

1 **REMOVAL OF PRIORITY AND EMERGING POLLUTANTS FROM AQUEOUS**  
2 **MEDIA BY ADSORPTION ONTO SYNTHETIC ORGANO-FUNCTIONALIZED**  
3 **HIGH-CHARGE SWELLING MICAS**

4

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26 **Abstract**

27 In this work, the removal of different types of emerging pollutants (four perfluoroalkyl  
28 compounds, two preservatives, three surfactants and nine pharmaceutical compounds) from  
29 aqueous solution by adsorption onto two novel synthetic clays, a high-charge swelling mica  
30 (Na-Mica-4) and an organo-functionalized mica (C<sub>18</sub>-Mica-4), was evaluated. Na-Mica-4 and  
31 C<sub>18</sub>-Mica-4 were prepared and characterized by X-Ray diffraction, Zeta potential, specific  
32 surface area, thermogravimetric analysis and transmission electron microscopy, before and  
33 after adsorption experiments.

34 The influence of the aqueous sample pH, salt addition and extraction time in the removal  
35 were evaluated. The results showed the high adsorption affinity of C<sub>18</sub>-Mica-4 for most of the  
36 emerging pollutants analysed after a removal time of 24 hours (14 out of 18 pollutants were  
37 effectively removed [70-100%]). A high correlation was observed between the log K<sub>ow</sub> of the  
38 selected emerging pollutants and the adsorption onto C<sub>18</sub>-Mica-4. The results also indicate  
39 that adsorption occurs in the interlayer space. While the removal rates with Na-Mica-4 were  
40 in the range 8% to 97% after seven days, some of the compounds, perfluorobutanoic acid and  
41 most of pharmaceutically active compounds, were not adsorbed onto the high-charge mica.  
42 C<sub>18</sub>-Mica-4 was effectively used for the removal of contaminants from four types of water  
43 samples.

44 **Keywords:** *Emerging pollutants; High-charge swelling micas; Organic functionalization;*  
45 *Water samples; Removal*

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## 51 **Introduction**

52 Preservation and improvement of water quality is paramount to keep the health and  
53 sustainability of the different ecosystems. The occurrence of natural or anthropogenic  
54 contaminants of emerging concern at levels between  $\text{ng L}^{-1}$  and  $\mu\text{g L}^{-1}$  has been reported in  
55 many publications including pesticides, industrial compounds, pharmaceuticals and personal  
56 care products, among others (Ruhí et al., 2016; Rodil et al., 2012; Bolong et al., 2009;  
57 Caliman et al., 2009). Conventional urban wastewater treatment plants (WWTPs) are not  
58 specifically designed to remove residual concentrations of organic compounds. Ultraviolet  
59 lamps have been used mainly for disinfection, while alternative technologies including  
60 advanced oxidation processes (such as ozonation with  $\text{H}_2\text{O}_2$  and the use of  $\text{Uv/H}_2\text{O}_2$ ),  
61 nanofiltration, reverse osmosis, and adsorption (Carmalin and Eder, 2018; Capodaglio, 2017;  
62 Grassi et al., 2012; Katsoyiannis et al., 2011; Liu et al., 2009), have been investigated but  
63 most of them hardly implemented as tertiary treatment in WWTPs.

64 Adsorption is one of the alternatives for the removal of emerging pollutants due to its high  
65 efficiency, selectivity, low cost, simplicity and the possibility of reusing and recycling the  
66 adsorbent (Carmalin and Eder, 2018; Martins et al., 2017; Méndez et al., 2017; Tapia-Orozco  
67 et al., 2016; Rashed, 2013; Park et al., 2011). The suitability of an adsorbent is determined by  
68 properties such as surface area, mechanical stability or pore size. Activated carbon (AC) is  
69 the most widespread adsorbent for the removal of organic pollutants because of its  
70 microporosity, which ensures good sorption capacities (Rigobello et al., 2013; Djilani et al.,  
71 2012; Ruiz et al., 2010; Yu et al., 2008; Nevskaia and Guerrero-Ruiz, 2001). However, the  
72 use of ACs is costly because only a percentage of carbons can be reused after the adsorption  
73 process (Sharma and Wankat, 2010), usually no more than 40% (Wang and Balasubramanian,  
74 2009). Moreover, thermal regeneration of activated carbons has been explored for emerging  
75 pollutants removal from effluent wastewater (Marques et al., 2017) but it was observed that

76 the regenerated activated carbon was not as efficient as new activated carbon. Therefore,  
77 alternative sorbents are desirable to overcome these drawbacks (Orta et al., 2018; Suna et al.,  
78 2017; Pazos et al., 2017). In this context, clay minerals have attracted much attention owing  
79 to their high cation exchange, swelling properties, and high surface areas (Lingya et al. 2016;  
80 Alba et al., 2009; Sánchez-Martín et al., 2008; Zadaca et al., 2007; Lagally, 2001).

81 Compared to other clay minerals like smectites or vermiculites, micas exhibit higher layer  
82 charge density. Naturally occurring micas do not swell in water and ion-exchange reactions  
83 with the interlayer cations would be extremely slow process (Kodama et al., 2000). In  
84 contrast, the synthetic highly charged mica Na-mica-4 has an unusual swelling behaviour and  
85 selective cation exchange properties, which may become potentially useful for hazardous  
86 cation separations from solutions (Alba et al., 2006; Park et al, 2002).

87 In addition, clay minerals can be modified in order to enhance their removal efficiency in  
88 aqueous media. The organo-functionalization of their surface allows for the effective sorption  
89 of non-ionic pollutants in the interface. The sorption of organic micropollutants by  
90 organoclays depends on the structure and size of alkylammonium ions, type of clay, cation  
91 exchange capacity, density and orientation of the alkyl chains on the surface, and features  
92 such as solute size, shape and relative solubility/hydrophobicity (Pazos et al., 2017; Alba et al,  
93 2011a). C18-mica prepared by a cation-exchange reaction between Na-mica-4 and primary  
94 alkylamine shows better expandability and structural properties than native Na-mica-4,  
95 improving its adsorption capacity (Pazos et al., 2012; Alba et al., 2011a). Up to now, few  
96 studies have examined the use of C18-Mica-4 as adsorbents for the retention of organic  
97 pollutants. Among them, Pazos et al. (2017) and Alba et al. (2011a) studied the adsorption of  
98 some pollutants from petroleum refineries such as benzene, toluene and phenol on these  
99 materials. More recently Orta et al. (2018) evaluated Na-Mica-4 and C18-Mica-4 for the  
100 removal of linear alkylbenzene sulfonates (LAS) from aqueous samples. More studies are

101 required to extend the use of this promising mica for the removal of other families of organic  
102 compounds.

103 In the present work, the adsorption of Na-Mica-4 and C<sub>18</sub>-Mica-4 is evaluated for the removal  
104 of eighteen micropollutants including priority substances (Directive 2013/39/EU), substances  
105 of the last watch list (Decision 2015/495/EU) and contaminants of emerging concern: two  
106 groups of industrial compounds (surfactants and perfluoroalkyl compounds), personal care  
107 products (preservatives), and multi-class pharmaceuticals (anti-inflammatory drugs,  
108 antibiotics, antiepileptic drugs,  $\beta$ -blockers, nervous system stimulants and lipid regulators).

109

## 110 **2. Materials and methods**

### 111 *2.1. Materials and reagents*

112 SiO<sub>2</sub> (Sigma Aldrich; CAS no. 112945-52-5, 99.8% purity), Al(OH)<sub>3</sub> (Sigma Aldrich; CAS  
113 no. 21645-51-2), MgF<sub>2</sub> (Sigma Aldrich; CAS no. 7783-40-6), and NaCl (Sigma Aldrich;  
114 CAS no. 7647-14-5,  $\geq 99.5\%$  purity) were purchased from Sigma-Aldrich for the synthesis of  
115 Na-Mica-4. Primary alkylamine octadecylamine salt (CAS no. 124-30-1,  $\geq 99.0\%$  purity) was  
116 purchased from Sigma Aldrich for the organo-functionalization of Na-Mica-4.

117 HPLC-grade acetonitrile (ACN), methanol (MeOH) and water were supplied by Romil Ltd.  
118 (Barcelona, Spain).

119 Hydrochloric acid, sodium hydroxide, sodium chloride (NaCl), and formic acid were  
120 obtained from Panreac (Barcelona, Spain). Ammonium formate and ammonium acetate were  
121 purchased from Sigma-Aldrich (Steinheim, Germany). All of them were analytical grade.

122 High purity standards of perfluorobutanoic acid (PFBuA), perfluoroheptanoic acid (PFHpA),  
123 perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), 4-nonylphenol (NP),  
124 methylparaben (MeP), and propylparaben (PrP) were supplied from Sigma-Aldrich  
125 (Steinheim, Germany). Sodium dodecylsulfate (AS-C12) and sodium octadecylsulfate (AS-

126 C18) were supplied by Alfa Aesar (Barcelona, Spain). Diclofenac (DIC), ibuprofen (IBU),  
127 salicylic acid (SAL), trimethoprim (TRI), carbamazepine (CAR), propranolol (PRO), caffeine  
128 (CAF), clofibric acid (CLOF), and gemfibrozil (GEM) were purchased from Dr. Ehrenstorfer  
129 (Augsburg, Germany).

130 Individual stock standard solutions of each compound were prepared in methanol and stored  
131 at 4 °C. Mixtures of the studied compounds at different concentration levels were prepared  
132 freshly before each experiment by dilution of the stock standard solutions in a mixture  
133 methanol:water (50:50, v/v). The acronym, pK<sub>a</sub> and log K<sub>ow</sub> of each analyte are shown in  
134 Table 1.

135

### 136 *2.2. Synthesis of swelling high charged micas*

137 Na-Mica-4 was synthesized by the NaCl melt method following a procedure described by  
138 Alba et al. (2006). Its cation exchange capacity (CEC) is 468 mequiv 100 g<sup>-1</sup> and its structural  
139 formula is Na<sub>4</sub>[Si<sub>4</sub>Al<sub>4</sub>]Mg<sub>6</sub>O<sub>20</sub>F<sub>4</sub> · nH<sub>2</sub>O. The starting products employed were SiO<sub>2</sub>, Al(OH)<sub>3</sub>,  
140 MgF<sub>2</sub> and NaCl. The reactants were weighed and mixed in an agate mortar until the mixture  
141 was homogeneous.

142 Heat treatments were carried out in a Pt crucible at 900 °C during 15 h using a heating rate of  
143 10 °C·min<sup>-1</sup>. The product was washed with distilled water, and the solid was separated by  
144 filtration, dried at room temperature, and then ground in agate mortar.

145

### 146 *2.3. Organo-functionalization of Na-mica-4*

147 The organomica C<sub>18</sub>-Mica-Na was prepared by a cation-exchange reaction between the mica  
148 and an excess of primary octadecylamine (2 CEC of Na-Mica-4) (Alba et al., 2011a). The  
149 primary amines were dissolved in an equivalent amount of HCl (0.1 M) and the resulting  
150 mixture was stirred for 3 h at 80 °C. The alkylammonium solution was then mixed with 0.6 g

151 of Na-Mica-4 and stirred for 3 h at 80 °C. Deionized water (50 mL at 50 °C) was added and  
152 the mixture was stirred for 30 min at 50 °C, and the dispersion was then centrifuged at 8,000  
153 rpm for 30 min at 5 °C. The product was dissolved in a hot ethanol:water mixture (1:1) and  
154 stirred for 1 h, centrifuged at 8,000 rpm for 30 min at 5 °C. Finally, the precipitate was left to  
155 dry at room temperature.

156

#### 157 *2.4. Sample collection*

158 Influent and effluent wastewater collected in September 2016 from a wastewater treatment  
159 plant located in Seville (Spain). Six daily-composite samples were obtained by mixing  
160 sample volumes collected every hour by an automatic device (Sigma 900 MAX Portable  
161 Sampler) over a 24-hour period. Surface water samples from the Guadalquivir River (Seville,  
162 Spain) and tap water samples were collected during the same period in Seville city. Water  
163 samples were taken in amber glass bottles pre-cleaned with acetone and methanol. Samples  
164 were stabilized with acetonitrile (final concentration 0.5% v/v) and were stored at 4 °C until  
165 analysis, which was carried out within 48 h after sample collection. Prior to the experiments,  
166 samples were filtered through a 1.2 µm glass-microfiber membrane filter GF/C™ (Whatman,  
167 Mainstone, UK) to remove suspended matter.

168

#### 169 *2.5. Adsorption experiments*

170 A volume of 8 mL of filtered sample was placed in a 25 mL flask containing 50 mg of Na-  
171 Mica-4 or C<sub>18</sub>-Mica-Na. A mixture of the selected pollutants was added to achieve  
172 concentration levels of 10 µg mL<sup>-1</sup>. The solution was stirred at 800 rpm for 24 h. The  
173 supernatants were then filtered through a 0.22 µm nylon filter and a 20 µL aliquot was  
174 injected into the chromatography instrument.

175 The parameters affecting pollutant adsorption, such as type of synthetic mica, sample pH and  
176 extraction time were optimised. The experiments were run in triplicate. Removal rates of the  
177 selected pollutants from water solution were calculated from the equation:  $C_{\text{spiked}} -$   
178  $C_{\text{blank}}/C_{\text{standard}}$ , where  $C_{\text{spiked}}$  is the concentration measured from spiked samples;  $C_{\text{blank}}$  is the  
179 concentration obtained from a blank of reagents; and  $C_{\text{standard}}$  is the concentration obtained by  
180 direct injection of standard solutions at the same concentration level. The linearity of the  
181 method was studied by analysing standard solutions in triplicate at concentrations ranging  
182 from  $0.1 \mu\text{g mL}^{-1}$  to  $10000 \mu\text{g mL}^{-1}$ .

183

## 184 2.6. Techniques

185 *X-ray diffraction* results were obtained in a Bruker D8 Advance A25 diffractometer (Bruker,  
186 Germany) in Bragg-Brentano configuration. The detector was a Lynxeye PSD detector  
187 (Bruker, Germany) equipped with a copper  $K\alpha$  radiation source (0.15405 nm wavelength).  
188 Measurements were taken with a  $2\theta$  range between  $1^\circ$  and  $70^\circ$ , a step of  $0.03^\circ$ , time per step  
189 of 0.1 s, and tube conditions of 40 kV and 30 mA. The diffractometer was calibrated  
190 mechanically according to the manufacturer specifications and corundum standard was used  
191 to check the resolution in a wide range of angles.

192 The *Zeta potential* was obtained from the mobility of the particles using the Smoluchowski  
193 equation (Smoluchowski, 1941). Before and after of adsorption experiments,  $C_{18}$ -Mica-Na  
194 was suspended in water ( $1 \text{ g L}^{-1}$ ) and the zeta potentials was measured on a Zetasizer  
195 Nanosystem system (Malvern Instruments, Southborough, MA). The pH of the solution was  
196 measured with Crison GLP 21 pH meter.

197 The *specific surface area* was determined by the Brunauer-Emmett-Teller (BET) method  
198 using an ASAP 2420 analyser (Micromeritics, USA) with  $\text{N}_2$  sorption (Brunauer S., Emmett  
199 P.H. and Teller, E., 1938).



200 Simultaneous *differential scanning calorimetry and thermal gravimetric analyses* (DSC-TGA)  
201 were performed on a Q600 STD (TA instruments, USA). The samples were heated from  
202 20 °C to 700 °C at a heating rate of 10 °C min<sup>-1</sup> in a nitrogen atmosphere.

203 *Transmission Electron Microscope* (TEM) images were acquired in a Talos Field Emission  
204 TEM (FEI, USA).

205 *Liquid Chromatography-tandem mass spectrometry* (LC-MS/MS) analyses were performed  
206 on an Agilent 1200 series HPLC system (Agilent, USA) equipped with a vacuum degasser, a  
207 binary pump, an autosampler and a thermostatic column compartment. MS analyses were  
208 done with a 6410 QqQ instrument equipped with an electrospray ionization source (ESI)  
209 (Agilent). Ionization of analytes was carried out using the following settings: MS capillary  
210 voltage 3000 V, drying-gas flow rate 9 L min<sup>-1</sup>, drying-gas temperature 350 °C, and nebulizer  
211 pressure 40 psi. Separation of analytes was carried out using a HALO C18 (50x4.6 mm i.d.;  
212 2.7 µm) analytical column (Teknokroma, Spain) protected by a HALO C18 (5x4.6 mm i.d.;  
213 2.7 µm) guard column (Teknokroma, Spain). Elution was performed at a flow rate of 0.6 mL  
214 min<sup>-1</sup> with a column temperature of 30 °C. More details about mobile phase and gradient  
215 elution applied to the separation of the studied compounds can be found in Supplementary  
216 material. Detection was performed in multiple reaction-monitoring mode (MRM), and  
217 positive and negative ionization were simultaneously monitored. Two MRM transitions were  
218 selected for each analyte, one was applied for quantification (MRM1) and another for  
219 confirmation (MRM2). MRM transitions, fragmentor voltage, collision energy and ionization  
220 mode are summarized in Table S1.

221

## 222 **3. Results and discussion**

### 223 **3.1. Characterization of adsorbents**

224 Le Bail analysis was conducted using the TOPAS 5 software (Le Bail, 2005). It is a profile  
225 fitting technique used to extract precise information about the position, intensity, width, and  
226 shape of each individual peak in a diffraction pattern (Orta et al. 2018). X-ray diffraction  
227 characterization tests showed an increase from 12 Å (Na-mica-4) to 49.9 Å (C<sub>18</sub>-Mica-4) in  
228 the interlayer space and a 49.0 Å decrease in the organomica after the adsorption assay. The  
229 difference in interlayer space between organomica and the organomica with adsorbed  
230 material was in the order of 1 Å (see Figure S1 and S2 in supplementary material). This  
231 difference is explained by the tilt angle ( $\alpha$ ) between the alkylammonium axis and the solid  
232 surface after adsorption of emerging pollutants in the interlayer space, which decreased from  
233 62.93° to 60.92°. The  $\alpha$  is calculated by plotting the basal spacing ( $d_{001}$ ) against the length of  
234 the alkylammonium ion chain length ( $n_c$ ), using the following equation (Alba et al., 2006):

$$235 \quad d_{001} = 2 [(n_c - 1) 0.126 + 0.131] \sin \alpha + 0.94 \text{ (nm)}$$

236 The results of the BET specific surface analysis (Brunauer, 1938) showed practically similar  
237 specific surface area for Na-mica-4, C<sub>18</sub>-Mica-4 and C<sub>18</sub>-Mica-4 after adsorption,  $4.2606 \pm$   
238  $0.0061 \text{ m}^2 \text{ g}^{-1}$ ,  $3.1918 \pm 0.1302 \text{ m}^2 \text{ g}^{-1}$  and  $3.3215 \pm 0.1188 \text{ m}^2 \text{ g}^{-1}$ , respectively.

239 The external surface charge of C<sub>18</sub>-Mica-4 before and after the adsorption assays was studied  
240 using the Zeta potential. At pH=5.3, the Zeta potential values were  $55.60 \pm 1.04 \text{ mV}$  and  $55.1$   
241  $\pm 1.09 \text{ mV}$ , before and after adsorption, respectively. These similar values in the external  
242 surface charge of C<sub>18</sub>-mica-4 and the results of the BET indicate that there is no adsorption of  
243 contaminants on the surface.

244 Figure 1 (a, b) shows the results of the DSC and TGA obtained for Na-mica-4, for C<sub>18</sub>-Mica-  
245 4, and for C<sub>18</sub>-Mica-4 after the adsorption assay. Initially, a weight loss of 7% occurred at a  
246 temperature lower than 100 °C, due to the evaporation of water retained in the interlayer  
247 space. This causes a decrease in the heat flow that corresponds to an endothermic peak as  
248 heat is required in the process (Figure 1b). Water loss for evaporation of the interstitial water

249 continued at a steady rate at 170 °C, followed by a moderate weight loss at 700 °C for the  
250 dehydroxylation of the layers (Alba et al., 2011b) (Figure 1a). Before and after the adsorption  
251 assays C<sub>18</sub>-Mica-4 showed a slight decrease of weight at about 170 °C due to the low amount  
252 of water present in it. A weight loss of up to 50% occurred between 170 °C and 450 °C,  
253 fundamentally due to degradation of the alkylammonium chains in the interlayer space (Alba  
254 et al., 2011a) (Figure 1a).

255 The Figure 1b shows exothermic and endothermic shoulders from 350 °C to 470 °C which  
256 correspond to the degradation of alkylammonium chains.

257 Image acquired by TEM shows parallel lines according to laminar silicates structure. The size  
258 of the interlaminar space is in concordance with the calculated by X-ray diffraction (Figure 2).

259

### 260 **3.2. Effect of operational variables on adsorption**

261 A study of the variables affecting the adsorption procedure was carried out to obtain the  
262 optimum conditions for all analytes. Type of adsorbent, sample pH, sodium chloride amount  
263 and extraction time were studied. The initial conditions were 8 mL of sample volume, 50 mg  
264 of adsorbent, and 24 h of extraction time. Experiments were carried out with 8 mL of sample  
265 volume in order to not require high adsorbent amounts. All samples were spiked with 10 µg  
266 mL<sup>-1</sup> of each analyte. Each experiment was run in triplicate.

267

#### 268 *3.2.1. Effect of the synthetic mica on the pollutant adsorption*

269 Removal rates for Na-Mica-4 and C<sub>18</sub>-Mica-4 are shown in Figure 3. Different behaviors  
270 were observed according to the type of mica and analyte. The C<sub>18</sub>-Mica-4 allowed removal  
271 rates in the range 70-100% after 24 h of extraction for all the industrial pollutants, except for  
272 MeP (removal rate: 50%). An increase of removal rates with the alkyl chain was observed for  
273 parabens and perfluoroalkyl compounds (50-70% and 70-91%, respectively). As for

274 pharmaceutical compounds, the optimum removal rates were observed in IBU, GEM, DIC,  
275 SAL and CLOF, while PRO, CAR, CAF and TRI removal rates were < 35%. As can be seen  
276 in Figure 4a, removal is highly dependent on the log K<sub>ow</sub> value of the target pollutants.  
277 Compounds with log K<sub>ow</sub> below 2.5 (such as MeP and some pharmaceutical compounds)  
278 were poorly retained onto the C<sub>18</sub>-Mica-4, probably due to their higher hydrophilicity.  
279 Organo-functionalization of mica increases the capacity to sorb effectively organic pollutants  
280 in the interface. According to the results of the characterization tests, which show no  
281 structural variation in the lamellar organization of the organomicas (only a decrease in the  
282 interlayer space), pollutants may be lodged between the alkylammonium chains, decreasing  
283 the the tilt angle of the chains. The main physical forces controlling adsorption are Van der  
284 Waals forces, hydrophobicity, hydrogen bonds, polarity and steric interaction or dipole-  
285 induced interaction (Ali et al., 2012). Similar results have been reported by Pazos et al. (2017)  
286 regarding the adsorption properties of C<sub>12</sub>-Mica-4, C<sub>14</sub>-Mica-4, C<sub>16</sub>-Mica-4, C<sub>18</sub>-Mica-4 for  
287 the removal of benzene, toluene and phenol.  
288 Generally Na-Mica-4 provides poor removal rates for the selected compounds, with the  
289 exception of PRO (97% after 24 h). Therefore, C<sub>18</sub>-Mica-4 was selected for subsequent  
290 studies.

291

### 292 3.2.2. *Effect of pH on pollutant adsorption*

293 A further pH study was developed using C<sub>18</sub>-Mica-4. Figure 4b shows the effect of the  
294 sample pH (from 0.5 to 12) on the removal efficiency of some selected analytes. Removal  
295 rates were not affected by sample pH in the range from 2 to 7 but decreased at extremely  
296 acidic (pH 1) and basic (pH 12) pH values. Therefore, no sample pH adjustment is necessary  
297 to apply to remove target compounds from water samples by adsorption onto C<sub>18</sub>-Mica-4.

298

### 299 3.2.3. *Effect of sodium chloride on pollutant adsorption*

300 The amount of contaminant adsorbed by C<sub>18</sub>-Mica-4 can be increased by addition of sodium  
301 chloride which results in a change in the ionic strength of the medium. Different % NaCl  
302 (from 0 to 20% w/v) were tested to reduce hydrophilicity and enhance the partitioning  
303 coefficient between C<sub>18</sub>-Mica-4 and the aqueous media. Nevertheless, removal rates of the  
304 target compounds by adsorption onto C<sub>18</sub>-Mica-4 were not affected by NaCl concentration.  
305 Only at a high NaCl content a slightly decrease of the removals occurs. These effect was  
306 observed for most of the compounds studied (except for PRO), irrespective of the log K<sub>ow</sub>.  
307 Therefore, addition of NaCl is not required for the removal of the target compounds by  
308 adsorption into C<sub>18</sub>-Mica-4.

309

### 310 3.2.4. *Effect of extraction time on pollutant adsorption*

311 Extraction times from 1 min to 7 days were tested. Figure 5 shows the extraction time  
312 profiles for selected pollutants. For most industrial pollutants (perfluoroalkyl compounds,  
313 alkyl sulphates and nonylphenol) the equilibrium is reached at 30 min. As for pharmaceutical  
314 compounds, 24 h were necessary to achieve equilibrium. As can be seen in Figure 5, after  
315 adsorption, compounds remain retained into the Mica at least seven days after extraction.  
316 Finally, parabens showed a significant increase in the removal rates at 7 days (from 50 to  
317 83% and from 70 to 95% for MeP and PrP, respectively). Therefore, after a removal time of  
318 24 hours 14 out of 18 pollutants were effectively removed [70-100%].

319

## 320 **3.3. Application of organomica in real environmental water samples**

321 The applicability of C<sub>18</sub>-Mica-4 to the removal of selected emerging pollutants from aqueous  
322 samples was tested in influent and effluent wastewater and surface and tap water. Removal  
323 efficiency was tested by spiking samples with a mixture of compounds at a concentration

324 level of  $10 \mu\text{g mL}^{-1}$ . Results are summarized in Table 2. C<sub>18</sub>-Mica-4 reduced considerably the  
325 concentration of selected pollutants in the four types of water analysed. This effect was  
326 slightly lower in influent wastewater what was probably due to the matrix effect of this  
327 sample. Typical chromatograms of a surface water sample before and after adsorption by the  
328 organomica are shown in Supplementary material (Figure S3).

329 The suitability of an adsorbent is determined by its properties such as surface area,  
330 mechanical stability or pore size. In this sense, and compared to other organoclays, C<sub>18</sub>-Mica-  
331 4 has proven to be an excellent adsorbent (better expandability, structural properties, control  
332 of the composition, purity, low cost and their ready availability). The results obtained support  
333 the high adsorption affinity of C<sub>18</sub>-Mica-4 for most of the selected pollutants analyzed after a  
334 removal time of 24 hours. Moreover no sample pH adjustment and no NaCl addition is  
335 required. In addition, to the date, most of studies about the application of organoclays as  
336 adsorbent for the removal of emerging pollutants from natural waters are focused in the  
337 removal of just one compound or a chemical group of organic compounds (De Oliveira et al.,  
338 2017; Lee et al., 2012; Park et al., 2011; Zhou et al., 2010; Yan et al., 2007; Polubesova et al.,  
339 2006; Yildiz et al., 2005). For instance, De Oliveira et al. (2017) evaluated the use of two  
340 cationic surfactants (benzyltrimethyltetradecyl ammonium (BDTA) and hexadecyl trimethyl  
341 ammonium bromide (HDTMA)) with a Na<sup>+</sup> exchanged montmorillonite for the removal of  
342 diclofenac from natural waters. The results indicate that adsorption of diclofenac is based on  
343 the mobilized cationic surfactants. Zhou et al. (2010) reported the use of organo-  
344 montmorillonite and hexadecyl trimethyl ammonium bromide (HDTMA) for the removal of  
345 PFOS from aqueous solutions. They observed a significant decrease of the interlayer space  
346 after PFOS sorption indicating the rearrangement of HDTMA in the organo-montmorillonite  
347 interlayer space. Polubesova et al., (2006) reported that benzyltrimethylhexadecylammonium  
348 (BDMHDA) modified montmorillonite was much more effective than the conventional

349 activated carbon treatment for the removal of tetracycline and sulfonamide antibiotics from  
350 contaminated water (Polubesova et al., (2006)). The evaluated C<sub>18</sub>-Mica-4 has only been  
351 applied to linear alkylbenzene sulphonates (Orta et al., 2018) and to benzene, toluene and  
352 phenol (Pazos et al., 2017).

353

#### 354 **4. Conclusions**

355 Na-mica-4 and C<sub>18</sub>-mica-4 were synthesized, characterized and applied for first time to the  
356 removal of different groups of emerging pollutants from water samples. The results obtained  
357 in the characterization indicate that the adsorption of pollutants occurs in the interlayer space.  
358 The X-ray diffraction of C<sub>18</sub>-Mica-4 showed a decrease in the interlayer space and degree of  
359 the tilt angle ( $\alpha$ ) between the alkylammonium axis and the solid surface. No structural  
360 variations were observed in the lamellar organization of C<sub>18</sub>-Mica-4.

361 The experiments revealed high adsorption affinity to the C<sub>18</sub>-Mica-4 for most of the emerging  
362 pollutants (14 out of 18 pollutants were effectively removed), while for Na-mica only 3 out of  
363 18 selected pollutants showed high adsorption. A high correlation was observed between the  
364 physicochemical properties of selected emerging pollutants ( $\log K_{ow}$ ) and the adsorption onto  
365 C<sub>18</sub>-Mica-4, so that compounds with  $\log K_{ow}$  higher than 2.5 were efficiently removed.

366 Our results show the high capacity of C<sub>18</sub>-Mica-4 for the removal of selected pollutants in  
367 wastewater, surface water and tap water samples. The reported data represent a promising  
368 area of research in the field of wastewater treatment technologies. The expansion capacity of  
369 organomicas as well as their ready availability, low cost, control of the composition and  
370 purity are promising developments for a bright future in the field of adsorption technology.  
371 Obtained results show that C<sub>18</sub>-Mica-4 is a promising synthetic clay material to remove  
372 organic pollutants from wastewater, surface water and tap water. Further studies should be  
373 carried out to extend the use of this promising clay to other organic compounds and types of

374 samples and also to be used as a sorbent material in sample treatments such as the removal of  
375 interfering compounds.

376

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382

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505

## 506 **FIGURE LEGENDS**

507 **Figure 1.** Thermal gravimetric (a) and differential scanning calorimetry (b) analysis for Na-  
508 4-Mica, C<sub>18</sub>-Mica-4 and C<sub>18</sub>-Mica-4 after adsorption.

509 **Figure 2.** Transmission Electron Microscopy picture of C<sub>18</sub>-Mica-4.

510 **Figure 3.** Effect of Na-Mica-4 and C<sub>18</sub>-Mica-4 on the removal of emerging pollutants (n=3).

511 **Figure 4.** (a) Influence of log K<sub>ow</sub> on the removals by using C<sub>18</sub>-Mica-4; (b) Effect of pH on  
512 the removals of the emerging pollutants (C<sub>18</sub>-Mica-4, n=3).

513 **Figure 5.** Effect of time on the removal of emerging pollutants (C<sub>18</sub>-Mica-4, n=3).

**Table 1.** Acronym and physico-chemical properties of the selected pollutants.

Compound	Acronym	pKa	Log Kow
Methylparaben	MeP	8.3	1.7
Propylparaben	PrP	8.2	2.6
Perfluorobutanoic acid	PFBuA	0.2-0.4	2.4
Perfluoroheptanoic acid	PFHpA	-	5.3
Perfluorooctanoic acid	PFOA	2.8	6.3
Perfluorooctane sulfonic acid	PFOS	-3.3	4.1
Nonylphenol	NP	10.7	4.5
Dodecyl sulfate	AS C12	<1	2.4
Octadecyl sulfate	AS C18	<1	2.6
Diclofenac	DIC	4.1	4
Ibuprofen	IBU	4.4	3.8
Salicylic acid	SAL	3.5	2.3
Trimethoprim	TRI	6.6	1.4
Carbamazepine	CAR	13.9	2.3-2.5
Propranolol	PRO	9.5	0.7
Caffeine	CAF	14	-0.1
Clofibric acid	CLOF	2.5-3.2	2.6
Gemfibrozil	GEM	4.7	4.8

**Table 2.** Pollutant removal (%) in real spiked water samples ( $10 \mu\text{g mL}^{-1}$ ) after  $\text{C}_{18}$ -Mica-4 adsorption (n=3).

Compound	Removal (%) in water samples			
	Tap water	Superficial water	Effluent wastewater	Influent wastewater
MeP	51	58	58	31
PrP	73	75	78	55
PFBuA	78	76	78	68
PFHpA	80	79	77	59
PFOA	87	94	91	84
PFOS	98	100	100	100
NP	98	99	99	99
ASC12	100	100	100	99
ASC18	100	103	100	100
DIC	91	85	78	76
IBU	87	88	78	75
SAL	96	100	90	70
TRI	54	53	55	40
CAR	61	42	58	59
PRO	41	39	15	17
CAF	56	30	52	49
CLOF	90	82	81	40
GEM	92	85	86	81

Figure 1  
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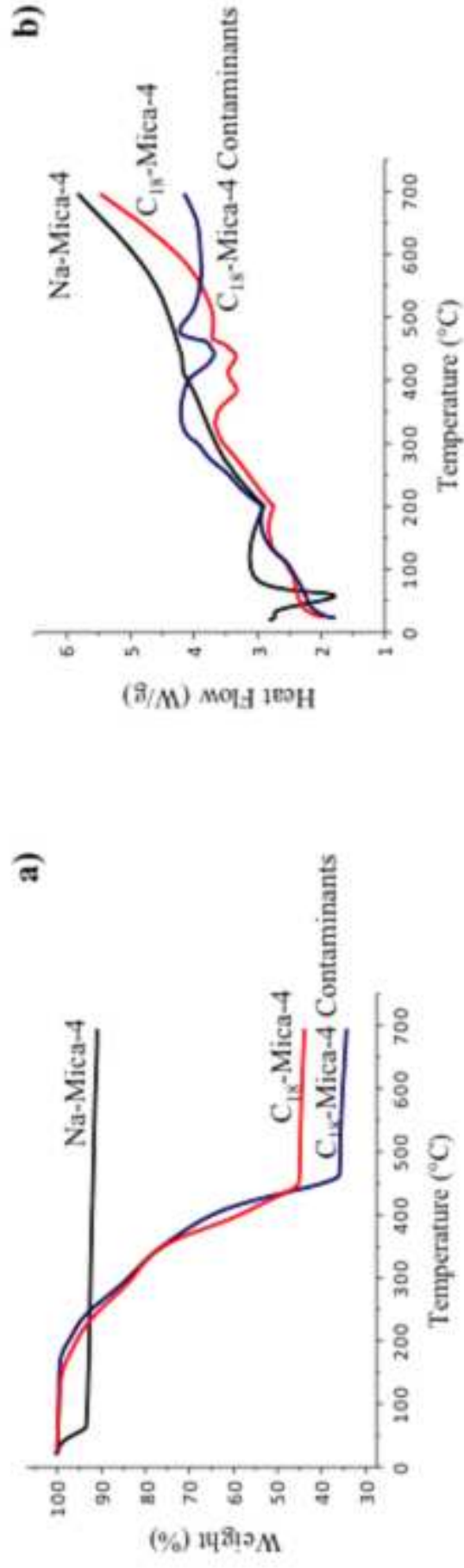




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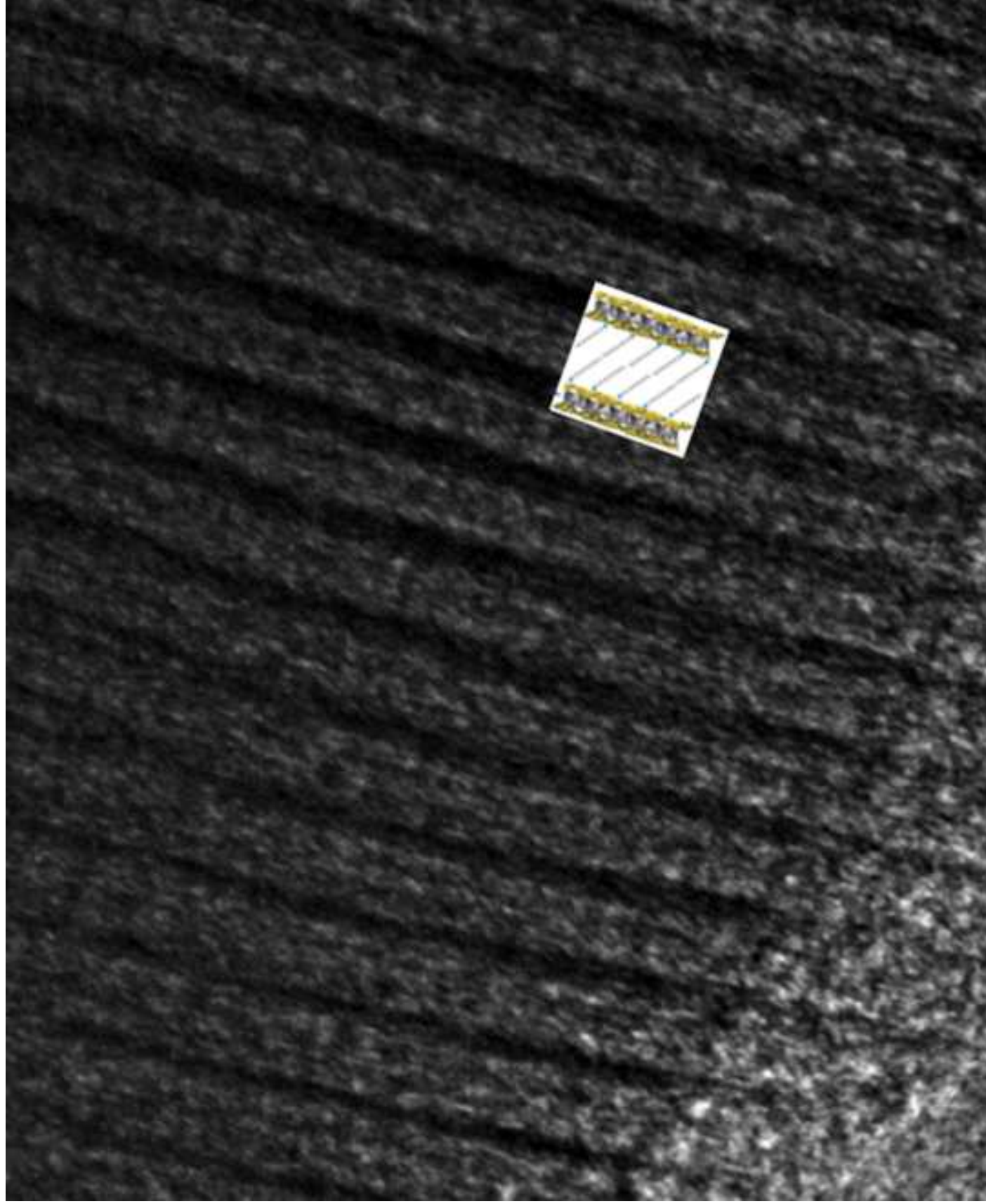


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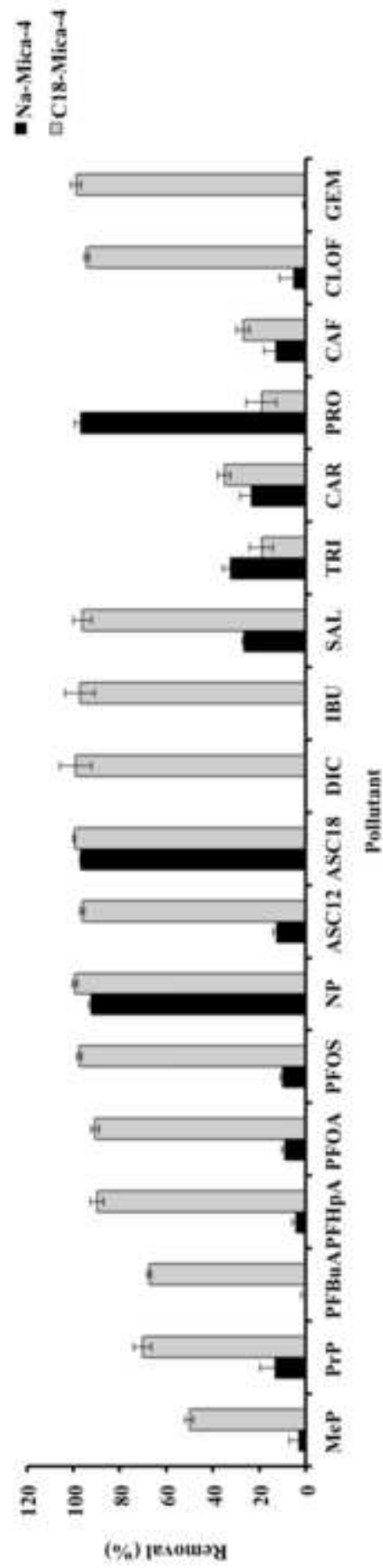
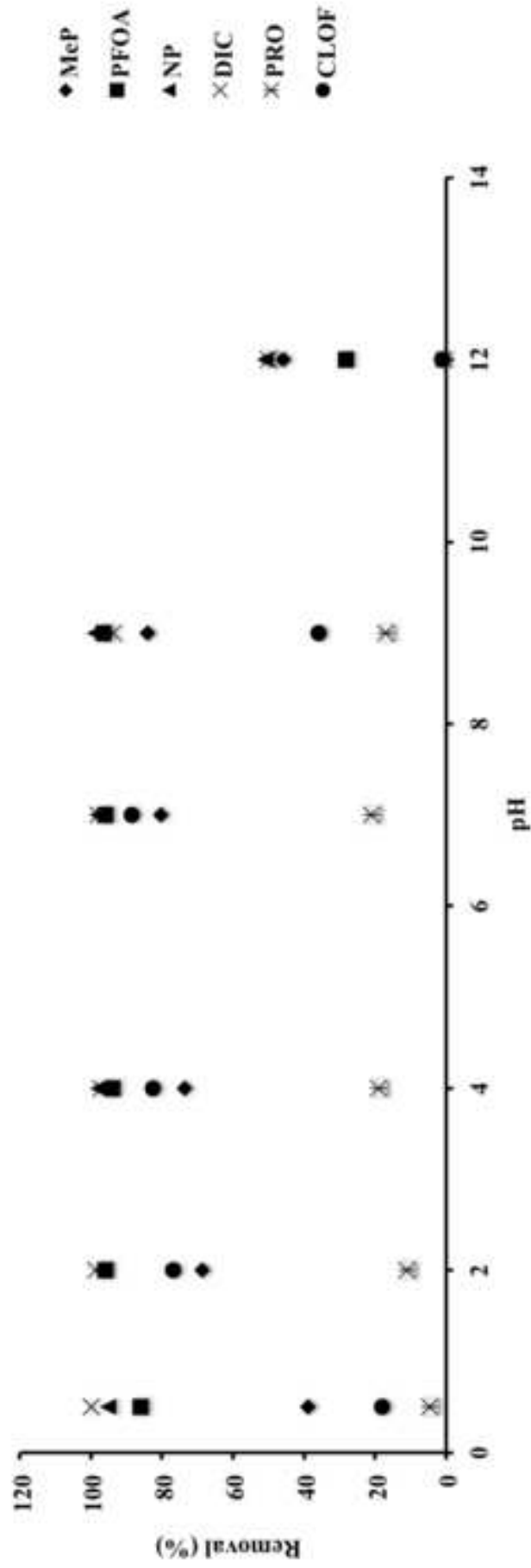
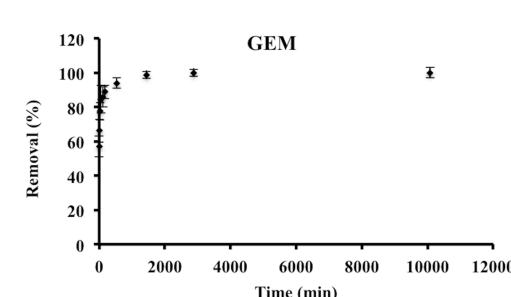
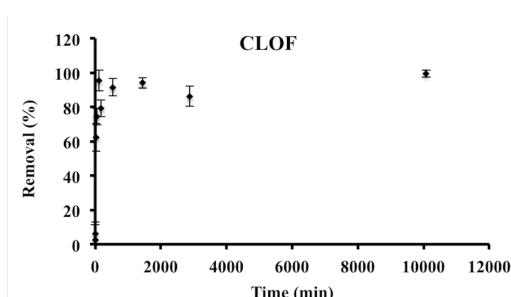
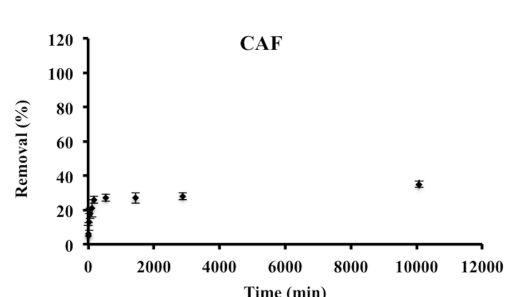
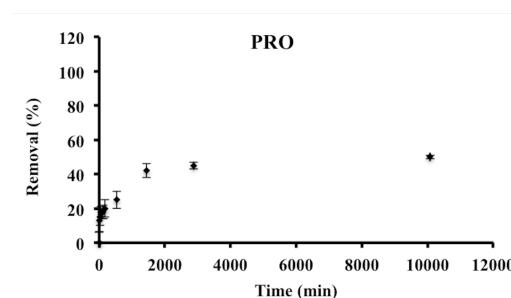
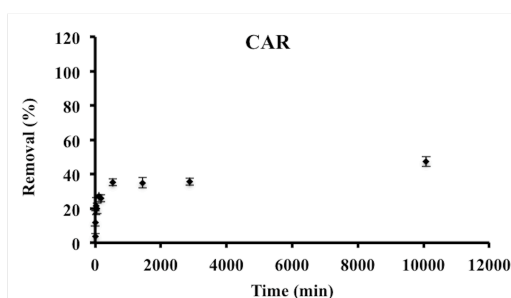
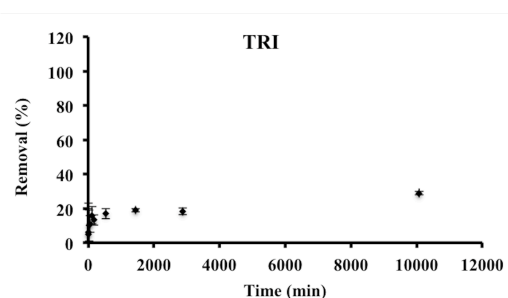
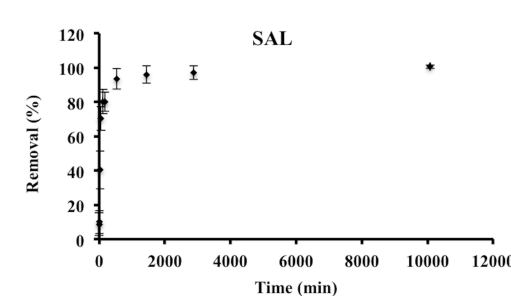
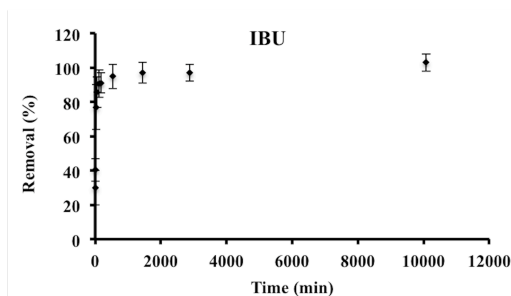
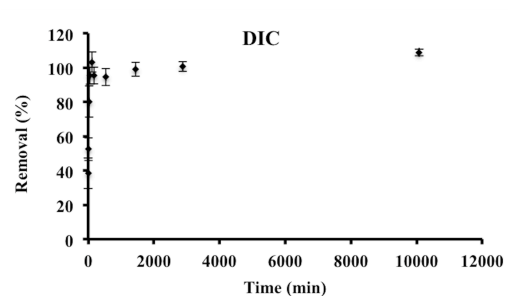
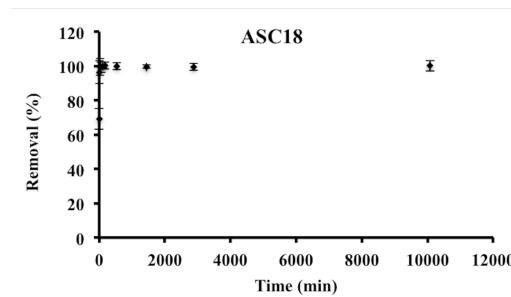
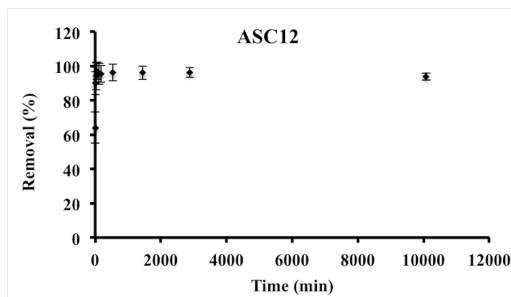
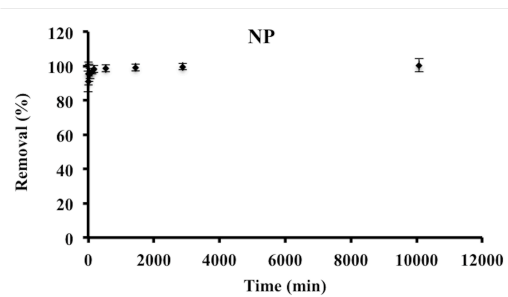
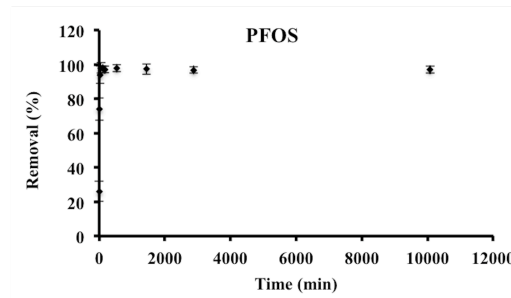
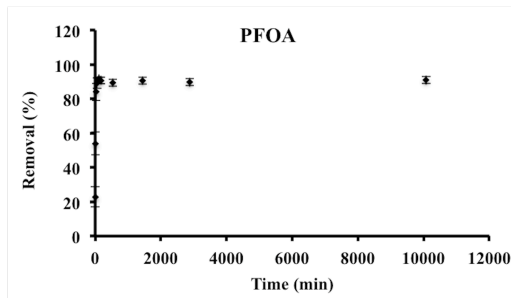
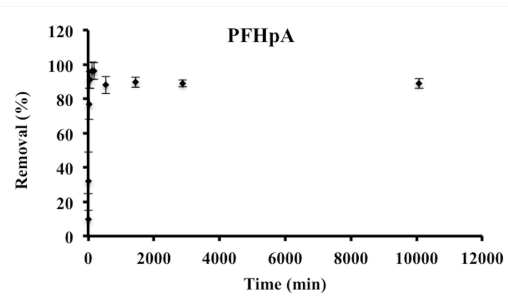
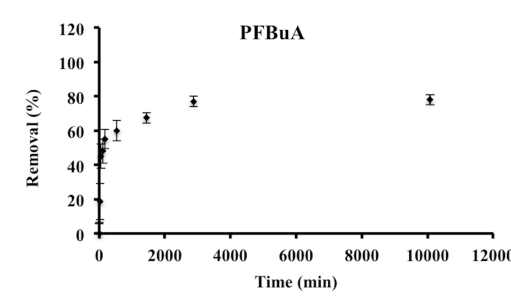
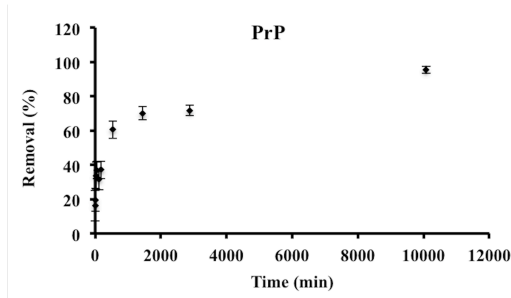
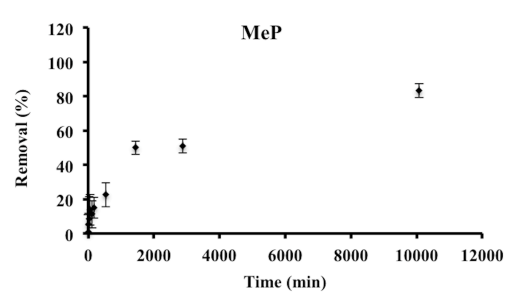


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