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Clayey-sand filter for the pharmaceuticals removal from wastewater effluent: Percolation experiments

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The objective of the study was to evaluate the sorption of a pool of pharmaceutically active compounds (PhACs) onto a clay-sand filter in a dynamic sorption experiment. The chosen adsorbent should have suitable chemical properties for the removal of the targeted PhACs and also consistent hydrodynamic behavior regarding field application. In this aim, the impact of interfoliar cation (Ca^{2+} or Na^+) intercalated into natural montmorillonite (Swy2) was tested by using different clay-sand ratios (from 0% to 100% of clay minerals). Only Ca-Swy2 showed a consistent hydraulic conductivity for field application with a value of $4.78 \times 10^{-8} \text{ m.s}^{-1}$ for 5%-95% clay-sand ratio. The sorption of PhACs onto this filter was investigated using oedometer cells by varying two parameters, the solution matrix (ultra-pure water or natural effluent) and the injection pressure (0.1 MPa and 0.2 MPa). PhACs were effectively adsorbed onto the filter for each experiment at different levels. The drop in injection pressure was a favorable factor for sorption whatever the matrix, with median global removal of $\sim 45\%$ at 0.2 MPa and $\sim 75\%$ at 0.1 MPa. The effect of the matrix exhibited two different trends as a function of the molecular charge of each PhAC. While cationic compounds were more effectively sorbed in the ultra-pure water matrix than in effluent matrix the sorption of anionic PhACs was more effective in the effluent matrix than in ultra-pure water. This indicates that the charge of the pollutant is a key parameter controlling the efficiency of the adsorbent. Despite these removal variations, the filter exhibited a significant sorption capacity especially at 0.1 MPa. It can therefore be an efficient solution for the removal of PhACs by tertiary filtration.

1 Introduction

Emerging Pollutants (EPs) represent a common form of pollution in numerous water compartments, from effluents to drinking water. Pharmaceutically Active Compounds (PhACs) account for more than 3,000 compounds among the most concentrated and persistent ones in the environment.^{1,2} They constitute a representative part of EPs due to their wide variety of chemical properties.^{3,4} Ever since the study by Richardson and Bowron highlighting the fate of pharmaceutical residues in the environment,⁵ several investigations have been conducted in this field over the last thirty years. Studies have focused on the removal of PhACs in Waste-Water Treatment Plants (WWTPs),^{6,7} and on improving the sensitivity of analytical methods in order to better characterize their occurrence in the environment.^{8,9} There are three main types of WWTPs: activated sludge treatment plants, phytoplanted filters or lagoon-based

systems, but the removal of EPs remains insufficient for all of them.¹⁰⁻¹² The main consequence of this lack of efficiency is the constant discharge of PhACs into the aquatic system. Even if PhACs are present in natural waters at relatively low concentrations, from several ng.L^{-1} to $\mu\text{g.L}^{-1}$,^{4,13} their toxicity has been widely proved,^{14,15} particularly for endocrine disruptors.^{16,17} Moreover, some PhACs can be concentrated in natural beings,¹⁸ and contaminate the whole trophic chain including humans with poorly-known consequences.¹⁹ While this contamination goes beyond issues of human health, it raises awareness of the hazards generated by EPs and particularly PhACs. Waste-water treatment is framed by two major factors, purification capacity and cost. Numerous innovative methods such as activated carbon or UV-oxidation exhibit excellent results for the removal of EPs but are often reserved for drinking water treatment due to prohibitive costs.²⁰ In addition, oxidation creates metabolites,²¹ whose toxicity is still unknown today. Ali et al. showed by a simple calculation between several removal techniques that adsorption mechanisms are the most appropriate and easiest way to remove both inorganic and organic micro-pollutants,²² since the adsorbent material has a large specific surface and a good affinity with the targeted micro-pollutants.^{23,24}

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† Footnotes relating to the title and/or authors should appear here.

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Drug	Abbreviation	CAS-Number	M _w	pKa	log K _{ow}	S _w	Charge
Atenolol C ₁₄ H ₂₂ N ₂ O ₃	ATE	29122-68-7	266.34	9.6	0.16	300	+
Codeine C ₁₈ H ₂₁ NO ₃	COD	76-57-3	299.36	8.21	1.2	79 x 10 ²	+
Diazepam C ₁₆ H ₁₃ ClN ₂ O	DIA	439-14-5	284.74	3.4	2.82	50	0
Diclofenac C ₁₄ H ₁₁ Cl ₂ NO ₂	DCF	15307-79-6	296.15	4.15	4.06	50 x 10 ³	-
Doxepin C ₁₉ H ₂₁ NO	DOX	1229-29-4	279.38	8.96	3.86	32 x 10 ³	+
Gemfibrozil C ₁₅ H ₂₂ O ₃	GEM	25812-30-0	250.33	4.8	4.33	4.97	-
Ibuprofen C ₁₃ H ₁₈ O ₂	IBU	15687-27-1	206.28	4.91	3.72	21	-
Ketoprofen C ₁₆ H ₁₄ O ₃	KET	22071-15-4	254.28	4.45	2.81	51	-
Metoprolol C ₁₅ H ₂₅ NO ₃	MET	56392-17-7	267.36	9.6	1.79	47 x 10 ²	+
Naproxen C ₁₄ H ₁₄ O ₃	NAP	22204-53-1	230.26	4.15	3	15.9	-
Oxazepam C ₁₅ H ₁₁ ClN ₂ O ₂	OXA	604-75-1	286.97	1.7- 11.6	2.31	20.71	0
Progesterone C ₂₁ H ₃₀ O ₂	PRO	57-83-0	314.46	-	4.04	8.81	0
Tramadol C ₁₆ H ₂₅ NO ₂	TRA	27203-92-5	263.37	9.41	2.51	75 x 10 ³	+
Trimethoprim C ₁₄ H ₁₈ N ₄ O ₃	TRI	738-70-5	290.32	7.2	0.38	400	0

With M_w, the molecular weight in g.mol⁻¹, pKa the acid dissociation constant, log K_{ow}, the octanol/water partition coefficient, S_w, the solubility in water at 25°C in mg.L⁻¹ and Charge, the dominant form at pH=7

Table 1: Selected pollutants and parameters used in this work

46 Natural materials such as clays offer a good balance
 47 between reactivity and cost for the treatment of
 48 effluents.²⁵ The efficiency of clays CEC (Cationic
 49 Exchange Capacity) in water is well documented.^{26–28}
 50 After all, numerous PhACs are not in cationic form but in
 51 neutral or anionic form in environmental
 52 conditions. Another key parameter is the influence of
 53 the solid-liquid ratio, which is often very remote from
 54 realistic applications.^{29,30} The latter two studies sought
 55 to gain a better understanding of sorption mechanisms
 56 for which starting concentrations are often largely
 57 overestimated compared to simulation approaching field
 58 conditions. To our knowledge, no study has investigated
 59 the sorption of PhACs at low starting concentrations (25
 60 µg.L⁻¹) onto natural clays. However sorption experiments
 61 with PhAC concentrations that are as close as possible to
 62 those found in natural environments and water
 63 purification plants are necessary in order to estimate the
 64 efficiency of sand and clay mixtures and the real
 65 affinities between the tested materials and the targeted
 66 pollutants.
 67 A similar concern also frames the choice of the
 68 geosorbents and their characteristics as interlayer
 69 cation, which controls the sorption capacity and
 70 hydrodynamic behavior.^{31,32}
 71 In view of the well-established capacity of clays to
 72 remove numerous compounds from water, the present
 73 study addressed three main issues: (i) the real capacity
 74 of slightly modified clay to treat a complex solution in
 75 pure water or effluent (ii) the impact of the kinetic
 76 transfer and the matrix effect on the sorption and (iii)

77 the feasibility of a clay-based filter for the removal of
 78 PhACs.

79 Materials and Methods

80 Filter: clay minerals and sand

81 The sand used was uniformly fine-grained Fontainebleau
 82 quartz sand (from the Paris basin, France) of analytical
 83 grade, and with a granulometry of 100-150 MESH.
 84 The clay mineral chosen was Swy2 Wyoming
 85 montmorillonite (Crook County Wyoming, United
 86 States), supplied by the Source Clays Repository of the
 87 Clay Minerals Society. After <2 µm fractionation by
 88 gravity sedimentation, the Swy2 sample was Na-
 89 exchanged by well-established procedures.³³ This Na-
 90 Swy2 was the starting material for the production of Ca-
 91 Swy2 with the same procedure, by replacing NaCl with
 92 CaCl₂. These two interlayer cations were chosen because
 93 of their predominance in the environment.
 94 Different proportions of sand and clay were tested to
 95 estimate the hydrodynamic properties of the resulting
 96 mix, with clay percentage in the filter of 5%, 10%, 50%
 97 and 100% (i.e. pure clay) and with a constant total mass
 98 of 8.0 ± 0.4g. For percolation tests with PhACs, a 5% clay
 99 filter was used.

100 PhACs and chemical reagents

101 The 14 PhAC standards (purity grade > 98%; see Table 1
 102 for details) were obtained from Sigma-Aldrich for ATE,
 103 COD, DIA, DOX (Doxepin Hydrochloride), GEM, KET, MET
 104 (Metoprolol Tartrate salt), NAP, OXA, PRO, TRA
 105 (Tramadol Hydrochloride), TRI, and from Acros Organics
 106 for DCF (Diclofenac Sodium) and IBU.

107 Chemical reagents of analytical grade, methanol (MeOH)
108 and pyridine were purchased from Fisher Scientific. N-
109 tert-Butyldimethylsilyl-N-methyltrifluoroacetamide
110 (MTBSTFA, >95%) was supplied by Sigma-Aldrich.

111 Percolation Experiments

112 Percolation experiments were carried out in oedometer
113 cells. This specific equipment was developed to
114 understand the hydrodynamic behavior of a solid sample
115 under different conditions.³⁴

116 The oedometer cell (internal diameter = 0.04 m) and the
117 injection syringe were both connected to a distinct
118 compressed-air system in order to apply respectively the
119 mechanical pressure on the sorbent material and the
120 injection pressure on the leaching solution. The
121 equipment scheme and further details are given in
122 Figure S1 and in Gautier et al.³⁵

123 For each experiment, 8 g of material (clay-sand mix) was
124 gradually compacted on the bottom side up to 0.5 MPa,
125 then totally unloaded, and compacted again at a
126 mechanical pressure of 0.3 MPa. The solution was
127 injected at the upper side into this compacted sample at
128 a constant pressure during experiments. The injection
129 pressure is the variable which controls the interaction
130 kinetic between the solution and the material. Indeed,
131 oedometer cells enable physical and hydraulic properties
132 to be jointly controlled. Two different injection pressures
133 were used in this study, 0.1 and 0.2 MPa.

134 In order to control impact of the matrix on the
135 adsorption of PhACs, two solutions were used in the
136 experiments: (i) a mix, hereafter called S, of each of the
137 14 selected PhACs at concentrations around 25 $\mu\text{g}\cdot\text{L}^{-1}$ in
138 ultra-pure water, and (ii) a mix between the 14 PhACs
139 and an effluent of a French rural WWTP, called N.
140 Although PhACs were present in this effluent their
141 maximum concentration around 200 $\text{ng}\cdot\text{L}^{-1}$ did not affect
142 our results by modifying starting concentrations
143 noticeably (Table S1 for details, and Table S2 for the
144 chemical parameters of the chosen effluent).

145 The choice of the starting concentration at 25 $\mu\text{g}\cdot\text{L}^{-1}$ for
146 each PhAC corresponds to the maximum PhAC
147 concentrations in some effluents.¹³

148 During percolation experiments, leachate samples were
149 collected each time that a volume of 100 mL solution
150 passed through the filter. A total of 1 L (10 x 100 mL) was
151 therefore used for each percolation experiment.

152 Leachate and clay analyses

153 Leachate analysis

154 Leachate solutions were concentrated by Solid-Phase
155 Extraction (SPE) and analyzed by Gas Chromatography
156 coupled to Mass Spectrometry (GC-MS).

157 PhAC extraction was carried out on a 6mL glass cartridge
158 filled with HR-X phase (Macherey-Nagel). Cartridges
159 were conditioned with 5 mL of MeOH then with 5mL of
160 ultra-pure water. Columns were filled with 100 mL of
161 sample and then rinsed with 5 mL of ultra-pure water
162 before drying for 30 minutes under vacuum. Finally,

163 elution was performed with 3 x 5 mL of MeOH.
164 Thereafter, internal standard was added to organic
165 layers, which were evaporated under reduced pressure.
166 Residues were derivatized with MTBSTFA according to
167 Schummer et al.³⁶

168 Analyses were performed on a Trace GC Ultra gas
169 chromatograph (GC) coupled to a TSQ Quantum XLS
170 mass spectrometer equipped with an AS 3000
171 autosampler (both from Thermo Scientific). The GC was
172 fitted with a Thermo Trace Gold TG-5 MS capillary
173 column (60 m, 0.25 mm i.d., 0.25 μm film thickness).

174 The temperature of the column was held at 50°C for 3
175 min, increased from 50 to 120°C at 30°C.min⁻¹, and from
176 120 to 310°C at 3°C.min⁻¹ with a final isothermal hold at
177 310°C for 21 min. 2 μL of sample was injected in splitless
178 mode at 280°C. Helium was the carrier gas (1 mL.min⁻¹).
179 The mass spectrometer was operated in EI mode at 70
180 eV, from m/z 50 to 500.

181 Clay characterization and global carbon analysis

182 X-ray diffraction (XRD) patterns were recorded between
183 2 and 64° (2 θ) using a Thermo Electron ARL'XTRA
184 diffractometer equipped with a Cu anode (Cu K α 1,2 =
185 1.5418 Å) coupled with a Si(Li) solid detector.
186 Experimental measurement parameters were 10s
187 counting time per 0.04°2 θ step. The diffractograms were
188 performed with dry powder samples (100 °C for 24 h).

189 Fourier transform infrared (FTIR) measurements were
190 recorded in the range 650-4000 cm⁻¹, using a Thermo
191 Nicolet 6700 FT spectrometer equipped with a
192 Deuterated Triglycine Sulfate (DTGS) detector and a
193 Nicolet Continuum microscope. The analyses were
194 performed in transmission mode and each spectrum was
195 the average of 256 scans collected at 2 cm⁻¹ resolution.
196 Carbon and nitrogen analyses were performed on
197 powdered samples by using a Thermo Scientific Flash
198 2000 organic analyzer assuming an analytical error of
199 0.05%.

200 Data analysis

201 To characterize the distribution of a compound between
202 a potential sorbent and the dissolved phase, the Log K_d
203 parameter is often used.³⁷ The computation
204 corresponding to its calculation is expressed as follows:

$$205 \log(K_d) = \log\left(\frac{q_s}{q_e}\right) \quad (1)$$

206 with K_d the solid-liquid distribution coefficient (L.kg⁻¹), q_s
207 the sorbed concentration (mg.kg⁻¹) and q_e the
208 equilibrium concentration (mg.L⁻¹).

209 Statistical tests were performed to verify the significance
210 of some hypothesis using the Student test with a chosen
211 statistical threshold of 0.01 for the resulting p -values.

212 To estimate the link between time and sorption capacity
213 and to describe the sorption dynamic, the first-order
214 Lagergren equation, the second-order kinetics model
215 and the Bangham equations are often used.³⁸

217

218 These equations are expressed in linear form by
 219 equations (2)-(4) respectively:

$$220 \log(q_m - q_t) = \log q_m - \frac{k_1}{2.303} t \quad (2)$$

$$221 \frac{t}{q_t} = \frac{1}{k_2 q_m^2} + \frac{1}{q_m} t \quad (3)$$

$$222 \log q_t = \log k_b + \frac{1}{n} \log t \quad (4)$$

223 with q_t the sorbed concentration in $\mu\text{g}\cdot\text{mg}^{-1}$ at the time t
 224 (min), q_m the pseudo-equilibrium sorbed concentration
 225 ($\mu\text{g}\cdot\text{mg}^{-1}$), k_1 (min^{-1}), k_2 ($\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) and k_b ($\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)
 226 respectively the first-order, the second-order and the
 227 Bangham sorption rate constants.

228 Each equation is based on different assumptions:

- 229 (i) the first-order Lagergren model considers
 230 that the quantity of unoccupied adsorption
 231 sites is proportional to the adsorption rate
 232 of adsorbate onto adsorption sites
 233 (ii) the second-order kinetic model assumes
 234 that the adsorption is chemically
 235 accomplished
 236 (iii) The Bangham equation considers a fast
 237 velocity of adsorption and a slow
 238 attainment of sorption equilibrium

239 These equations were applied to the experimental
 240 results.

241 Results and discussion

242 Hydrodynamic properties

243 Percolation experiments were first performed with
 244 water solution in order to determine the hydraulic
 245 conductivity (K) of the different clay-sand materials. K ,
 246 expressed in $\text{m}\cdot\text{s}^{-1}$, was calculated from Darcy's law,
 247 using the expression developed for a saturated
 248 medium:³⁹

$$249 K = \frac{Q}{i \cdot S}$$

250 where Q is the measured volumetric flow rate ($\text{m}^3\cdot\text{s}^{-1}$) at
 251 the steady state, i is the hydraulic gradient and S is the
 252 cross-sectional area of the oedometer cell (m^2).

253 For a potential environmental application, the clay-sand
 254 filter should have hydrodynamic properties that
 255 correspond to the hydraulic conductivities operable in
 256 actual treatment installations, whereas clays are a
 257 natural barrier used for example to trap nuclear
 258 wastes.⁴⁰

Clays	SSA	CEC	ϵ_{max}	θ_{max}
Na-Swy2	45.4 ^a	85.0±2.7 ^a	37% ^a	75%
Ca-Swy2	46.0 ^b	85.1±0.01 ^b	1.5%	62%

With SSA, Specific Surface Area ($\text{m}^2\cdot\text{g}^{-1}$); CEC, Cationic Exchange Capacity
 (meq.100g⁻¹ of clays); ϵ_{max} the maximum axial swelling strain for 100% clay
 sample; θ_{max} the maximum water content for 100% clay sample and ^a 33^b41

259 Table 2: Main properties of the selected clays saturated with Na⁺ and Ca²⁺ as
 260 interfoliar cations

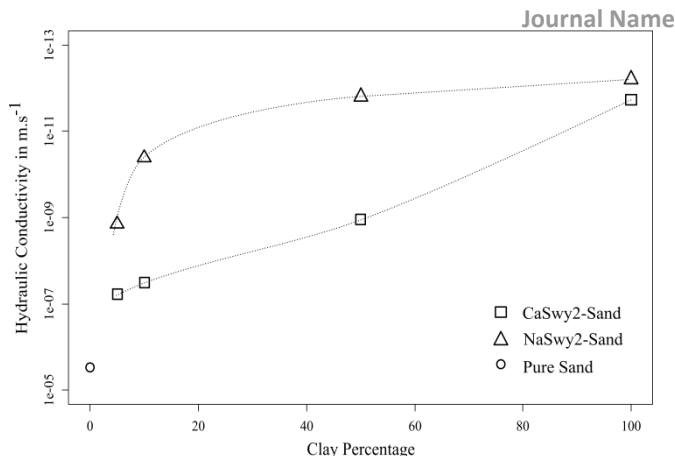


Figure 1: Hydraulic Conductivity as a function of the clay percentage in the clay-sand filter with circle: pure sand, triangles: clay-sand filters with Na-Swy2 and squares: clay-sand filters with Ca-Swy2

261 This specific application should find a good balance
 262 between high permeable Fontainebleau sand and Na- or
 263 Ca-Swy2 clay with a low permeability.

264 Different clay-sand ratios were tested for both Na- and
 265 Ca-SWy2 in order to simulate and calculate the
 266 maximum flow of solution that can pass through the
 267 filter.

268 In accordance with the aim of this work, the ideal clay-
 269 sand ratio should include a low proportion of clay. As
 270 expected, the decrease in K was correlated with the finer
 271 texture related to the increase in clay percentage.
 272 Nevertheless, this evolution differed between the two
 273 clay materials tested (Figure 1):

- 274 - The NaSwy2-Sand mix can be considered as a
 275 waterproof material with K values between
 276 $1.35\text{e}^{-9} \text{ m}\cdot\text{s}^{-1}$ (5% clays) and $1.5\text{e}^{-12} \text{ m}\cdot\text{s}^{-1}$ (50%
 277 clays)
- 278 - The CaSwy2-Sand mix allowed a better
 279 percolation at a low clay proportion with K
 280 between $4.76\text{e}^{-8} \text{ m}\cdot\text{s}^{-1}$ (5% clays) and 1.11e^{-9}
 281 $\text{m}\cdot\text{s}^{-1}$ (50% clays)

282 This permeability gap between the two materials can be
 283 explained by the differences in physico-chemical clay
 284 properties. Whereas the specific surface area and the
 285 cationic exchange capacity were similar for both Na- and
 286 Ca-Swy2 (Table 2), their macroscopic swelling
 287 performance varied greatly impacting their θ_{max} value.

Injection Pressure	0.1 MPa		0.2 MPa	
	S	N	S	N
Matrix Abbreviation	S1	N1	S2	N2
Q	9	9.1	17.9	18
Filter thickness (mm)	4.39	4.24	4.05	3.95
pH	6.5	6.7	6.5	6.7

with S, the ultra-pure water matrix; N, the effluent matrix; Q, the flow in mL.min⁻¹ and pH of the initial solution

288 Table 3 Experimental conditions for percolation experiments with PhACs in
 289 solution through a filter composed of 5% of Ca-Swy2 and 95% of Fontainebleau
 290 sand

291

292 The maximum axial swelling strain ε_{max} , deduced from
 293 the measured axial displacements of the piston,
 294 revealed a high degree of swelling for the Na-Swy2
 295 smectite compared to Ca-Swy2, 37% and 1.5%
 296 respectively (Table 2).

297 The high swelling capacity of Na-Swy2 influenced the
 298 decrease in K especially at a low clay percentage (5%).
 299 Conversely the extremely low macroscopic swelling for
 300 Ca-Swy2 indicates a textural and crystalline swelling
 301 control on the decrease in K . 5% was the clay proportion
 302 selected for the percolation experiments with PhACs in
 303 solution.

304 Ca-Swy2 presents another advantage compared to Na-
 305 Swy2 for a field use: the high macroscopic swelling
 306 capacity of Na-Swy2 under wet conditions could damage
 307 installations which are subjected to dry/wet cycles.
 308 While the mechanical behavior of the Ca-Swy2 smectite
 309 in association with sand was very similar to non-swelling
 310 clay (such as kaolinites) with a low impact of dry/wet
 311 cycles, this adsorbent was characterized by a high
 312 specific surface area, making it suitable for interaction
 313 experiments with emerging organic pollutants.

314 In view of the very low permeability of the NaSwy2-sand
 315 mix, percolation experiments with the PhACs in solution
 316 were carried out only with CaSwy2-sand materials as
 317 filter. The experimental conditions for the percolation
 318 tests with a 5-95% CaSwy2-sand mix are presented in
 319 Table 3.

320 Drug Removal

321 The global removal of the PhAC pool can be used to
 322 estimate the efficiency of the filter in different
 323 experimental conditions.

324 The term C_0 was calculated by the addition of the initial
 325 concentrations of the 14 PhACs and C corresponds to the
 326 addition of the 14 PhAC concentrations for one collected
 327 sample.

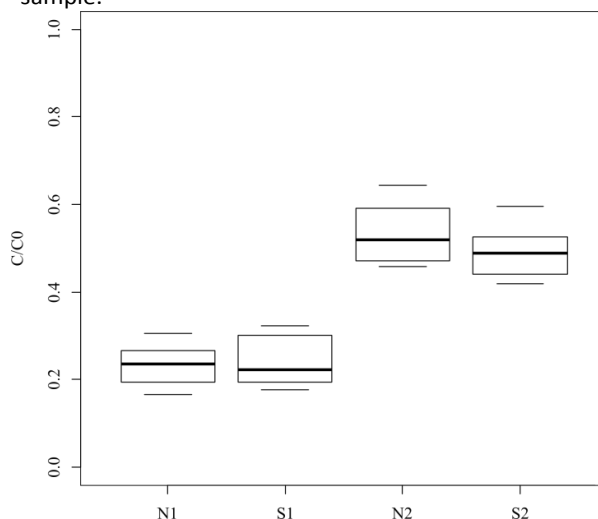


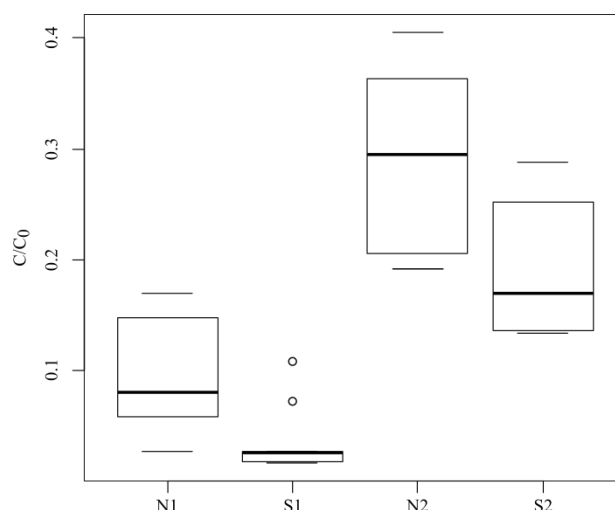
Figure 3: Additive sorption (C/C_0) of all the pharmaceuticals for each experiment: boxes were computed from the removal values added for the 14 pollutants for 10 independent measurements. The line within the box marks the median, boundaries indicate the 25th and 75th percentiles, and error bars indicate the maximum and the minimum removal measurements

328 The spread of the ten values is around 10% of the total
 329 removal (Figure 2) indicating a good regularity in the
 330 sorption capacity of the tested material. The adsorption
 331 capacity was significant (i.e. > 40%) for all the
 332 experimental conditions and the total removal reached
 333 was between the extreme values of 35 and 85%. No
 334 significant differences in total C/C_0 in the global removal
 335 were observed for the two matrices at the same
 336 pressure ($p = .04$ and $.06$ at 0.1 and 0.2 MPa
 337 respectively). The median removal was around 75% at
 338 0.1 MPa and 50% at 0.2 MPa whatever the matrix. The
 339 enrichment of the matrix with natural organic matter
 340 (NOM) and electrolytes (matrix N) appeared to have no
 341 impact on global removal whereas the drop in injection
 342 pressure significantly enhanced removal ($p < .01$ between
 343 N1 and N2 and between S1 and S2).

344 Partition and removal efficiency of targeted PhACs

345 The solid-liquid distribution coefficient (K_d) is often used
 346 to determine the ability of a material to sorb compounds
 347 from a solution. This parameter was used to calculate
 348 the partition between the solution and the sorbent for
 349 each collected sample and estimate its variability
 350 between the ten samples for each percolation
 351 experiment. Unlike modeling equations of sorption
 352 kinetic, the K_d value does not directly depend on the
 353 duration of the experiment.

354 Due to the chosen solid-liquid ratio, PhACs were half-
 355 sorbed (50:50) if, $\text{Log } K_d = 3.40 \text{ L.kg}^{-1}$, and the starting
 356 concentration is precisely $25 \mu\text{g.L}^{-1}$.



357 Figure 2: Additive sorption (C/C_0) of the cationic pharmaceuticals for each
 358 experiment: boxes were computed from the removal values added for the 14
 359 pollutants for 10 independent measurements. The line within the box marks the
 360 median, boundaries indicate the 25th and 75th percentiles, and error bars
 361 indicate the maximum and the minimum removal measurements

362 Cationic Species

363 Two major trends emerged from the analysis of the total
 364 C/C_0 values for the cationic species (Figure 3).

365 The decrease in the injection pressure, corresponding to
 366 a slowdown of the flux was a favorable factor for
 367 sorption. For all the compounds, the transition from S2
 368 to S1 was accompanied by a significant increase in the
 369 $\text{Log } K_d$ ($p < .01$ for the whole cationic compounds)
 370 together with an increase in the total removal (Figure 3).

	S1		N1		S2		N2		onto Sludge
	Log K_d	MRv	Log K_d	MRv	Log K_d	MRv	Log K_d	MRv	Log K_d
Cationic Species									
ATE	4.99 ± 0.03	97.0 ± 0.04	4.34 ± 0.04	87.6 ± 0.09	3.43 ± 0.05	46.2 ± 0.41	3.31 ± 0.04	37.2 ± 0.39	1.58 ^a
COD	4.74 ± 0.02	95.2 ± 0.03	4.31 ± 0.04	88.6 ± 0.11	4.03 ± 0.06	73.2 ± 0.24	4.26 ± 0.02	86.4 ± 0.09	1.15 ^{a,b}
DOX	5.79 ± 0.01	99.6 ± 0.01	4.86 ± 0.02	96.2 ± 0.03	5.38 ± 0.01	98.9 ± 0.01	4.57 ± 0.02	93.2 ± 0.03	2.14 ^b
MET	5.09 ± 0.03	96.9 ± 0.03	4.34 ± 0.03	89.0 ± 0.08	4.01 ± 0.03	77.2 ± 0.16	3.96 ± 0.01	75.8 ± 0.12	1.81 ^b
TRA	4.63 ± 0.03	94.3 ± 0.04	3.96 ± 0.04	74.6 ± 0.24	3.94 ± 0.02	77.2 ± 0.14	3.65 ± 0.02	60.4 ± 0.19	1.67 ^b
TRI	4.76 ± 0.02	95.3 ± 0.06	4.90 ± 0.04	96.4 ± 0.03	4.87 ± 0.05	95.0 ± 0.04	4.36 ± 0.02	91.4 ± 0.07	1.15 ^b
Neutral Species									
DIA	4.20 ± 0.03	86.5 ± 0.07	4.19 ± 0.03	86.1 ± 0.09	3.45 ± 0.04	44.4 ± 0.46	4.33 ± 0.04	90.1 ± 0.59	1.72 ^b
OXA	3.78 ± 0.01	71.6 ± 0.09	3.84 ± 0.01	74.4 ± 0.12	2.01 ± 0.13	2.0 ± 0.56	3.17 ± 0.01	34.4 ± 0.19	1.11 ^b
PRO	4.92 ± 0.01	97.4 ± 0.01	4.76 ± 0.02	96.1 ± 0.03	5.80 ± 0.03	99.5 ± 0.01	5.77 ± 0.03	99.6 ± 0.01	3.28 ^a
Anionic Species									
DCF	3.45 ± 0.02	55.3 ± 0.12	3.60 ± 0.02	59.8 ± 0.19	2.99 ± 0.02	26.2 ± 0.35	3.01 ± 0.02	28.9 ± 0.36	1.2 ^c
GEM	3.76 ± 0.02	71.6 ± 0.09	3.72 ± 0.02	67.2 ± 0.18	2.71 ± 0.05	13.9 ± 0.72	3.48 ± 0.01	52.6 ± 0.16	0.95 ^a
IBU	3.07 ± 0.02	34.2 ± 0.35	3.35 ± 0.01	48.3 ± 0.22	2.08 ± 0.04	5.1 ± 0.58	2.61 ± 0.04	12.5 ± 0.93	2.23 ^a
KET	4.11 ± 0.04	81.9 ± 0.03	4.12 ± 0.02	84.5 ± 0.09	3.44 ± 0.04	40.0 ± 0.56	3.99 ± 0.01	79.8 ± 0.05	-
NAP	3.12 ± 0.02	40.4 ± 0.29	3.55 ± 0.02	53.7 ± 0.41	2.26 ± 0.12	6.1 ± 0.86	2.96 ± 0.01	24.5 ± 0.27	2.08 ^a

with Log K_d in $L \cdot kg^{-1}$, MRv in %, Relative Standard Deviation values equal to Average/Standard Deviation for $n=8$ (clipped for the two extreme samples) and values onto sludge from a^{42} , b^{43} and c^{44}

371 Table 4: Log K_d values and Mean Removal values (in %) for selected pollutants
 372 ± Relative Standard Deviation for each experiment, compared to Log K_d values
 373 found for PhACs onto sludge in the literature

374 Whereas for the S2 experiment, Log K_d values varied
 375 between ATE (3.43) and DOX (5.38), Log K_d values were
 376 more homogeneous for the S1 experiment (Table 4).
 377 Whatever the injection pressure, the retention of
 378 cationic PhACs was generally favored in the case of ultra-
 379 pure water (S), except for TRI at 0.1 MPa and COD at 0.2
 380 MPa for which the opposite was recorded. The cationic
 381 PhACs were probably in competition with other
 382 components (organic or inorganic) contained in the
 383 wastewater effluent. As a result, the adsorption of
 384 cationic PhACs was lower in matrix N than S ($p < .01$ for
 385 the two injection pressures).

386 Anionic species

387 For anionic PhACs, the shift to a lower injection pressure
 388 was also favorable for sorption (Figure 4), especially for
 389 IBU in ultra-pure water (S2 vs S1) (Table 4). These results
 390 indicated that the interaction kinetic is an important
 391 component of the sorption, as for cationic PhACs.
 392 The complexation of the matrix, especially at 0.2 MPa,
 393 significantly increased the sorption of all the anionic
 394 PhACs ($p < .01$ at 0.1 and 0.2 MPa). Between S1 and N1,
 395 except for IBU, DCF and NAP (e.g. 3.10 to 3.54
 396 respectively), the variations in Log K_d values were not
 397 statistically significant ($p = .44$ and $.36$ for GEM and KET
 398 respectively).

399 Neutral Species

401 The solid-liquid distribution variations for the three
 402 neutral PhACs did not follow a trend. It was therefore
 403 difficult to evaluate the impact of the matrix or of the
 404 injection pressure. Whereas PRO was well sorbed
 405 whatever the experimental conditions, for DIA and OXA,
 406 variations in the Log K_d values were closer to the
 407 behavior of anionic species (Table 4).

408 Partition control factors

409 The effect of ionic strength or of the presence of organic
 410 matter in water, which can favor the sorption of anionic
 411 species, was confirmed by the experimental results as
 412 suggested in other studies.⁴⁵ This assumption can be
 413 explained by the adsorption of organic compounds or
 414 electrolytes which could enhance the anionic sorption
 415 capacities of the clay material.⁴⁶
 416 Kinetic transfer is the second major influence on the
 417 sorption capacity. The sorption improvement is
 418 particularly strong on anionic species, whose sorption
 419 kinetic is known to be slower to reach equilibrium,⁴⁷
 420 than that of cationic species (Figure 4).²⁷
 421 Measurements of Log K_d values are generally performed
 422 onto sludge to better understand the partition of PhACs
 423 during waste-water treatment.⁴²⁻⁴⁴ Thus, sorption on
 424 sludge can be considered as a removal despite the

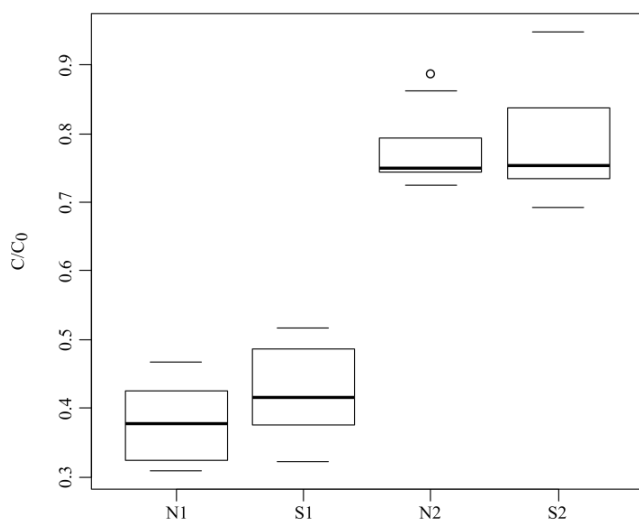


Figure 4: Additive sorption (C/C_0) of the anionic pharmaceuticals for each experiment: boxes were computed from the removal values added for the 14 pollutants for 10 independent measurements. The line within the box marks the median, boundaries indicate the 25th and 75th percentiles, and error bars indicate the maximum and the minimum removal measurements

425 variable further use of sludge. If we compare the Log K_d
 426 values onto secondary sludge in the literature for each
 427 compound (Table 4), there is no link between the charge
 428 of the pollutant and the Log K_d . IBU or NAP are well
 429 sorbed onto sludge whereas other anionic compounds
 430 have a Log $K_d < 2$. These compounds were also among
 431 the three anionic compounds to be significantly better
 432 sorbed in N matrix than S (Table 4) at 0.1 MPa. The
 433 combination of these two factors demonstrated the
 434 NOM impact on the sorption of some anionic PhACs.
 435 For cationic species, only one value (for DOX) exceeds 2
 436 and only the neutral compound PRO is well sorbed by
 437 sludge.

438 The affinity of our material with PhACs was far greater
 439 than that of sludge, with Log K_d values up to at least for
 440 the N1 experiment, indicating that the chosen material
 441 has better trapping properties than sludge.

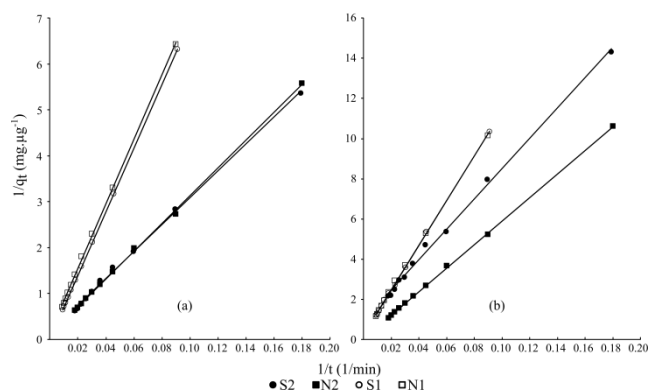
442 The greater complexity of sludge in terms of chemical
 443 reactivity results in a variable affinity with the targeted
 444 PhACs that does not depend only on the charge of the
 445 pollutants,⁴⁸ whereas with clay material, the charge
 446 seems to play the most important role in the control of
 447 sorption.

448 Sorption kinetics modeling

449 Based on the obtained correlation coefficients of the
 450 three models tested that spread out from 0.90 to 0.999
 451 (Tables S3, S4 and S5), it appears that the experimental
 452 data are better adjusted with Bangham equation (r^2
 453 comprised between 0.970 and 0.999). Nevertheless, the
 454 whole models used here provide similar trends. The
 455 efficiency of the adsorption is enhanced at high pressure
 456 as shown by k_1 constants (first-order Lagergren). Figures
 457 5 and 6 confirm and highlights the sorption rate was
 458 higher at 0.2 MPa than at 0.1 MPa indicating a better
 459 sorption efficiency at higher kinetic percolation.

460 The second-order Lagergren (Table S4) and Bangham
 461 (Table S5) equations suggested a good regularity of the
 462 removal quality of the material as Log K_d standard
 463 deviation values expressed.

464 For the best sorbed compounds DOX, PRO and TRI, the
 465 comparison of k_2 and q_m values indicated the same
 466 trends as those observed with the Log K_d analysis on the
 467 matrix effect. An increase in log k_2 corresponding with a
 468 drop in q_m between respectively S and N (for each
 469 injection pressure) indicated a matrix effect that was
 470 unfavorable for the adsorption of cationic compounds.



471 Figure 6: Pseudo second-order fits (solid lines) for (a) Metoprolol
 472 (cationic) and (b) Diazepam (neutral) for each experiment

473 The exact opposite was observed for IBU, OXA and NAP,
 474 with a lower log k_2 and a higher q_m for N than S. For the
 475 other compounds, the data can be interpreted as shown
 476 in Figure 5. For cationic species, there was a slight
 477 unfavorable effect of the N matrix whereas the opposite
 478 was observed for anionic species.

479 Unlike the Log K_d values, the modeling and resulting
 480 sorption efficiency values gave contrasting results. The
 481 main controlling factor for the sorption capacity of Ca-
 482 Swy2 towards PhACs is the chemical properties of the
 483 molecule. As this material has a greater cationic than
 484 anionic exchange capacity, cationic compounds were
 485 strongly favored for sorption.

486 Otherwise, the sorption of anionic compounds was
 487 slightly better in effluent matrix than in ultra-pure water
 488 but it remained significantly lower than for cationic
 489 compounds. This enhancement of anionic species
 490 adsorption by the addition of NOM or electrolytes has
 491 already been reported for IBU alone onto
 492 montmorillonite, indicating that without a saturation
 493 effect, the behavior of a pool of PhACs with Ca-Swy2 is
 494 similar to that of a single PhAC.

495 Model fittings demonstrated that Ca-Swy2 has a large
 496 sorption capacity spectrum even if the molecular charge
 497 remained a key factor for the removal ratio.

498 While the better removal efficiency at a lower injection
 499 pressure seemed to improve sorption, modeling results
 500 showed that the sorption rate was higher for higher
 501 injection pressures. With a view to optimizing the kinetic
 502 transfer through the filter, further data need to be
 503 obtained to combine the best removal efficiency with
 504 the best sorption rate constant.

505 Clays characterization

506 Clays were separated from sand after the leachate test
 507 for further characterization. Two methods were applied
 508 to investigate the adsorbent reaction to the leachate,
 509 XRD and FTIR analysis.

510 XRD and FTIR exhibited no significant layer expansion or
 511 band stretching respectively after experiments.

512 Elemental analyses were carried out on the clay minerals
 513 after the percolation of 1 liter in order to estimate the

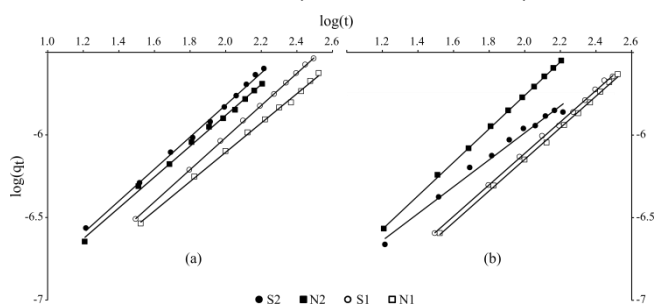


Figure 5: Bangham fits (solid lines) for (a) Tramadol (cationic) and (b) Ketoprofen (anionic) for each experiment

514 total sorbed concentration based on the carbon
515 percentage of the clays (Figure 7).

516 The comparison between elemental analyses on clays
517 and leachate sample analyses exhibited similar results
518 for the ultra-pure water matrix. This is consistent with
519 the assumption that clays are responsible for most of
520 the sorption in comparison with sand. Similar results
521 between clays and water samples also indicated that
522 PhACs are effectively adsorbed onto Ca-Swy2 and not
523 degraded furthermore.

524 In accordance with previous results obtained from
525 solution analyses, the total sorbed concentration was
526 higher for S1 than S2, with a total removal of 65.7% and
527 48.2% respectively.

528 For N matrices, the elemental analysis results are
529 significantly higher than those of the leachate samples.
530 This indicates that the material adsorbed more than
531 PhACs from the effluent matrix. The additional organic
532 compounds that were adsorbed may possibly explain the
533 better sorption for anionic compounds in the effluents.⁴⁹

534 Sorption Mechanisms

535 Despite the excellent removal efficiency of the prepared
536 mineral mixture in this study, sorbed PhACs amounts
537 remain low due to the selected starting concentrations
538 that were $25 \mu\text{g}\cdot\text{L}^{-1}$. Since the sorbed amounts for the
539 whole PhACs were rather low, it was rather hard to
540 probe any changes through the use of classical analytical
541 techniques such as FTIR or XRD, which may acknowledge
542 us about conformation of molecules and their
543 localization for a proper description of the adsorption
544 processes.

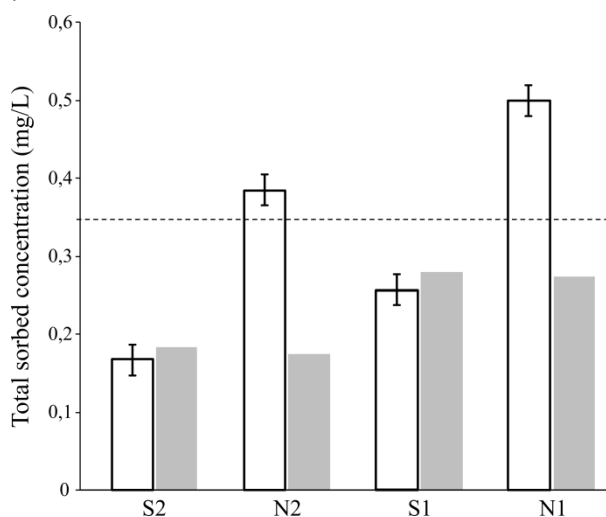


Figure 7: Comparison between the total sorbed concentrations calculated by elemental analysis of clays (white bars) and from the leachate samples (gray bars) for each percolation test. The dotted line corresponds to the total injected concentration of PhACs

545 Nevertheless, it appears that the sorption of anionic
546 PhACs is particularly enhanced for clay mineral with Ca^{2+}
547 as compensating cations. Indeed, Ca^{2+} is divalent and
548 showed its ability to sorb anionic species by cationic
549 bridges.⁵⁰ Here, the results suggest a better sorption
550 efficiency of anionic species in contrast to previous
551 studies using sodium exchanged Na-Swy2.^{49,51} However
552 electrostatic interactions or even hydrogen bonds cannot
553 be excluded that may play also as driving forces for the
554 adsorption. Further experiments need to be carried out
555 to better point out the sorption mechanisms.

556 Cationic species are usually adsorbed on clay mineral
557 through cation exchanges and it may also the case for
558 PhACs here. This mechanism is thermodynamically
559 spontaneous,²⁷ but only compensating cations on the
560 external surfaces are involved since no changes in the
561 diffraction patterns were observed.

562 Conclusions

563 From the results of this study, the following conclusions
564 can be drawn:

- 565 - Natural Ca-saturated smectite (Ca-Swy2)
566 incorporated into a sand-filter allowed a flow
567 consistent with *in-situ* applications whereas Na-
568 saturated smectite (Na-Swy2) is a waterproof
569 material that is not adapted to the sorption of
570 pollutants in a simulation of dynamic sorption
571 close to field reality
- 572 - Ca-Swy2 exhibited a large adsorption capacity
573 even for cationic, neutral and anionic PhACs at
574 similar wastewater pH. With the values of the
575 relative standard deviation of samples, it seems
576 that the sorption efficiency in time is steady.
577 The sorption capacity is guided by two major
578 parameters, infiltration kinetics and the
579 composition of the matrix.
- 580 - The effluent matrix played a contrasting role on
581 the sorption efficiency, depending on the
582 molecular charge and the speciation at the
583 tested pH: anionic species were favored by this
584 complex matrix in contrast to cationic ones, for
585 which the sorption efficiency was lower. Some
586 NOM and/or electrolytes of the effluent were
587 also adsorbed onto the filter and played a key
588 role in the sorption of anionic compounds
589 whereas they were in competition with cationic
590 species. Further analyses need to be carried out
591 to characterize them.
- 592 - The applied models fitted our data well, but
593 due to the pseudo equilibrium that was
594 reached, the calculated constants did not
595 correspond to previous observations for all the
596 models. However, even a low kinetic (0.1 MPa)
597 favored sorption processes, and at higher
598 injection pressure sorption processes were
599 more efficient

600 - Natural Ca-smectite is a slightly modified
601 material that could significantly improve the
602 removal efficiency of current treatment chains,
603 especially concerning the removal of PhACs.
604 - The key role played by the interlayer cation can
605 direct the choice of geosorbent for further
606 studies, using clays minerals that are naturally
607 saturated by Ca²⁺, rather than by Na⁺
608 - Implementation in the field of the tertiary
609 treatment technique presented here requires
610 further experiments. Nevertheless, this study
611 stresses out the relevance of the material in a
612 field application for a good removal efficiency
613 especially in comparison with tertiary
614 treatments using chemical products, potentially
615 toxic for the environment. The main question
616 now is the management costs induced by this
617 technique, especially concerning the durability
618 of the filter.

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625

626 Notes and references

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