



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-02989392>

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

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

Introduction

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

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

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

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

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

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

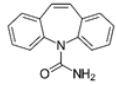
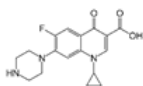
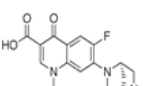
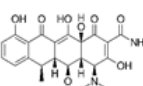
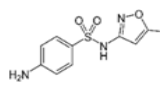
In this work, we developed and tested clay-silica nanoparticle hybrid nanostructures that can be an economic alternative to the activated carbon conventionally used in water treatment. The silica to clay ratio was adjusted to optimize the adsorption capacity of the nanocomposites (NCs). The efficiency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

Materials and Methods

Targeted pharmaceutical molecules

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

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

Pharmaceutical class	Antiepileptic	Antibiotics			
Compounds	Carbamazepine	Ciprofloxacin	Danofloxacin	Doxycycline	Sulfamethoxazole
Chemical formula	$C_{15}H_{12}N_2O$	$C_{17}H_{15}FN_3O_3$	$C_{19}H_{20}FN_2O_3$	$C_{22}H_{24}N_2O_5$	$C_{10}H_{11}N_2O_3S$
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

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

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

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

Nanocomposite synthesis

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

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

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

Characterization of the materials

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

Removal efficiency of ciprofloxacin in a model effluent

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

Nanocomposite dispersibility and potential for recovery after treatment

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

Removal efficiency in real groundwater

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

Groundwater from the Paris region (France) was used for this experiment ($\text{pH} = 7.5$, dissolved organic carbon: 1.5 mg/L, UV absorbance at 254 nm = 4 m^{-1} , expressed as optical density). The main chemical elements constituting the geochemical composition were analyzed. Results are 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 order to control the presence of residual pollutants in this groundwater before exposition, the concentration of the five studied micropollutants was determined. Only carbamazepine and

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

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

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

Results

1. Characterization of materials

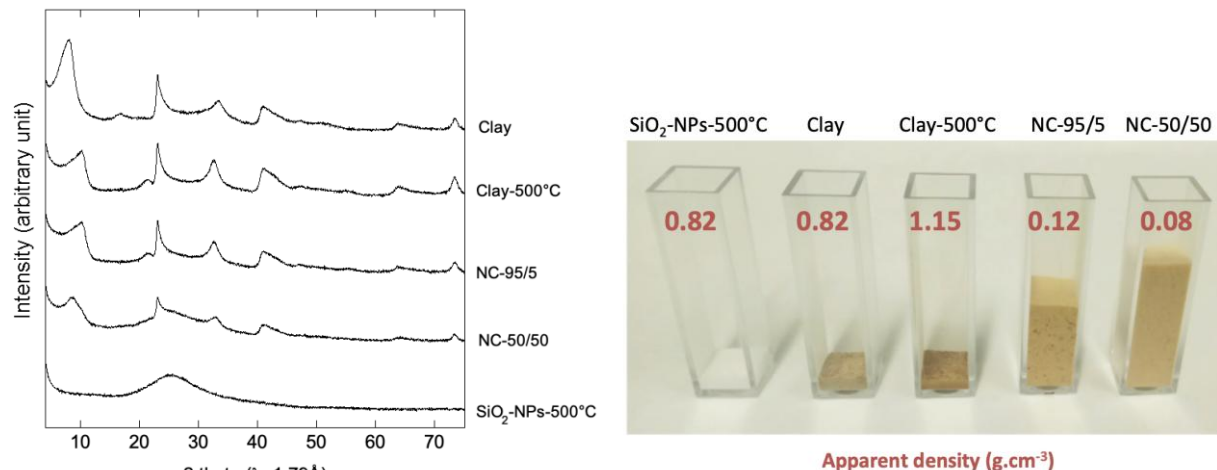


Figure 1. X-ray diffraction patterns (left) and apparent density measured in a volume of 230 mg of material (right) of the initial clay, nanocomposites and references heated at 500°C

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

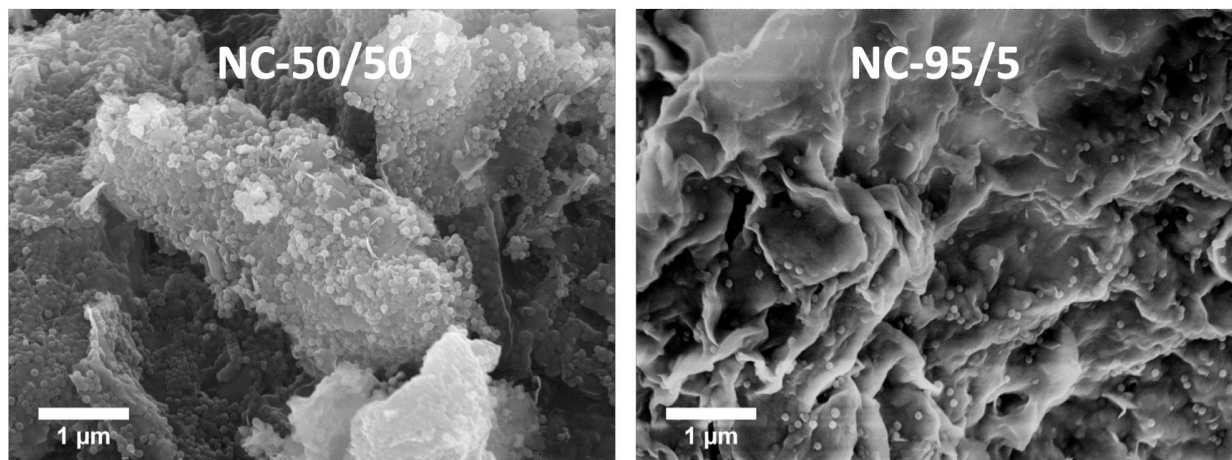


Figure 2. SEM images of NC-50/50 (left) and NC-95/5 (right)

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

2. Removal efficiency of ciprofloxacin in model effluents

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

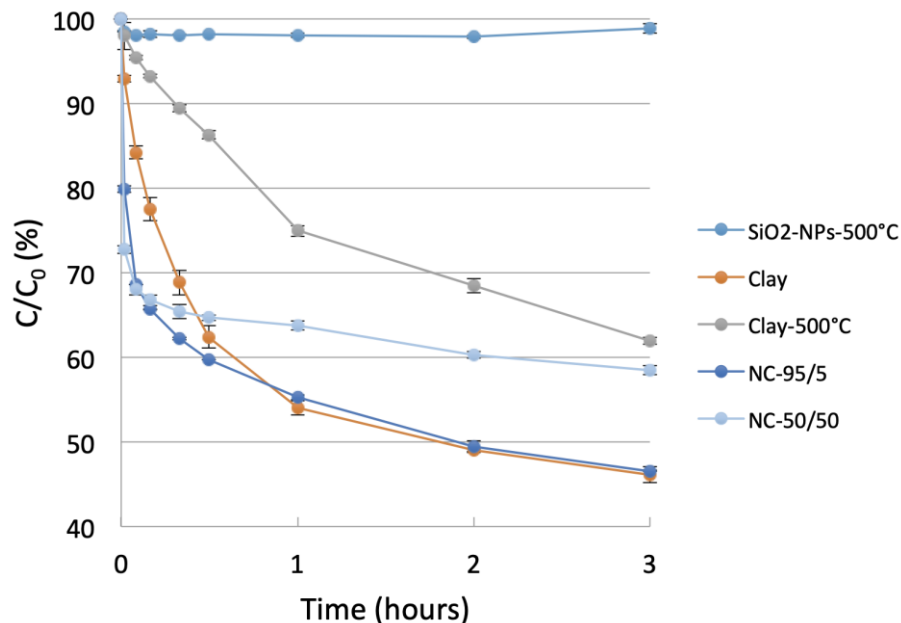


Figure 3. Removal kinetics of ciprofloxacin from a model of surface water by adsorption to the sorbent materials: clay, SiO₂-NPs-500°C and NCs

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

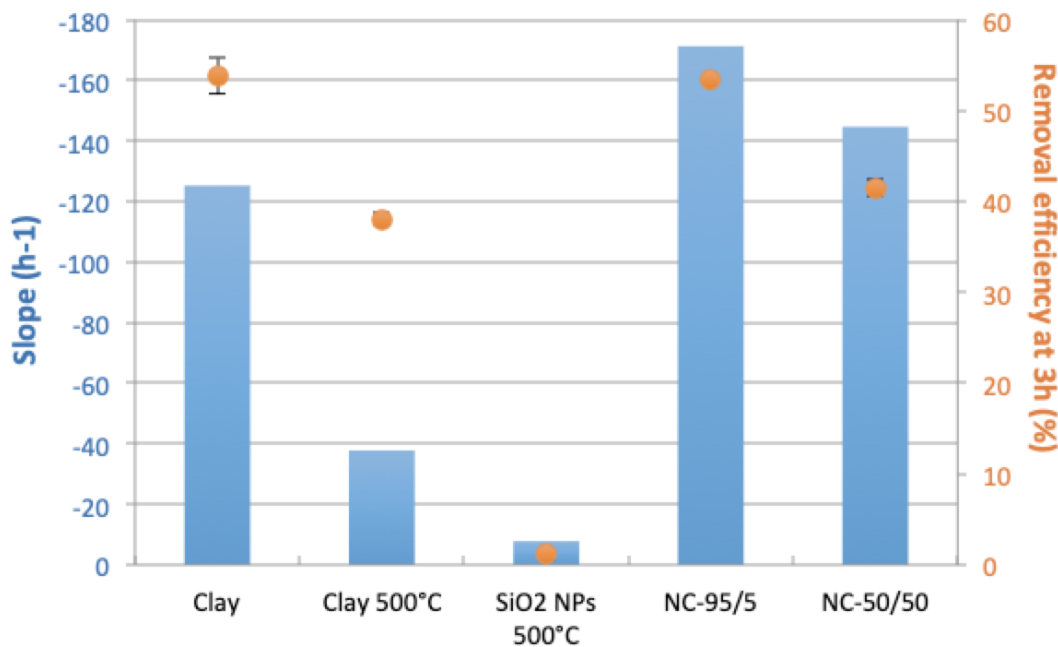


Figure 4. Removal kinetics (Figure 3) calculated on the first 4 experimental points (after 10 minutes of reaction) are represented on the primary y-axis (blue bars). Removal efficiencies after 3 hours are represented on the secondary y-axis (orange dots).

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

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

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

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

The mineralogy of NC-95/5 is preserved after adsorption as shown in Figure S1. The (001) reflection distance is shifted from 9.6Å (before adsorption) to 14.4Å (after adsorption). This basal reflection observed after adsorption of ciprofloxacin is typical of hydrated Ca-montmorillonite which is consistent with the fact that Evian water contains 80 mg/L of Ca^{2+} . In addition to NC-95/5, calcium carbonate phases were detected which is, once again, consistent with the ionic composition of Evian water that contains bicarbonates (360 mg/L) which has favored the precipitation of calcite and aragonite (Figure S1).

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

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

3. Nanocomposite and clay recovery from liquid media

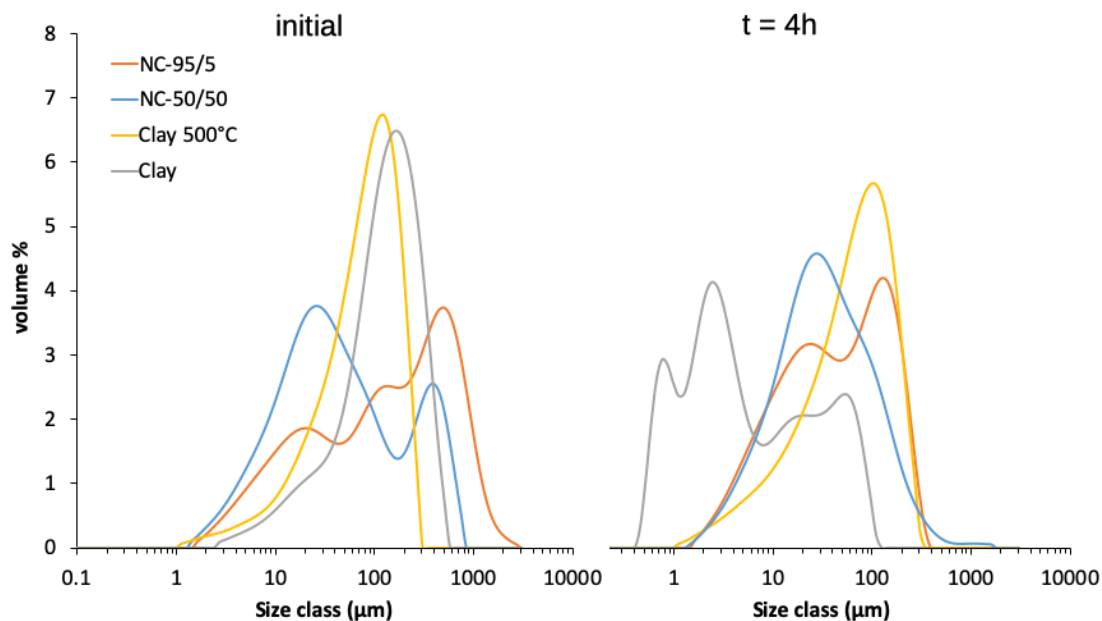


Figure 5: Size distribution of the clay and NCs in synthetic surface water, at t_0 (left, just after dispersion) and after 4h of agitation (right).

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

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

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

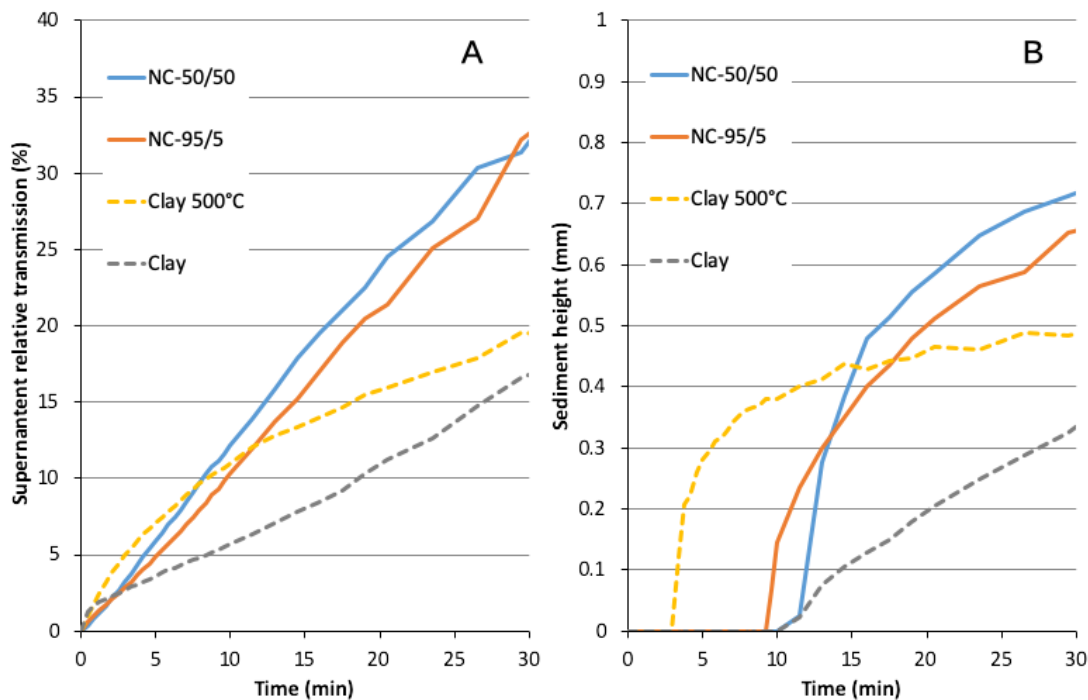


Figure 6: Kinetics of supernatant clarification (A) and sediment formation (B) measured respectively by light transmission and backscattering in the upper 39 mm and bottom 1 mm of the sedimentation tube for clay-based materials

4. Removal efficiency in groundwater

Table 2. Adsorption performances of the 5 micropollutants on activated carbon, NCs and the 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%
-------------------------------	----	----	----	-----	----

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

Conclusion

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

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

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

- Akpınar, I., Yazaydin, A.O. (2017) Rapid and Efficient Removal of Carbamazepine from Water by UiO-67. *Industrial & Engineering Chemistry Research* 56, 15122-15130.
- Ali, M., Ahmed, M. (2017) Adsorption behavior of doxycycline antibiotic on NaY zeolite from wheat (*Triticum aestivum*) straws ash. *Journal of the Taiwan Institute of Chemical Engineers* 81, 218-224.
- Arp, H.P.H., Brown, T.N., Berger, U., Hale, S.E. (2017) Ranking REACH registered neutral, ionizable and ionic organic chemicals based on their aquatic persistency and mobility. *Environmental Science: Processes & Impacts* 19, 939-955.
- Banković, P., Milutinović-Nikolić, A., Mojović, Z., Jović-Jovičić, N., Perović, M., Spasojević, V., Jovanović, D. (2013) Synthesis and characterization of bentonites rich in beidellite with incorporated Al or Al-Fe oxide pillars. *Microporous and Mesoporous Materials* 165, 247-256.
- Besnault, S., Ruel, S., Baig, S., Esperanza, M., Budzinski, H., Miege, C., Boucher, C., Menach, K., Coquery, M. (2014) Technical, economic and environmental evaluation of advanced tertiary treatments for micropollutants removal (oxidation and adsorption). *ECOSTP* (Verone, Italy),
- Bizi, M. (2012) Stability and flocculation of nanosilica by conventional polymer. *Natural Science* 04, 372-385.
- Bizi, M. (2019) Activated Carbon and the Principal Mineral Constituents of a Natural Soil in the Presence of Carbamazepine. *Water* 11, 2290-2306.
- Bizi, M., El Bachra, F.E. (2020) Evaluation of the ciprofloxacin adsorption capacity of common industrial minerals and application to tap water treatment. *Powder Technology* 362, 323-333.
- Brindley, G.W., Sempels, R.E. (2018) Preparation and properties of some hydroxy-aluminium beidellites. *Clay Minerals* 12, 229-237.
- De Cazes, M., Abejón, R., Belleville, M.-P., Sanchez Marcano, J. (2014a) Membrane Bioprocesses for Pharmaceutical Micropollutant Removal from Waters. *Membranes* 4, 692-729.
- De Cazes, M., Belleville, M.P., Mougél, M., Kellner, H., Sanchez-Marcano, J. (2015) Characterization of laccase-grafted ceramic membranes for pharmaceuticals degradation. *Journal of Membrane Science* 476, 384-393.
- De Cazes, M., Belleville, M.P., Petit, E., Llorca, M., Rodríguez-Mozaz, S., de Gunzburg, J., Barceló, D., Sanchez-Marcano, J. (2014b) Design and optimization of an enzymatic membrane reactor for tetracycline degradation. *Catalysis Today* 236, 146-152.
- Djebbar, M., Djafri, F., Bouchekara, M., Djafri, A. (2012) Adsorption of phenol on natural clay. *Applied Water Science* 2, 77-86.
- Essington, M.E. (1994) Adsorption of aniline and toluidines on montmorillonite. *Soil Science* 158, 181-188.
- Furlong, E.T., Batt, A.L., Glassmeyer, S.T., Noriega, M.C., Kolpin, D.W., Mash, H., Schenck, K.M. (2017) Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States: Pharmaceuticals. *Science of The Total Environment* 579, 1629-1642.
- Guégan, R., De Oliveira, T., Le Gleuher, J., Sugahara, Y. (2020) Tuning down the environmental interests of organoclays for emerging pollutants: Pharmaceuticals in presence of electrolytes. *Chemosphere* 239, 124730.
- He, Q., Liang, J.-J., Chen, L.-X., Chen, S.-L., Zheng, H.-L., Liu, H.-X., Zhang, H.-J. (2020) Removal of the environmental pollutant carbamazepine using molecular imprinted adsorbents: Molecular simulation, adsorption properties, and mechanisms. *Water Research* 168, 115164.

- Horner, O., Neveu, S., Montredon, S., Siaugue, J.-M., Cabuil, V. (2009) Hydrothermal synthesis of large maghemite nanoparticles: Influence of the pH on the particle size. *Journal of Nanoparticle Research* 11, 1247-1250.
- Jolivet, J.-P., Chanéac, C., Tronc, E. (2004) Iron Oxide Chemistry. From Molecular Clusters to Extended Solid Networks. *Chemical communications (Cambridge, England)* 35, 481-7.
- Knappe, D.R.U., Li, L., Quinlivan, P.A., Wagner, T.B. (2003) Effects of activated carbon characteristics on organic contaminant removal. Awwa Research Foundation, Denver, CO :.
- Labille, J., Thomas, F., Milas, M., Vanhaverbeke, C. (2005) Flocculation of colloidal clay by bacterial polysaccharides: Effect of macromolecule charge and structure. *Journal of colloid and interface science* 284, 149-56.
- Lee, D.C., Jang, L.W. (1996) Preparation and characterization of PMMA–Clay hybrid composite by emulsion polymerization. *Journal of Applied Polymer Science* 61, 1117-1122.
- Li, S., Zhang, X., Huang, Y. (2017) Zeolitic imidazolate framework-8 derived nanoporous carbon as an effective and recyclable adsorbent for removal of ciprofloxacin antibiotics from water. *Journal of Hazardous Materials* 321, 711-719.
- Liu, S., Xu, W., Liu, Y.-g., Tan, X., Zeng, G.-m., Li, X., Liang, J., Zhou, Z., Yan, Z.-l., Cai, X.-x. (2017) Facile synthesis of Cu(II) impregnated biochar with enhanced adsorption activity for the removal of doxycycline hydrochloride from water. *Science of The Total Environment* 592.
- Magnan, E., Catarino, I., Paolucci-Jeanjean, D., Preziosi-Belloy, L., Belleville, M.P. (2004) Immobilization of lipase on a ceramic membrane: activity and stability. *Journal of Membrane Science* 241, 161-166.
- Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M., Barry, D. (2013) Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? *The Science of the total environment* 461-462C, 480-498.
- Pavithra, K.G., Kumar, P.S., Jaikumar, V., Rajan, P.S. (2019) Removal of colorants from wastewater: A review on sources and treatment strategies. *Journal of Industrial and Engineering Chemistry* 75, 1-19.
- Prasannamedha, G., Kumar, P.S. (2020) A review on contamination and removal of sulfamethoxazole from aqueous solution using cleaner techniques: Present and future perspective. *Journal of Cleaner Production* 250, 119553.
- Rostamian, R., Behnejad, H. (2017) A unified platform for experimental and quantum mechanical study of antibiotic removal from water. *Journal of Water Process Engineering* 17, 207-215.
- Stackelberg, P., Gibs, J., Furlong, E., Meyer, M., Zaugg, S., Lippincott, R. (2007) Efficiency of Conventional Drinking-Water-Treatment Processes in Removal of Pharmaceuticals and Other Organic Compounds. *The Science of the total environment* 377, 255-72.
- Sudhakaran, S., Maeng, S.K., Amy, G. (2013) Hybridization of natural systems with advanced treatment processes for organic micropollutant removals: New concepts in multi-barrier treatment. *Chemosphere* 92.
- Wang, Y.X., Ngo, H.H., Guo, W.S. (2015) Preparation of a specific bamboo based activated carbon and its application for ciprofloxacin removal. *Science of The Total Environment* 533, 32-39.
- Yu, Z., Peldszus, S., Huck, P.M. (2008) Adsorption characteristics of selected pharmaceuticals and an endocrine disrupting compound—Naproxen, carbamazepine and nonylphenol—on activated carbon. *Water Research* 42, 2873-2882.
- Zhang, W., Ding, Y., Boyd, S.A., Teppen, B.J., Li, H. (2010) Sorption and desorption of 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