopores. The pharmaceutical molecules studied in this work are quite large to be accommodated in the narrower micropores. As an example, the maximum molecular sizes of diclofenac, carbamazepine, sulfamethoxazole and metoprolol, are in the range 1.2-1.6 nm (Figoli *et al.*, 2017; Mitran *et al.*, 2016; Nielsen *et al.*, 2014). Another factor to be considered to select the

406 appropriate μGAC is the price that in the case of chemical activated μGACs is the double than
407 the steam activated μGACs.

408 Results obtained in the experiment with spiked water cannot be extrapolated to the results
409 obtained with the secondary effluent wastewater (Figure 8) since the presence of background
410 organic matter plays an important role in the adsorption mechanisms of the pharmaceuticals into
411 μGAC. Previous authors (Mailler et al., 2016) have proved that the presence and nature of the
412 background organic matter, specially protein-like molecules, affects the adsorption of
413 micropollutants in AC. So, it is important to use real water matrices in order to assess the
414 efficiency of adsorbents in the removal of OMP: as shown in Figure 8 the presence of
415 background organic matter negatively affected the adsorption in most cases (MWV-2, MWV-1,
416 CLG-1 and CMV-1); however, some μGAC (DST-2 and NRT-2) presented higher adsorption
417 efficiencies in the experiments with the effluent water.

418 In the case of the experiments with secondary effluent wastewater, the textural properties
419 do not seem to play the most important role during the adsorption of pharmaceuticals. Best
420 performing μGAC in experiments with wastewater was MWV-1, which also showed a good
421 efficiency removal in spiked water experiments. Curiously, the second best adsorbent with
422 effluent water was DST-2, a μGAC that has a relatively low surface area and mesoporous
423 volume. So, this good adsorption performance could be explained by the chemical properties of
424 the μGAC. As it has been previously shown, there were slight correlations between the removal
425 of pharmaceuticals and some specific oxygen surface groups, such as carboxylic, ether and
426 lactones. Nielsen *et al*., (2014) proved that oxygen groups incorporated to the carbon matrix,
427 besides attracting polar molecules, also react with functional groups of the pollutants, especially
428 with amines, resulting in very strong adsorption. Moreover, the ability of a carbon surface to
429 activate oxygen can result in the partial oxidation of the adsorbed species (Nielsen *et al*., 2014).
430 Also the surface charge seems to be an important parameter. In this study, it was also observed
431 that in the adsorbents with similar pore development, a high $pH_{(pzc)}$ which implies a higher
432 surface positive charge, can enhance the adsorption of pharmaceuticals.

The presence of positive charges on the pharmaceuticals seems to improve the adsorption of the compound into μGACs, in agreement with results obtained with PAC by other authors (De Ridder *et al*., 2011; Mailler *et al*., 2014; Margot *et al*., 2013). This is particularly relevant in the presence of background organic matter in the water: The adsorption of background organic matter, generally negatively charged in wastewater, on activated carbon surface can switch (if initially neutral or positive) or increase (if already negative) the charge, resulting overall in a surface negatively charged (Mailler *et al*., 2014; Margot *et al*., 2013). In this case the μGAC surface has negative charges inducing strong electrostatic attraction of positive compounds. This also corroborates the importance of oxygenated groups on the μGAC for the adsorption of pharmaceuticals. Positive molecules, that have loose electrons, can receive electrons from oxygenated groups present in the surface of the adsorbent materials. Also, some functional groups may enhance adsorption of pharmaceuticals such as aromaticity and N-heterocycles (Delgado *et al*., 2012), explaining the high removal of ofloxacin although this compound was negatively charged (Figure 4). For instance, ofloxacin and diclofenac (both anionic at working pH) have three heterocycles, known to enhance adsorption on activated carbon (Delgado *et al*., 2012), while sulfamethoxazole (also anionic) has only one heterocycle. As it can be observed in Figure 4, sulfamethoxazole exhibited a lower adsorption than ofloxacin and diclofenac in both sets of experiments.

Removal efficiencies obtained in this work were compared in Table S4 with those achieved by other authors working with different μGAC, PAC and GAC (De Ridder et al., 2011; Kårelid et al., 2017; Mailler et al., 2016, 2014; Sheng et al., 2016; Streicher et al., 2016; Westerhoff et al., 2005; Zietzschmann et al., 2014). Mailler *et al*., (2016) explored the use of a different μGAC in a pilot plant for the removal of 39 pharmaceuticals (some different to those studied in this work) obtaining high removals (> 70 %) for ciprofloxacin, erythromycin, ofloxacine, trimethoprim, carbamazepine, bezafibrate, diclofenac, iopromide and ketoprofen. Similar efficiencies with the optimal μGAC (MWV-1) were achieved in the present study, in the lab scale batch experiments with WWTP effluent, obtaining the highest removals (> 65 %) for

ciprofloxacin, azithromycin, trimethoprim, ofloxacine, carbamazepine and venlafaxine. According to Table S4 it seems that the compounds that are less prone to get adsorbed into AC are sulfamethoxazole, valsartan, iopromide and gemfibrozil *(*De Ridder *et al.,* 2011*;* Mailler *et al.,* 2014*;* Mailler *et al.,* 2016*;* Sheng *et al*., 2016; Zietzschmann *et al*., 2014). Also this study reports the first adsorption efficiencies in AC material for the following pharmaceuticals: azithromycin, valsartan and furosemide.

The UV_{254} removal correlated well with the average pharmaceutical removal in for all the studied compounds both in the presence and in the absence of background organic matter in the water. The monitoring of the UV_{254} can be used as an indicator to control the dose μGAC in tertiary treatments.

5. CONCLUSIONS

Physical properties of the adsorbents are very important in the adsorption of pharmaceuticals in clean water matrices. Mesoporosity, high in materials like MWV-2 and MWV-1, is the most important parameter, since pharmaceutical molecules can be allocated in mesopores better than in narrower micropores. However, chemical properties, such as the presence of oxygenated functional groups on the μGAC surface and the $pH_{(pzc)}$, seems to be also important on the adsorption of pharmaceuticals in presence of background organic matter, i.e effluent WWTP. Concerning physical-chemical properties of pharmaceuticals, positively charged pharmaceuticals seems to be better adsorbed into the μGAC when treating WWTP effluents. Finally, UV_{254} can be used as an indicator of pharmaceutical removal efficiency in order to control the dose of μGAC in tertiary treatments.

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Table 1. Physical-chemical properties of pharmaceuticals used in this study

Table 2. Textural properties, oxygen-containing functionalities obtained from XPS and TPD analysis and $pH_{(pzc)}$ of the μGAC. Adapted from (Cabrera-Codony *et al*., 2014).

Table 1. Physical-chemical properties of pharmaceuticals used in this study

Compound	Characteristics				
	Type	MW [g mol^{-1}]	Log K_{ow}	Log D (pH=8)	Prevalent Charge
Azithromycin	antibiotic	749.0	0.80	-1.73	Cation
Ciprofloxacin	antibiotic	331.4	1.57	-1.16	Cation / Anion
Erythromycin	antibiotic	733.9	1.22	0.69	Cation
Ofloxacine	antibiotic	361.4	1.51	-0.89	Anion
Sulfamethoxazole	antibiotic	253.3	1.04	-0.03	Anion
Trimethoprim	antibiotic	290.3	1.05	0.99	Neutral
Carbamazepine	antidepressant	236.3	3.22	3.22	Neutral
Fluoxetine	antidepressant	309.3	4.19	2.39	Cation
Venlafaxine	antidepressant	277.3	2.25	1.30	Cation
o-desmehtylvenlafaxine	antidepressant *	263.4	2.22	1.26	Cation
Bezafibrate	lipid-lowering	361.8	3.52	-0.04	Anion
Atorvastatin	lipid-lowering	558.7	5.00	1.61	Anion
Gemfibrozil	lipid-lowering	250.3	4.22	1.00	Anion
Diclofenac	anti-inflammatory	296.2	3.97	0.45	Anion
Ketoprofen	anti-inflammatory	254.3	3.46	-0.08	Anion
Irbesartan	antihypertensive	428.5	5.74	4.23	Neutral
Valsartan	antihypertensive	435.5	5.63	0.77	Anion
Metoprolol	β-blocker	267.3	1.49	-0.18	Cation
Metoprolol Acid	β-blocker *	267.3	1.13	-1.87	Cation / Anion
Furosemide	diuretic	330.7	1.66	-1.76	Anion
Iopromide	x-ray contrast	791.1	-0.72	-0.72	Neutral
Loratadine	antihistamine	382.9	4.48	4.48	Neutral
Salbutamol	bronchodilator	239.2	0.61	-1.06	Cation

(MarvinSketch, 2017)
* metabolite

Table 2. Textural properties, oxygen-containing functionalities obtained from XPS and TPD analysis and $pH_{(pzc)}$ of the μGAC. Adapted from (Cabrera-Codony *et al.*, 2014).

	DST-2	NRT-2	CLG-1	CMV-1	MWV-1	MWV-2
Origin	Anthracite	Peat	Coal	Coal	Wood	Wood
Activation	Steam	Steam	Steam	Steam	Chemical	Chemical
Textural properties						
S_{BET} [m^2 g^{-1}]	933	1183	1276	850	1757	2142
V_t [cm^3 g^{-1}]	0.46	0.53	0.75	0.52	1.19	1.52
VDR_{N2} [cm^3 g^{-1}]	0.38	0.45	0.48	0.38	0.67	0.76
VDR_{CO2} [cm^3 g^{-1}]	0.09	0.24	0.13	0.22	0.15	0.16
V_{meso} [cm^3 g^{-1}]	0.08	0.08	0.27	0.14	0.52	0.76
XPS [%]						
C=O	23.7	20.3	17.0	31.1	17.1	29.8
COH COC	24.1	39.3	17.6	24.6	32.2	8.2
COOCO	16.3	9.2	20.6	14.3	6.5	28.6
COOH	24.8	23.4	26.1	14.5	37.7	8.6
XPS O/C	0.148	0.193	0.109	0.16	0.172	0.201
TPD [μmol g^{-1}]						
Carboxylic	61.1	120	44.4	109.4	208.3	180
Lactone	26.0	16.7	9.0	19.8	33.1	15.9
Anhydride	64.5	129.9	77.8	243.9	192.5	242.6
Phenolic	296.1	536.5	163.9	831.4	1386.5	1866.1
Carbonyl	543.8	671.8	148.5	362.7	443.5	221.9
Ether	10.3	18.1	118.9	98.1	374.8	117.8
TPD O/C	0.026	0.034	0.013	0.045	0.069	0.076
pH						
$pH_{(pzc)}$	10.4	8.9	8.5	7.8	6.2	4.8
Surface charge (at pH = 8)	++	+	0/+	0/-	-	--

Figure 1. D80 values in mg L^{-1} of adsorbent for the removal of 20 μg L^{-1} of pharmaceutical. Solid lines corresponds to the average D80 for each μGAC.

Figure 2. Influence of the A) molecular weight and the B) log D and C) charge of the pharmaceuticals on the average D80 of the studied pharmaceuticals with μGACs. Error bars on C correspond to the standard deviation for all the pharmaceuticals studied (cationic n=7, neutral n=5 anionic n=9).

Figure 3. Influence of the A) mesopore volume and the B) percentage of mesopore (V_{meso}/Vt) on the D80 for the average removal of the studied pharmaceuticals with μGACs. Error bars correspond to the standard deviation for all the pharmaceuticals studied (n=23).

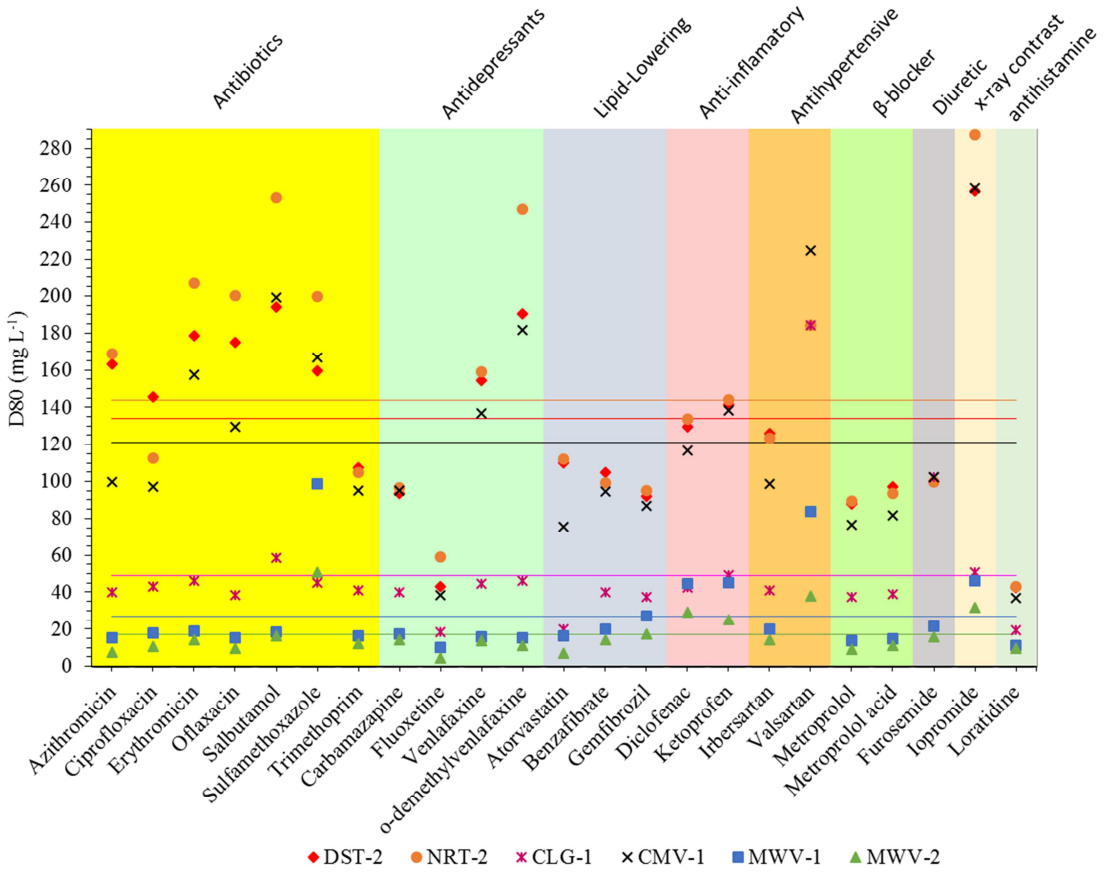
Figure 4. A) Removal percentage of pharmaceuticals for each μGAC in the experiments with effluent water. The μGAC concentration was 20 mg L^{-1} in all experiment. Solid lines corresponds to the total pharmaceutical removal percentage for each μGAC. Initial concentration of the effluent water is represented as grey bars referred to secondary axis stand and standard deviation as error bars (n=3). B) Average removal of each pharmaceutical with 6 μGAC using an adsorbent concentration of 20 mg L^{-1} with effluent and spiked water. Error bars correspond to standard deviation (n=6).

Figure 5. Influence of A) oxygenated groups and B) $pH_{(pzc)}$ of μGAC on the % of removal of pharmaceuticals with the effluent water experiment.

Figure 6. Linear relationship between pharmaceutical removal and UV_{254} removal in the experiments with spiked and effluent experiments.

Figure 7. Total pharmaceutical removal with different μGAC concentrations in spiked water (20 μg L^{-1} of each pharmaceutical). Dashed line for chemical activated AC and solid line for steam activated AC were drawn as guides to the eye.

Figure 8. Total removal of pharmaceuticals obtained with each μGAC using an adsorbent concentration of 20 mg L^{-1} with effluent and spiked water. Error bars correspond to the standard deviation (n=16).



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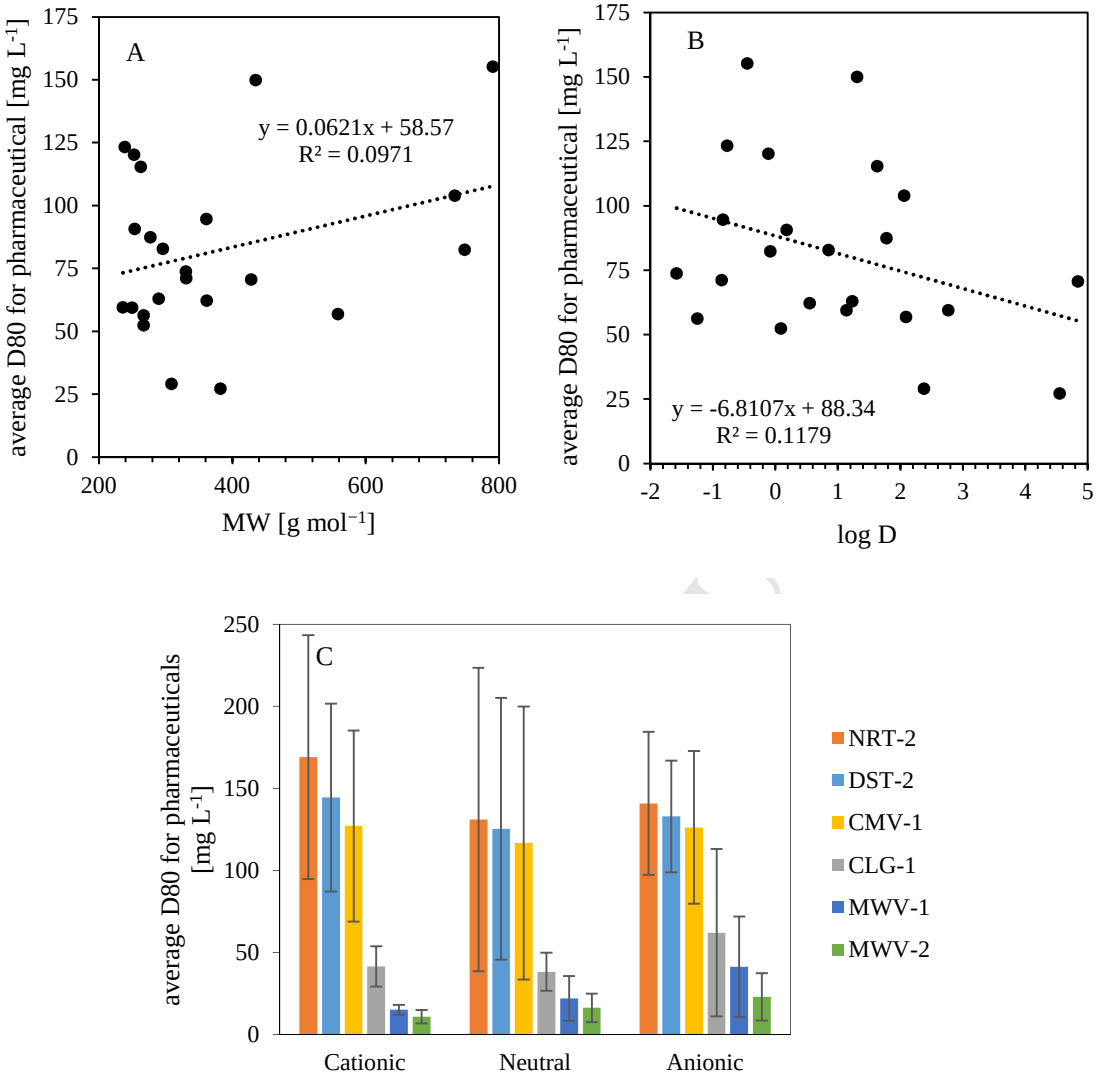


Figure 2. Influence of the A) molecular weight and the B) log D and C) charge of the pharmaceuticals on the average D80 of the studied pharmaceuticals with μGACs. Error bars on C correspond to the standard deviation for all the pharmaceuticals studied (cationic n=7, neutral n=5 anionic n=9).

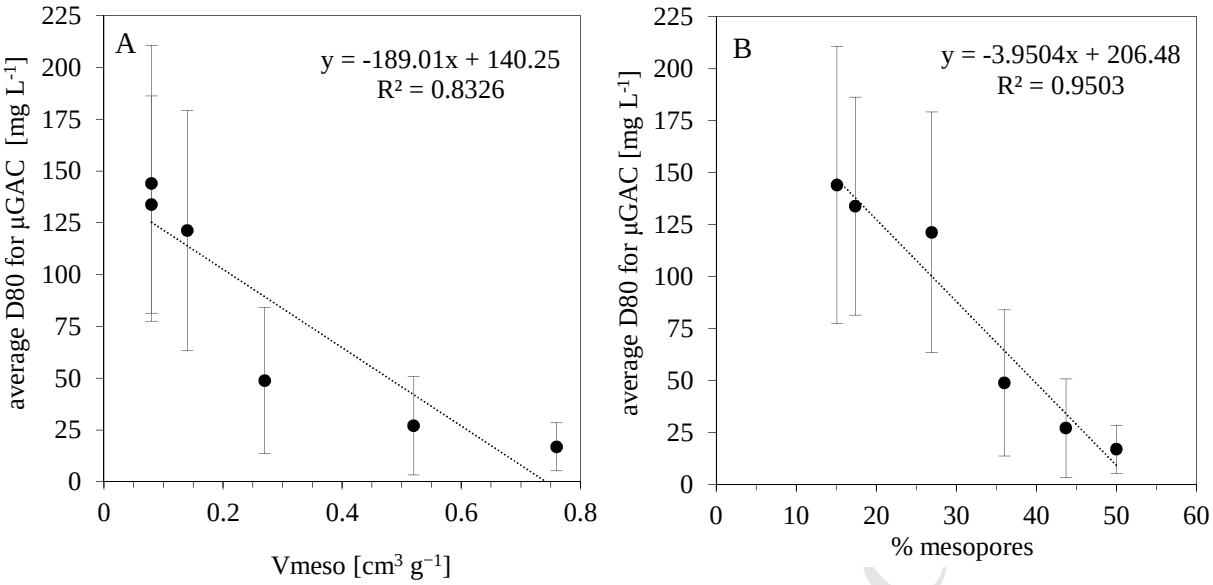


Figure 3. Influence of the A) mesopore volume and the B) percentage of mesopore (V_{meso}/Vt) on the D80 for the average removal of the studied pharmaceuticals with µGACs. Error bars correspond to the standard deviation for all the pharmaceuticals studied (n=23).

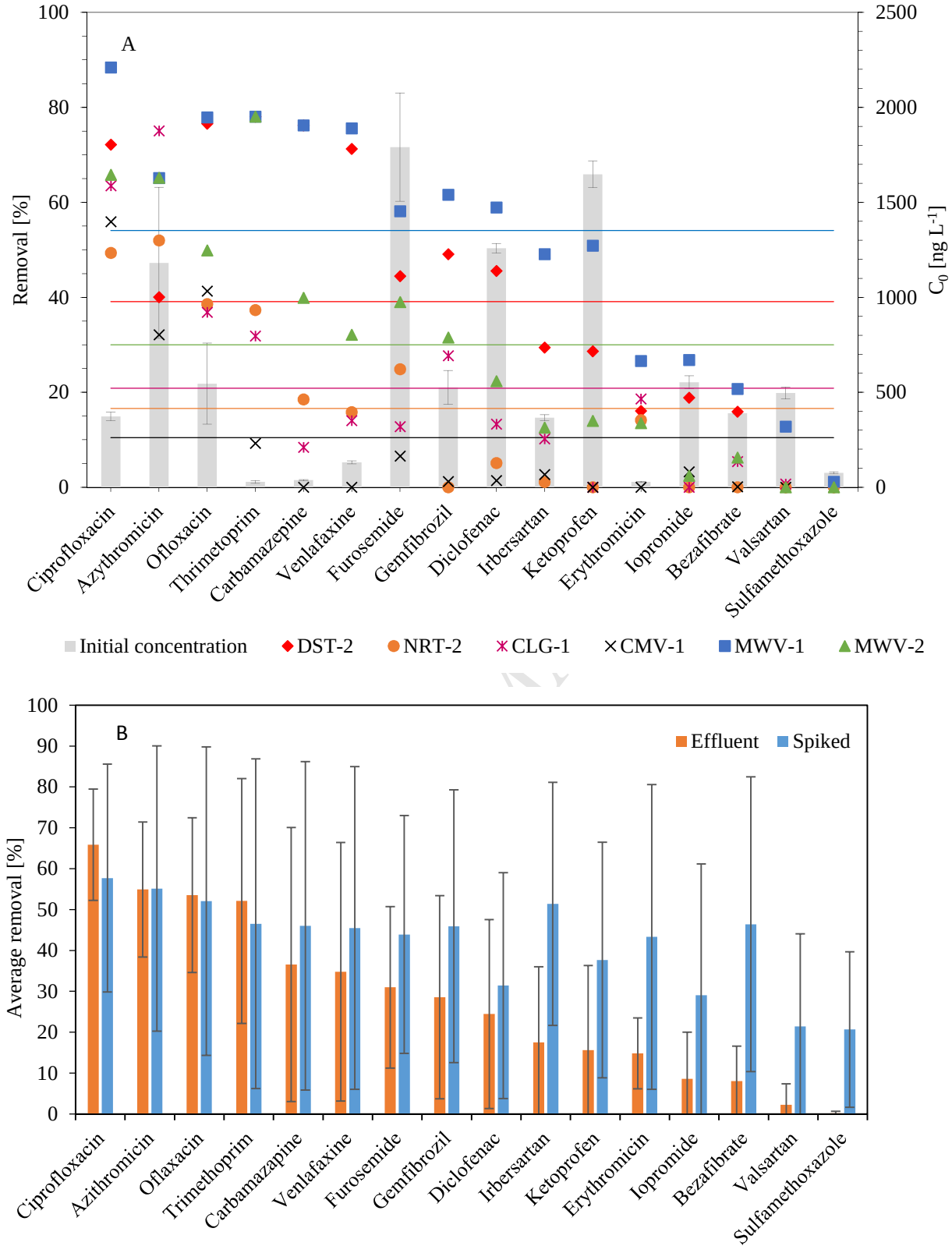
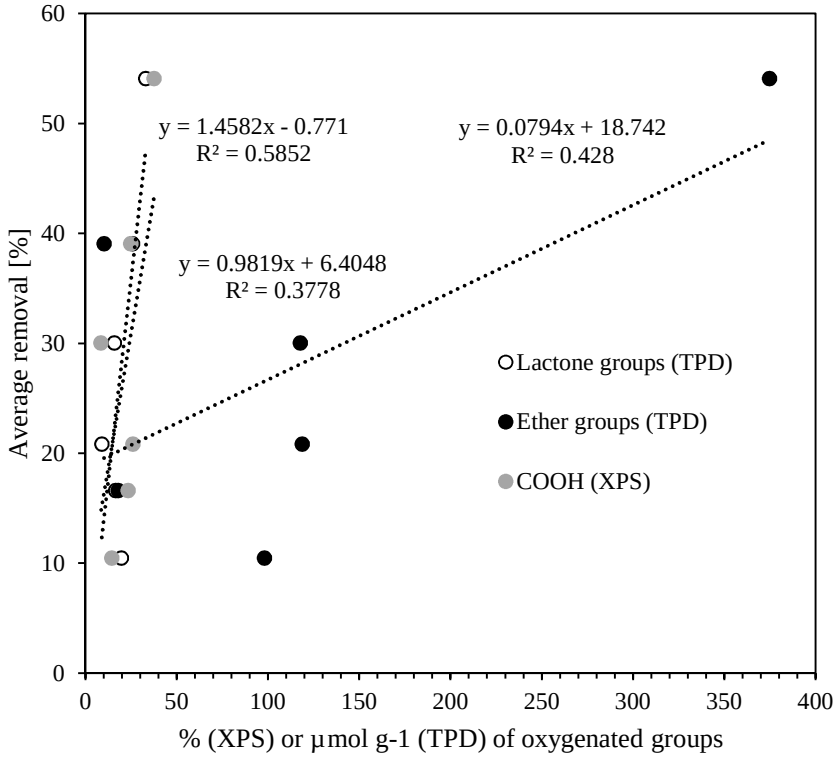


Figure 4. A) Removal percentage of pharmaceuticals for each μGAC in the experiments with effluent water. The μGAC concentration was 20 mg L^{-1} in all experiment. Solid lines corresponds to the total pharmaceutical removal percentage for each μGAC. Initial concentration of the effluent water is represented as grey bars referred to secondary axis stand and standard deviation as error bars (n=3). B) Average removal of each pharmaceutical with 6 μGAC using an adsorbent concentration of 20 mg L^{-1} with effluent and spiked water. Error bars correspond to standard deviation (n=6).



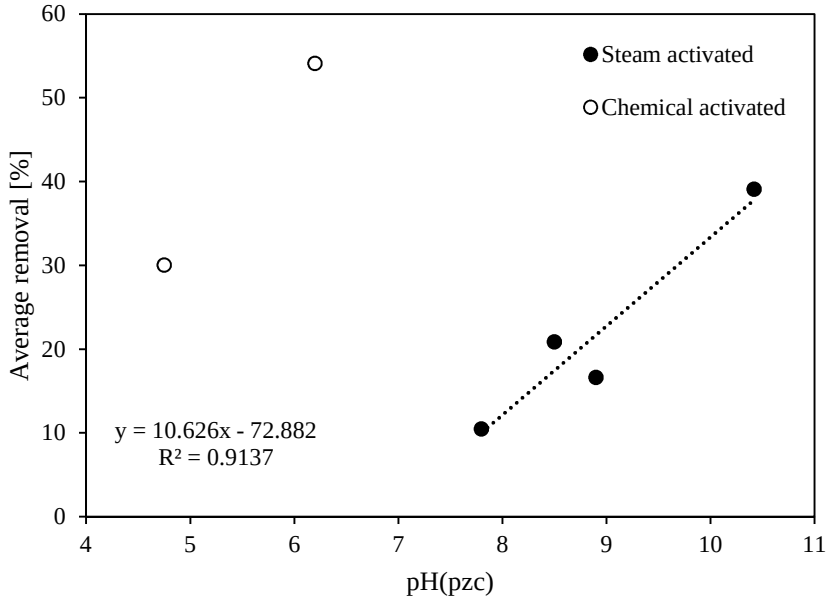


Figure 5. Influence of A) oxygenated groups and B) $pH_{(pzc)}$ of µGAC on the % of removal of pharmaceuticals with the effluent water experiment.

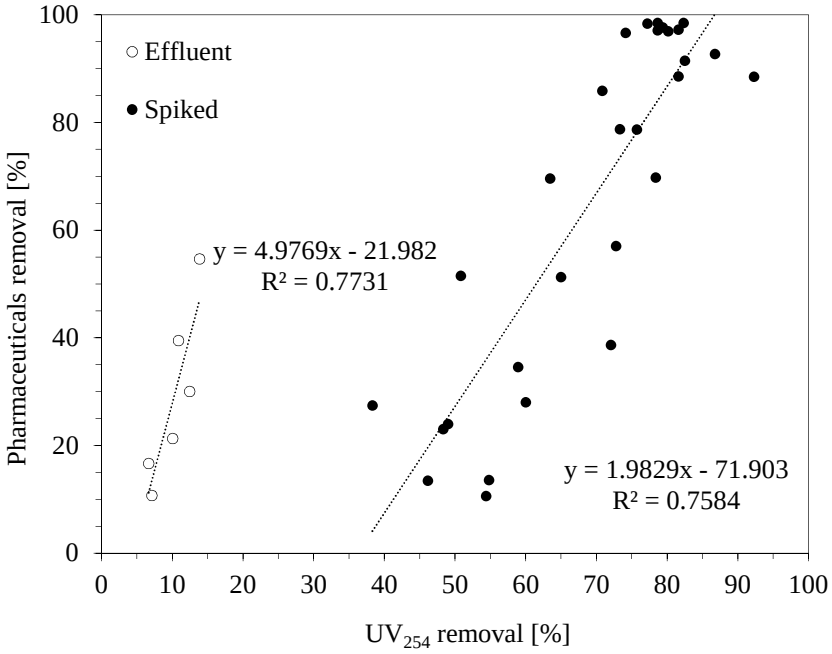


Figure 6. Linear relationship between pharmaceutical removal and UV_{254} removal in the experiments with spiked and effluent experiments.

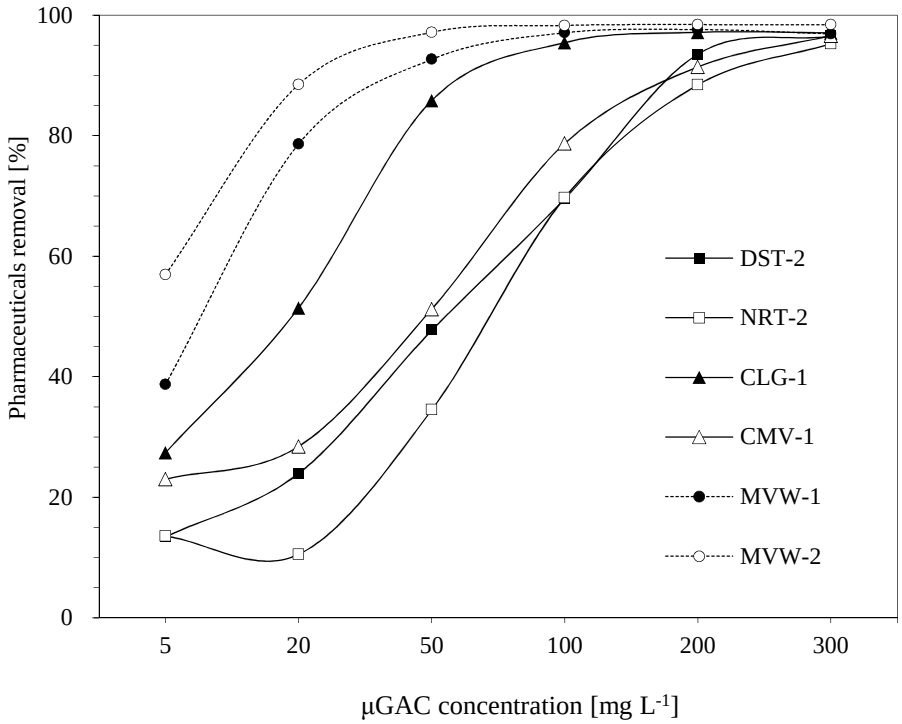


Figure 7. Total pharmaceutical removal with different μGAC concentrations in spiked water (20 μg L^{-1} of each pharmaceutical). Dashed line for chemical activated AC and solid line for steam activated AC were drawn as guides to the eye.

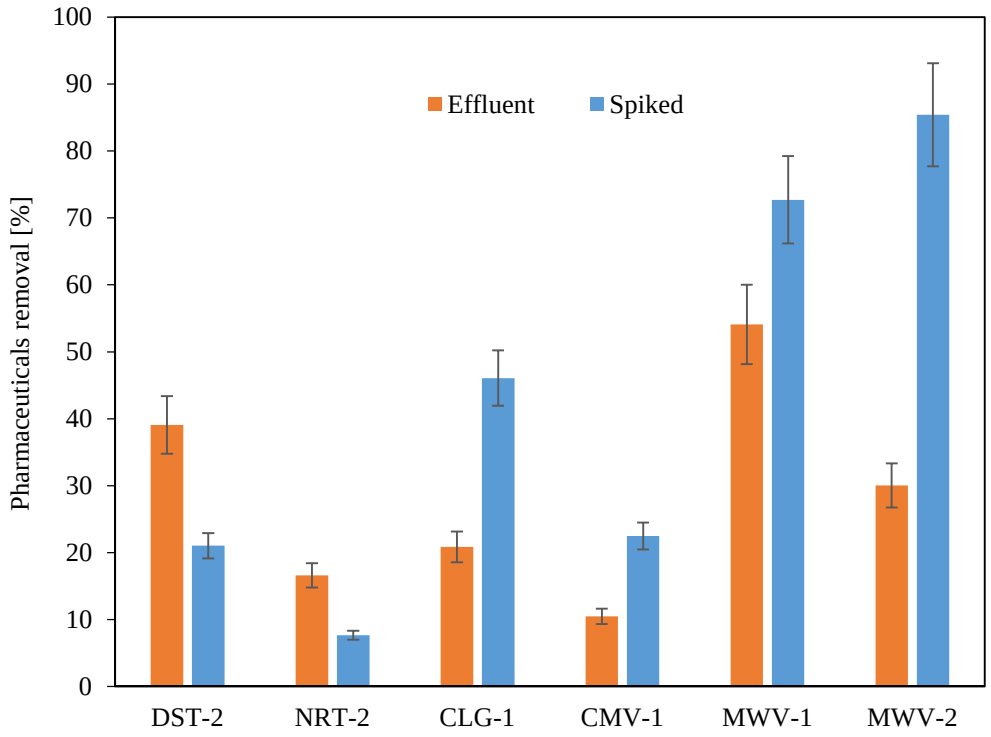


Figure 8. Total removal of pharmaceuticals obtained with each μGAC using an adsorbent concentration of 20 mg L^{-1} with effluent and spiked water. Error bars correspond to the standard deviation (n=16).

Highlights:

- Results in spiked water cannot be extrapolated to effluent water.
- Mesopores are important in the adsorption without background organic matter.
- µGAC chemical properties are relevant in adsorption with background organic matter.
- Positive charges in pharmaceuticals improve the adsorption.
- UV_{254} is a promising parameter to control pharmaceuticals adsorption.