



HAL
open science

Silica-clay nanocomposites for the removal of antibiotics in the water usage cycle

Clément Levard, Karima Hamdi-Alaoui, Isabelle Baudin, Amélie Guillon,
Daniel Borschneck, Andrea Campos, Mohamed Bizi, Florence Benoit, Corinne
Chanéac, Jérôme Labille

► To cite this version:

Clément Levard, Karima Hamdi-Alaoui, Isabelle Baudin, Amélie Guillon, Daniel Borschneck, et al..
Silica-clay nanocomposites for the removal of antibiotics in the water usage cycle. *Environmental Science and Pollution Research*, 2021, 28 (6), pp.7564-757. 10.1007/s11356-020-11076-5 . hal-02989392

HAL Id: hal-02989392

<https://hal.science/hal-02989392v1>

Submitted on 5 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Silica-clay nanocomposites for the removal of antibiotics in the water usage cycle

Clément Levard^{1*}, Karima Hamdi-Alaoui¹, Isabelle Baudin², Amélie Guillon², Daniel Borschneck¹, Andrea Campos³, Mohamed Bizi⁴, Florence Benoit⁵, Corinne Chaneac⁵ and Jérôme Labille¹

¹ Aix Marseille Univ, CNRS, IRD, INRAE, Coll France, CEREGE, Aix-en-Provence, France

² SUEZ-CIRSEE. 38, rue du président Wilson, 78230 Le Pecq.

³ Aix-Marseille Université, CP2M, Faculté des Sciences, Campus de St Jérôme, F-13397 Marseille, France

⁴ BRGM, Water, Environment, Process Development and Analysis Division 3, Avenue C. Guillemin, 45060 Orléans Cedex 2, France

⁵ Sorbonne Université, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 4 Place Jussieu, F-75005 Paris, France

* Corresponding author: levard@cerege.fr

Keywords: micropollutant; sustainable treatment; clay nanohybrid, antibiotics, water usage cycle

Abstract

The increasingly frequent detection of resistant organic micropollutants in waters calls for better treatment of these molecules that are recognized to be dangerous for human health and the environment. As an alternative to conventional adsorbent material such as activated carbon, silica-clay nanocomposites were synthesized for the removal of pharmaceuticals in contaminated water. Their efficiency with respect to carbamazepine, ciprofloxacin, danofloxacin, doxycycline and sulfamethoxazole was assessed in model water and real groundwater spiked with the five contaminants. Results showed that the efficacy of contaminant removal depends on the chemical properties of the micropollutants. Among the adsorbents tested, the nanocomposite made of 95% clay and 5% SiO₂ NPs was the most efficient and was easily recovered from solution after treatment compared to pure clay, for example. The composite is

31 thus a good candidate in terms of operating costs and environmental sustainability for the
32 removal of organic contaminants.

33 **Introduction**

34 Antibiotics are massively used in human and veterinary therapeutic applications. Their
35 production and use lead to increasing detection of antibiotics in the environment, especially in
36 effluents from wastewater treatment plants, but also in surface water and even groundwater.
37 The presence of these compounds in the water cycle can affect the quality of drinking water.
38 The resistance of some of these compounds to the conventional processes applied in drinking
39 water supply chains has been evidenced in several national surveys. For example, in the United
40 States, a federal survey identified 118 pharmaceutical micropollutants at the outlet of 25
41 drinking water production plants (FURLONG *et al.*, 2017).

42
43 In this context, it is indispensable to strengthen the monitoring and treatment of these
44 pharmaceutical pollutants at different stages of the water cycle. Two main treatment routes for
45 pharmaceutical compounds are during the production of drinking water or during tertiary
46 treatment of wastewater refining: the adsorption route and the chemical or biological oxidation
47 route that were also widely explored for the elimination of other organic contaminants (PAVITHRA
48 *et al.*, 2019).

49
50 Activated Carbon (AC) is the most commonly used adsorbent medium for water treatment in
51 industrial scale applications. The performance of AC in retaining a large number of pollutants is
52 undeniable but is nevertheless sometimes insufficient. A wide range of other media are currently
53 available for direct or polishing water treatment, with different characteristics (origin, activity,
54 porosity, size, density, etc.). The best media for water treatment can be selected based on
55 these properties in order to optimize the removal of the targeted pollutant and to be integrated in
56 the existing treatment plant. On one hand, powdered activated carbon (PAC) in suspension can
57 be directly added to the water to be treated, which has the advantage of being flexible as the
58 dose can be adapted to the concentration of the pollutant. However, the main disadvantage of
59 PAC is its high operating cost when used continuously, and the difficulty involved in separating
60 the medium from the sludge or waste by settling or filtration at the disposal step. Granular
61 activated carbon (GAC), on the other hand, uses a fixed-bed filter, usually located in one or two
62 steps of the water treatment plant, for clarification and polishing. Compared with PAC, GAC is

63 the most economical solution in larger systems or where organic contamination has to be
64 controlled continuously. GAC performance and treatment reliability for the removal of organics
65 are closely linked to the frequency of the carbon regeneration or replacement. In turn, the
66 frequency is highly dependent on the adsorption affinity of the pollutants and on competition
67 with the organic matter present in the water. This is particularly true with GAC used at the
68 clarification step (KNAPPE *et al.*, 2003).

69
70 Considering the economic and technical limitations involved in the use of activated carbon in
71 water treatment, developing an alternative process or material would be of great interest for
72 water treatment suppliers. To be viable and applicable, such new processes should fulfill
73 numerous conditions, including efficient pollutant elimination, easy integration into existing water
74 treatment plants as an additional refining step, easy removal from the treated water after use,
75 environmental sustainability, and low cost (PRASANAMEDHA AND KUMAR, 2020).

76 Clay-based materials appear to be good alternative candidates in this context as they have a
77 good adsorption capacity and ion exchange properties that can efficiently and selectively retain
78 many micropollutants (BESNAULT *et al.*, 2014; ZHU *et al.*, 2016). Clays can be modified, e.g. by
79 bridging or grafting nanoparticles, to increase the surface exchange by avoiding the stacking of
80 the clay layers, to adjust the interlayer distance to the size of the targeted micropollutants and in
81 turn, improve the performance and adsorption selectivity (LEE AND JANG, 1996; JOLIVET *et al.*,
82 2004; HORNER *et al.*, 2009; BANKOVIĆ *et al.*, 2013; BRINDLEY AND SEMPELS, 2018; GUÉGAN *et al.*,
83 2020).

84
85 In this work, we developed and tested clay-silica nanoparticle hybrid nanostructures that can be
86 an economic alternative to the activated carbon conventionally used in water treatment. The
87 silica to clay ratio was adjusted to optimize the adsorption capacity of the nanocomposites
88 (NCs). The efficiency of the resulting silica-clay NCs for the removal of ciprofloxacin was first
89 tested on a model water. In the second step, real water contaminated by a selection of
90 pharmaceutical micropollutants that are currently among the most recalcitrant to conventional
91 treatments used in industrialised countries was used to assess the performance of the different
92 NCs in realistic conditions.

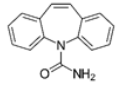
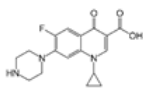
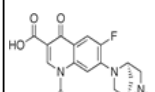
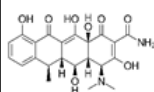
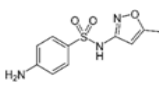
93 Materials and Methods

94 Targeted pharmaceutical molecules

95 The pharmaceutical substances studied here were chosen based on consumption, occurrence
 96 in the water cycle, recalcitrance to conventional treatments, and potential risk for the
 97 environment. Based on these criteria, four antibiotics, doxycycline, ciprofloxacin, danofloxacin
 98 and sulfamethoxazole, and an anticonvulsant, carbamazepine, were selected (Table 1).

99

100 Table 1. Main use and characteristics of the pharmaceuticals studied here

Pharmaceutical class	Antiepileptic	Antibiotics			
Compounds	Carbamazepine	Ciprofloxacin	Danofloxacin	Doxycycline	Sulfamethoxazole
Chemical formula	C ₁₅ H ₁₂ N ₂ O	C ₁₇ H ₁₈ FN ₂ O ₃	C ₁₉ H ₂₀ FN ₂ O ₃	C ₂₂ H ₂₄ N ₂ O ₅	C ₁₀ H ₁₁ N ₂ O ₃ S
Chemical structure					
Molecular mass (g/mol)	236.27	331.34	357.38	444.43	253.28
pKa	13.9	5.86 ; 8.24	6.07 ; 8.56	3.09 ; 8 ; 9.2	1.83 ; 5.57
Solubility (mg/L)	18	30 000	20 000	630	610
Log Kow	2.45	0.28	-0.3	-0.02	0.89
Type of use	Human use	Human use	Veterinary use	Human and veterinary use	Human and veterinary use

101

102

103 The treatability of chemical compounds in water by adsorption on an hydrophobic medium, such
 104 as activated carbon, is often classified according to their respective log Kow (measurement of
 105 the differential solubility of chemical compounds in two different media), higher log Kow giving
 106 higher expected adsorption. Carbamazepine and sulfamethoxazole are thus expected to
 107 undergo strong adsorption, while ciprofloxacin is expected to adsorb more weakly, and
 108 danofloxacin and doxycycline should be less adsorbed. Performance tests have been carried
 109 out at laboratory, pilot and industrial scale for the elimination of carbamazepine (SUDHAKARAN *et al.*,
 110 2013; AKPINAR AND YAZAYDIN, 2017; BIZI, 2019; HE *et al.*, 2020) and sulfamethoxazole
 111 (STACKELBERG *et al.*, 2007). Efficient removal of both compounds was obtained by adsorption
 112 on PAC (MARGOT *et al.*, 2013; BESNAULT *et al.*, 2014).

113 AC is also well known as a non-specific but efficient treatment solution for removal of a wide
 114 range of hydrophobic compounds in various matrixes (resources, drinking water, wastewater,
 115 industrial effluents, etc.). However, the cost of AC is high and finding less costly alternative media
 116 is a real challenge for water treatment. That is why several works on different alternative

117 adsorbent materials applied for micro-pollutants treatment have been undertaken. The materials
118 include clay-based media (YU *et al.*, 2008; ZHANG *et al.*, 2010) which have shown some
119 adsorption capacity. The elimination of ciprofloxacin has been studied at laboratory scale on
120 various media including carbon, clay, and zeolites (WANG *et al.*, 2015; LI *et al.*, 2017;
121 ROSTAMIAN AND BEHNEJAD, 2017; BIZI AND EL BACHRA, 2020). However, these authors did not
122 study the application or the treatment efficiency of clay-based nanocomposites in realistic
123 conditions for the removal of several compounds with different solubility, size, hydrophobicity
124 and charge, such as the ones targeted here. Finally, few laboratory-scale studies on
125 danofloxacin and doxycycline treatments have focused on the difficulty of treating doxycycline
126 by adsorption (ALI AND AHMED, 2017; LIU *et al.*, 2017).

127 Nanocomposite synthesis

128
129 The clay material used in this work was collected from Nador under the trade name Monador
130 (North East Morocco, North Africa). It consists of a relatively pure Na,Ca montmorillonite. The
131 cationic exchange capacity of the raw clay sieved to 20 μm was determined at 141 meq/100g.
132 For this study, the finest fraction of the clay ($< 2 \mu\text{m}$) was recovered for the synthesis of the
133 silica-clay NCs as follows: 20 g of the sieved clay were dispersed in 500 mL of ultrapure water
134 by magnetic stirring at 500 rpm for 24 h. After 30 minutes, ultrasonic treatment was performed
135 for 10 minutes. The clay suspension was then poured into a 25 cm glass column and left to
136 settle for 20 h. According to Stokes law and considering a clay density of $2.6 \text{ g}\cdot\text{cm}^{-3}$, 20 h
137 correspond to a sedimentation cutoff close to 2 μm at 25 cm in height. The supernatant
138 containing the size fraction below 2 μm was recovered and freeze dried, for further preparation.
139 The silica nanoparticles used in this work were obtained from “Clariant Corporation” under the
140 trade name Klebosol® 30R50. They were characterised by a primary particle size of 80 nm (Bizi,
141 2012), also confirmed in hydrodynamic size in pure water measured by dynamic light scattering
142 ($82.4 \pm 0.6 \text{ nm}$).

143 Silica-clay nanocomposites (NCs) were synthesized as follows. Clay was dispersed in Milli-Q
144 water at a concentration of 20 g/L. The suspension was stirred for 24 h at 500 rpm to favor layer
145 exfoliation. Then, a volume of SiO_2 nanoparticles was added to the suspension to reach 5 or 50
146 wt% of the clay substrate. At this neutral pH, both clay and silica are negatively charged and are
147 stable in suspension. The mixture was homogenized by magnetic stirring for one minute, and
148 then immediately frozen in liquid nitrogen to maintain the homogenous distribution of silica and

149 clay components. Water was then removed by freeze drying, and the recovered solid material
150 was heated at 500°C for 4 hours to consolidate the architecture of the aggregates. In order to
151 obtain material reference, separate pure silica and clay materials were also heated at 500°C for
152 comparison with NCs referred as SiO₂-NP-500°C and Clay-500°C.

153 Characterization of the materials

154
155 Scanning electron microscopy (SEM) analysis was carried out using a Zeiss Gemini 500 high
156 resolution field emission scanning electron microscope equipped with an in-lens secondary
157 electron detector. Images of uncoated samples were acquired at low voltages for surface
158 sensitivity and also to avoid beam damage. X-ray diffraction (XRD) analysis was performed
159 using a Panalytical X'Pert Pro diffractometer running at 40kV and 40mA equipped with Co K α
160 radiation ($\lambda = 1.79 \text{ \AA}$). Samples were deposited on low background silicon plates and scanned
161 in a 2 θ range of 4-75° with a step size of 0.033° and a time step of 5.1s.

162 Removal efficiency of ciprofloxacin in a model effluent

163 Elimination of ciprofloxacin from a model effluent was studied as a preliminary approach to
164 optimize the synthesis of the sorbent material. Evian water (pH= 7.5-7.8) was used to mimic the
165 ionic composition of a typical surface water. Ciprofloxacin in the aqueous medium was
166 quantified by measuring the specific absorbance peak at 272 nm wavelength. A Jasco V-650
167 UV-visible spectrophotometer (Jasco, Japan) was used for this purpose, with quartz cells of 1
168 cm optical pathway. A calibration curve was first measured showing good linearity from 0.5 to
169 20 mg/L ($R^2 = 0.9999$). Every absorbance measurement was processed in triplicate.
170 Ciprofloxacin was first spiked into water at 5 mg/L. The sorbent material was then added at a
171 concentration of 50 mg/L and the reactor was kept under agitation for three hours by magnetic
172 stirring at 650 rpm. Aliquots of the mixture were sampled at different times and filtered at 0.45
173 μm to remove the sorbent material and the retained ciprofloxacin. The supernatant was then
174 analysed by UV absorbance to measure the concentration of ciprofloxacin remaining free in
175 solution. X-ray Photoelectron Spectroscopy (XPS) was performed using a Kratos – Axis NOVA
176 XPS equipped with a monochromatic Al K α source to assess adsorption mechanism (150 Watts).

177 Nanocomposite dispersibility and potential for recovery after treatment

178 After use as a sorbent material during a tertiary or polishing treatment step, the NCs should be
179 easily recovered from the liquid medium in an additional quaternary step before the treated
180 water is released. This can be achieved by the rapid sedimentation of the material in the liquid
181 batch when agitation is stopped, which depends on the size and density of the dispersed units.
182 Dispersion or sedimentation of the synthesized materials in aqueous medium was measured
183 using laser diffraction and turbidity profiles. Firstly, 200 mg/L of NC was introduced in Evian
184 water, that mimicked the ionic composition of a typical surface water, and maintained under
185 constant agitation by magnetic stirring for four hours. A Malvern Mastersizer 3000 (Malvern
186 Instruments, Worcester, UK) connected to the agitated system via a peristaltic pump in
187 recirculation mode was used to measure the size distribution of the different NCs over time. For
188 comparison with reference clay materials, the same procedure was used for pure
189 montmorillonite clay before and after calcination at 500°C. Secondly, at $t = 4\text{h}$, a 20 mL aliquot
190 of the medium was sampled under agitation and poured into the sedimentation tube. A
191 Turbiscan apparatus (Formulaction, Toulouse, France) was used to measure the turbidity profile
192 along the tube height according to time. Measurements were recorded every 25 sec during 30
193 minutes. The suspension clarification was analyzed via the intensity of the transmitted light
194 increasing with time, while the formation of sediments was measured via the backscattered light
195 intensity in the bottom of the tube (lower 1 mm). A 2% relative increase was reasonably used to
196 distinguish the top of the solid deposit from the initial background backscattered by the liquid
197 suspension.

198 Removal efficiency in real groundwater

199 After optimization of the synthesis and tests of NCs efficiency in model water, clay-silica NCs
200 were tested in real groundwater spiked with the five selected micropollutants at realistic
201 concentrations. Activated carbon, currently used in conventional water treatment, was also
202 studied for the purpose of comparison.

203 Groundwater from the Paris region (France) was used for this experiment ($\text{pH} = 7.5$, dissolved
204 organic carbon: 1.5 mg/L, UV absorbance at 254 nm = 4 m^{-1} , expressed as optical density). The
205 main chemical elements constituting the geochemical composition were analyzed. Results are
206 given in mg/L: Al (< 0.05), Ca (72.4), K (3.3), Mg (8.59), Na (15.3), P (< 0.05) and Zn (0.04). In
207 order to control the presence of residual pollutants in this groundwater before exposition, the
208 concentration of the five studied micropollutants was determined. Only carbamazepine and

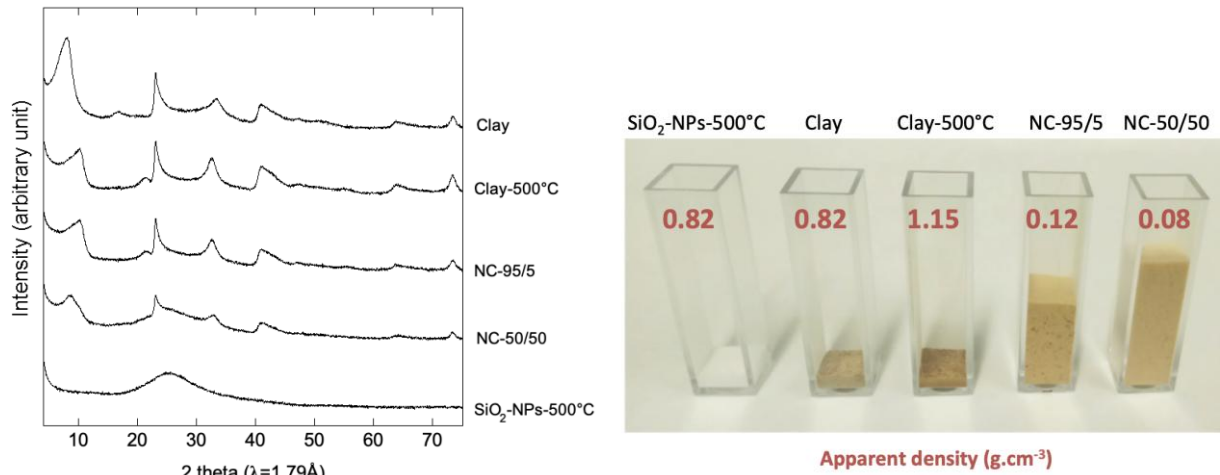
209 sulfamethoxazole were detected in the groundwater, at respectively 10 and 5 ng/L, giving the
210 chemical background.

211
212 The five micropollutants ciprofloxacin, danofloxacin, doxycycline, carbamazepine and
213 sulfamethoxazole were spiked into water at individual concentrations of 2 µg/L. The sorbent
214 material was then added to the medium at a concentration of 50 mg/L, as processed in
215 preliminary tests on the model effluent, and the mixture was agitated continuously for 48 h.
216 Filtration at 0.45 µm on a glass fiber filter was then processed to remove the sorbent material
217 and other particulate matter from the liquid medium.

218 An analytical method was developed to quantify the targeted micropollutants in this matrix and
219 also in other complex waters (surface water, wastewater, etc.). Solid phase extraction on HLB
220 cartridge (Waters) at pH 3 was performed. Then, after washing and drying, an elution was
221 realised with 5 mL methanol. Analyses were liquid chromatography coupled with mass
222 spectrometry. A triple quadrupole mass spectrometer, TSQ Quantum (Thermo Fisher Scientific)
223 equipped with a HSS T3 column (Waters®) was used. The mobile phase followed a
224 water/methanol gradient + 0.1% formic acid, circulating at a solvent flow rate of 200 µL/min, with
225 an injected volume of 10 µL and a temperature of 30°C. Detection was achieved by two MS/MS
226 transitions in positive ionization mode with electrospray source. Quantification was performed by
227 internal calibration using compounds labelled with D or ¹³C. The limits of detection obtained
228 ranged between 1 and 5 ng/L.

229 **Results**

230 1. Characterization of materials



231
232 Figure 1. X-ray diffraction patterns (left) and apparent density measured in a volume of 230 mg
233 of material (right) of the initial clay, nanocomposites and references heated at 500°C

234
235 Since silica is amorphous, the X-ray diffraction pattern of the clay-based materials is consistent
236 with a montmorillonite (Figure 1, left). The first peak corresponds to the (001) reflection (basal
237 spacing) and is characteristic of layer stacking. For raw clay, the interlayer distance is 12.5Å,
238 typical of hydrated Na-montmorillonite. When heated to 500°C, the lamellar structure is
239 preserved and the (001) reflection is shifted to 9.6Å, indicating interlayer dehydration. Regarding
240 NCs, although NC-95/5 was very similar to Clay-500°C, the first NC-50/50 peak became less
241 intense and broader with a slight shift at lower angles, suggesting increased disorder in layer
242 stacking and increased interlayer distance. However, no change in the order inside the layer
243 was observed. The increase in structural disorder is in good agreement with the measured
244 apparent density (Figure 2, right) that is more than one-order lower for NC-50/50 than for Clay-
245 500°C (decrease in the apparent density by a factor of 14). In addition, -although not observed by
246 X-ray diffraction, 5% of SiO₂ Nps in NC-95/5 is enough to strongly affect apparent density by
247 one order of magnitude compared to Clay-500°C.

248

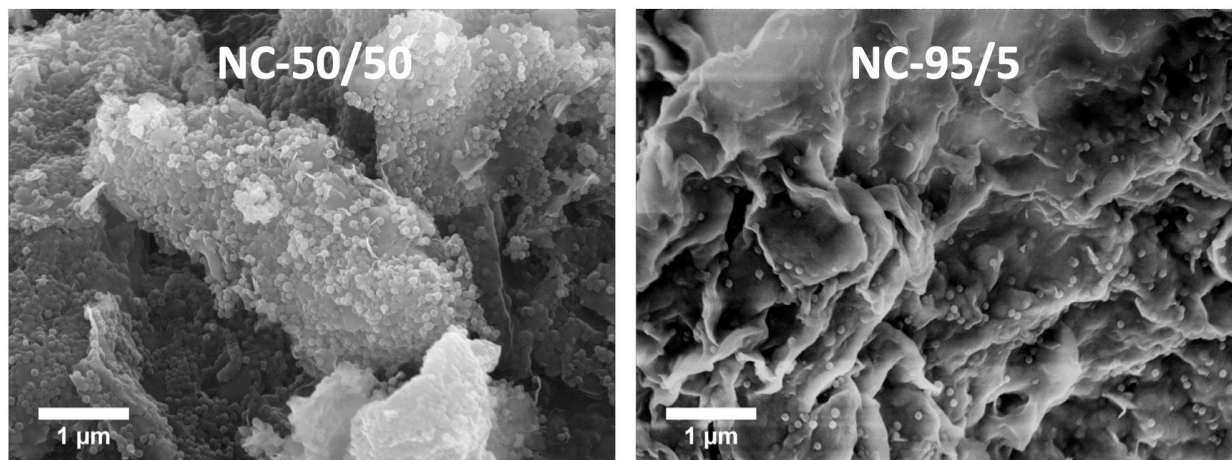


Figure 2. SEM images of NC-50/50 (left) and NC-95/5 (right)

249
250
251
252 SEM analysis was performed on NC-95/5 and NC-50/50 (Figure 2). Although SEM cannot
253 provide evidence for the intercalation of SiO_2 -NPs in the interlayers, it can give an idea of the
254 surface coverage and dispersion of SiO_2 -NPs at the surface of the clay sheets. For the lowest
255 loading of SiO_2 -NPs (NC-95/5)(Figure 2, right), NPs are well-dispersed in the clayey matrix and
256 are isolated from each other while NC-50/50 (Figure 2, left) exhibits a relatively high surface
257 coverage of the SiO_2 -NPs at the clay surface. The randomly dispersed distribution of the SiO_2 -
258 NPs observed on the clay substrate for NC-95/5 confirms that the method of preparation used
259 here satisfactorily delivered an apparently homogenous hybrid material. Moreover, irregularities,
260 microcavities and the non-compact and very porous nature of the observed structures in
261 addition to the low apparent density (probable high macroporosity) will favor the rapid diffusion
262 of water and micropollutants. Beyond these structural considerations, the reactivity of the NCs
263 was assessed in both model effluents and in realistic conditions.

264

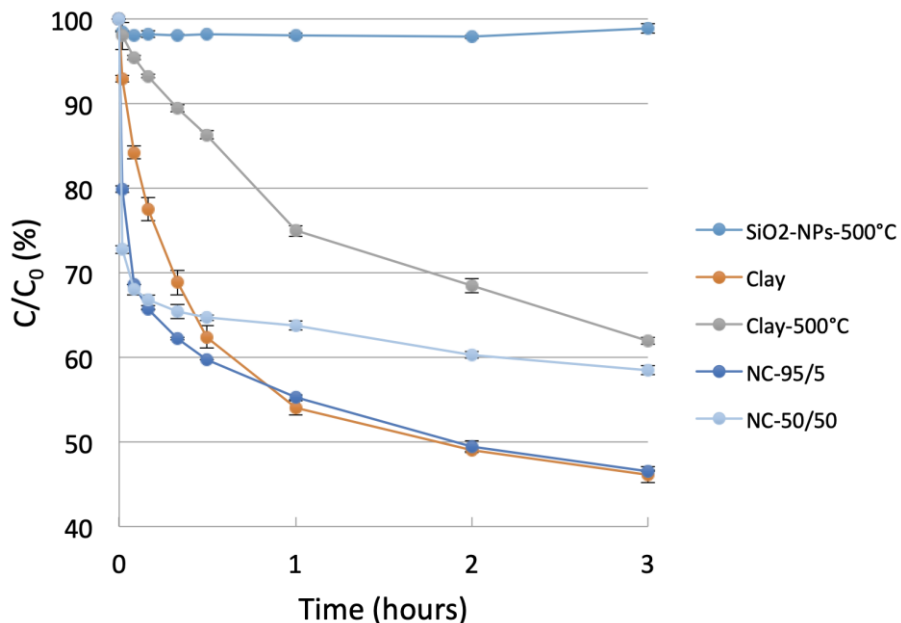
265 2. Removal efficiency of ciprofloxacin in model effluents

266

267 Ciprofloxacin was used for this first proof of concept thanks to the ease of UV-visible
268 spectroscopy.

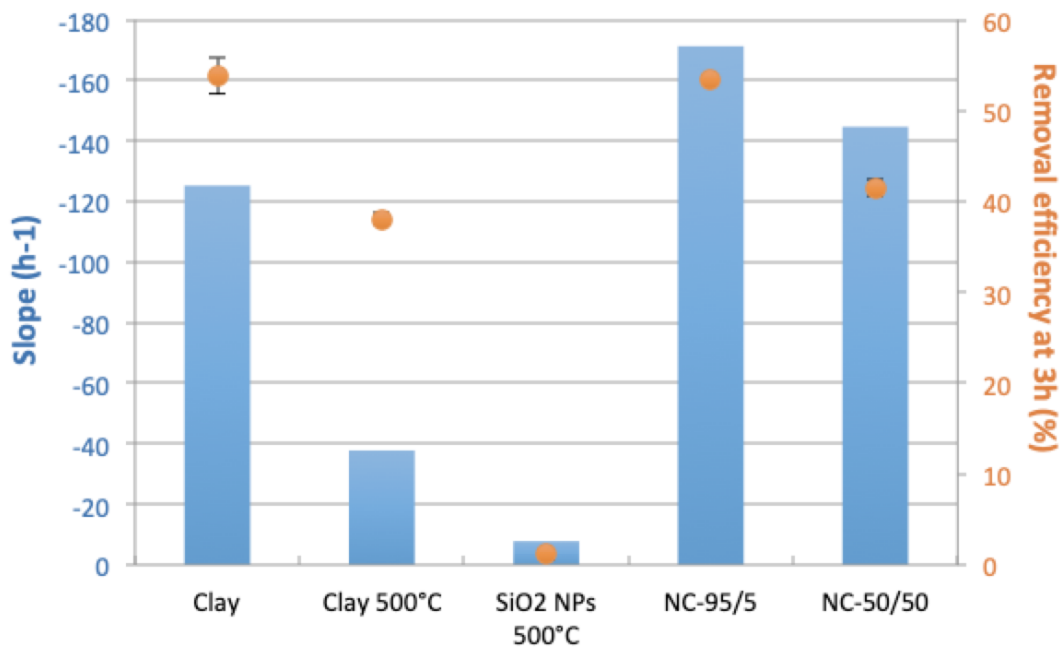
269

270



271
 272 Figure 3. Removal kinetics of ciprofloxacin from a model of surface water by adsorption to the
 273 sorbent materials: clay, SiO₂-NPs-500°C and NCs
 274

275 The time-resolved removal of ciprofloxacin from the model water (Figure 3) provided insights
 276 into the adsorption kinetics on clay (raw or heated at 500°C), SiO₂-NPs-500°C and NCs. While
 277 no removal of ciprofloxacin was obtained with SiO₂NP-500°C, significant but contrasted
 278 adsorption behaviors were observed in clay and NC sorbents. The behaviors were
 279 characterized by a first removal step lasting around 10 minutes, followed by a slower reaction
 280 step that may correspond to saturation of the material. The slope of the curves measured over
 281 the 10 first minutes (first 4 points) was used to obtain insight into the initial kinetic of the reaction
 282 (Figure 4, blue bars). Three behaviors can be distinguished as (i) a rapid initial adsorption rate
 283 with NC-95/5 and NC-50/50, (ii) a moderate initial adsorption rate obtained with clay and (iii) a
 284 relatively slow adsorption rate with clay-500°C. Thus, the presence of SiO₂-NPs in NC-95/5 and
 285 NC-50/50 significantly increased the adsorption kinetics of ciprofloxacin.



286
 287 Figure 4. Removal kinetics (Figure 3) calculated on the first 4 experimental points (after 10
 288 minutes of reaction) are represented on the primary y-axis (blue bars). Removal efficiencies
 289 after 3 hours are represented on the secondary y-axis (orange dots).

290
 291 In addition to the initial kinetics, the removal efficiency measured after 3 hours provides insight
 292 into sorbent capacity (Figure 4, orange dots), which ranged from 1% for SiO₂-NPs-500°C to
 293 53.5% for clay and NC-95/5. The best results were obtained for raw clay and NC-95/5 with a
 294 removal efficiency > 50%. Both products were well-hydrated after 3 hours and probably had
 295 similar surface areas and therefore similar adsorption capacity. This was not the case of NC-
 296 50/50, which showed reasonable but lower removal efficiency than for NC-95/5 and clay that
 297 can be attributed to the high fraction of SiO₂-NPs in the nanocomposite that has no affinity for
 298 ciprofloxacin, as shown in Figure 3.

299 The reason why NCs are more efficient sorbent material than clay-500°C is certainly linked to
 300 the disordered and porous structure obtained in the NCs compared to clay-500°C, which is
 301 more favorable for fast diffusion of water and pollutants inside the material. In absence of NP
 302 inside the clay, the heating step at 500°C leads to sheet stacking that results in a dense
 303 structure that does not have the desired properties.

304 Although not responsive to ciprofloxacin, SiO₂-NPs play a significant positive role in the kinetics
 305 of ciprofloxacin adsorption. Based on kinetic and removal efficiencies, NC-95/5 appears to be
 306 the most appropriate candidate for efficient removal of ciprofloxacin. Further analysis of the NC-

307 95/5 sample was performed to check its crystallinity after adsorption of ciprofloxacin using XRD
308 and to assess adsorption mechanism using XPS.

309
310 The mineralogy of NC-95/5 is preserved after adsorption as shown in Figure S1. The (001)
311 reflection distance is shifted from 9.6Å (before adsorption) to 14.4Å (after adsorption). This
312 basal reflection observed after adsorption of ciprofloxacin is typical of hydrated Ca-
313 montmorillonite which is consistent with the fact that Evian water contains 80 mg/L of Ca²⁺. In
314 addition to NC-95/5, calcium carbonate phases were detected which is, once again, consistent
315 with the ionic composition of Evian water that contains bicarbonates (360 mg/L) which has
316 favored the precipitation of calcite and aragonite (Figure S1).

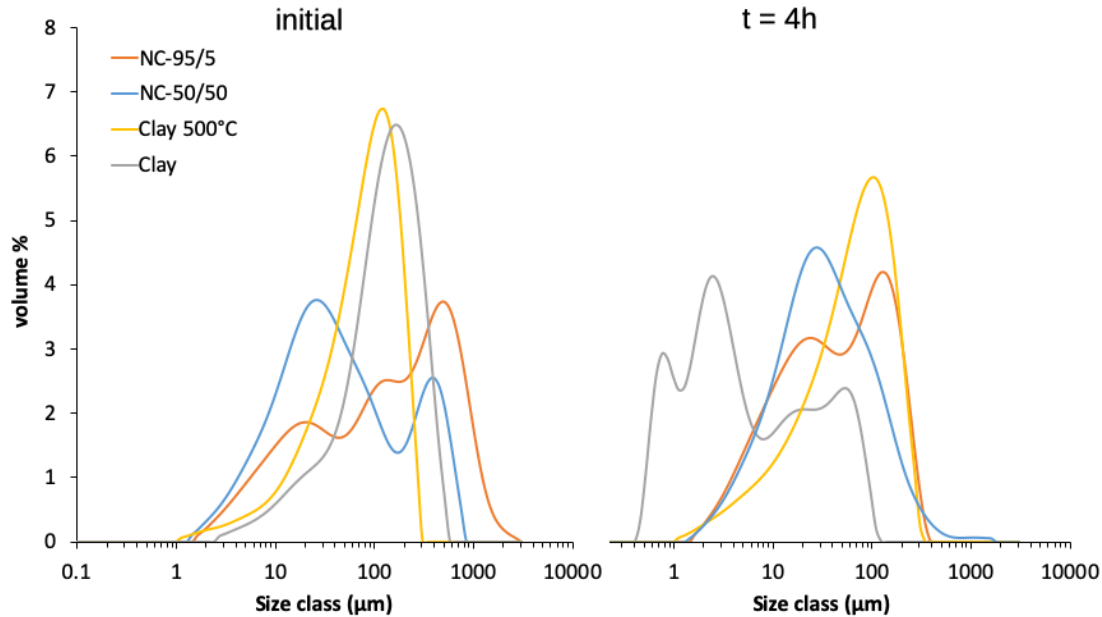
317
318 XPS analysis was performed on NC-95/5 before and after sorption of ciprofloxacin to
319 investigate sorption mechanism. However, although XPS confirms the presence of ciprofloxacin
320 on the NC-95/5 substrate (specific signature of Fluor), it does not allow to identify the sorption
321 mechanisms mainly because of the presence of a significant fraction of adventitious carbon
322 classically observed in XPS measurements (see Figures S2, S3, S4 and S5 in SI).

323
324 In addition to surface reactivity, the recoverability of the particles after treatment is an important
325 aspect to be taken into consideration and was tested on the different sorbents NC-95/5,
326 NC50/50, clay and clay-500.

327

328 3. Nanocomposite and clay recovery from liquid media

329



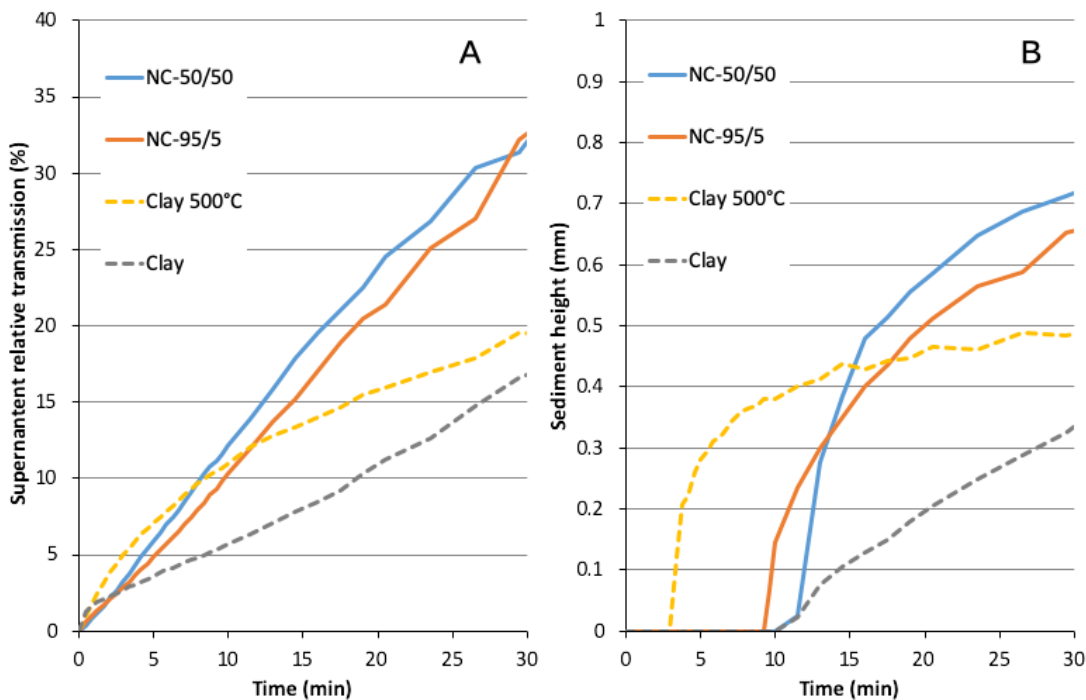
330
 331 Figure 5: Size distribution of the clay and NCs in synthetic surface water, at t_0 (left, just after
 332 dispersion) and after 4h of agitation (right).

333
 334 Laser diffraction was used to measure the dispersion of the hybrid material in water compared
 335 to raw clay and to clay-500°C. It proved that heating at 500°C causes the formation of
 336 irreversible aggregates that can withstand the dispersion step in aqueous medium. Indeed, after
 337 4 h of agitation in water, neither clay-500°C nor the NCs displayed a particle size below 1 μm ,
 338 which is roughly the upper limit of the colloidal size range. These three materials remained in an
 339 aggregated form with sizes ranging from 5 to 200 μm , while after 4 h of agitation, the clay was
 340 rapidly dispersed in sub-micrometer units. Colloidal dispersion of the montmorillonite clay
 341 usually implies continuous swelling, due to hydration of the inter-lamellar cations toward multiple
 342 layers of water molecules. Here the calcination step at 500°C led to dehydration of those cations
 343 and shrinkage of the interlamellar space, which likely reduced access to the water molecules
 344 from the outside when the material was redispersed in water. This resulted in the irreversible
 345 aggregation of the clay particles with no noticeable difference between the NCs and the clay-
 346 500°C.

347 The larger aggregate size obtained here certainly favors more rapid sedimentation of the NCs,
 348 which should facilitate recovery from the water treatment plant after use. This was confirmed by
 349 the sedimentation trends shown in figure 6. After 4 h of agitation of the materials in synthetic
 350 surface water, the sedimentation rate was measured in terms of supernatant clarification and of
 351 formation of a sediment layer. The NCs clearly showed the highest sedimentation rates,

352 reaching 30-35% of average supernatant clarification in 30 minutes (Figure 6A). In comparison,
353 the pure clay, which still contained sub-micrometer dispersed units, sedimented at the lowest
354 rate, reaching only 15-20% in the same time period. Clay-500°C displayed different
355 sedimentation behavior characterized by a higher rate in the first 5 minutes, followed by a
356 slower rate. This suggests coexistence of high-density aggregates that settled out rapidly, and
357 of lower density aggregates that remained in suspension longer. These respective behaviors
358 are corroborated by the formation of the sediment layer shown in Figure 6B. The change in
359 sediment height over time points to higher kinetics of the nanocomposites than of pure clay,
360 reaching approximately 0.7 mm for NCs compared with 0.35 mm in 30 min for pure clay. Again,
361 clay-500°C underwent more rapid sediment formation in the first 5 minutes, after which the
362 process slowed down. It is important to note that the change in sediment height over time
363 results not only from the sedimentation rate but also from apparent sediment density. As the
364 NCs are characterized by lower apparent density than pure clay, the sediments formed are
365 expected to result in a thicker layer at a given mass of material. Such a contribution of the
366 material density cannot be distinguished from that of the sedimentation rate in Figure 6B.
367 Of note, in the water treatment, the sedimentation efficiency of particulate matter is usually
368 adjusted by the adding chemicals such as coagulants and/or flocculants. So any increase in
369 sedimentation caused by the sorbent material, as obtained in our case, could also lead to lower
370 chemical dosage and new sludge characteristics and behavior (more compact, easier to treat
371 and to dispose of).

372



373
 374 Figure 6: Kinetics of supernatant clarification (A) and sediment formation (B) measured
 375 respectively by light transmission and backscattering in the upper 39 mm and bottom 1 mm of
 376 the sedimentation tube for clay-based materials

377 4. Removal efficiency in groundwater

378 Table 2. Adsorption performances of the 5 micropollutants on activated carbon, NCs and the
 379 reference materials

Sorbent (50 mg/L)	Cipro.	Dano	Sulfa	Doxy	Carba
Activated carbon	100%	100%	100%	100%	100%
MMT/SiO ₂ (50/50)	99%	99%	0%	34%	3%
MMT/SiO ₂ (95/5)	100%	100%	0%	60%	0%
clay-500	94%	95%	0%	41%	0%

SiO₂ NP-500	0%	0%	0%	11%	0%
-------------------------------	----	----	----	-----	----

380

381

382 SiO₂-NPs-500°C showed no reaction to the five micropollutants tested in this study. NC-95/5
 383 and NC-50/50 removal efficiencies were ranked in the following decreasing order Ciprofloxacin
 384 = Danofloxacin > Doxycycline > Sulfamethoxazole = Carbamazepine. Further mechanistic
 385 studies are now needed to explain this trend. However, based on the chemical composition of
 386 the different compounds, one can hypothesize that some properties may control the affinity
 387 between NCs and organics. The two antibiotics that are efficiently removed by NCs are the only
 388 ones that have a carboxylic functional group (Table 1), which is known to be a good complexing
 389 group, with pKa values of 5.86/8.24 and 6.07/8.56 for Ciprofloxacin and Danofloxacin,
 390 respectively. At neutral pH, the carboxylic groups are deprotonated and most probably react
 391 with the positive Al groups of the clay (LABILLE *et al.*, 2005). Na-Montmorillonite has also been
 392 shown to have good affinity for phenolic compounds (DJEJBAR *et al.*, 2012), which may explain
 393 the relatively good removal efficiency of doxycycline. Finally, the last two contaminants that
 394 were not removed at all have neither carboxylic nor phenolic groups. They both have amino
 395 groups that were neutrally charged at the pH of our experiment. Adsorption of aniline (the
 396 phenyl group attached to an amino group) on Montmorillonite has been studied in the past and
 397 showed maximum adsorption when the pH of the solution was approximately equal to the pKa
 398 of the anilinium ion deprotonation reaction (pH 4.5-5) (ESSINGTON, 1994). Minimum adsorption
 399 was observed at pH above 7, which could partially explain the low affinity of clay for
 400 sulfamethoxazole and carbamazepine.

401 **Conclusion**

402

403 Silica-clay nanocomposites were designed specifically for the removal of antibiotics in potable
 404 water treatment plants as an alternative to powder activated carbon. Among the five
 405 pharmaceuticals tested, the silica-clay nanocomposites enabled efficient removal of three
 406 molecules, ciprofloxacin, danofloxacin and doxycyclin, making them promising sorbent
 407 materials. In the hybrid structure of the nanocomposites, although non-reactive, the SiO₂-NPs
 408 are homogenously distributed and strongly affect clay stacking by creating disorder which
 409 appears to favor the diffusion of water and micropollutants in the material. NC-95/5 showed the

410 highest reactivity among the synthesized products. In addition, the design of the
411 nanocomposites includes a calcination step, which resulted in the formation of non-reversible
412 aggregates > 1 μm . After being used use as a sorbent in suspension, the material can thus
413 easily be recovered from the water using normal filtration or sedimentation techniques. Finally,
414 the use of natural clay is beneficial from an environmental point of view and the low loading of
415 SiO_2 -NPs is advantageous in terms of the cost of synthesis.

416 As a possible next step in this work, NCs could be tested with other specific pollutants that are
417 not easily treated by activated carbon due to their unique properties (hydrophilic, polar, mobile,
418 small molecules), such as persistent and mobile organic compounds (PMOCs) (ARP *et al.*,
419 2017). PMOCs, such as pesticide metabolites, per- and poly fluoro alkyl substances etc., are
420 sufficiently mobile in an aquatic environment to enter drinking water resources, and sufficiently
421 persistent to survive current water treatment processes. Treatment of such compounds is a real
422 challenge for environmental and sanitary risk management. Another possible perspective is to
423 increase the efficiency of NCs by replacing the poorly reactive SiO_2 -NPs by Al- or Fe-based NPs
424 that have a stronger affinity for these micropollutants. Finally, as an alternative to micropollutant
425 removal through adsorption, recent publications pointed to the interest of oxydoreductases
426 (such as peroxidases, polyphenol oxidases), hydrolases (such as proteases, esterases, lipases
427 and cellulases) and lyases for wastewater treatment and especially for the degradation of
428 phenol, aromatic compounds and hormones (DE CAZES *et al.*, 2014a). The interest of using
429 laccases and esterases for the degradation of antibiotics has recently been demonstrated and
430 more generally, the biodegradation treatment by enzymes fixed on an adsorbent support like
431 clay or membrane has been proposed as promising treatment solution (MAGNAN *et al.*, 2004; DE
432 CAZES *et al.*, 2014a; DE CAZES *et al.*, 2014b; DE CAZES *et al.*, 2015). In this perspective, NCs
433 could be used as a support for enzyme grafting.

434 **Ethics approval and consent to participate**

435 Not applicable

436 **Consent for publication**

437 Not applicable

438 **Availability of data and materials**

439 The datasets used and/or analysed during the current study are available from the
440 corresponding author on reasonable request.

441 **Competing interests**

442 The authors declare that they have no competing interests

443 **Funding**

444 This study was done within the framework of the POLPHARMA Project ANR-15-CE04-0007.
445 The authors gratefully acknowledge the French National Research Agency for financial support.

446 **Authors' contributions**

447 CL, IB, AG and JL have designed the experiment, CL, KH-A, DB, AC, IB, AG and JL have
448 performed the experiments, All authors have actively participated to the interpretation of the
449 data, writing of the manuscript and approved the final manuscript.

450 **References**

451

452 Akpinar, I., Yazaydin, A.O. (2017) Rapid and Efficient Removal of Carbamazepine from Water
453 by UiO-67. *Industrial & Engineering Chemistry Research* 56, 15122-15130.

454 Ali, M., Ahmed, M. (2017) Adsorption behavior of doxycycline antibiotic on NaY zeolite from
455 wheat (*Triticum aestivum*) straws ash. *Journal of the Taiwan Institute of Chemical*
456 *Engineers* 81, 218-224.

457 Arp, H.P.H., Brown, T.N., Berger, U., Hale, S.E. (2017) Ranking REACH registered neutral,
458 ionizable and ionic organic chemicals based on their aquatic persistency and mobility.
459 *Environmental Science: Processes & Impacts* 19, 939-955.

460 Banković, P., Milutinović-Nikolić, A., Mojović, Z., Jović-Jovičić, N., Perović, M., Spasojević, V.,
461 Jovanović, D. (2013) Synthesis and characterization of bentonites rich in beidellite with
462 incorporated Al or Al-Fe oxide pillars. *Microporous and Mesoporous Materials* 165, 247-
463 256.

464 Besnault, S., Ruel, S., Baig, S., Esperanza, M., Budzinski, H., Miege, C., Boucher, C., Menach,
465 K., Coquery, M. (2014) Technical, economic and environmental evaluation of advanced
466 tertiary treatments for micropollutants removal (oxidation and adsorption). *ECOSTP*
467 (Verone, Italy),

468 Bizi, M. (2012) Stability and flocculation of nanosilica by conventional polymer. *Natural Science*
469 04, 372-385.

470 Bizi, M. (2019) Activated Carbon and the Principal Mineral Constituents of a Natural Soil in the
471 Presence of Carbamazepine. *Water* 11, 2290-2306.

472 Bizi, M., El Bachra, F.E. (2020) Evaluation of the ciprofloxacin adsorption capacity of common
473 industrial minerals and application to tap water treatment. *Powder Technology* 362, 323-
474 333.

475 Brindley, G.W., Sempels, R.E. (2018) Preparation and properties of some hydroxy-aluminium
476 beidellites. *Clay Minerals* 12, 229-237.

477 De Cazes, M., Abejón, R., Belleville, M.-P., Sanchez Marcano, J. (2014a) Membrane
478 Bioprocesses for Pharmaceutical Micropollutant Removal from Waters. *Membranes* 4,
479 692-729.

480 De Cazes, M., Belleville, M.P., Mougel, M., Kellner, H., Sanchez-Marcano, J. (2015)
481 Characterization of laccase-grafted ceramic membranes for pharmaceuticals
482 degradation. *Journal of Membrane Science* 476, 384-393.

483 De Cazes, M., Belleville, M.P., Petit, E., Llorca, M., Rodríguez-Mozaz, S., de Gunzburg, J.,
484 Barceló, D., Sanchez-Marcano, J. (2014b) Design and optimization of an enzymatic
485 membrane reactor for tetracycline degradation. *Catalysis Today* 236, 146-152.

486 Djebbar, M., Djafri, F., Boucekara, M., Djafri, A. (2012) Adsorption of phenol on natural clay.
487 *Applied Water Science* 2, 77-86.

488 Essington, M.E. (1994) Adsorption of aniline and toluidines on montmorillonite. *Soil Science*
489 158, 181-188.

490 Furlong, E.T., Batt, A.L., Glassmeyer, S.T., Noriega, M.C., Kolpin, D.W., Mash, H., Schenck,
491 K.M. (2017) Nationwide reconnaissance of contaminants of emerging concern in source
492 and treated drinking waters of the United States: Pharmaceuticals. *Science of The Total*
493 *Environment* 579, 1629-1642.

494 Guégan, R., De Oliveira, T., Le Gleuher, J., Sugahara, Y. (2020) Tuning down the
495 environmental interests of organoclays for emerging pollutants: Pharmaceuticals in
496 presence of electrolytes. *Chemosphere* 239, 124730.

497 He, Q., Liang, J.-J., Chen, L.-X., Chen, S.-L., Zheng, H.-L., Liu, H.-X., Zhang, H.-J. (2020)
498 Removal of the environmental pollutant carbamazepine using molecular imprinted
499 adsorbents: Molecular simulation, adsorption properties, and mechanisms. *Water*
500 *Research* 168, 115164.

501 Horner, O., Neveu, S., Montredon, S., Siaugue, J.-M., Cabuil, V. (2009) Hydrothermal synthesis
502 of large maghemite nanoparticles: Influence of the pH on the particle size. *Journal of*
503 *Nanoparticle Research* 11, 1247-1250.

504 Jolivet, J.-P., Chanéac, C., Tronc, E. (2004) Iron Oxide Chemistry. From Molecular Clusters to
505 Extended Solid Networks. *Chemical communications (Cambridge, England)* 35, 481-7.

506 Knappe, D.R.U., Li, L., Quinlivan, P.A., Wagner, T.B. (2003) Effects of activated carbon
507 characteristics on organic contaminant removal. Awwa Research Foundation, Denver,
508 CO :.

509 Labille, J., Thomas, F., Milas, M., Vanhaverbeke, C. (2005) Flocculation of colloidal clay by
510 bacterial polysaccharides: Effect of macromolecule charge and structure. *Journal of*
511 *colloid and interface science* 284, 149-56.

512 Lee, D.C., Jang, L.W. (1996) Preparation and characterization of PMMA–Clay hybrid composite
513 by emulsion polymerization. *Journal of Applied Polymer Science* 61, 1117-1122.

514 Li, S., Zhang, X., Huang, Y. (2017) Zeolitic imidazolate framework-8 derived nanoporous carbon
515 as an effective and recyclable adsorbent for removal of ciprofloxacin antibiotics from
516 water. *Journal of Hazardous Materials* 321, 711-719.

517 Liu, S., Xu, W., Liu, Y.-g., Tan, X., Zeng, G.-m., Li, X., Liang, J., Zhou, Z., Yan, Z.-l., Cai, X.-x.
518 (2017) Facile synthesis of Cu(II) impregnated biochar with enhanced adsorption activity
519 for the removal of doxycycline hydrochloride from water. *Science of The Total*
520 *Environment* 592.

521 Magnan, E., Catarino, I., Paolucci-Jeanjean, D., Preziosi-Belloy, L., Belleville, M.P. (2004)
522 Immobilization of lipase on a ceramic membrane: activity and stability. *Journal of*
523 *Membrane Science* 241, 161-166.

524 Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L., Abegglen, C., Thonney,
525 D., Chèvre, N., Schärer, M., Barry, D. (2013) Treatment of micropollutants in municipal
526 wastewater: Ozone or powdered activated carbon? *The Science of the total environment*
527 461-462C, 480-498.

528 Pavithra, K.G., Kumar, P.S., Jaikumar, V., Rajan, P.S. (2019) Removal of colorants from
529 wastewater: A review on sources and treatment strategies. *Journal of Industrial and*
530 *Engineering Chemistry* 75, 1-19.

531 Prasannamedha, G., Kumar, P.S. (2020) A review on contamination and removal of
532 sulfamethoxazole from aqueous solution using cleaner techniques: Present and future
533 perspective. *Journal of Cleaner Production* 250, 119553.

534 Rostamian, R., Behnejad, H. (2017) A unified platform for experimental and quantum
535 mechanical study of antibiotic removal from water. *Journal of Water Process*
536 *Engineering* 17, 207-215.

537 Stackelberg, P., Gibs, J., Furlong, E., Meyer, M., Zaugg, S., Lippincott, R. (2007) Efficiency of
538 Conventional Drinking-Water-Treatment Processes in Removal of Pharmaceuticals and
539 Other Organic Compounds. *The Science of the total environment* 377, 255-72.

540 Sudhakaran, S., Maeng, S.K., Amy, G. (2013) Hybridization of natural systems with advanced
541 treatment processes for organic micropollutant removals: New concepts in multi-barrier
542 treatment. *Chemosphere* 92.

543 Wang, Y.X., Ngo, H.H., Guo, W.S. (2015) Preparation of a specific bamboo based activated
544 carbon and its application for ciprofloxacin removal. *Science of The Total Environment*
545 533, 32-39.

546 Yu, Z., Peldszus, S., Huck, P.M. (2008) Adsorption characteristics of selected pharmaceuticals
547 and an endocrine disrupting compound—Naproxen, carbamazepine and nonylphenol—
548 on activated carbon. *Water Research* 42, 2873-2882.

549 Zhang, W., Ding, Y., Boyd, S.A., Teppen, B.J., Li, H. (2010) Sorption and desorption of
550 carbamazepine from water by smectite clays. *Chemosphere* 81, 954-960.

551 Zhu, R., Chen, Q., Zhou, Q., Xi, Y., Zhu, J., He, H. (2016) Adsorbents based on montmorillonite
552 for contaminant removal from water: A review. *Applied Clay Science* 123, 239-258.
553