Clayey-sand filter for the removal of pharmaceuticals from wastewater effluent: Percolation experiments
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To cite this version:
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T. Thiebault, M. Boussafir, R. Guégan, C. Le Milbeau and L. Le Forestier

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 $4.78 \times 10^{-6}$ m.s$^{-1}$ for 5%-95% clay-sand ratio. The sorption of PhACs onto this filter was investigated using edometer 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 ~45% at 0.2 MPa and ~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.
pure water or effluent of slightly modified clay to treat a complex solution in study addressed three main remove numerous compounds from water, the present hydrodynamic behavior. Cation, which geosorbent affinities between the tested materials and the targeted pollutants. Those found in natural environments and water purification plants are necessary in order to estimate the efficiency of sand and clay mixtures and the real affinities between the tested materials and the targeted pollutants. A similar concern also frames the choice of the geosorbents and their characteristics as interlayer cation, which controls the sorption capacity and hydrodynamic behavior. In view of the well-established capacity of clays to remove numerous compounds from water, the present study addressed three main issues: (i) the real capacity of slightly modified clay to treat a complex solution in pure water or effluent (ii) the impact of the kinetic transfer and the matrix effect on the sorption and (iii) the feasibility of a clay-based filter for the removal of PhACs.

Natural materials such as clays offer a good balance between reactivity and cost for the treatment of effluents. The efficiency of clays CEC (Cationic Exchange Capacity) in water is well documented. After all, numerous PhACs are not in cationic form but in neutral or anionic form in environmental conditions. Another key parameter is the influence of the solid-liquid ratio, which is often very remote from realistic applications. The latter two studies sought to gain a better understanding of sorption mechanisms for which starting concentrations are often largely overestimated compared to simulation approaching field conditions. To our knowledge, no study has investigated the sorption of PhACs at low starting concentrations (25 µg.L⁻¹) onto natural clays. However sorption experiments with PhAC concentrations that are as close as possible to those found in natural environments and water purification plants are necessary in order to estimate the efficiency of sand and clay mixtures and the real affinities between the tested materials and the targeted pollutants. Materials and Methods Filter: clay minerals and sand

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

PhACs and chemical reagents

<table>
<thead>
<tr>
<th>Drug</th>
<th>Abbreviation</th>
<th>CAS-Number</th>
<th>Mw</th>
<th>pKa</th>
<th>log Kow</th>
<th>Sw</th>
<th>Charge</th>
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<tbody>
<tr>
<td>Atenolol</td>
<td>ATE</td>
<td>29122-68-7</td>
<td>266.34</td>
<td>9.6</td>
<td>0.16</td>
<td>300</td>
<td>+</td>
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<tr>
<td>Codeine</td>
<td>COD</td>
<td>76-57-3</td>
<td>299.36</td>
<td>8.21</td>
<td>1.2</td>
<td>79 x 10⁷</td>
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<tr>
<td>Diazepam</td>
<td>DIA</td>
<td>439-14-5</td>
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<td>3.4</td>
<td>2.82</td>
<td>50</td>
<td>0</td>
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<tr>
<td>Diclofenac</td>
<td>DCF</td>
<td>15307-79-6</td>
<td>296.15</td>
<td>4.15</td>
<td>4.06</td>
<td>50 x 10⁷</td>
<td>-</td>
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<tr>
<td>Doxepin</td>
<td>DOX</td>
<td>1229-29-4</td>
<td>279.38</td>
<td>8.96</td>
<td>3.86</td>
<td>32 x 10⁷</td>
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<tr>
<td>Gemfibrozil</td>
<td>GEM</td>
<td>25812-30-0</td>
<td>250.33</td>
<td>4.8</td>
<td>4.33</td>
<td>4.97</td>
<td>-</td>
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<tr>
<td>Ibuprofen</td>
<td>IBU</td>
<td>15687-27-1</td>
<td>206.28</td>
<td>4.91</td>
<td>3.72</td>
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<tr>
<td>Ketoprofen</td>
<td>KET</td>
<td>22071-15-4</td>
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<td>4.45</td>
<td>2.81</td>
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<td>Metoprolol</td>
<td>MET</td>
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<td>1.79</td>
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<tr>
<td>Naproxen</td>
<td>NAP</td>
<td>22204-53-1</td>
<td>230.26</td>
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<td>3</td>
<td>15.9</td>
<td>-</td>
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<tr>
<td>Oxazepam</td>
<td>OXA</td>
<td>604-75-1</td>
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<td>1.7</td>
<td>11.6</td>
<td>2.31</td>
<td>20.71</td>
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<td>Progesterone</td>
<td>PRO</td>
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<td>-</td>
<td>4.04</td>
<td>8.81</td>
<td>0</td>
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<tr>
<td>Tramadol</td>
<td>TRA</td>
<td>27203-92-5</td>
<td>263.37</td>
<td>9.41</td>
<td>2.51</td>
<td>75 x 10⁷</td>
<td>+</td>
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<td>Trimethoprim</td>
<td>TRI</td>
<td>738-70-5</td>
<td>290.32</td>
<td>7.2</td>
<td>0.38</td>
<td>400</td>
<td>0</td>
</tr>
</tbody>
</table>

With Mw, the molecular weight in g.mol⁻¹, pKa the acid dissociation constant, log Kow, the octanol/water partition coefficient, Sw, 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
Percolation Experiments

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

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

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

In order to control impact of the matrix on the adsorption of PhACs, two solutions were used in the experiments: (i) a mix, hereafter called S, of each of the 14 selected PhACs at concentrations around 25 µg.L⁻¹ in ultra-pure water, and (ii) a mix between the 14 PhACs and an effluent of a French rural WWTP, called N. Although PhACs were present in this effluent their maximum concentration around 200 ng.L⁻¹ did not affect our results by modifying starting concentrations noticeably (Table S1 for details, and Table S2 for the chemical parameters of the chosen effluent).

The choice of the starting concentration at 25 µg.L⁻¹ for each PhAC corresponds to the maximum PhAC concentrations in some effluents.  

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

Leachate and clay analyses

Leachate analysis

Leachate solutions were concentrated by Solid-Phase Extraction (SPE) and analyzed by Gas Chromatography coupled to Mass Spectrometry (GC-MS). PhAC extraction was carried out on a 6mL glass cartridge filled with HR-X phase (Macherey-Nagel). Cartridges were conditioned with 5 mL of MeOH then with 5mL of ultra-pure water. Columns were filled with 100 mL of sample and then rinsed with 5 mL of ultra-pure water before drying for 30 minutes under vacuum. Finally, evaporation was performed with 3 x 5 mL of MeOH.

Thereafter, internal standard was added to organic layers, which were evaporated under reduced pressure. Residues were derivatized with MTBSTFA according to Schummer et al.  

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

The temperature of the column was held at 50°C for 3 min, increased from 50 to 120°C at 30°C.min⁻¹, and from 120 to 310°C at 3°C.min⁻¹ with a final isothermal hold at 310°C for 21 min. 2 µL of sample was injected in splitless mode at 280°C. Helium was the carrier gas (1 mL.min⁻¹).

The mass spectrometer was operated in El mode at 70 eV, from m/z 50 to 500.

Clay characterization and global carbon analysis

X-ray diffraction (XRD) patterns were recorded between 2 and 64° (2θ) using a Thermo Electron ARL’XTRA diffractometer equipped with a Cu anode (Cu Kα1,2 = 1.5418 Å) coupled with a Si(li) solid detector. Experimental measurement parameters were 10s counting time per 0.04°2θ step. The diffractograms were performed with dry powder samples (100°C for 24 h).

Fourier transform infrared (FTIR) measurements were recorded in the range 650-4000 cm⁻¹, using a Thermo Nicolet 6700 FT spectrometer equipped with a Deuterated Triglycine Sulfate (DTGS) detector and a Nicolet Continuum microscope. The analyses were performed in transmission mode and each spectrum was the average of 256 scans collected at 2 cm⁻¹ resolution.

Carbon and nitrogen analyses were performed on powdered samples by using a Thermo Scientific Flash 2000 organic analyzer assuming an analytical error of 0.05%.

Data analysis

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

\[ \log(K_d) = \frac{d}{q_s} \]

with \( K_d \) the solid-liquid distribution coefficient (L.kg⁻¹), \( d \) the sorbed concentration (mg.kg⁻¹) and \( q_s \) the equilibrium concentration (mg.L⁻¹).

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

To estimate the link between time and sorption capacity and to describe the sorption dynamic, the first-order Lagergren equation, the second-order kinetics model and the Bangham equations are often used.
These equations are expressed in linear form by equations (2)-(4) respectively:

\[
\log(q_m - q_t) = \log q_m - \frac{k_1}{z \cdot 303} t
\]  
(2)

\[
\frac{q_t}{q_m} = 1 - \frac{t}{k_2 q_m} + \frac{1}{q_m} t
\]  
(3)

\[
\log q_t = \log k_b + \frac{t}{n} \log t
\]  
(4)

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

Each equation is based on different assumptions:

(i) the first-order Lagergren model considers that the quantity of unoccupied adsorption sites is proportional to the adsorption rate of adsorbate onto adsorption sites

(ii) the second-order kinetic model assumes that the adsorption is chemically accomplished

(iii) The Bangham equation considers a fast velocity of adsorption and a slow attainment of sorption equilibrium

These equations were applied to the experimental results.

Results and discussion

Hydrodynamic properties

Percolation experiments were first performed with water solution in order to determine the hydraulic conductivity (K) of the different clay-sand materials. K, expressed in m.s\(^{-1}\), was calculated from Darcy’s law, using the expression developed for a saturated medium:

\[
K = \frac{Q}{\delta S}
\]

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

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

<table>
<thead>
<tr>
<th>Clays</th>
<th>SSA (m(^2).g(^{-1}))</th>
<th>CEC (meq.100g(^{-1}))</th>
<th>( \varepsilon_{\text{max}} )</th>
<th>( \Theta_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Swy2</td>
<td>45.4</td>
<td>85.0±2.7</td>
<td>37%</td>
<td>75%</td>
</tr>
<tr>
<td>Ca-Swy2</td>
<td>46.0</td>
<td>85.1±0.01</td>
<td>1.5%</td>
<td>62%</td>
</tr>
</tbody>
</table>

With SSA, Specific Surface Area (m\(^2\).g\(^{-1}\)); CEC, Cationic Exchange Capacity (meq.100g\(^{-1}\) of clays); \( \varepsilon_{\text{max}} \), the maximum axial swelling strain for 100% clay sample; \( \Theta_{\text{max}} \), the maximum water content for 100% clay sample.

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

- The Na-Swy2-Sand mix can be considered as a waterproof material with K values between 1.35e\(^{-9}\) m.s\(^{-1}\) (5% clays) and 1.5e\(^{-12}\) m.s\(^{-1}\) (50% clays)
- The Ca-Swy2-Sand mix allowed a better percolation at a low clay proportion with K between 4.76e\(^{-9}\) m.s\(^{-1}\) (5% clays) and 1.11e\(^{-9}\) m.s\(^{-1}\) (50% clays)

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

<table>
<thead>
<tr>
<th>Injection Pressure</th>
<th>0.1 MPa</th>
<th>0.2 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>S</td>
<td>N</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>S1</td>
<td>N1</td>
</tr>
<tr>
<td>Q</td>
<td>9</td>
<td>9.1</td>
</tr>
<tr>
<td>Filter thickness</td>
<td>4.39</td>
<td>4.24</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>6.7</td>
</tr>
</tbody>
</table>

with S, the ultra-pure water matrix; N, the effluent matrix; Q, the flow in mL.min\(^{-1}\) and pH of the initial solution.

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

Different clay-sand ratios were tested for both Na- and Ca-Swy2 in order to simulate and calculate the maximum flow of solution that can pass through the filter.

Table 2: Main properties of the selected clays saturated with Na\(^+\) and Ca\(^{2+}\) as interfoliar cations

Table 3 Experimental conditions for percolation experiments with PhACs in solution through a filter composed of 5% of Ca-Swy2 and 95% of Fontainebleau sand
The maximum axial swelling strain $\varepsilon_{\text{max}}$ deduced from the measured axial displacements of the piston, revealed a high degree of swelling for the Na-Swy2 smectite compared to Ca-Swy2, 37% and 1.5% respectively (Table 2). The high swelling capacity of Na-Swy2 influenced the decrease in $K$ especially at a low clay percentage (5%). Conversely the extremely low macroscopic swelling for Ca-Swy2 indicates a textural and crystalline swelling control on the decrease in $K$. 5% was the clay proportion selected for the percolation experiments with PhACs in solution.

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

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

**Drug Removal**

The global removal of the PhAC pool can be used to estimate the efficiency of the filter in different experimental conditions. The term $C_0$ was calculated by the addition of the initial concentrations of the 14 PhACs and $C$ corresponds to the addition of the 14 PhAC concentrations for one collected sample.

The spread of the ten values is around 10% of the total removal (Figure 2) indicating a good regularity in the sorption capacity of the tested material. The adsorption capacity was significant (i.e. > 40%) for all the experimental conditions and the total removal reached was between the extreme values of 35 and 85%. No significant differences in total C/C$_0$ in the global removal were observed for the two matrices at the same pressure ($p = .04$ and .06 at 0.1 and 0.2 MPa respectively). The median removal was around 75% at 0.1 MPa and 50% at 0.2 MPa whatever the matrix. The enrichment of the matrix with natural organic matter (NOM) and electrolytes (matrix N) appeared to have no impact on global removal whereas the drop in injection pressure significantly enhanced removal ($p<.01$ between N1 and N2 and between S1 and S2).

**Partition and removal efficiency of targeted PhACs**

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

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

**Cationic Species**

Two major trends emerged from the analysis of the total C/C$_0$ values for the cationic species (Figure 3). The decrease in the injection pressure, corresponding to a slowdown of the flux was a favorable factor for sorption. For all the compounds, the transition from S2 to S1 was accompanied by a significant increase in the $\log K_d$ ($p<.01$ for the whole cationic compounds) together with an increase in the total removal (Figure 3).
indicate the maximum and the minimum removal measurements between the 25th and 75th percentiles, and error bars indicate the maximum and the minimum removal measurements.

Whereas for the S2 experiment, Log $K_d$ values varied between ATE (3.43) and DOX (5.38), Log $K_d$ values were more homogeneous for the S1 experiment (Table 4). Whereas the injection pressure, the retention of cationic PhACs was generally favored in the case of ultra-pure water (S), except for TRI at 0.1 MPa and COD at 0.2 MPa for which the opposite was recorded. The cationic PhACs were probably in competition with other components (organic or inorganic) contained in the wastewater effluent. As a result, the adsorption of cationic PhACs was lower in matrix N than S (p<0.01 for the two injection pressures).

For anionic PhACs, the shift to a lower injection pressure was also favorable for sorption (Figure 4), especially for IBU in ultra-pure water (S2 vs S1) (Table 4). These results indicated that the interaction kinetic is an important component of the sorption, as for cationic PhACs.

The complexation of the matrix, especially at 0.2 MPa, significantly increased the sorption of all the anionic PhACs (p<0.01 at 0.1 and 0.2 MPa). Between S1 and N1, except for IBU, DCF and NAP (e.g. 3.10 to 3.54 respectively), the variations in Log $K_d$ values were not statistically significant (p = .44 and .36 for GEM and KET respectively).

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

The effect of ionic strength or of the presence of organic matter in water, which can favor the sorption of anionic species, was confirmed by the experimental results as suggested in other studies. This assumption can be explained by the adsorption of organic compounds or electrolytes which could enhance the anionic sorption capacities of the clay material.

Kinetic transfer is the second major influence on the sorption capacity. The sorption improvement is particularly strong on anionic species, whose sorption kinetic is known to be slower to reach equilibrium, than that of cationic species (Figure 4).

Measurements of Log $K_d$ values are generally performed onto sludge to better understand the partition of PhACs during waste-water treatment. Thus, sorption on sludge can be considered as a removal despite the
variable further use of sludge. If we compare the Log $K_d$
values onto secondary sludge in the literature for each
compound (Table 4), there is no link between the charge
of the pollutant and the Log $K_d$. IBU or NAP are well
sorbed onto sludge whereas other anionic compounds
have a Log $K_d < 2$. These compounds were also among
the three anionic compounds to be significantly better
sorbed in N matrix than S (Table 4) at 0.1 MPa. The
combination of these two factors demonstrated the
NOM impact on the sorption of some anionic PhACs.
For cationic species, only one value (for DOX) exceeds 2
and only the neutral compound PRO is well sorbed by
sludge.

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

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

**Sorption kinetics modeling**

Based on the obtained correlation coefficients of the
three models tested that spread out from 0.90 to 0.999
(Tables S3, S4 and S5), it appears that the experimental
data are better adjusted with Bangham equation ($r^2$
comprised between 0.970 and 0.999). Nevertheless, the
whole models used here provide similar trends. The
efficiency of the adsorption is enhanced at high pressure
as shown by $k_2$ constants (first-order Lagergren). Figures
5 and 6 confirm and highlights the sorption rate was
higher at 0.2 MPa than at 0.1 MPa indicating a better
sorption efficiency at higher kinetic percolation.

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

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

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

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and only the neutral compound PRO is well sorbed by
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removal quality of the material as Log $K_d$ standard
deviation values expressed.

For the best sorbed compounds DOX, PRO and TRI, the
comparison of $k_2$ and $q_m$ values indicated the same
trends as those observed with the Log $K_d$ analysis on the
matrix effect. An increase in log $k_2$ corresponding with a
drop in $q_m$ between respectively S and N (for each
injection pressure) indicated a matrix effect that was
unfavorable for the adsorption of cationic compounds.
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.29
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 μg 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.](image)

545 Nevertheless, it appears that the sorption of anionic
546 PhACs is particularly enhanced for clay mineral with Ca²⁺
547 as compensating cations. Indeed, Ca²⁺ 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
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) incorporated into a sand-filter allowed a flow consistent with in-situ applications whereas Na-
saturated smectite (Na-Swy2) is a waterproof material that is not adapted to the sorption of pollutants in a simulation of dynamic sorption
566 close to field reality
567 - Ca-Swy2 exhibited a large adsorption capacity even for cationic, neutral and anionic PhACs at
568 similar wastewater pH. With the values of the relative standard deviation of samples, it seems that the sorption efficiency in time is steady.
569 The sorption capacity is guided by two major parameters, infiltration kinetics and the
570 composition of the matrix.
571 - The effluent matrix played a contrasting role on the sorption efficiency, depending on the molecular charge and the speciation at the tested pH: anionic species were favored by this complex matrix in contrast to cationic ones, for which the sorption efficiency was lower. Some NOM and/or electrolytes of the effluent were also adsorbed onto the filter and played a key role in the sorption of anionic compounds whereas they were in competition with cationic species. Further analyses need to be carried out to characterize them.
572 - The applied models fitted our data well, but due to the pseudo equilibrium that was reached, the calculated constants did not correspond to previous observations for all the models. However, even a low kinetic (0.1 MPa) favored sorption processes, and at higher injection pressure sorption processes were more efficient
Natural Ca-smectite is a slightly modified material that could significantly improve the removal efficiency of current treatment chains, especially concerning the removal of PhACs.

The key role played by the interlayer cation can direct the choice of geosorbent for further studies, using clays minerals that are naturally saturated by Ca$^{2+}$, rather than by Na$^+$. Implementation in the field of the tertiary treatment technique presented here requires further experiments. Nevertheless, this study stresses out the relevance of the material in a field application for a good removal efficiency especially in comparison with tertiary treatments using chemical products, potentially toxic for the environment. The main question now is the management costs induced by this technique, especially concerning the durability of the filter.

Acknowledgements

The work received financial support from the HArPE Project (2012-00073536) funded by the Région Centre-Val de Loire. The authors would also like to thank Fabrice Muller for XRD and FTIR analysis and Marielle Hatton for carbon analysis.

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