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1 **Title**

2 Influence of dissolved organic matter on the removal of 12 organic micropollutants from
3 wastewater effluent by powdered activated carbon adsorption

4 **Authors**

5 Ronan Guillosoy¹, Julien Le Roux^{1*}, Romain Mailler², Caroline Soares Pereira-Derome¹,
6 Gilles Varrault¹, Adèle Bressy¹, Emmanuelle Vulliet³, Catherine Morlay⁴, Fabrice Nauleau⁵,
7 Vincent Rocher², Johnny Gasperi^{1*}

8 ¹ Ecole des Ponts ParisTech, Université Paris-Est Créteil, AgroParisTech, Laboratoire Eau
9 Environnement et Systèmes Urbains, UMR MA 102, Créteil, France

10 ² Service public de l'assainissement francilien (SIAAP), Direction Innovation et
11 Environnement, Colombes

12 ³ Université de Lyon, CNRS, Université Claude Bernard Lyon 1, INSA-Lyon, MATEIS,
13 UMR 5510, Villeurbanne, France

14 ⁴ Université de Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences
15 Analytiques, UMR 5280, Villeurbanne, France

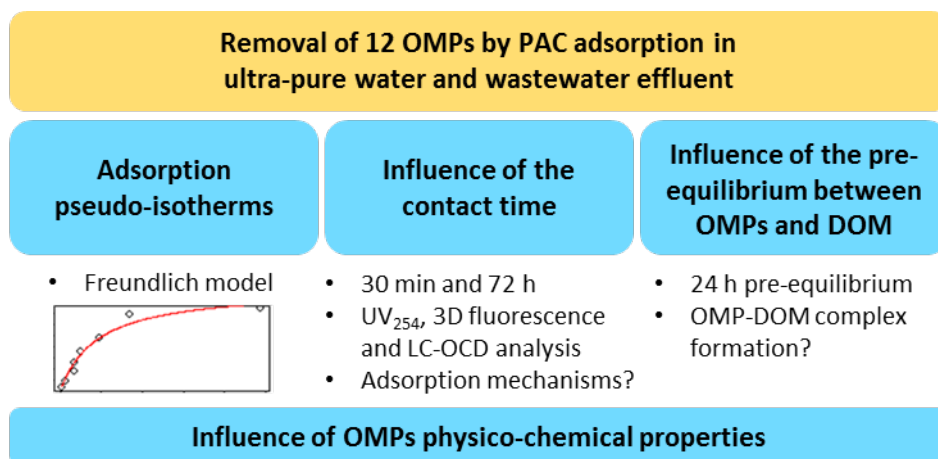
16 ⁵ Saur, Direction de la Recherche et du Développement, Maurepas, France

17 * Corresponding author. gasperi@u-pec.fr ; julien.le-roux@u-pec.fr

18 **Highlights**

- 19 • OMPs removal was lower in WWTP effluent than ultra-pure water due to DOM
20 adsorption
- 21 • Pore blockage was the main negative effect rather than competition for adsorption sites
- 22 • OMPs charge had an impact on their adsorption rate in presence of wastewater
- 23 • A pre-equilibrium between OMPs and DOM decreased DOM negative effects

24 Graphical abstract



25

26 Abstract

27 The presence of dissolved organic matter (DOM) in wastewater effluents is recognized as the
28 main factor limiting the adsorption of organic micropollutants (OMPs) onto activated
29 carbon. The degree of the negative effect that DOM, depending on its quality, exerts on
30 OMPs adsorption is still unclear. The influence of the interactions between DOM and OMPs
31 on their removal is also not fully understood. Adsorption isotherms and conventional batch
32 tests were performed in ultra-pure water and in wastewater effluent to study the influence of
33 DOM on the adsorption of 12 OMPs onto powdered activated carbon. Best fit of adsorption
34 pseudo-isotherms was obtained with the Freundlich equation and showed, as expected, that
35 OMPs adsorption was higher in ultra-pure water than in wastewater effluent due to the
36 presence of DOM leading to pore blockage and competition for adsorption sites. LC-OCD
37 analysis revealed that biopolymers and hydrophobic molecules were the most adsorbed
38 fractions while humic acids were not removed after a contact time of either 30 min or 72 h.
39 The presence of DOM had a negative impact on the removal of all OMPs after 30 min of
40 adsorption, but similar removals to ultra-pure water were obtained for 6 OMPs after 72h of
41 adsorption. This demonstrated that competition between DOM and OMPs for adsorption

42 sites was not a major mechanism as compared to pore blockage, which only slowed down
43 the adsorption and did not prevent it. The charge of OMPs had a clear impact: the adsorption
44 of negatively charged compounds was reduced in the presence of wastewater effluent due to
45 repulsive electrostatic interactions with the adsorbed DOM and the PAC surface. On the
46 other hand, the removal of positively charged compounds was improved. A 24h pre-
47 equilibrium between OMPs and DOM improved their removal onto PAC, which suggest that
48 OMPs and DOM interact in solution which decreased the negative effects caused by the
49 presence of DOM, e.g. through co-adsorption of an OMP-DOM complex.

50 **Keywords**

51 Wastewater advanced treatment; Organic micropollutants; Dissolved organic matter;
52 Activated carbon adsorption.

53 **1. Introduction**

54 The presence of organic micropollutants (OMPs) in aquatic bodies is a concern due to their
55 potential persistence and suspected negative effects on ecosystems (Courtier et al., 2019;
56 Desbiolles et al., 2018; Zenker et al., 2014). One of the main sources of OMPs are
57 wastewater effluents since wastewater treatment plants (WWTPs) are not designed for their
58 removal (Yang et al., 2017). Some compounds can however be well removed during the
59 biological treatment (e.g. acetaminophen, ibuprofen, ketoprofen or naproxen), but their
60 concentrations in the wastewater effluent is still an issue (ranging from ng/L levels up to tens
61 or even hundreds of $\mu\text{g/L}$) (Guillossou et al., 2019; Jelic et al., 2011; Joss et al., 2005;
62 Verlicchi et al., 2012). Different processes commonly employed to eliminate OMPs for
63 drinking water production (e.g. activated carbon adsorption or oxidation processes such as
64 ozonation) are gaining interest for wastewater treatment (Altmann et al., 2014; Bourgin et
65 al., 2018; Margot et al., 2013). Activated carbon adsorption offers the advantage of being

66 able to remove a wide range of compounds, and of being easy to use and flexible, with no
67 risk of toxic byproducts generation (Kårelid et al., 2017; Mailler et al., 2016a, 2015; Meinel
68 et al., 2015).

69 Adsorption is a complex process driven by the properties of OMPs and the properties of
70 activated carbon, and is also influenced by the water quality, mainly the presence of
71 dissolved organic matter (DOM). Some authors proposed that activated carbon adsorption
72 was driven by the hydrophobicity of OMPs (de Ridder et al., 2010; Westerhoff et al., 2005)
73 but this was mostly observed for neutral compounds and not for charged compounds (de
74 Ridder et al., 2011; Kovalova et al., 2013; Mailler et al., 2015; Margot et al., 2013). DOM
75 affects the adsorption of OMPs onto activated carbon through direct competition for
76 available surface/adsorption sites and pore blockage, depending on its nature (i.e. average
77 molecular weight, hydrophobicity) and the activated carbon porosity (Newcombe et al.,
78 1997). Newcombe et al. (2002) reported that low molecular weight DOM (≈ 200 Da)
79 reduced the equilibrium adsorption capacity of 2-methylisoborneol by competition for
80 adsorption sites and blockage of micropores. The medium (200-600 Da) and high molecular
81 weight DOM (> 1000 Da) could not access micropores but reduced the adsorption rate by
82 restricting direct access to adsorption sites through macro- and mesopores, necessitating a
83 more tortuous diffusion path for 2-methylisoborneol. OMPs can also interact through
84 electrostatic attraction/repulsion, van der Waals, π - π or hydrogen bonds with the DOM.
85 Interactions between DOM and OMPs in the dissolved phase were observed during the
86 treatment of effluents by membrane filtration, leading to an increase of OMPs rejection
87 (Majewska-Nowak et al., 2002; Tödtheide et al., 1997). Many studies have been conducted
88 on the interactions between pesticides and DOM (Caupos et al., 2015; Ilani et al., 2005; Lee
89 et al., 2003), but little data is available for other OMP families such as pharmaceuticals.
90 Hernandez-Ruiz et al. (2012) demonstrated that bisphenol-A could interact with microbial

91 byproduct-like and humic acid-like DOM components from wastewater, and carbamazepine
92 and ibuprofen with fulvic acid-like components. The influence of these interactions on the
93 adsorption by activated carbon has been barely studied, especially with wastewater DOM.
94 Jin et al. (2018) observed that zwitterionic compounds could interact with humic acids in
95 solution, be adsorbed onto activated carbon and also interact with humic acids adsorbed on
96 the activated carbon surface. The presence of humic acids increased the removal of
97 tetracycline and ciprofloxacin thanks to interactions with humic acids which trapped OMPs.
98 However, these interactions between OMPs and DOM were observed under specific
99 conditions (low dose of activated carbon and very high concentrations of DOM and OMPs)
100 that are not representative of the real conditions encountered in drinking water plants or
101 wastewater treatment plants.

102 Only a few studies were conducted to assess the influence of DOM originating from
103 wastewater effluents on the adsorption of OMPs onto activated carbon. Wastewater DOM is
104 a complex mixture, generally considered to be composed of large organic molecules
105 (biopolymers, humic substances and building blocks) and smaller molecules (low molecular
106 weight acids and neutrals) (de Ridder et al., 2011; Pernet-coudrier et al., 2008). Some
107 authors proposed that the main negative effect of DOM was the competition for adsorption
108 sites rather than pore blockage: Zietzschmann et al. (2014) fractionated DOM using
109 nanofiltration and obtained a lower adsorption of 5 OMPs in the presence of low molecular
110 weight DOM (competition for adsorption sites phenomenon) compared to raw and high
111 molecular weight DOM (pore blockage phenomenon). They reported that the impact of the
112 small DOM molecules was more important for medium and weakly adsorbing OMPs.
113 Moreover, the DOM adsorbed onto the activated carbon is globally negatively charged at the
114 pH of the wastewater and can decrease the adsorption of negatively charged OMPs through
115 repulsive electrostatic interactions (de Ridder et al., 2011). A negative influence of DOM on

116 the adsorption of negatively charged compounds was also observed by Hu et al. (2016).
117 Alves et al. (2018) reported that in the absence of DOM, the textural properties (i.e. the
118 porosity) of micro-grain activated carbons (μ GACs) played the most important role in the
119 adsorption of OMPs, while in the presence of DOM the surface chemistry of μ GACs (i.e.
120 point of zero charge, surface functional groups) had a predominant impact and positively
121 charged compounds were better removed.

122 While the negative effect of DOM on OMPs adsorption is known, the degree of this effect
123 (i.e. quantification of the decrease in adsorption rates) in relation to the DOM composition is
124 still unclear. The influence of OMPs-DOM interactions on OMPs adsorption is also not fully
125 understood and was not comprehensively studied in conditions close to realistic wastewater
126 treatment applications (i.e. synthetic water, low OMPs concentrations and activated carbon
127 doses). In this context, the present work evaluated the adsorption of 12 OMPs onto powdered
128 activated carbon (PAC) under various conditions by following 3 approaches. As a first step,
129 short-term adsorption capacity at various concentrations of the 12 OMPs (i.e. pseudo-
130 isotherms) was evaluated in two different matrices (ultra-pure water and wastewater effluent)
131 to assess the influence of DOM on OMPs removal. Batch tests in ultra-pure and wastewater
132 effluent were then performed at short and long contact times with PAC (30 min and 72 h) to
133 compare the short-term capacity with a long-term adsorption equilibrium and thus to
134 characterize the underlying adsorption mechanisms. DOM adsorption was examined in
135 parallel through LC-OCD, UV_{254} and fluorescence excitation/emission analyses to better
136 understand its adsorption and its effect on OMPs removal. Finally, the influence of a pre-
137 equilibrium between OMPs and DOM before adsorption was examined to study the possible
138 interactions between OMPs and DOM. The links between OMPs physico-chemical
139 properties and their adsorption were discussed for each experiment.

140 **2. Materials and methods**

141 *2.1. Materials*

142 Wastewater effluent samples were punctually collected from the Seine Centre WWTP
143 (SIAAP, Colombes, France), treating wastewater of about 800,000 inhabitant equivalents
144 with a flow of 240,000 m³/day. After pre-treatment (screening, grit and oil removal), a
145 physico-chemical lamellar settling unit removes particles and colloids, 3 biofiltration stages
146 remove nutrients then the effluent is discharged into the Seine river (Rocher et al., 2012).
147 The pH of the wastewater effluent ranges from 7.8 to 8 (SIAAP data). The PAC used for all
148 adsorption experiments was PB-170 (DaCarb, see physico-chemical properties summarized
149 in Table S1) and was previously studied in a large-scale pilot and in batch experiments
150 (Mailler et al., 2016b, 2015). Organic micropollutants were purchased from Sigma-Aldrich
151 and their physico-chemical properties are described in Table 1 (molecular weight,
152 hydrophobicity/log D and charge) and Table S2 (van der Waals volume, minimal projection
153 area, polar surface area and hydrogen bonds).

154 *2.2. Experimental methods*

155 The 12 employed OMPs (Table 1) were selected based on their occurrence and
156 concentrations in Parisian wastewater effluents (Mailler et al., 2015). They were commonly
157 found in WWTP effluents and present a broad range of physical and chemical properties (i.e.
158 charge, size, hydrophobicity).

159 Short-term adsorption capacity of the 12 OMPs was studied after 30 min at room
160 temperature (20 °C) and at 8 different concentrations (ranging from 0.04-1.7 µg/L to 1.2-52
161 µg/L depending on the OMPs, concentrations C1-C8 in Table S3) in ultra-pure water (pH
162 adjusted to 8.0) and wastewater effluent, resulting in pseudo-isotherm curves (since an
163 adsorption isotherm is assumed to be obtained at reaction equilibrium, which was not

164 reached after 30 min) (experiment 1). The Freundlich equation (Freundlich, 1906) was used
 165 to model adsorption pseudo-isotherms (Equation 1):

$$166 \quad q_t = K_F C_t^{\frac{1}{n}}$$

167 (1)

168 where q_t ($\mu\text{g}/\text{mg}$) is the amount of adsorbate uptake, K_F ($\mu\text{g}/\text{mg}/(\mu\text{g}/\text{L})^{1/n}$) is the Freundlich
 169 constant, C_t ($\mu\text{g}/\text{L}$) is the adsorbate concentration and $1/n$ (dimensionless) is the Freundlich
 170 intensity parameter related to the intensity of the adsorption driving force or the surface
 171 heterogeneity.

172 The modeling parameters (K_F and $1/n$) and p -values from the Student test were obtained for
 173 each OMP and each matrix (ultra-pure water or wastewater effluent) via non-linear least
 174 squares regression with the *nlstools* package (Baty et al., 2015) using *R* software (R Core
 175 Team, 2007).

176 Table 1. Name, type and main physico-chemical properties of OMPs used in this study. LOQ: limit of
 177 quantification (ng/L); MW: molecular weight (g/mol); log K_{ow} : partition coefficient between water and octanol
 178 (MarvinSketch, ChemAxon); log D: log K_{ow} at pH = 8.0. Charge : average charge based on the presence
 179 percentage of each OMP species (anionic, cationic, neutral, zwitterionic) at pH 8 (MarvinSketch, ChemAxon).

Compound	Type	LOQ (ng/L)	MW (g/mol)	Log D (pH = 8)	Charge (pH = 8)
Acetaminophen	Analgesic	0.5	151	0.90	-0.03
Atenolol	Beta-blocker	1	266	-1.25	0.98
Carbamazepine	Anticonvulsant	1	236	2.77	0.00
Diclofenac	Analgesic	0.5	296	0.26	-1.00
Erythromycin	Antibiotic	4	734	2.07	0.71
Ibuprofen	Analgesic	6	207	0.69	-0.99
Lorazepam	Antidepressant	1.5	321	3.53	0.00
Ofloxacin	Antibiotic	1	361	-1.12	-0.99
Oxazepam	Antidepressant	2	287	2.92	0.00
Roxithromycin	Antibiotic	0.5	837	1.89	0.92
Sulfadiazine	Antibiotic	1	250	-0.66	-0.91
Trimethoprim	Antibiotic	2	290	1.22	0.12

180 The influence of contact time was studied by conducting comparative adsorption tests in
 181 ultra-pure water and wastewater effluent during 30 min and 72 h at an average OMPs
 182 concentration (0.48-20 $\mu\text{g}/\text{L}$ depending on the OMPs, concentration C5 in Table S3)

183 (experiment 2). DOC, DOM fractions from LC-OCD chromatograms, UV_{254} and the
184 intensity of 6 fluorescence indexes from excitation/emission matrices were determined
185 before and after adsorption.

186 Finally, adsorption experiments were performed with and without a 24 h pre-equilibrium
187 between the wastewater effluent and spiked OMPs (at the lowest working concentrations,
188 i.e. 0.04-1.7 $\mu\text{g/L}$ depending on the OMPs, concentration C1 in Table S3) to study the
189 influence of the contact between DOM and OMPs prior to adsorption (during 30 min and
190 72h) (experiment 3).

191 A dose of 10 mg/L of PAC was added to the working solutions during all the experiments.
192 This dose was previously demonstrated to maximize differences between molecules in terms
193 of removal, which allows the observation of relationships between physico-chemical
194 properties of OMPs and their removal (Mailler et al., 2016b). Experiments were conducted
195 only one time because previous results indicated that the variability of OMPs removal was
196 low (<10%) in similar conditions (Guillossou et al., 2020). Batch systems were placed under
197 strong stirring during the required contact time. Pre-determined volumes of the stock
198 solution containing the 12 OMPs were spiked in working solutions of 1.5 L to reach the
199 targeted concentrations for each experiment. Volumes of the spiked solution were chosen to
200 maintain a low percentage of solvent (methanol) added to the working solution (< 0.05%).
201 The targeted concentrations of OMPs in the working solution were chosen to ensure that all
202 OMPs were not completely adsorbed onto the PAC after the chosen contact times and that
203 residual concentrations were above limits of quantification (LOQ, Table 1). Unless
204 specifically mentioned, OMPs were always spiked in the wastewater effluent 24 h prior to
205 PAC addition to simulate the interactions between DOM and OMPs occurring during sewer
206 transfer and inside WWTPs.

207 *2.3. Analytical procedures*

208 OMPs were analyzed within 48 h at the Institute of Analytical Sciences (ISA – Villeurbanne,
209 France) by liquid chromatography coupled to tandem mass spectroscopy. Prior to analysis,
210 all samples were homogenized and filtered on 0.7 μm GF/F glass filters (Whatman). More
211 information on the analytical methods can be found in the literature (Vulliet et al., 2011).
212 LOQs of the 12 OMPs ranged between 0.5 and 6 ng/L (Table 1). If the concentration of
213 some pharmaceuticals was below the LOQ after adsorption, their removal from the liquid
214 phase and the quantity adsorbed onto the solid phase were estimated as if their concentration
215 was equal to LOQ/2.

216 Dissolved organic carbon (DOC) was analyzed for each experiment by the certified SIAAP
217 laboratory filtration on 0.45 μm polyvinylidene fluoride filters (Milex[®], Merck) (limit of
218 quantification = 0.3 mgC/L). Liquid size-exclusion chromatography was coupled with
219 organic carbon detection (LC-OCD, DOC-Labor Dr. Huber, Germany) to study the
220 adsorption of different DOM fractions including biopolymers, humic acids, building blocks
221 and low molecular weight acids and neutrals (Huber et al., 2011).

222 Spectroscopic measurements were performed for experiment 2 and 3 at room temperature
223 directly after sampling and filtration on 0.45 μm polyvinylidene fluoride filters (Milex[®],
224 Merck). UV_{254} was measured in a 1 cm quartz cuvette using a spectrophotometer (Genesys
225 10S UV-Vis, Thermo Scientific). Fluorescence emission-excitation matrices (EEMs) were
226 obtained using a 1 cm quartz cuvette and a spectrofluorometer (FP-8300, 150-W Xenon
227 lamp, Jasco) with excitation wavelengths ranging from 240 nm to 450 nm with an interval of
228 5 nm, and emission wavelengths ranging from 250 nm to 600 nm with an interval of 2 nm.
229 When UV_{254} was higher than 0.080 1/cm, the samples were diluted with ultrapure water to
230 avoid inner filter effects due to adsorbing species present in the wastewater (Alberts and

231 Takács, 2004). EEMs of ultrapure water were subtracted from the sample EEMs, which were
232 also normalized by the Raman peak of ultrapure water (excitation wavelength of 350 nm) to
233 obtain fluorescence data in Raman units (R.U.) (Lawaetz and Stedmon, 2009). EEMs were
234 characterized by using a set of excitation/emission wavelengths based on maximum
235 localization of 6 specific PARAFAC components (C1-C6) that were previously obtained
236 from wastewater samples of the Seine Centre WWTP (Goffin et al. 2018). The index C1
237 (275/304 nm) is related to tyrosine-like compounds, C2 (285/344 nm) to
238 tyrosine/tryptophan-like compounds, C3 (275/378 nm) to tryptophan-like compounds, C4
239 (295/404 nm) to humic-like compounds from a recent biological activity and C5 (360/434
240 nm) and C6 (275/464 nm) to humic-like compounds.

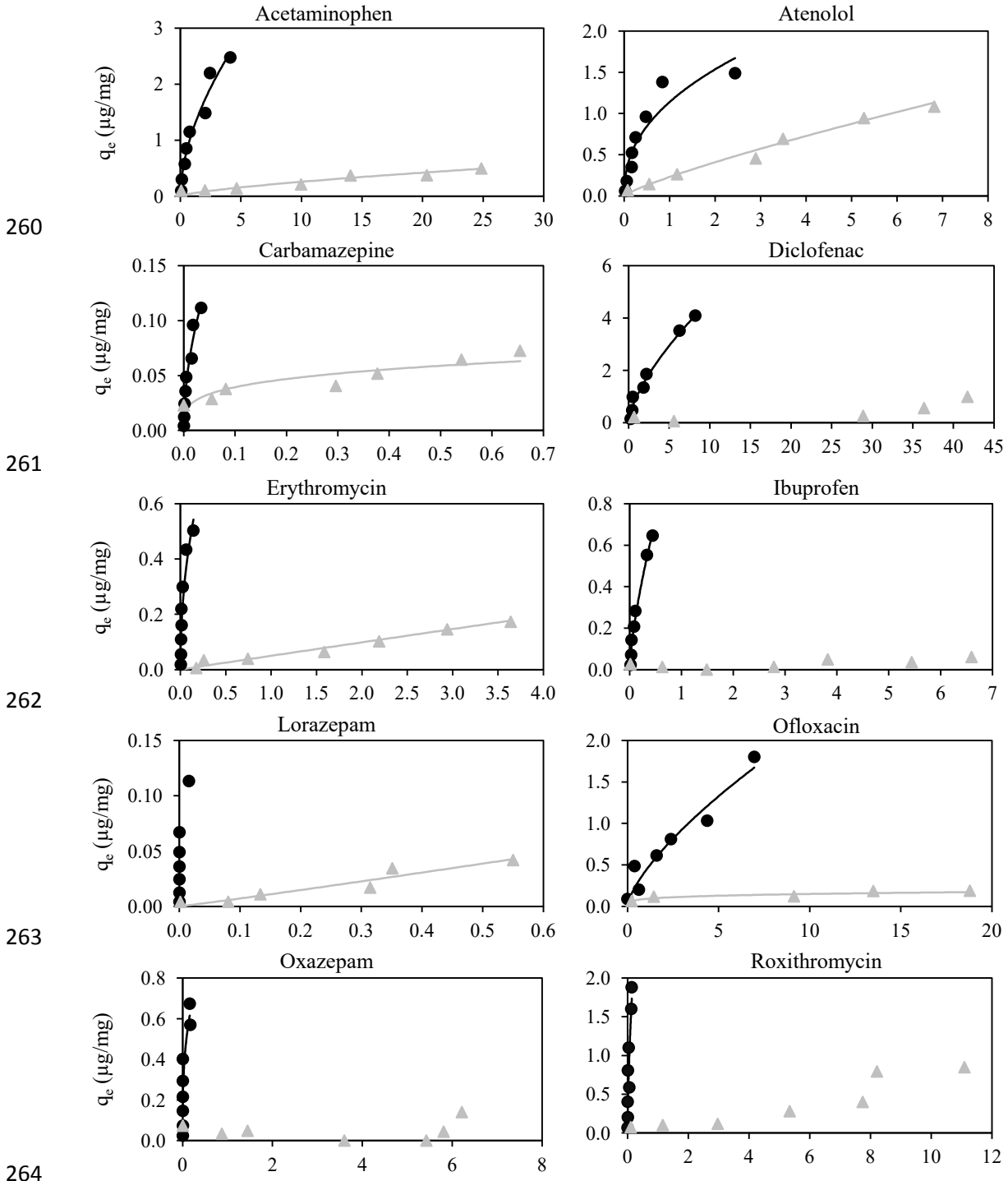
241 **3. Results and discussion**

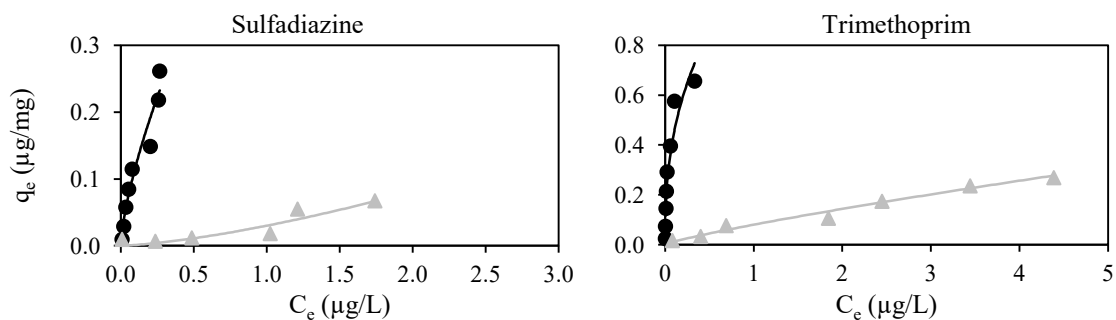
242 *3.1. Adsorption pseudo-isotherms*

243 Pseudo-isotherms representing the short-term (30 min) adsorption capacity of OMPs in each
244 matrix are presented in Figure 1 and the best-fit isotherms parameters are summarized in
245 Table 2 (experiment 1). Most pseudo-isotherms were correctly fitted with the Freundlich
246 equation (Student-test, p -value < 0.05 for the estimated K_F or $1/n$). In ultra-pure water, only
247 lorazepam could not be fitted by the Freundlich equation because no residual concentration
248 was detected in most bottles after 30 min of contact time. In wastewater effluent, diclofenac,
249 ibuprofen, oxazepam and roxithromycin were not correctly fitted (p -value > 0.05 for the
250 estimated K_F or $1/n$) and their Freundlich parameters were therefore not reported in Table 2.

251 As expected, the adsorption capacity (i.e. q_t value for a given initial concentration) was
252 systematically higher in ultra-pure water than in wastewater effluent for all OMPs, and all
253 Freundlich constants (K_F) obtained after fitting the data were higher in ultra-pure water than
254 in wastewater effluent accordingly. For most OMPs, the Freundlich intensity parameter ($1/n$)

255 was also higher in wastewater effluent than in ultra-pure water, which shows that the
 256 presence of DOM makes adsorption less favorable. The Freundlich intensity parameter was
 257 lower in wastewater effluent than in ultra-pure water only for carbamazepine and ofloxacin.
 258 This could be due to modelling issues because of analytical errors at some concentrations,
 259 leading to shifted points on the isotherm (C_t and q_t values).





265
266 Figure 1. OMPs adsorption pseudo-isotherms after 30 min of contact time with PAC and a pre-equilibrium of
267 24 h between the matrix and OMPs before adsorption (experiment 1). ● Ultra-pure water. ▲ Wastewater
268 effluent. Lines correspond to the best-fit obtained by the Freundlich model.

269 Table 2. Best-fit isotherms parameters of OMPs adsorption after 30 min of contact time with PAC and a
270 pre-equilibrium of 24 h between the matrix and OMPs before adsorption (Freundlich constant K_F , intensity
271 parameter $1/n$ and coefficient of determination R^2 of the model) (experiment 1). p -values from the Student-test
272 are given for each parameter.

Compound	Matrix	Freundlich				R^2
		K_F ($\mu\text{g}/\text{mg}$)/($\mu\text{g}/\text{L}$) $^{1/n}$	p -value	$1/n$	p -value	
Acetaminophen	Ultra-pure water	1.16	<0.001	0.56	<0.001	0.96
	Wastewater effluent	0.05	0.042	0.71	0.003	0.96
Atenolol	Ultra-pure water	1.14	<0.001	0.43	0.001	0.88
	Wastewater effluent	0.23	<0.001	0.83	<0.001	0.98
Carbamazepine	Ultra-pure water	0.67	0.006	0.52	<0.001	0.96
	Wastewater effluent	0.07	<0.001	0.25	0.048	0.72
Diclofenac	Ultra-pure water	1.00	<0.001	0.67	<0.001	0.98
	Wastewater effluent	-	-	-	-	-
Erythromycin	Ultra-pure water	1.38	0.006	0.48	0.001	0.88
	Wastewater effluent	0.05	<0.001	0.98	<0.001	0.97
Ibuprofen	Ultra-pure water	1.17	<0.001	0.70	<0.001	0.99
	Wastewater effluent	-	-	-	-	-
Lorazepam	Ultra-pure water	-	-	-	-	-
	Wastewater effluent	0.08	0.017	1.05	0.019	0.92
Ofloxacin	Ultra-pure water	0.43	0.010	0.70	0.006	0.95
	Wastewater effluent	0.09	0.010	0.22	0.047	0.96
Oxazepam	Ultra-pure water	1.13	0.012	0.33	0.012	0.71
	Wastewater effluent	-	-	-	-	-
Roxithromycin	Ultra-pure water	6.08	0.040	0.64	0.007	0.83
	Wastewater effluent	-	-	-	-	-
Sulfadiazine	Ultra-pure water	0.58	0.002	0.69	<0.001	0.94
	Wastewater effluent	0.03	0.010	1.44	0.039	0.88
Trimethoprim	Ultra-pure water	0.13	<0.001	0.40	<0.001	0.90
	Wastewater effluent	0.08	<0.001	0.84	<0.001	0.98

273 The adsorption isotherm is favorable when $1/n < 1$, which suggests a good affinity between
274 the adsorbate and the adsorbent (i.e. chemisorption), while it is unfavorable when $1/n > 1$,
275 the first adsorbate molecules are hardly adsorbed but improve the adsorption of the

276 following, probably through multilayer adsorption favorized by van der Waals interactions
277 (i.e. physisorption). The adsorption of sulfadiazine was unfavorable ($1/n = 1.44$) and the
278 adsorption of erythromycin and lorazepam was almost linear ($1/n = 0.98$ and 1.05 ,
279 respectively). Erythromycin is positively charged and one of the largest molecules (MW >
280 700 g/mol) and could be more impacted by the presence of DOM (i.e., by pore blockage and
281 steric hindrance).

282 Attractive electrostatic interactions with the negatively charged DOM were probably not
283 sufficient to counterbalance pore blockage. Sulfadiazine is negatively charged and thus was
284 probably subjected to repulsive electrostatic interactions with the adsorbed DOM, as well as
285 diclofenac and ibuprofen. No correlation was obtained between Freundlich parameters and
286 any physico-chemical property of the 12 OMPs (Table 1 and Table S2), suggesting that the
287 adsorption of OMPs depends on various mechanisms and parameters governing their affinity
288 with the PAC, and also their interactions with the DOM both present in solution and
289 adsorbed at the surface of the activated carbon.

290 *3.2. Influence of the contact time with PAC*

291 3.2.1 DOM adsorption

292 DOC removal was low (4%) after 30 min of adsorption and close to values obtained in a
293 previous study (Mailler et al., 2016b) (Table 3, experiment 2). The DOC removal was higher
294 after 72 h (15%) but was still low despite a longer contact time. LC-OCD analyses (see
295 Figure 2) showed that the wastewater effluent DOM was mainly composed of humic-like
296 substances (2.58 mgC/L), followed by biopolymers, building blocks and low molecular
297 weight neutrals (1.26-1.38 mgC/L) and to a lesser extent of hydrophobic molecules (0.75
298 mgC/L). Only biopolymers (especially the smallest biopolymers eluted at 33-40 min of
299 retention time) were significantly removed after 30 min of adsorption (11 %), while almost

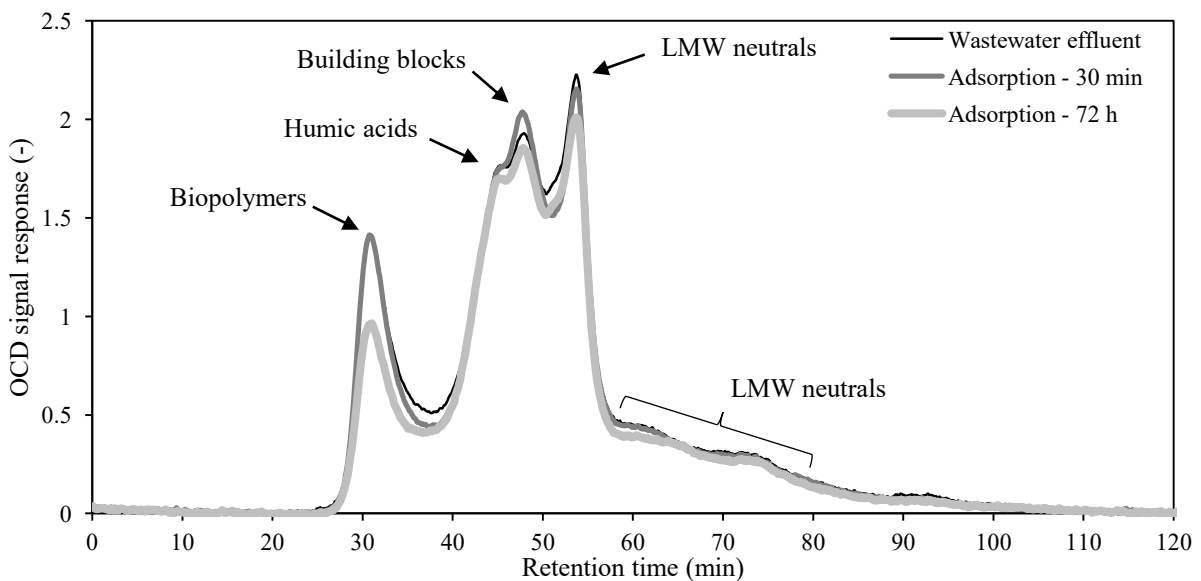
300 no removal (< 3%) was observed for humic acids, building blocks and low molecular weight
301 neutrals. The hydrophobic fraction, which is the remaining fraction of DOC retained on the
302 chromatographic column and not eluted, reached similar removal as biopolymers (8 %).
303 These results show that only specific DOM fractions are adsorbed and are thus responsible
304 for the mechanisms preventing OMPs adsorption and occurring at the surface of the AC (i.e.
305 competition for adsorption sites and pore blockage). The removal of most DOM fractions
306 increased after a 72 h contact time with PAC. The most adsorbed fractions were again
307 biopolymers (34%) and hydrophobic molecules (32%), followed by building blocks (10%)
308 and low molecular weight neutrals (14%). However, humic acids were still not removed
309 (2%) despite being the main DOM fraction. The LC-OCD effluent profile shows a much
310 lower proportion of humic-like substances compared to a natural water (Schulz et al., 2017)
311 and conventional wastewater profile (Zietzschmann et al., 2014) and humic acid adsorption
312 was more important in these two studies. The lower adsorption in this study could be due to
313 the presence of biopolymers, unlike the other studies, which are much larger and could
314 hinder the diffusion of humic acids to the adsorption sites. The difference in PAC used could
315 also explain the observed differences for the adsorption of humic acids, particularly the point
316 of zero charge.

317 Table 3. DOC, DOM fractions from LC-OCD, UV₂₅₄ and fluorescence indexes removal after adsorption for 30
318 min and 72 h (PAC, 10 mg/L) (experiment 2).

Dissolved organic matter fraction	Wastewater effluent level	Removal (%)	
		30 min	72 h
DOC	7.31 mgC/L	4	15
Biopolymers	1.35 mgC/L	11	34
Humic acids	2.58 mgC/L	2	2
Building blocks	1.26 mgC/L	0	10
LMW neutrals	1.38 mgC/L	3	14
Hydrophobic fraction	0.75 mgC/L	8	32
UV ₂₅₄	0.167 l/cm	12	24
C1 – Tyrosine-like compounds	0.59 R.U.	18	44
C2 – Tyrosine/tryptophan-like compounds	1.40 R.U.	18	46
C3 – Tryptophan-like compounds	1.35 R.U.	16	39
C4 – Humic-like compounds from a recent biological activity	1.36 R.U.	15	34

C5 – Humic-like compounds	1.77 R.U.	18	41
C6 – Humic-like compounds	1.27 R.U.	6	35

319 A removal of 12% was obtained for UV₂₅₄ after 30 min of adsorption, while the intensity of
320 fluorescence indexes was slightly more affected (15-18%) except for the index C6 (6%).
321 After 72 h of adsorption, the decrease in UV₂₅₄ intensity (24%) and fluorescence indexes
322 (34-46%) was in agreement with the higher removal of DOM observed from DOC and
323 LC-OCD measurements. However, at both contact time, the decrease in UV₂₅₄ intensity and
324 fluorescence indexes was proportionally higher than the removal of DOC and DOM
325 fractions. Especially, 3 fluorescence indexes related to humic substances (i.e., C4, C5, C6)
326 exhibited a decrease higher than 30% after 72h of adsorption while only 2% of humic acids
327 as analyzed by LC-OCD were removed. Fluorescing molecules represent a very small
328 portion of the DOM (Wünsch et al., 2015) and these results indicate that they were
329 preferentially adsorbed as compared to the bulk of humic substances.



330 Figure 2. LC-OCD chromatograms of wastewater effluent before and after adsorption for 30 min and 72 h
331 (PAC, 10 mg/L) (experiment 2) with fraction indicators (Huber et al., 2011). LMW : low molecular weight.
332

333 3.2.2. OMPs removal

334 The removal of OMPs by activated carbon was determined after 30 min and 72 h of contact
335 time in ultra-pure water and wastewater effluent (Table 4, experiment 2). In ultra-pure water,

336 removals were important (> 94%) and similar between 30 min and 72 h (less than 6%
 337 difference) for almost all OMPs with the exception of diclofenac (89 and 97% at 30 min and
 338 72 h, respectively) and ofloxacin (77 and 91%, respectively). Diclofenac and ofloxacin being
 339 negatively charged compounds, their lower removal at 30 min was possibly due to repulsive
 340 electrostatic interactions with the negatively charged PAC ($\text{pH}_{\text{pzc}} = 5.0$). However, ibuprofen
 341 and sulfadiazine are also negatively charged molecules but their removal was not affected,
 342 which suggests that other mechanisms favored their adsorption. Ofloxacin has a higher MW
 343 than ibuprofen and sulfadiazine, and diclofenac comprises large chlorine atoms, so
 344 differences in the diffusion rates into the activated carbon pores due to both repulsive
 345 interactions and steric hindrance effects may explain the various removals obtained for these
 346 negatively charged compounds.

347 Table 4. Removal of pharmaceuticals by adsorption onto PAC (10 mg/L) in ultra-pure water and wastewater
 348 effluent after 30 min and 72 h of contact time (experiment 2). A pre-equilibrium of 24 h between the matrix and
 349 OMPs before adsorption was realized. *: removal calculated using LOQ/2 as OMP concentration after
 350 adsorption.

Compound	Removal (%)			
	Ultra-pure water		Wastewater effluent	
	30 min	72 h	30 min	72 h
Acetaminophen	94	99*	17	57
Atenolol	96	99*	60	88
Carbamazepine	99	99	57	99*
Diclofenac	89	97	9	27
Erythromycin	99	99	27	99
Ibuprofen	96	99	4	24
Lorazepam	99*	99*	34	73
Ofloxacin	77	91	11	86
Oxazepam	99*	99*	7	57
Roxithromycin	99	99	33	99
Sulfadiazine	94	99*	15	31
Trimethoprim	99	99*	36	89

351 In the wastewater effluent and after 30 min, removals were low (< 40%) except for atenolol
 352 and carbamazepine (60 and 57%, respectively). These low removals could be attributed to
 353 pore blockage and competition for adsorption sites caused by the presence of DOM.
 354 Biopolymers, consisting of very large molecules (> 10 kDa), were the main DOM fraction
 355 adsorbed onto PAC and thus are potentially responsible for the pore blockage. The

356 hydrophobic fraction of DOM, which was also better adsorbed onto PAC and can be
357 considered in the case of wastewater as a mixture of lipids, fatty acids and
358 lipopolysaccharides of various sizes, could also be responsible of pore blockage but also
359 competition for adsorption sites. The positively charged and the neutral compounds were
360 better removed than the negatively charged compounds (average removal of 40, 30 and 10%,
361 respectively). As already observed in ultra-pure water, the occurrence of repulsive
362 interactions between anionic OMPs and the negatively-charged PAC surface can explain
363 these results, and these interactions can be intensified by the negatively-charged DOM
364 adsorbed onto PAC. Conversely, the better adsorption of atenolol (presenting a positive
365 charge at the pH of the wastewater effluent) could be attributed to attractive electrostatic
366 interactions with the negatively charged PAC surface and the adsorbed DOM. Erythromycin
367 and roxithromycin were again poorly removed because of steric hindrance with the DOM
368 adsorbed in the PAC pores.

369 After 72 h, the removal of all OMPs increased and the highest removals (ranging from 86 to
370 99%) were achieved for atenolol, carbamazepine, erythromycin, ofloxacin, roxithromycin
371 and trimethoprim, which indicates that, as expected, 30 min of contact time was not
372 sufficient to reach the equilibrium. The difference between adsorption rates at 30 min and 72
373 h suggests that, for these 6 compounds, the negative effect of DOM was negligible and that
374 the adsorbed fractions of DOM (which should exacerbate higher pore blockage and
375 competition for adsorption sites) did not prevent their adsorption in the long term. The access
376 to adsorption sites was thus not totally prevented by DOM and no competition inside the
377 pores occurred in the long term. Another possible mechanism is the formation of DOM-
378 OMPs complexes that are progressively adsorbed onto the PAC surface. Pore blockage was
379 thus the main negative effect of DOM inhibiting the adsorption of these OMPs at 30 min,
380 which was finally counterbalanced by their slow diffusion either through the adsorbed DOM

381 or inside PAC pores. The removal of the 6 other OMPs was lower, which indicates that
382 DOM still had a negative effect on their adsorption, either by pore blockage, competition for
383 adsorption sites, or electrostatic repulsion from DOM moieties. The positively charged and
384 the neutral compounds were better removed than the negatively charged compounds
385 (average removal of 95, 75 and 42%, respectively). Erythromycin and roxithromycin were
386 well removed despite their size, probably because of attractive interactions with both the
387 adsorbed DOM and the PAC rather than diffusion into the PAC pores. On the contrary, low
388 removals (ranging from 24 to 31%) were still observed for the negatively charged
389 compounds (diclofenac, ibuprofen and sulfadiazine) and may be attributed to repulsive
390 electrostatic interactions with both the adsorbed DOM and the PAC in addition to
391 competition for adsorption sites. Even after a longer contact time, the presence of DOM had
392 a higher negative effect on the adsorption of negatively charged compounds. Despite its
393 predominant negative charge, ofloxacin was well removed in the presence of DOM (86%
394 after 72 h) and it could be due to interactions with DOM favored by its high polar surface
395 and number of possible hydrogen bonds in comparison to other negative OMPs. No trend
396 was observed between the physical and chemical properties of neutral pharmaceuticals and
397 their removals after 30 min and 72 h.

398 *3.3. Influence of the pre-equilibrium between DOM and OMPs on adsorption*

399 The removal of OMPs by adsorption onto PAC for 30 min and 72 h was examined with and
400 without a pre-equilibrium time of 24 h between the wastewater effluent and OMPs (Table 5)
401 (experiment 3). The 24 h pre-equilibrium between DOM and OMPs increased the removal of
402 all OMPs after 30 min of adsorption. The increase was particularly high for lorazepam
403 (+38%) but also acetaminophen (+26%), diclofenac (+27%) and roxithromycin (+22%),
404 which were poorly or not removed without precontact with DOM (0-11%). A significant
405 increase was observed for atenolol (+15%), erythromycin (+15%), ibuprofen (+13%),

406 oxazepam (+18%), sulfadiazine (+13%) and trimethoprim (+14%). These OMPs were also
407 poorly removed without a pre-equilibrium with DOM (4-23%) except atenolol (34%) and
408 trimethoprim (45%). However, the pre-equilibrium with DOM had little impact on the
409 removal of carbamazepine (+7%) and ofloxacin (+8%) which were already well adsorbed
410 without a pre-equilibrium with DOM (41 and 47 %, respectively). Those results confirm that
411 OMPs and DOM interacted in solution. Such association between OMPs and DOM (through
412 hydrophobic, hydrogen bonding, van der Waals or dipole-dipole interactions) has been
413 extensively studied, especially with natural organic matter (Caupos et al., 2015; Hernandez-
414 Ruiz et al., 2012; Mott, 2002). Its influence on the adsorption of OMPs, specifically onto
415 activated carbon, is however scarcely documented. Some studies demonstrated that DOM
416 prevent the adsorption of organic compounds on river or wastewater particles but this effect
417 could not be attributed to either DOM-OMP association in solution or to competitive
418 adsorption (Hassett and Anderson, 1982). The co-adsorption of DOM and hydrophobic
419 organic compounds has been reported at the surface of mineral materials (e.g. clay, kaolinite)
420 and found to be enhanced by ionic strength (i.e. the presence of divalent cations) (Brunk et
421 al., 1996; Wu et al., 2011). One study reported the enhanced adsorption of pentachlorophenol
422 by PAC after a 3-day pre-equilibrium with fulvic acids, which was attributed to binding at
423 the surface of PAC or to the modification of PAC surface properties by fulvic acid
424 adsorption (Lafrance et al., 1991). Our results demonstrate that the DOM-OMP complexes
425 formed after some pre-equilibration time could be subsequently adsorbed onto the PAC. The
426 pre-equilibrium with DOM thus balances the negative effects caused by DOM presence.
427 Further investigations would be needed to determine the potential role of inorganic ions
428 present in wastewater effluents on the formation of these DOM-OMP complexes and their
429 adsorption.

430 The precontact of 24 h between DOM and OMPs had no impact on the removal of most
 431 OMPs after 72 h of adsorption. An increase was only observed for ibuprofen (+28%) and
 432 sulfadiazine (+36%) and in a lesser extent for lorazepam (+9%) and roxithromycine (+8%).
 433 The removal of these 4 OMPs after 72 h of adsorption and without a precontact with DOM
 434 was low (16-68%) in comparison to the other OMPs (77-98%), which didn't need
 435 interactions with DOM to be well adsorbed.

436 These results suggest that the precontact time between DOM and OMPs occurring during
 437 sewer transfer and inside WWTPs, therefore the processes used for primary and biological
 438 treatment, could have an impact on OMPs removal by activated carbon adsorption. DOM-
 439 OMPs complexes could also be formed at the surface of the PAC after long contact times,
 440 allowing the high removals obtained after 72h even without the 24h pre-equilibrium. These
 441 results also imply that a pre-equilibrium time between DOM and OMPs may be necessary in
 442 laboratory experiments when OMPs are spiked (e.g. adsorption isotherms) in order to have
 443 similar DOM-OMPs interactions to what can be expected in wastewater effluents.

444 Table 5. Removal of pharmaceuticals (initial concentration range: 0.04-1.7 µg/L, Table S2) by adsorption onto
 445 PAC (10 mg/L) with or without a pre-equilibrium time of 24 h between wastewater effluent and OMPs after 30
 446 min and 72 h of contact time (experiment 3).

Compound	Removal (%)			
	Without 24 h precontact		With 24 h precontact	
	30 min	72 h	30 min	72 h
Acetaminophen	9	89	35	90
Atenolol	34	91	49	92
Carbamazepine	41	93	48	95
Diclofenac	11	77	38	80
Erythromycin	20	79	35	83
Ibuprofen	4	36	17	64
Lorazepam	2	59	40	68
Ofloxacin	47	98	55	98
Oxazepam	23	86	41	88
Roxithromycin	0	68	22	76
Sulfadiazine	6	16	19	52
Trimethoprim	45	96	59	98

447 4. Conclusion

- 448 • Adsorption pseudo-isotherms showed, as expected, that OMPs adsorption was higher
449 in ultra-pure water than in wastewater effluent due to the presence of DOM leading to
450 pore blockage and competition for adsorption sites. Various molecular properties
451 (e.g. charge, MW, solubility, hydrophobicity) are involved in the adsorption
452 mechanisms of OMPs, leading to differences in the adsorption capacity of different
453 OMPs.
- 454 • LC-OCD analysis revealed that biopolymers and hydrophobic molecules were the
455 two major fractions of DOM adsorbed on the PAC (~ 30% after 72h). Other fractions
456 were adsorbed after a contact time of 72 h (~ 10%) except humic acids despite being
457 the main DOM fraction. The removal of DOM as analyzed by UV₂₅₄ and
458 fluorescence indexes was higher than the removal calculated from LC-OCD analyses,
459 which could be explained by different adsorption behaviors between the
460 spectroscopically active DOM and the non-active one.
- 461 • The presence of DOM had a negative impact on the removal of all OMPs after 30
462 min of adsorption, but similar removals to ultra-pure water were obtained after a
463 contact time of 72 h for 6 OMPs. A sufficient contact time was thus able to allow
464 high removals of these OMPs despite an increase of DOM adsorption, either by slow
465 diffusion of OMPs through the adsorbed DOM or the PAC pores. Another possible
466 mechanism is the formation of DOM-OMPs complexes that are progressively
467 adsorbed at the PAC surface. Competition for adsorption sites is thus not always the
468 main negative effect in the presence of DOM. Pore blockage, due to the adsorption of
469 biopolymers, hydrophobic molecules of DOM, first strongly prevents the adsorption
470 of OMPs, but is compensated at longer contact times by the potential mechanisms
471 described above.

- 472 • OMPs charge had an impact on their adsorption both in the presence and absence of
473 DOM. The adsorption rate of negatively charged compounds in the presence of
474 wastewater effluent was reduced due to repulsive electrostatic interactions with the
475 adsorbed DOM and the PAC surface (i.e. both negatively charged). Positively
476 charged compounds were globally better adsorbed, possibly due to attractive
477 electrostatic interactions, but steric hindrance hindered the adsorption rate of some
478 large molecules.
- 479 • A pre-equilibrium of 24 h between OMPs and DOM improved their removal onto
480 PAC, which confirm that OMPs and DOM interact in solution. These results are in
481 accordance with the formation of DOM-OMPs complexes in solution which
482 increased the overall removal of OMPs, especially at short contact times.
- 483 • Additional studies should be conducted to identify the nature of the interactions
484 between DOM and OMPs, to determine the influence of various pre-equilibrium
485 times (i.e. a kinetic study) between DOM and OMPs and optimal conditions of pre-
486 equilibrium and adsorption contact times, as well as the influence of DOM quality
487 (i.e. wastewater from activated sludges, biofilters, membrane bioreactors) and
488 fractions (e.g. biopolymers or hydrophobic molecules), and the potential role of
489 inorganic ions (e.g. divalent cations).

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