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

Clément Levard<sup>1\*</sup>, Karima Hamdi-Alaoui<sup>1</sup>, Isabelle Baudin<sup>2</sup>, Amélie Guillon<sup>2</sup>, Daniel Borschneck<sup>1</sup>, Andrea Campos<sup>3</sup>, Mohamed Bizi<sup>4</sup>, Florence Benoit<sup>5</sup>, Corinne Chaneac<sup>5</sup> and Jérôme Labille<sup>1</sup>

<sup>1</sup> Aix Marseille Univ, CNRS, IRD, INRAE, Coll France, CEREGE, Aix-en-Provence, France

<sup>2</sup> SUEZ-CIRSEE. 38, rue du président Wilson, 78230 Le Pecq.

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

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

<sup>5</sup> 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

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## 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% SiO<sub>2</sub> 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.

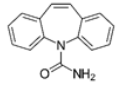
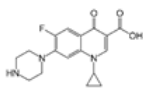
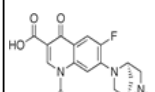
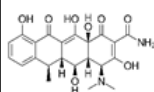
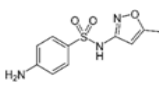
## 93 Materials and Methods

### 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 <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	C <sub>17</sub> H <sub>18</sub> FN <sub>2</sub> O <sub>3</sub>	C <sub>19</sub> H <sub>20</sub> FN <sub>2</sub> O <sub>3</sub>	C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub>	C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> 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*  
 110 *al.*, 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  $\mu\text{m}$  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  $\mu\text{m}$  at 25 cm in height. The supernatant  
138 containing the size fraction below 2  $\mu\text{m}$  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  $\text{SiO}_2$  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 SiO<sub>2</sub>-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 $\alpha$   
160 radiation ( $\lambda = 1.79 \text{ \AA}$ ). Samples were deposited on low background silicon plates and scanned  
161 in a  $2\theta$  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  $\mu\text{m}$  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 $\alpha$  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 =  $4\text{ m}^{-1}$ , 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



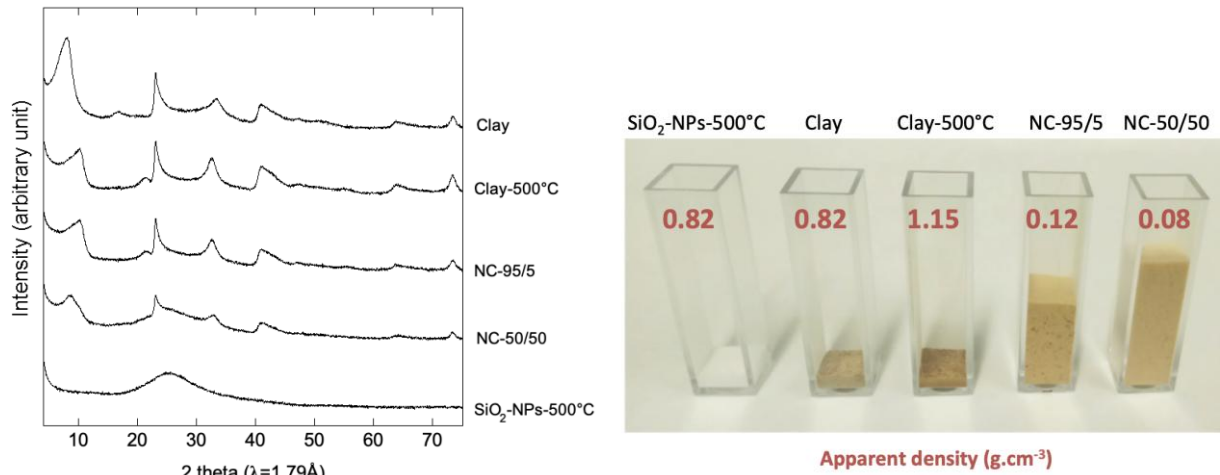
209 sulfamethoxazole were detected in the groundwater, at respectively 10 and 5 ng/L, giving the  
210 chemical background.

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 <sup>13</sup>C. 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 SiO<sub>2</sub> Nps in NC-95/5 is enough to strongly affect apparent density by  
247 one order of magnitude compared to Clay-500°C.

248

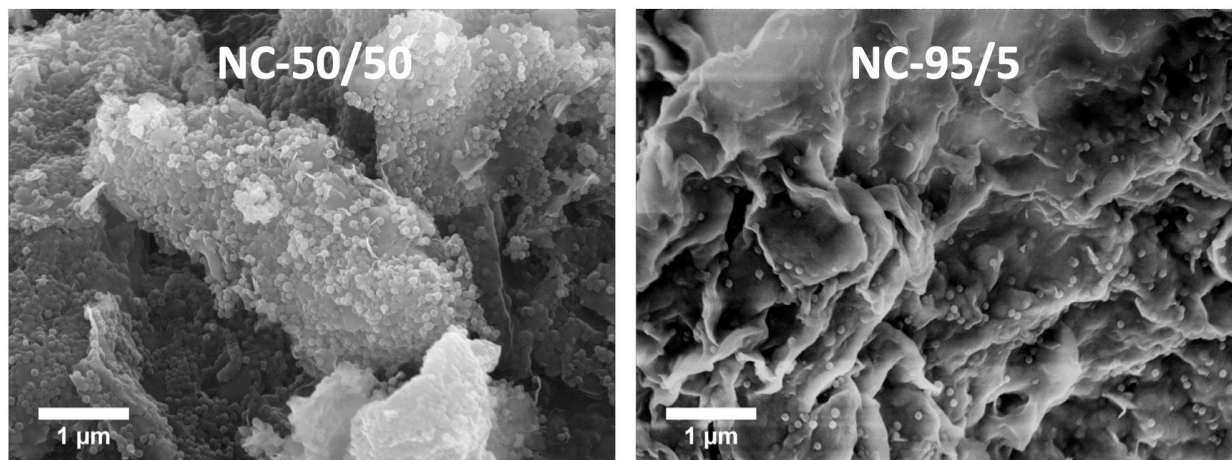


Figure 2. SEM images of NC-50/50 (left) and NC-95/5 (right)

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  $\text{SiO}_2$ -NPs in the interlayers, it can give an idea of the  
254 surface coverage and dispersion of  $\text{SiO}_2$ -NPs at the surface of the clay sheets. For the lowest  
255 loading of  $\text{SiO}_2$ -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  $\text{SiO}_2$ -NPs at the clay surface. The randomly dispersed distribution of the  $\text{SiO}_2$ -  
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

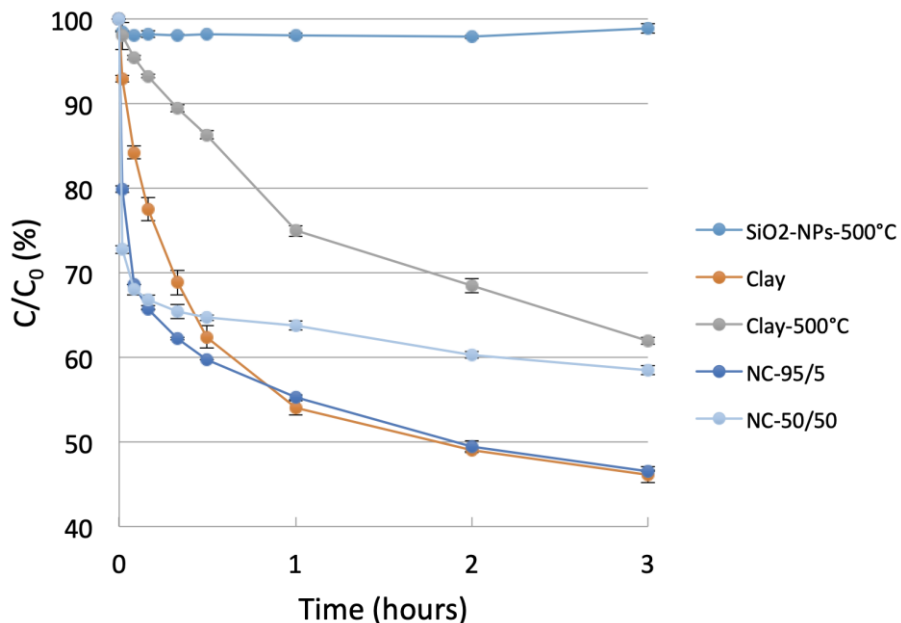
## 265 2. Removal efficiency of ciprofloxacin in model effluents

266

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

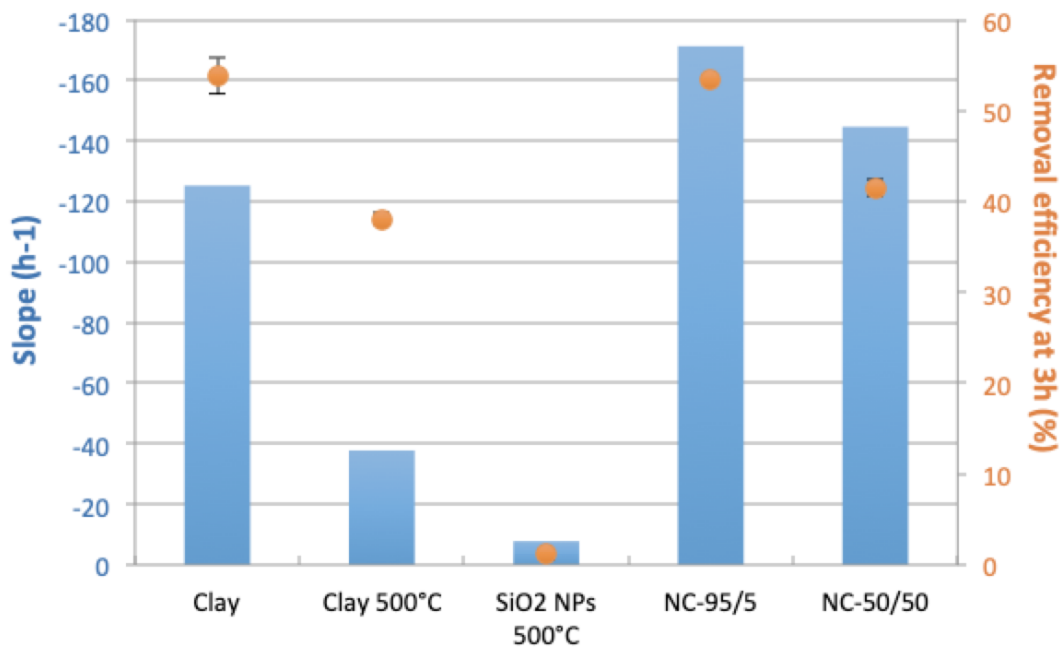
269

270



271  
 272 Figure 3. Removal kinetics of ciprofloxacin from a model of surface water by adsorption to the  
 273 sorbent materials: clay, SiO<sub>2</sub>-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), SiO<sub>2</sub>-NPs-500°C and NCs. While  
 277 no removal of ciprofloxacin was obtained with SiO<sub>2</sub>NP-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 SiO<sub>2</sub>-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 SiO<sub>2</sub>-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 SiO<sub>2</sub>-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, SiO<sub>2</sub>-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 Ca<sup>2+</sup>. 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).

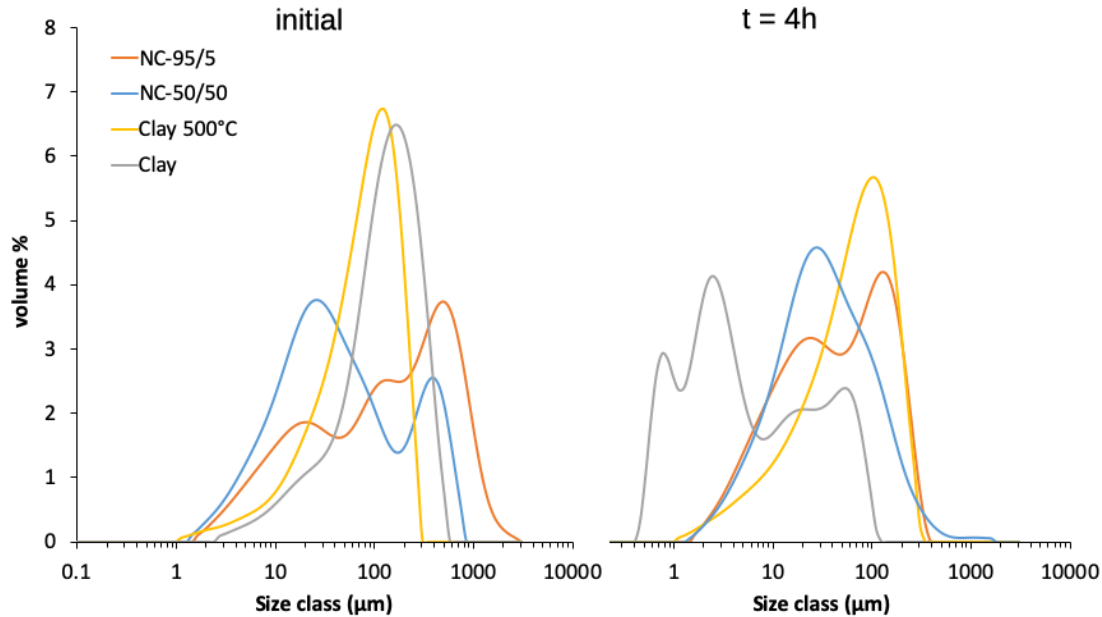
317  
318 XPS analysis was performed on NC-95/5 before and after sorption of ciprofloxacin to  
319 investigate sorption mechanism. However, although XPS confirms the presence of ciprofloxacin  
320 on the NC-95/5 substrate (specific signature of Fluor), it does not allow to identify the sorption  
321 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).

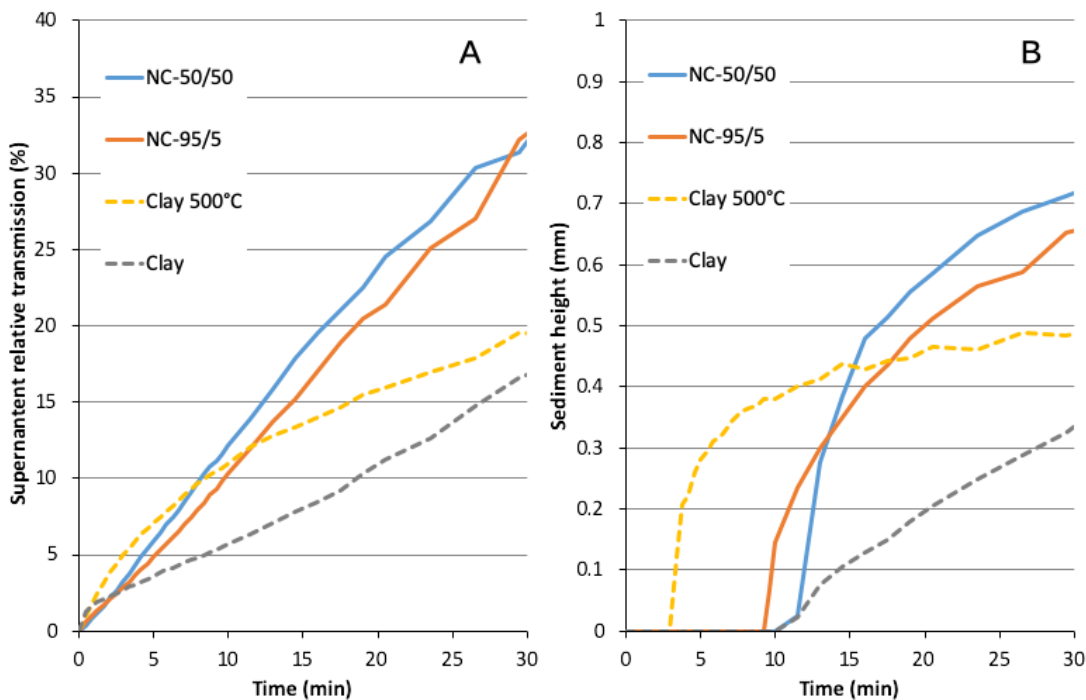
333  
 334 Laser diffraction was used to measure the dispersion of the hybrid material in water compared  
 335 to raw clay and to clay-500°C. It proved that heating at 500°C causes the formation of  
 336 irreversible aggregates that can withstand the dispersion step in aqueous medium. Indeed, after  
 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 <sub>2</sub> (50/50)	99%	99%	0%	34%	3%
MMT/SiO <sub>2</sub> (95/5)	100%	100%	0%	60%	0%
clay-500	94%	95%	0%	41%	0%

<b>SiO<sub>2</sub> NP-500</b>	0%	0%	0%	11%	0%
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380

381

382 SiO<sub>2</sub>-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 SiO<sub>2</sub>-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  $\mu\text{m}$ . 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  $\text{SiO}_2$ -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  $\text{SiO}_2$ -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

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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.

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