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# Journal Pre-proof

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Pharmaceuticals in presence of electrolytes

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1 Tuning down the environmental interests of organoclays for emerging  
2 pollutants: pharmaceuticals in presence of electrolytes

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11 **Abstract**

12 The impact of electrolytes on the adsorption of emerging pollutants: pharmaceuticals onto  
13 layered materials: a raw clay mineral and its nonionic and cationic organoclay derivatives was  
14 studied. The selected pharmaceuticals: amoxicillin, norfloxacin, sulfamethoxazole,  
15 metoprolol, carbamazepine, and trimethoprim show different electric charges: zwitterionic,  
16 anionic, cationic and neutral and hydrophobic character (different LogP). Without any salts,  
17 the set of complementary data obtained by UV and infrared spectroscopies, X-ray diffraction  
18 points out the importance of the electric charge which represents a key parameter in both the  
19 spontaneity and feasibility of the adsorption. In contrast, the hydrophobicity of the analytes  
20 plays a minor role but determines the magnitude of the adsorbed amount of pharmaceuticals  
21 onto organoclays. With a dual hydrophilic and hydrophobic behavior, nonionic organoclay  
22 appears to be the most polyvalent material for the removal of the pharmaceuticals. In the

23 presence of electrolytes (NaCl at a concentration of  $1 \times 10^{-2}$  mol L<sup>-1</sup>), both nonionic and  
24 cationic organoclays show a decrease of their efficiencies, whereas the adsorption is  
25 particularly enhanced for Na-Mt except for the cationic species (trimethoprim and  
26 metoprolol). Thus, in realistic experimental conditions close to those of natural effluents, raw  
27 clay mineral appears as the most appropriate sorbent for the studied pharmaceuticals while it  
28 raises the question of the usefulness of organoclays in water remediation strategy.

29

## 30 **1. Introduction**

31 The chemical modification of swelling-type clay minerals, by using surfactants of  
32 different nature: cationic, nonionic, zwitterionic to get organoclays, enhances the adsorption  
33 efficiency but also extends the range of adsorbed organic molecules (Stockmeyer 1991,  
34 Stapleton et al. 1994, Liu and Gonzalez 1999, El-Nahhal and Safi 2004, Groisman et al. 2004,  
35 Shen 2004, Gao and Pedersen 2005, Polubesova et al. 2005, Bekçi et al. 2006, Deng et al.  
36 2006, Polubesova et al. 2006, Guégan et al. 2009, Guégan 2010, Sarkar et al. 2010, Zhang et  
37 al. 2010, Guégan 2011, Lee et al. 2011, Park et al. 2011, Guegan 2013, Zha et al. 2013,  
38 Guégan et al. 2015, Thiebault et al. 2015, De Oliveira and Guégan 2016, De Oliveira et al.  
39 2017, Guégan et al. 2017, De Oliveira et al. 2018). Thus, numerous studies pointed out the  
40 interests of organoclays as adsorbents, going as far as to suggest these materials as perennial  
41 and realistic solutions for the remediation of wastewater or as tertiary treatment for drinking  
42 water (Stockmeyer 1991, Polubesova et al. 2005, Polubesova et al. 2006, Undabeytia et al.  
43 2008). In the latter case, the adsorption displays the main interest to avoid any degradation of  
44 the molecules but requires a recycling of the hybrid materials after being in contact with  
45 pollutants. The efficient adsorption of diverse organic pollutants: pharmaceuticals, and other  
46 phytosanitary products in batch experimental conditions illustrates the interests of cationic  
47 organoclays (Alther 2002, Park et al. 2011). Due to their dual hydrophilic-hydrophobic

48 behaviors and possible cation exchange capacity, nonionic organoclays represent polyvalent  
49 adsorbents towards many organic products (Deng 2003, Guégan et al. 2015, De Oliveira et al.  
50 2018). The previous batch adsorption experiments were conducted under unrealistic  
51 conditions (i.e. use of synthetic water without any organic matter or with only monomolecular  
52 matrix), quite distant from those in natural effluents. Indeed, in effluents, several antagonistic  
53 effects may occur: competition between molecules and organic matter, electrolytes which  
54 may tune down the interests of organoclays as adsorbents.

55 In a natural context, the presence of electrolytes and their fluctuations of concentration  
56 may affect the adsorption/desorption equilibrium lead to a release of adsorbed pollutants onto  
57 layered materials playing the role of carrier phases for pollutants. Besides the complexity of  
58 the whole interaction that may be involved, the impact of ionic strength on the adsorption of  
59 both organic and inorganic species can be considered now as being well established for clay  
60 minerals (Liu and Gonzalez 1999, Gao and Pedersen 2005, Wang et al. 2009): Electrolytes  
61 can act as a screening effect which limits the transfer of the analytes, or enhances the  
62 adsorption through ionic bridges. If the effects of the ionic strength for clay minerals are  
63 relatively well understood, interestingly, research works focusing on organoclays and organic  
64 pollutants including pharmaceuticals appear scarce (Stapleton et al. 1994, El-Nahhal and Safi  
65 2004, Anirudhan and Ramachandran 2006).

66 Pharmaceutical products are frequently found in large quantities in numerous  
67 effluents, with compounds identified as persistent in the natural environment due to their  
68 molecular complexity but also possible associations with mineral phases that may preserve  
69 them. These molecules of relatively moderate molecular masses show various degrees of  
70 freedom and complex molecular behaviors as diverse as their therapeutic actions with  
71 hydrophobic features and acid-base properties that modulate their electrical charge with pH.  
72 Their presence in the natural environment at concentrations reaching several nanograms is

73 recognized to cause adverse effects on many ecosystems and represents a public health matter  
74 involving the interests of numerous scientists focusing on the development of novel  
75 adsorbents (Adriano et al. 2005, Bekçi et al. 2006, Kim et al. 2010, Liu et al. 2011, Moussavi  
76 et al. 2013, Kodešová et al. 2015, De Oliveira and Guégan 2016, Nielsen and Bandosz 2016,  
77 De Oliveira et al. 2017, Limousy et al. 2017).

78         The objective of this study concerns the understanding about the adsorption and  
79 possible desorption of diverse pharmaceuticals onto cationic and nonionic organoclays in the  
80 presence of electrolytes that mimic the experimental conditions of the natural context. Thus,  
81 this research work represents a rupture to the previous studies aiming at characterizing the  
82 adsorption of pharmaceuticals onto organoclays in batch situation with synthetic waters where  
83 only thermal or kinetic parameters were investigated. To understand the impact of the ionic  
84 strength, six pharmaceutical products (PPs) with different features: electric charges (cationic,  
85 zwitterionic, nonionic, anionic or neutral products), hydrophobic character with LogP ranging  
86 from -1.03 to 2.45, were adsorbed onto both nonionic and cationic organoclays. The  
87 effectiveness of adsorption of PPs onto organoclays was compared to: a sodium exchanged  
88 montmorillonite (from Wyoming) via a multi-technique approach including X-ray diffraction,  
89 infrared and UV-Visible spectroscopies, providing important insights in the different  
90 interactional mechanisms and their evolutions in the presence of electrolytes.

91

## 92 **2. Materials and techniques**

### 93 **2.1. Materials**

94 The montmorillonite (Mt) used in that study was obtained from the Source Clay Minerals  
95 Repository, University of Missouri (Columbia, MO). This clay mineral (from Wyoming) was  
96 used as a starting material for organoclay preparation but also as a referenced adsorbent. The  
97 structural formula can be expressed as:  $(Ca_{0.12}Na_{0.32}K_{0.05})[Al_{3.01}Fe(III)_{0.41}Mn_{0.01}Mg_{0.54}Ti_{0.02}]$ -  
98  $[Si_{7.98}Al_{0.02}]O_{20}(OH)_4$ . Mt was fractioned below 2  $\mu m$  by gravity sedimentation. Then, the  
99 resulting clay mineral was purified and sodium ( $Na^+$ ) exchanged. This montmorillonite (Na-  
100 Mt) exhibits a cation exchange capacity (CEC) of 93 meq per 100 g clay.

101 Polyoxyethylene (20) oleyl ether (Brij<sup>®</sup>-O20) and Benzyldimethyltetradecylammonium  
102 (BDTA) chemicals were supplied from Sigma Aldrich Chemical company. These two  
103 chemicals: Brij and BDTA are nonionic and cationic surfactants respectively. Aqueous  
104 solutions of surfactants with Millipore deionized water were prepared at a concentration of 1  
105 time the CEC of Mt clay for BDTA, and at about  $1.13 \times 10^{-3} \text{ mol.L}^{-1}$  for Brij-O-20. Then,  
106 these surfactant solutions were mixed to Mt aqueous dispersions before being stirred at 300  
107 rpm for 24 h. At the end of this procedure, the solutions were centrifuged at 3000 rpm for 20  
108 min and the supernatants were removed and the solid fractions (organoclays) were recovered.  
109 The resulting organoclays were dried at 100°C for 24 h before using them as adsorbents or  
110 prior any analyses.

### 111 **2.2. Experimental techniques**

112 The concentration of the six pharmaceutical compounds before and after being in contact with  
113 the layered adsorbents: raw clay mineral and organoclays was obtained by UV-Visible  
114 analysis using an Evolution 220 spectrophotometer (Thermo Scientific). Fourier transform  
115 infrared (FTIR) measurements in the range  $650\text{-}4000 \text{ cm}^{-1}$ , were recorded using a Thermo

116 Nicolet 6700 FT spectrometer equipped with a Deuterated Triglycine Sulfate (DTGS) detector  
117 and a Nicolet Continuum microscope. The powder samples were spread over a NaCl window  
118 of the microscope. The analyzed sample area was a square of side 100  $\mu\text{m}$  chosen under the  
119 microscope 15X Infinity Reflexchromat objective. The analyses were performed in  
120 transmission mode and each spectrum corresponded to the average of 256 scans collected at 2  
121  $\text{cm}^{-1}$  resolution. The  $d_{001}$  spacing's of the layered materials before and after being in contact  
122 with the antibiotics were determined by the first  $00l$  reflection from the X-rays patterns which  
123 were recorded in a conventional  $\theta$ - $\theta$  Bragg-Brentano configuration by using a Thermo  
124 Electron ARL'XTRA diffractometer equipped with a Cu anode ( $\text{CuK}_{\alpha} = 1.5418 \text{ \AA}$ ) coupled  
125 with a Si(Li) solid detector. The diffractograms on dry samples (100°C for 24 h) were  
126 performed between 1 and 24° ( $2\theta$ ) with an angular and time steps of 0.04° and 10 s,  
127 respectively.

### 128 **2.3. Adsorption of PPs**

129 Amoxicillin (AMX) or 6-(p-hydroxy- $\alpha$ -aminophenylacetamido) penicillanic acid),  
130 Norfloxacin (NFX) or 1-Ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-  
131 quinolinecarboxylic acid, Sulfamethoxazole (SMX) or (4-Amino-N-(5-methyl-3-isoxazolyl))  
132 benzenesulfonamide), Trimethoprim (TRI) (5-[(3,4,5-Trimethoxyphenyl)methyl]-2,4-  
133 pyrimidinediamine), Metoprolol (MTP) or 1-(isopropylamino)-3-[4-(2-  
134 methoxyethyl)phenoxy]propan-2-ol, and carbamazepine (CBZ) or 5-Carbamoyl-5H-  
135 dibenz(b,f)azepine were purchased from Sigma-Aldrich Chemical, and assumed to have a  
136 purity > 98%. These products were used in batch adsorption experiments onto raw clay  
137 mineral and its nonionic and cationic organoclays derivatives using at least 10 initial aqueous  
138 solutions ranging from 10  $\text{mg L}^{-1}$  up to 4  $\text{g L}^{-1}$  (for AMX, or below the possible maximum  
139 concentration according to the solubility of each pharmaceutical compound).



140 AMX displays a LogP of about 0.87 and 2  $pK_a$  couples of 3.23 and 7.43 while NFX show a  
141 LogP of -1.03 and owns 2  $pK_a$  of 5.77 and 8.68 (for strongest acidic and basic form), leading  
142 to cationic-zwitterionic-anionic behavior respectively along the pH range 0-14 (Table 1). In  
143 contrast, SMX with a LogP of 0.89 (solubility in water about  $610 \text{ mg L}^{-1}$  at  $37^\circ\text{C}$ ) shows a  
144  $pK_a$  couple of 6.16 and 1.97 for strongest acidic and basic form respectively, driving to a  
145 cationic-neutral-anionic sequence following the pH. TRI shows a LogP of 1.28 and has a  
146 water solubility of  $400 \text{ mg L}^{-1}$  (at  $25^\circ\text{C}$ ) and exhibits a cationic to neutral behavior  
147 ( $pK_a=7.16$ ). With a similar water solubility of about  $400 \text{ mg L}^{-1}$ , MTP displays the same acid  
148 base behavior with a cationic to neutral sequence ( $pK_a=9.67$ ) and shows a LogP of 1.88.  
149 Finally, CBZ has the largest LogP value at about 2.45 among the selected PPs in this study  
150 and is neutral (or nonionic hydrophobic compound) on the whole pH range with a poor  
151 solubility in water of about  $18 \text{ mg L}^{-1}$ . At a pH value close to that of effluents (pH=6.5 of a  
152 study), AMX and NFX are mainly zwitterionic, with a predominance of about 90 and 80%  
153 and anionic (10%) and cationic (20%) respectively (checked by chromatography analyses and  
154 consolidated by some literature data). SMX shows a neutral–anionic behavior with a ratio of  
155 30/70%. TRI is essentially in its cationic form with a frequency of 80% (20% other species  
156 are in neutral forms) while only MTP cations are present (Table 1).

157 The solid to liquid ratio was identical with 100 mg of sorbents used for 50 mL of PPs aqueous  
158 solutions in centrifuge tubes. Samples were shaken on a rotary shaker at 50 rpm during 24 h  
159 in order to reach the equilibrium and then centrifuged at 5000 rpm for 25 min. Both  
160 supernatants and sorbents after contact with the PPs were removed and analyzed through UV-  
161 Visible spectroscopy. The effect of the ionic strength was achieved by the addition of NaCl  
162 salts at a concentration of  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ . The amount of adsorbed PPs was calculated by  
163 the difference between the initial and equilibrium final concentrations that allowed us to  
164 determine the equilibrium adsorption isotherms. Prior XRD and FTIR characterizations, the

165 entire resulting organoclays and Mt after adsorption of PPs were dried at 100°C for 48 h. No  
166 release of organic compounds was observed based on prior thermal gravimetry analyses (i.e.  
167 organic compounds have large molecular masses with poor volatility and are usually degraded  
168 in the temperature range 250-350°C).

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### 170 3. Results and discussion

#### 171 3.1. Organoclay Characteristics

172 The whole layered materials: BDTA-Mt, Brij<sub>0.4</sub>-Mt organoclays, and Na-Mt were  
173 characterized by both XRD and FTIR (supporting data) analyses. As expected, the proper  
174 intercalation of the surfactants within the interlayer space of the starting Na-Mt was  
175 confirmed by a shift at low angle values ( $2\theta$ ) of the  $00l$  reflections. With the introduced  
176 concentrations (1 time the value of the CEC for the cationic surfactant and a similar amount  
177 for the Brij), the expansion of the interlayer space reaches 18.3 Å for both BDTA-Mt and  
178 Brij<sub>0.4</sub>-Mt organoclays, corresponding to lateral bilayers organization (Figure 1). FTIR spectra  
179 confirm such surfactant organization and show typical features characteristics of the organic  
180 compounds, such as the absorption bands at 2840-2920  $\text{cm}^{-1}$  relative to the symmetric and  
181 antisymmetric  $\text{CH}_2$  stretching vibrations of the surfactant alkyl chains, of which frequencies  
182 stress out gauche conformation of the molecules (Guégan et al. 2009, Guégan 2010, Guegan  
183 2013, Guegan et al. 2016) (supporting data).

184 Since the adsorption properties of the organoclays mainly depend on the kind of surfactants  
185 used, two different surfactants of different nature (nonionic and cationic) and saturated and  
186 unsaturated were used. Thus, the prepared materials display complementary properties: from  
187 cation exchange capacity, and hydrophilicity for untreated Na-Mt, dual hydro-  
188 philicity/phobicity for Brij<sub>0.4</sub>-Mt; to hydrophobicity or organophilicity and even possible  
189 anion adsorption ability for BDTA-Mt (Guégan et al. 2015, De Oliveira and Guégan 2016, De  
190 Oliveira et al. 2017, De Oliveira et al. 2018). In addition, the difference

191

192

193

194

## 195 **3.2. Interaction mechanisms of the PPs onto layered materials without electrolytes**

### 196 *3.2.1. Case of cationic species: Metoprolol and Trimethoprim*

197 The Figure 2 shows the equilibrium adsorption isotherms of the whole pharmaceuticals onto  
198 the three sorbents in this study. These isotherms represent the adsorbed amounts of the  
199 pharmaceuticals onto the layered materials after being in contact for 24 hours under stirring  
200 (batch experiments), as a function of the equilibrium concentration of pharmaceuticals. As  
201 expected for cationic compounds that can be ion-exchanged with the inorganic cations located  
202 within the interlayer space of untreated or raw swelling clay minerals, the adsorption  
203 isotherms onto Na-Mt reveal a Langmuir or L-type line shape, which is well known for  
204 adsorption cases (Figure 2) (Bekçi et al. 2006, Guégan et al. 2015, Thiebault et al. 2015, De  
205 Oliveira et al. 2018). Interestingly similar behavior can be observed onto both nonionic and  
206 cationic organoclays, which thus confirms the proper adsorption of the two cationic  
207 pharmaceuticals (metoprolol and trimethoprim) on the three adsorbents. Interestingly, with a  
208 similar water solubility value as TRI, the adsorption of metoprolol (MTP) displays a different  
209 behavior without any notable saturation for both Na-Mt and Brij<sub>0.4</sub>-Mt, whereas it appears  
210 rather limited onto BDTA-Mt as it could be expected for cationic species (Guégan et al. 2015,  
211 De Oliveira et al. 2018). In the latter case, the adsorbed amount reaches a maximum value of  
212 about  $1.26 \times 10^{-4} \text{ mol g}^{-1}$ , in contrast to those of  $5.08 \times 10^{-4}$  and  $5.62 \times 10^{-4} \text{ mol g}^{-1}$  for Brij<sub>0.4</sub>-  
213 Mt and Na-Mt respectively. Similar trends about the small affinity of the PPs with BDTA-Mt  
214 are reflected with the fitting parameters derived from both the Langmuir and Freundlich  
215 models which are minimum. The Freundlich constant  $K_F$  represents the volume of water that  
216 can be treated per gram of material. By using this parameter to list a material adsorption  
217 capacity, it is possible to find a similar degree of affinity of both MTP and TRI with the  
218 adsorbents: Brij<sub>0.4</sub>-Mt ( $K_F = 8.35 \times 10^{-3} \text{ Lg}^{-1}$ ) > Na-Mt ( $K_F = 4.72 \times 10^{-2} \text{ Lg}^{-1}$ ) > BDTA-Mt  
219 (Table 2).

220 As expected with organic cations proportion of both TRI and MTP, a limited adsorption onto  
221 BDTA-Mt is observed. For cationic species, the adsorption is mainly driven by electrostatic  
222 interaction through cation exchange with the inorganic cations ( $\text{Na}^+$ ) in the case of Na-Mt and  
223 Brij<sub>0.4</sub>-Mt (Bekçi et al. 2006, Guégan et al. 2015, Thiebault et al. 2015, De Oliveira et al.  
224 2018). In BDTA-Mt, such cation exchange is no more possible due to the presence of cationic  
225 surfactant within the interlayer space. Despite the lack of any electrostatic interaction, the  
226 organophilic character of both adsorbent (BDTA-Mt) and the analytes (here MTP and TRI),  
227 contributes to a favorable adsorption, as the parameter  $1/n$  comprised between 0.1 and 1  
228 underlines (Kodešová et al. 2015). With 20% of neutral-species for TRI, the repulsion forces  
229 are reduced by enhancing the transfer of mass of organic species. For both Na-Mt and Brij<sub>0.4</sub>-  
230 Mt materials (for which the whole inorganic cations are presumed to be accessible), the main  
231 driving force for adsorption involves electrostatic interaction with cation exchanges between  
232  $\text{Na}^+$  and amine moieties of TRI and MTP (Bekçi et al. 2006). Additionally, due to the  
233 presence of a hydrophobic environment and the versatility of the material with a dual  
234 hydrophobic/hydrophilic behavior, Brij<sub>0.4</sub>-Mt offers supplementary adsorption sites leading to  
235 an increase of the adsorption of TRI in contrast to Na-Mt, and their intercalation within the  
236 interlayer space of the whole layered materials. This intercalation cannot be observed for  
237 organoclays where the intercalated surfactants already increased an interlayer space. In  
238 contrast, the intercalation with similar amount of adsorbed PPs could be highlighted in Na-Mt,  
239 with an extension of the phyllosilicate galleries reaching about 15.5 and 14.7 Å for TRI and  
240 MTP respectively, comparatively to that of Na-Mt: 9.6 Å (Figure 3).

241

### 242 3.2.2. Adsorption of zwitterionic species: case of the Amoxicillin and Nofloxacin

243 Amoxicillin (AMX) shows a great affinity to the whole adsorbents with an adsorption at large  
244 amount ( $5.68 \times 10^{-3} \text{ mol g}^{-1}$ ) onto the whole layered materials, with a bold affinity of AMX

245 for BDTA-Mt. By using  $K_F$  (Table 2 and Figure 2n and  $q_{max}$ ), the affinity of AMX is as  
246 follows: BDTA-Mt > Brij<sub>0.4</sub>-Mt > Na-Mt. The slight excess of BDTA<sup>+</sup> combined with their  
247 hydrophobic character favor the adsorption of AMX with its CO<sub>2</sub><sup>-</sup> moieties through  
248 electrostatic and hydrophobic interactions (Adriano et al. 2005, Putra et al. 2009, Belhachemi  
249 and Djelaila 2017). In contrast, AMX can be cation exchanged in Na-Mt, leading to its  
250 intercalation with an increase of the interlayer spacing to nearly 15 Å in agreement with a  
251 molecular size of AMX, driving to an adsorbed amount larger than the value of the CEC ( $9.29$   
252  $\times 10^{-4}$  mol g<sup>-1</sup>) (Figure 3). This suggests that additional forces such as ion-dipole and even  
253 hydrophobic interaction contribute also in the adsorption in a second step but in a lesser  
254 extent. Similar mechanisms can be found in Brij<sub>0.4</sub>-Mt with a larger adsorption of PP due to  
255 the hydrophobic nature of the organo-layered material.

256 Norfloxacin (NFX) displays a great affinity to Na-Mt with an adsorbed amount close to the  
257 CEC:  $8.48 \times 10^{-4}$  mol g<sup>-1</sup> and a  $K_F$  of  $7.80 \times 10^{-2}$  L g<sup>-1</sup>. Indeed, at a pH=6.5, NFX shows 17%  
258 cationic and 83% zwitterionic species, driving to possible substitution of Na<sup>+</sup> cations in both  
259 Na-Mt and Brij<sub>0.4</sub>-Mt. However, in the latter case, the presence of a nonionic surfactant may  
260 restrict the proper diffusion and ion-exchange to occur, diminishing in that way the number of  
261 accessible Na<sup>+</sup> to be exchanged. The adsorbed amount of NFX onto Brij<sub>0.4</sub>-Mt at about  $4.24 \times$   
262  $10^{-4}$  mol g<sup>-1</sup> represents half the value of the CEC, suggesting that 50% of the exchangeable  
263 inorganic cations can be mobilized in the adsorption of NFX, and thus leads to a lower  $K_F$  (in  
264 comparison to that of Na-Mt) of  $5.66 \times 10^{-2}$  L g<sup>-1</sup>. With an adsorbed amount of only  $2.39 \times 10^{-}$   
265  $4$  mol g<sup>-1</sup>, the adsorption onto BDTA-Mt appears rather low. This trend is also confirmed with  
266 the parameter derived from Freundlich equation. Such low affinity of NFX to a cationic  
267 organoclay is nevertheless normal due to (i) the repulsive forces between analyte and BDTA-  
268 Mt, (ii) the limitation to perform any ion-exchange and (iii) the hydrophilic nature of NFX  
269 (LogP = -1.03). However, as a zwitterionic compound, NFX displays also some negative

270 charges that may be responsible of its adsorption onto BDTA-Mt. Indeed, for organoclays  
271 prepared at concentration above 1 CEC with additional , surfactant can be organized in  
272 paraffin structure with a wide expansion making it easier the intercalation of organic  
273 compounds and even anionic species.

274 With the observation of additional bands related to those of the pharmaceuticals, FTIR  
275 technique confirms proper the adsorption of NFX onto layered materials onto layered  
276 materials (Figure 4). Additionally, this technique can give new insights in the moieties of the  
277 molecules in interaction with the layered materials as it could be discussed in previous  
278 research works (Guégan et al. 2015, De Oliveira and Guégan 2016, De Oliveira et al. 2017).

279 The integrated intensity of the absorption bands characteristics of the NFX in the reduced  
280 spectral range between 1270 and 1570  $\text{cm}^{-1}$  related to the modes of elongation of CO of the  
281 ester and acid functions allows one to follow the evolution of the adsorption with an analysis  
282 onto a solid as it could be possible with adsorption isotherms determined through UV  
283 spectroscopy with difference of concentrations in liquid samples. The resulting evolution of  
284 the integrated intensities of the vibration bands of NFX shows similar trends as the adsorption  
285 isotherms highlighted with a better affinity of NFX to Na-Mt > Brij<sub>0.4</sub>-Mt > BDTA-Mt  
286 (Figure 5).

287

288 *3.2.3. Adsorption of a neutral or nonionic hydrophobic compound: case of the*  
289 *Carbamazepine*

290 CBZ shows a limited solubility in water ( $18 \text{ mg L}^{-1}$ ) due to its hydrophobic character and may  
291 be one of the main reasons about its persistence in numerous effluents. Thus, the adsorbed  
292 amount of this pharmaceutical onto the whole layered materials appears quite low, one order  
293 of magnitude lower than the other studied PPs in this study. Nevertheless, the resulting  
294 adsorption isotherms at the equilibrium point out the affinity of CBZ for the whole adsorbents

295 which is enhanced for BDTA-Mt > Brij<sub>0.4</sub>-Mt and Na-Mt with a maximum adsorbed amount  
296 reaching about  $2.53 \times 10^{-5}$ ,  $1.18 \times 10^{-5}$  and  $4.14 \times 10^{-6}$  mol g<sup>-1</sup> respectively. As expected, the  
297 hydrophobic character of CBZ limits the transfer of mass onto Na-Mt while the hydrophobic  
298 environment in the organoclays allows its proper adsorption.

299 Besides being nonionic and hydrophobic compound, CBZ can be weakly ionizable and holds  
300 punctual partial electric charge allowing possible physisorption processes that could be  
301 responsible for an adsorption (Zhang et al. 2010, Kodešová et al. 2015). Thus, CBZ may be  
302 sorbed onto Na-Mt through possible hydrogen bonds with the surface silanol groups (located  
303 in the edges of the phyllosilicate sheets in very small amounts) and for both organoclays with  
304 weak molecular hydrophobic interaction in addition with possible  $\pi$ - $\pi$  interactions in the case  
305 of BDTA-Mt explaining the large adsorbed amount in the latter case.

306

#### 307 *3.2.4. Adsorption of an anionic compound: the sulfamethoxazole*

308 The adsorption of sulfamethoxazole (SMX) is effective for the three materials as the  
309 adsorption isotherms revealed with a gradual growth of the adsorbed amount as the  
310 concentration is increased without reaching any plateau (Figure 2). The affinity of SMX is  
311 particularly enhanced for BDTA-Mt > Brij<sub>0.4</sub>-Mt > Na-Mt as both  $q_m$  and  $K_F$  stressed out  
312 (Table 2). At a pH of 6.5, SMX is mainly anionic (67%) and neutral (33%). Thus, as  
313 expected, the adsorption of this pharmaceutical onto Na-Mt is considerably limited. However,  
314 neutral SMX can be totally adsorbed through probable ion-dipole interaction, leading to its  
315 intercalation besides its hydrophobic character, as it could be observed by X-ray diffraction  
316 data (Figure 3). Indeed,  $q_m$  reaches  $2.56 \times 10^{-4}$  mol g<sup>-1</sup> onto Na-Mt which matches with a  
317 deviation of only 4% of the amount of SMX in its neutral form. However, the existence of  
318 negative charge at the surface of Na-Mt associated to weak polarizability of SMX  
319 considerably prevents further adsorption due to repulsive effects (Gao and Pedersen 2005).



320 Indeed, the deprotonated form of sulfamethoxazole significantly decreases the ability of the  
321 sulfonamide group of sulfamethoxazole to be able to perform  $\pi$ - $\pi$  interactions with the  $\pi$ -  
322 donor functions of the materials (Chen et al. 2014). In Brij<sub>0,4</sub>-Mt, the introduction of  
323 surfactant shields these repulsive forces while introducing a hydrophobic environment,  
324 leading to an adsorption in a larger proportion than Na-Mt. Thus, neutral SMX can be  
325 adsorbed onto the nonionic organoclay through accessible inorganic Na<sup>+</sup> cations, while the  
326 hydrophobic environment due to the presence of surfactant, allows a larger adsorption of the  
327 other species. With similar hydrophobic environment combined with a slight excess of  
328 BDTA<sup>+</sup>, SMX is adsorbed in large amount with deprotonated moieties ( $\pi$ - $\pi$  electron donor-  
329 acceptor interaction), and also hydrophobic-type molecular interactions (Rostamian and  
330 Behnejad 2016).

### 331 **3.3 Impact of the ionic strengths on the adsorption of organoclays to PPs**

332 Besides not being the most efficient sorbent, the adsorption efficiency of the layered materials  
333 in this study reasonably appears quite suitable for pharmaceuticals. However, depending on  
334 the nature of the organic pollutants, their adsorption capacities that can be similar to activated  
335 carbons. The experiments were essentially performed in synthetic water without any change  
336 of electrolytes. In a natural context, effluents show diverse electrolytes at different  
337 concentrations that may significantly perturb the magnitude of the adsorption or lead to a  
338 possible desorption. Thus, as described previously, the main driving force for the adsorption  
339 of pharmaceuticals results from electrostatic interactions, which are known to be sensitive to  
340 any change of the ionic strengths with usually the observation of an increase of the adsorbed  
341 amount (Gao and Pedersen 2005, Bekçi et al. 2006).

342 As it was expected, the ionic strength plays on the magnitude of the adsorption of the whole  
343 pharmaceuticals. Both line shapes and evolution of the isotherms follow the same trend as  
344 before but, except metoprolol the values of the maximum adsorbed amount of

345 pharmaceuticals as well as the parameters derived from the fitting procedure and more  
346 particularly  $K_F$  which appears affected with a change of the experimental conditions (Figure 2  
347 and Table 2). However, both nonionic and cationic organoclays show a decrease of their  
348 efficiencies, in contrast to Na-Mt for which the adsorption is particularly enhanced except for  
349 the cationic species (TRI and MTP) and thus appears as the most appropriate sorbent for the  
350 studied pharmaceuticals in the presence of NaCl at a concentration of  $1 \times 10^{-2} \text{ mol L}^{-1}$ .

351 For the cationic species (TMP and TRI), the addition of electrolytes reduces the total  
352 adsorption capacity of the three materials. For TRI, a decrease in the adsorbed quantities of  
353 about 8.4%, 34.2% and 25.1% can be observed whereas for MTP, it reaches a variation of  
354 8.0%, 1.6% and 15.7% for Na-Mt, BDTA-Mt and Brij<sub>0.4</sub>-Mt respectively. By focusing on  $K_F$ ,  
355 the same trend is confirmed. As expected for BDTA-Mt, organic cations are poorly adsorbed  
356 and can be mainly adsorbed through hydrophobic interaction and it is verified in the case of  
357 MTP where the NaCl salts do not affect the adsorbed amount, nor  $K_F$ . It is interesting to  
358 observe how the speciation of the organic compounds plays again on the adsorption. With the  
359 presence of an electrolyte, the transfer of nonionic TRI is considerably reduced and explains  
360 why the decrease of the adsorbed amount onto BDTA-Mt. Indeed, the presence of  $\text{Na}^+$  cations  
361 may shield the sites of adsorption and induces a competition effect which does not favor the  
362 sorption of neutral species to cationic organoclay. Moreover,  $\text{Na}^+$  ions are known to perturb  
363 electron-acceptor  $\pi$ - $\pi$ -electron interactions and may explain also the decrease of TRI onto  
364 BDTA-Mt. For sorbents where exchange of cations process is possible (i.e. Na-Mt and Brij<sub>0.4</sub>-  
365 Mt)  $\text{Na}^+$  ions in solution compete to other organic cations, here the pharmaceuticals and thus  
366 limits the adsorption. An intercalation of  $\text{Na}^+$  was confirmed by atomic absorption  
367 spectroscopy (not shown) and also observed through X-ray diffraction patterns (Figure 3),  
368 with a shift to large  $2\theta$  angle values of the 00l reflection where the interlayer space decreases

369 from 15.01 to 14.48 Å and from 14.66 to 14.23 Å for both TRI and MTP respectively after the  
370 addition of salts.

371 With  $q_{max}$  amount and  $K_F$  as main parameters to appreciate the affinity between analytes to  
372 sorbents, the presence of NaCl does induce any large change in the sequence of affinity of  
373 both AMX and NFX with the layered materials (Figure 2 and Table 2). However, the presence  
374 of the electrolytes reduces the transfer of the pharmaceuticals onto organoclays with a  
375 decrease of the adsorbed amounts for AMX of about 25% and 27% and for NFX by 49% and  
376 70% for both BDTA-Mt and Brij<sub>0,4</sub>-Mt respectively. In contrast, Na-Mt shows a clear  
377 improvement of the adsorption capacities in the presence of NaCl. Indeed, the maximum  
378 adsorbed amounts are  $2.69 \times 10^{-3}$  and  $9.91 \times 10^{-4}$  molg<sup>-1</sup> for AMX and NFX respectively  
379 representing an increase of 190% and 17%. The study of the solid phase by FTIR of Na-Mt  
380 also brings a confirmation of the improvement of the adsorption in the presence of electrolyte  
381 and confirms the general trends observed with the isotherms (Figures 4-5).

382 The addition of salts may change the solubility and hydrophobicity of substances in solution  
383 that can reduce the adsorption capacity of adsorbents (Anirudhan and Ramachandran 2006,  
384 Bui and Choi 2010). A loss of hydrophobicity could indeed penalize the interactions of the  
385 similar range of energy involved in the adsorption of pharmaceuticals to organoclays.  
386 Electrolytes in solution may also combine with pharmaceuticals and reduce considerably their  
387 diffusion at a surface of the layered materials. The grafting of surfactant onto the surface of  
388 the layered materials acting as a brush may prevent a possible diffusion within the interlayer  
389 space of the pharmaceuticals or probably the presence of salts aside the organoclays shield the  
390 possibility of adsorption of zwitterionic compounds (Figure 6) (Vinu et al. 2006).

391 The presence of NaCl that amplifies the polarizability of the molecules via ionic bridges and  
392 thus causes a drop-in of the hydrophobicity (Anirudhan and Ramachandran 2006) is likely to  
393 explain the change of affinity between CBZ and Na-Mt. The addition of salts does affect the

394 main driving force (hydrophobic interaction) for the adsorption of CBZ to organoclays  
395 allowing one to obtain similar adsorbed amounts. However, the possibility to interact through  
396 ionic bridges to Na-Mt enhances considerably the adsorption capacity showing an ability to  
397 adsorb CBZ at even larger extent than organoclays (Figure 2). Similarly, Na-Mt represents the  
398 best suitable material for anionic compounds in presence of electrolytes, where the adsorbed  
399 amounts show an increase by reaching 170% to reach  $7.01 \times 10^{-4} \text{ mol g}^{-1}$ . The addition of salts  
400 must change the state of charge of SMX with the possible formation of ion complexes of  
401 which nature is different from the surface properties of organoclays and therefore limit its  
402 mass transfer. This combination of sodium ions with the deprotonated groups of the  
403 molecules leads to the establishment of repulsive forces in regards to the cationic organoclay  
404 and decreases its adsorption capacity. Such ion-molecule complexations may explain an  
405 improvement in the adsorption in the opposite case of initially repulsive interactions which  
406 can be extended to the results obtained for Na-Mt.

#### 407 **4. Conclusions**

408 With a study of six pharmaceuticals showing diverse chemical nature (zwitterionic, anionic,  
409 cationic and neutrals as well as displaying different hydrophobicity) onto layered materials  
410 based on clay minerals with diverse properties (cation exchange, organophilicity, anion  
411 adsorption ability) without any electrolytes, electrostatic interactions appear to be the main  
412 adsorption mechanisms while hydrophobic parameter plays a second role. However, this latter  
413 feature is important since the intercalation of surfactant drives to an organic environment with  
414 novel adsorption sites, thus improving the adsorption of pharmaceuticals.

415 As expected with adsorption mechanisms that bear on electrostatic interactions, the ionic  
416 strength strongly affects the adsorption processes of pharmaceuticals with a drastic reduction  
417 of the efficiency of both cationic and nonionic organoclays. Such decrease results from (i) a  
418 competition effect between salts and the organophilic surface of organoclays to the

419 pharmaceuticals, and (ii) a noticeable change in the properties of the aqueous solution that  
420 may decrease the hydrophobic character of organic compounds. In contrast, the improvement  
421 of the adsorption properties of Na-Mt in the presence of electrolytes can be explained by  
422 electric double layers or Debye model and the screening of the electrostatic repulsions with  
423 the introduction counter-ions at a surface of the phyllosilicate sheets. Indeed, with monovalent  
424 salts, the Debye screening length is quite reduced and decreases the magnitude of the  
425 repulsion relative to the van der Waals attraction. This phenomenon obviously favors the  
426 adsorption of organic compounds onto Na-Mt, where ion-dipole interaction through the  
427 presence of counter-ions located at the surface of the phyllosilicate sheets. In organoclays, the  
428 presence of surfactant already reduces the repulsion forces between the inorganic sheets but  
429 generates a hydrophobic environment with the grafting of an organic layer or brush. This  
430 combination contributes to the improvement of the adsorption efficiency of organoclays  
431 without any electrolytes. However, with salts, their adsorption abilities for pharmaceuticals  
432 remain identical or appear considerably reduced. In Na-Mt, salts are located to a surface  
433 which lessen the Debye screening length. In contrast, for organoclays the introduced ions  
434 remain in solution and may interact with organic compounds, leading to a backward shift of  
435 the desorption/adsorption equilibrium. This can go farer since the adsorption of organic  
436 compounds to a clay mineral generates step by step a hybrid material, equivalent to  
437 organoclays obtained with surfactants, of which efficiency is decreased. Worse, it can drive to  
438 the desorption of the adsorbed organic compounds as we could observed (not shown here) and  
439 thus raises the question of the usefulness of organoclays in water remediation strategy.

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443

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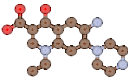


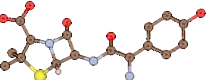



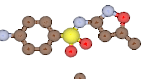


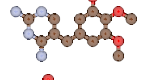


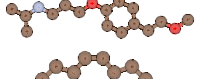


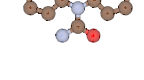

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557

558

559 Table 1: Characteristics of the pharmaceutical products used in this study: solubility, pKa,  
 560 LogP and speciation. LogP corresponds to the value of the hydrophobic character of the  
 561 compounds (a LogP equals to zero corresponds to a compound with an equilibrated balance  
 562 between its hydrophobic and hydrophilic moieties, while a Log P negative and positive  
 563 represents a hydrophilic and hydrophobic compound). The red, green, blue and association of  
 564 blue and red circles symbolizes the electric charge of the pharmaceuticals at a pH=6.5:  
 565 positive, neutral, negative and zwitterion respectively.

Pharmaceutical products		Solubility (mg L <sup>-1</sup> )	LogP	pKa	Speciation (pH=6.5)
Norfloxacin (NFX)		178 000	-1.03	5.77 - 8.68	10%  /  90%
Amoxicillin (AMX)		3430	0.87	3.23 - 7.43	80%   /  20%
Sulfamethoxazole (SMX)		610	0.89	1.97 - 6.16	33%  /  70%
Trimethoprim (TRI)		400	0.91	7.12	20%  /  80%
Metropolol (MTP)		0.402	1.88	9.7	10%  /  90%
Carbamazepine (CBZ)		0.152	2.45	—	

566

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569 Table 2: Adsorption isotherm constants determined with Langmuir, Freundlich model fits for  
 570 the adsorption of the whole pharmaceuticals: Amoxicillin (AMX), Sulfamethoxazole (SMX),  
 571 Trimethoprim (TRI), Metoprolol (MTP), Norfloxacin (NFX) and Carbamazepine (CBZ) onto  
 572 untreated Na exchanged montmorillonite: Na-Mt, BDTA-Mt and Brij<sub>0.4</sub>-Mt with and without  
 573 salts (NaCl at a concentration of 1 mol L<sup>-1</sup>).  
 574

575

Adsorbant	Analytes	Langmuir				Freundlich		
		q <sub>max</sub> (mol.g <sup>-1</sup> )	K <sub>L</sub> (L.mol <sup>-1</sup> )	ΔG° (kJ.mol <sup>-1</sup> )	r <sup>2</sup>	K <sub>F</sub> (L.g <sup>-1</sup> )	1/n	r <sup>2</sup>
Na-Mt	AMX	9.29 x 10 <sup>-4</sup>	9.73 x 10 <sup>1</sup>	-11.72	0.988	4.71 x 10 <sup>-2</sup>	0.94	0.984
	AMX + NaCl	2.69 x 10 <sup>-3</sup>	9.98 x 10 <sup>1</sup>	-11.79	0.984	1.60 x 10 <sup>-1</sup>	0.95	0.966
BDTA-Mt	AMX	5.68 x 10 <sup>-3</sup>	1.46 x 10 <sup>2</sup>	-12.76	0.972	2.07 x 10 <sup>-1</sup>	0.81	0.983
	AMX + NaCl	4.28 x 10 <sup>-3</sup>	1.15 x 10 <sup>2</sup>	-12.15	0.994	1.87 x 10 <sup>-1</sup>	0.87	0.992
Brij <sub>0.4</sub> -Mt	AMX	4.44 x 10 <sup>-3</sup>	1.31 x 10 <sup>2</sup>	-12.48	0.996	2.04 x 10 <sup>-1</sup>	0.88	0.997
	AMX + NaCl	3.23 x 10 <sup>-3</sup>	1.02 x 10 <sup>2</sup>	-11.85	0.993	1.79 x 10 <sup>-1</sup>	0.94	0.991
Na-Mt	SMX	2.56 x 10 <sup>-4</sup>	4.87 x 10 <sup>2</sup>	-15.85	0.967	1.24 x 10 <sup>-2</sup>	0.73	0.964
	SMX + NaCl	7.01 x 10 <sup>-4</sup>	3.30 x 10 <sup>3</sup>	-20.75	0.988	3.18 x 10 <sup>-2</sup>	0.57	0.957
BDTA-Mt	SMX	9.73 x 10 <sup>-4</sup>	4.78 x 10 <sup>3</sup>	-21.69	0.976	4.55 x 10 <sup>-2</sup>	0.59	0.961
	SMX + NaCl	6.98 x 10 <sup>-4</sup>	1.63 x 10 <sup>3</sup>	-18.95	0.958	2.88 x 10 <sup>-2</sup>	0.58	0.991
Brij <sub>0.4</sub> -Mt	SMX	6.97 x 10 <sup>-4</sup>	5.06 x 10 <sup>2</sup>	-15.95	0.976	2.43 x 10 <sup>-2</sup>	0.66	0.930
	SMX + NaCl	3.21 x 10 <sup>-4</sup>	4.90 x 10 <sup>2</sup>	-15.87	0.989	2.06 x 10 <sup>-2</sup>	0.77	0.986
Na-Mt	TRI	3.80 x 10 <sup>-4</sup>	5.98 x 10 <sup>3</sup>	-22.27	0.982	3.44 x 10 <sup>-3</sup>	0.33	0.901
	TRI + NaCl	3.48 x 10 <sup>-4</sup>	5.15 x 10 <sup>3</sup>	-21.89	0.998	2.92 x 10 <sup>-3</sup>	0.33	0.899
BDTA-Mt	TRI	2.78 x 10 <sup>-4</sup>	4.46 x 10 <sup>3</sup>	-21.52	0.922	2.79 x 10 <sup>-3</sup>	0.36	0.907
	TRI + NaCl	1.83 x 10 <sup>-4</sup>	6.76 x 10 <sup>2</sup>	-16.69	0.995	2.47 x 10 <sup>-3</sup>	0.51	0.999
Brij <sub>0.4</sub> -Mt	TRI	4.13 x 10 <sup>-4</sup>	7.59 x 10 <sup>4</sup>	-28.78	0.928	8.35 x 10 <sup>-3</sup>	0.40	0.996
	TRI + NaCl	3.61 x 10 <sup>-4</sup>	5.20 x 10 <sup>3</sup>	-21.92	0.992	3.15 x 10 <sup>-3</sup>	0.34	0.997
Na-Mt	NFX	8.48 x 10 <sup>-4</sup>	4.54 x 10 <sup>3</sup>	-21.57	0.984	7.80 x 10 <sup>-2</sup>	0.62	0.997
	NFX + NaCl	9.91 x 10 <sup>-4</sup>	4.96 x 10 <sup>3</sup>	-21.79	0.983	8.96 x 10 <sup>-2</sup>	0.61	0.988
BDTA-Mt	NFX	2.39 x 10 <sup>-4</sup>	9.53 x 10 <sup>2</sup>	-17.57	0.980	9.74 x 10 <sup>-3</sup>	0.64	0.975
	NFX + NaCl	1.23 x 10 <sup>-4</sup>	5.33 x 10 <sup>2</sup>	-16.08	0.998	2.64 x 10 <sup>-3</sup>	0.61	0.994
Brij <sub>0.4</sub> -Mt	NFX	4.24 x 10 <sup>-4</sup>	4.42 x 10 <sup>3</sup>	-21.50	0.958	5.66 x 10 <sup>-2</sup>	0.66	0.977
	NFX + NaCl	1.26 x 10 <sup>-4</sup>	6.47 x 10 <sup>2</sup>	-16.58	0.840	6.27 x 10 <sup>-3</sup>	0.73	0.864
Na-Mt	CBZ	4.14 x 10 <sup>-6</sup>	5.63 x 10 <sup>4</sup>	-28.02	0.873	2.26 x 10 <sup>-3</sup>	0.65	0.972
	CBZ + NaCl	2.54 x 10 <sup>-5</sup>	1.80 x 10 <sup>5</sup>	-30.99	0.976	3.22 x 10 <sup>-2</sup>	0.66	0.975
BDTA-Mt	CBZ	2.53 x 10 <sup>-5</sup>	1.41 x 10 <sup>5</sup>	-30.38	0.977	2.75 x 10 <sup>-3</sup>	0.67	0.943
	CBZ + NaCl	2.33 x 10 <sup>-5</sup>	1.34 x 10 <sup>5</sup>	-30.24	0.984	2.26 x 10 <sup>-2</sup>	0.66	0.985

Brij <sub>0.4</sub> -Mt	CBZ	$1.18 \times 10^{-5}$	$1.10 \times 10^5$	-29.76	0.966	$2.49 \times 10^{-3}$	0.54	0.939
	CBZ + NaCl	$1.99 \times 10^{-5}$	$1.24 \times 10^5$	-30.05	0.981	$6.11 \times 10^{-3}$	0.56	0.981
Na-Mt	MTP	$5.62 \times 10^{-4}$	$3.07 \times 10^3$	-20.57	0.967	$4.72 \times 10^{-2}$	0.65	0.936
	MTP + NaCl	$5.17 \times 10^{-4}$	$2.98 \times 10^3$	-20.50	0.978	$3.04 \times 10^{-2}$	0.61	0.905
BDTA-Mt	MTP	$1.26 \times 10^{-4}$	$1.63 \times 10^3$	-18.95	0.964	$3.47 \times 10^{-3}$	0.55	0.988
	MTP + NaCl	$1.24 \times 10^{-4}$	$1.32 \times 10^3$	-18.41	0.879	$1.52 \times 10^{-3}$	0.46	0.923
Brij <sub>0.4</sub> -Mt	MTP	$5.08 \times 10^{-4}$	$1.95 \times 10^3$	-19.40	0.974	$2.91 \times 10^{-2}$	0.63	0.960
	MTP + NaCl	$4.28 \times 10^{-4}$	$1.68 \times 10^3$	-19.02	0.962	$2.85 \times 10^{-2}$	0.66	0.900

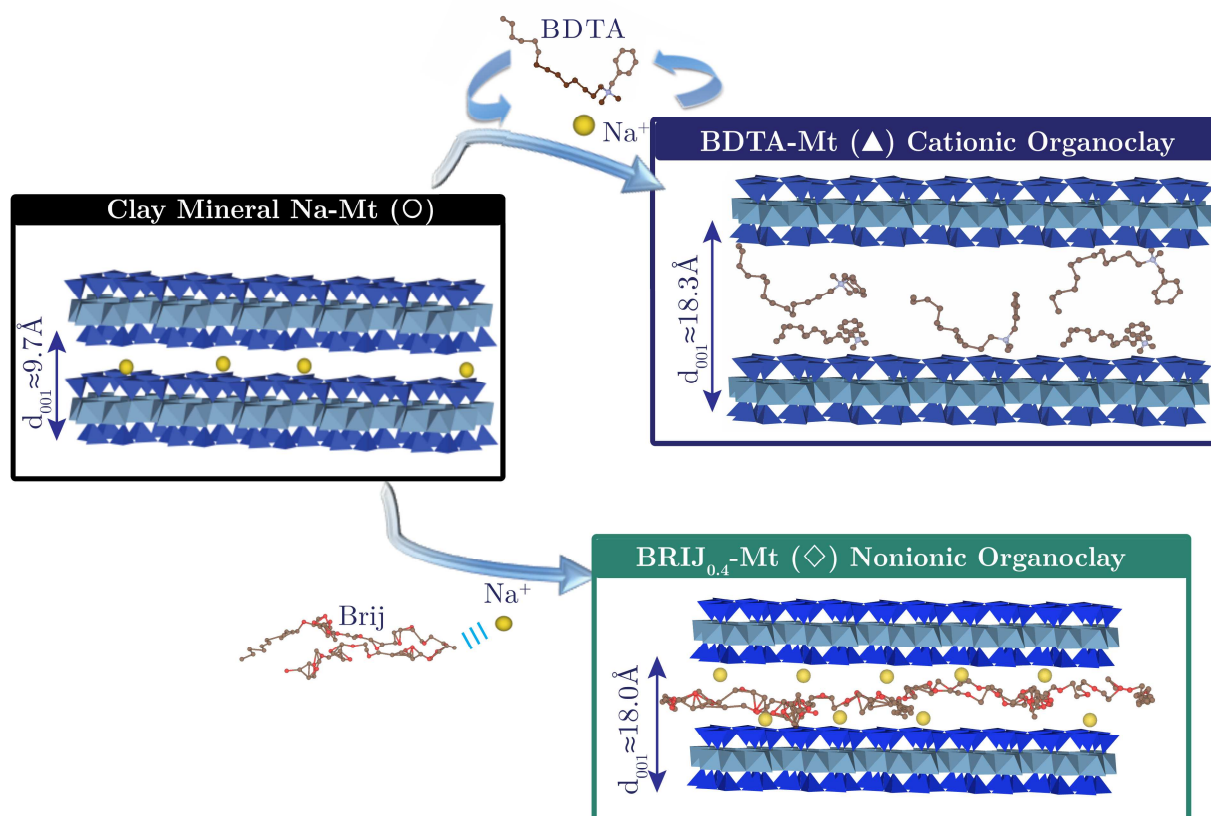


Figure 1: Schematic representation of the whole geo-sorbents used in this study: Na-Mt clay mineral, BDTA-Mt (100% of the compensations cations are substituted to BDTA through cation exchange) and Brij<sub>0.4</sub>-Mt, a nonionic organoclay (where the inorganic cations are kept within the interlayer space and Brij is intercalated involving ion-dipole interaction) showing lateral bilayers organization. The sorbents used in this study display singular adsorption properties: hydrophobicity/philicity, cation/anion retention which will be highlighted with six pharmaceuticals of different chemical nature.

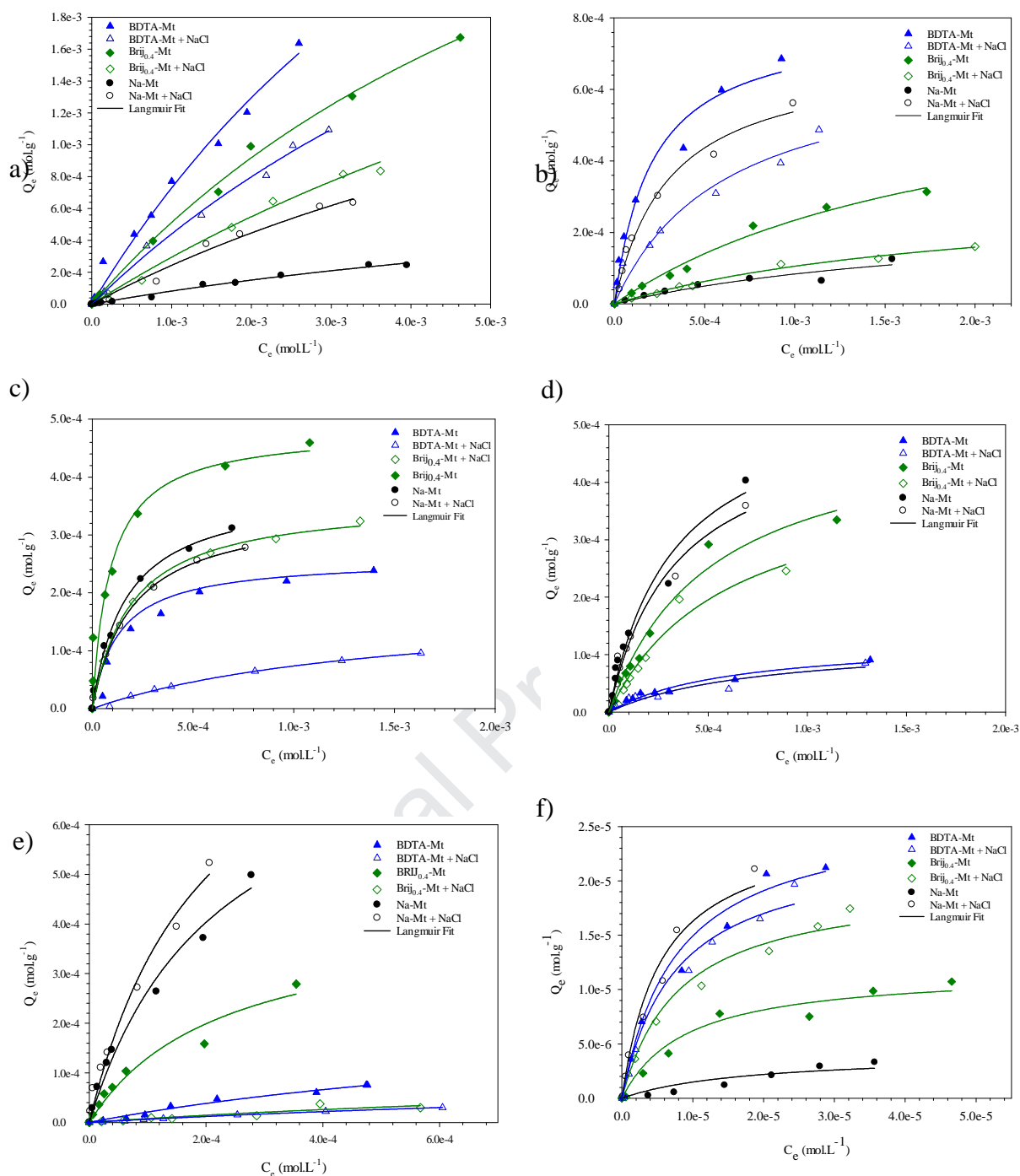


Figure 2: Effect of the ionic strength with the addition of NaCl electrolytes ( $10^{-2}$  M) on the equilibrium adsorption isotherms of a) Amoxicillin (AMX), b) Sulfamethoxazole (SMX), c) Trimethoprim (TRI), d) Metoprolol (MTP), e) Norfloxacin (NFX) and f) Carbamazepine (CBZ) onto untreated Na exchanged montmorillonite: Na-Mt (circle), BDTA-Mt (triangle top) and Brij<sub>0.4</sub>-Mt (diamond).  $Q_e$  represents the adsorbed amount of pharmaceutical while  $C_e$  is the equilibrium pharmaceutical concentration. The solid lines represent the fits by using the Langmuir equation model.

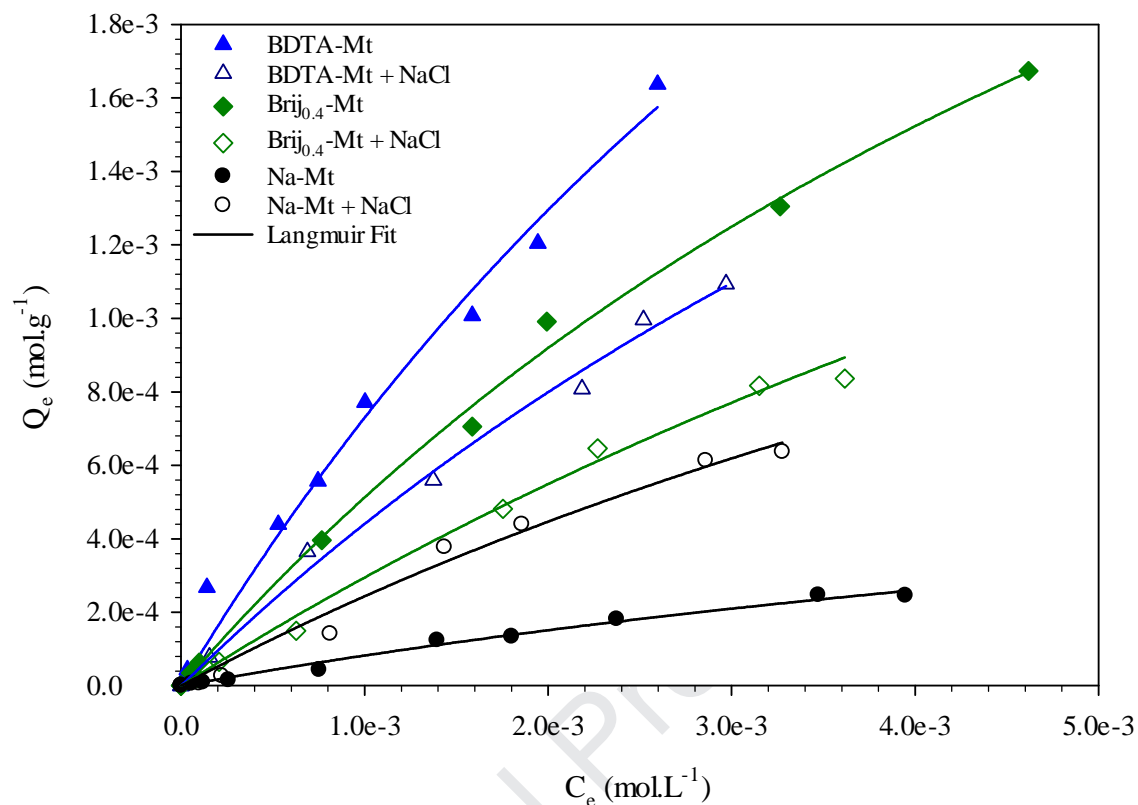


Figure 2a: Effect of the ionic strength with the addition of NaCl electrolytes ( $10^{-2}$  M) on the equilibrium adsorption isotherms of Amoxicillin (AMX) onto untreated Na exchanged montmorillonite: Na-Mt (circle), BDTA-Mt (triangle top) and Brij<sub>0.4</sub>-Mt (diamond).  $Q_e$  represents the adsorbed amount of pharmaceutical while  $C_e$  is the equilibrium pharmaceutical concentration. The solid lines represent the fits by using the Langmuir equation model.

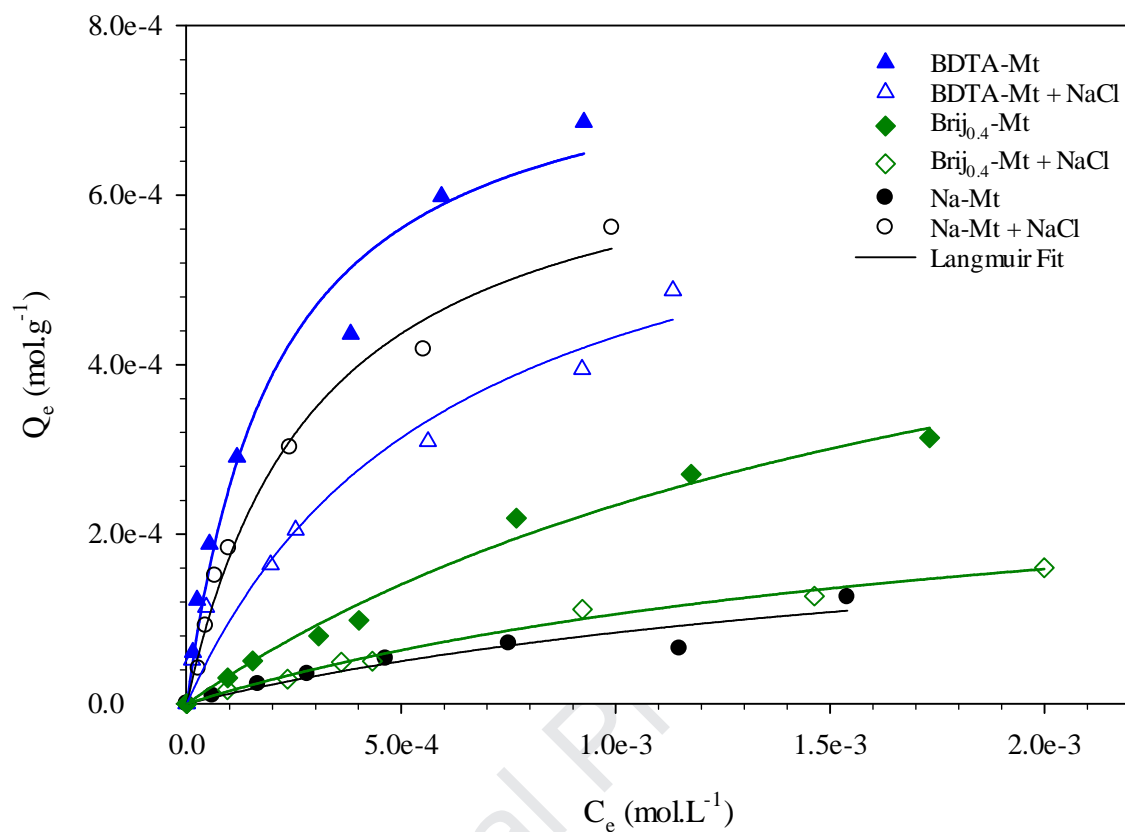


Figure 2b: Effect of the ionic strength with the addition of NaCl electrolytes ( $10^{-2}$  M) on the equilibrium adsorption isotherms of Sulfamethoxazole (SMX) onto untreated Na exchanged montmorillonite: Na-Mt (circle), BDTA-Mt (triangle top) and Brij<sub>0.4</sub>-Mt (diamond).  $Q_e$  represents the adsorbed amount of pharmaceutical while  $C_e$  is the equilibrium pharmaceutical concentration. The solid lines represent the fits by using the Langmuir equation model.



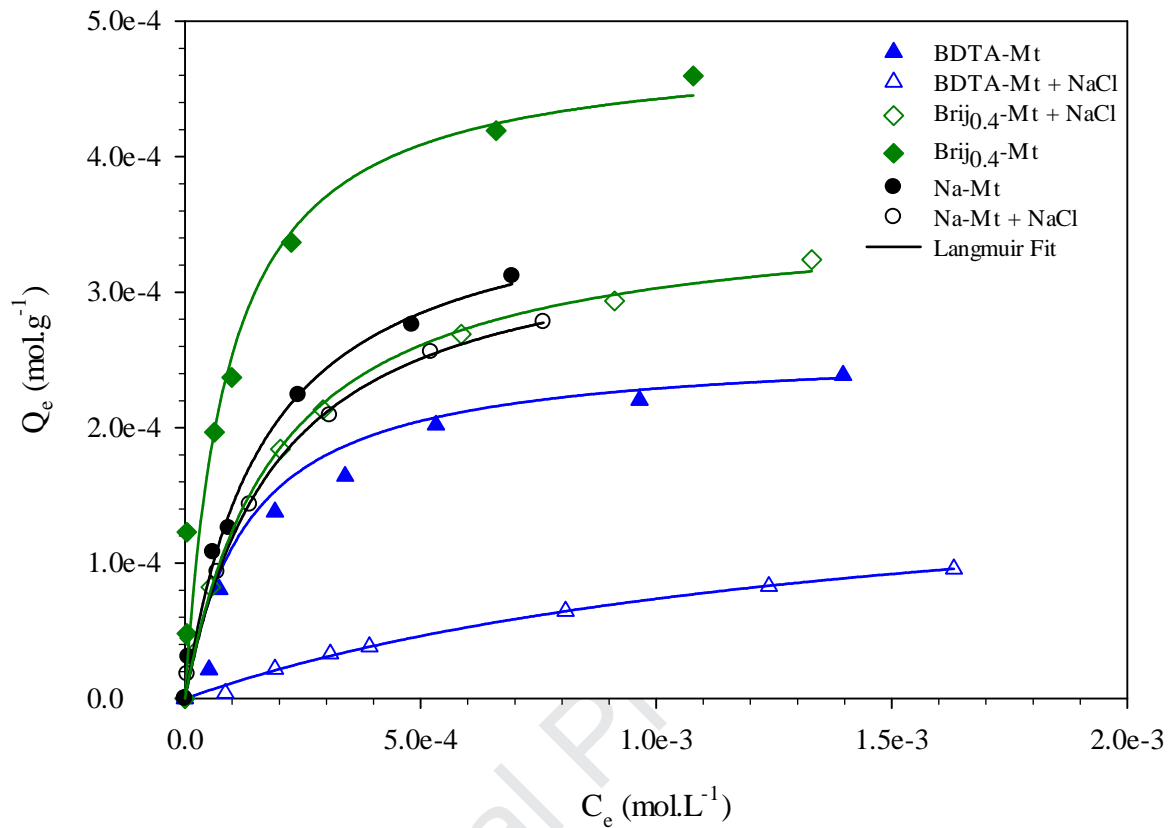


Figure 2c: Effect of the ionic strength with the addition of NaCl electrolytes ( $10^{-2}$  M) on the equilibrium adsorption isotherms of Trimethoprim (TRI) onto untreated Na exchanged montmorillonite: Na-Mt (circle), BDTA-Mt (triangle top) and Brij<sub>0.4</sub>-Mt (diamond).  $Q_e$  represents the adsorbed amount of pharmaceutical while  $C_e$  is the equilibrium pharmaceutical concentration. The solid lines represent the fits by using the Langmuir equation model.

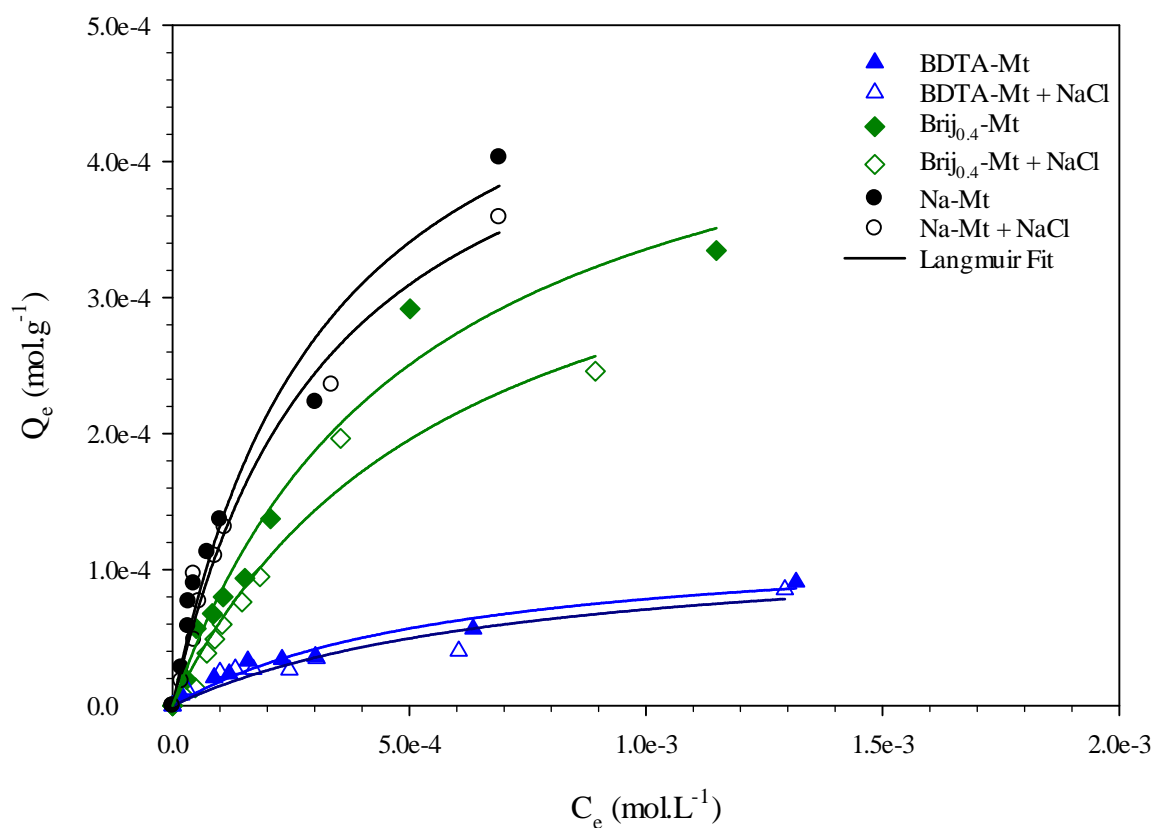


Figure 2d: Effect of the ionic strength with the addition of NaCl electrolytes ( $10^{-2}$  M) on the equilibrium adsorption isotherms of Metoprolol (MTP) onto untreated Na exchanged montmorillonite: Na-Mt (circle), BDTA-Mt (triangle top) and Brij<sub>0.4</sub>-Mt (diamond).  $Q_e$  represents the adsorbed amount of pharmaceutical while  $C_e$  is the equilibrium pharmaceutical concentration. The solid lines represent the fits by using the Langmuir equation model.

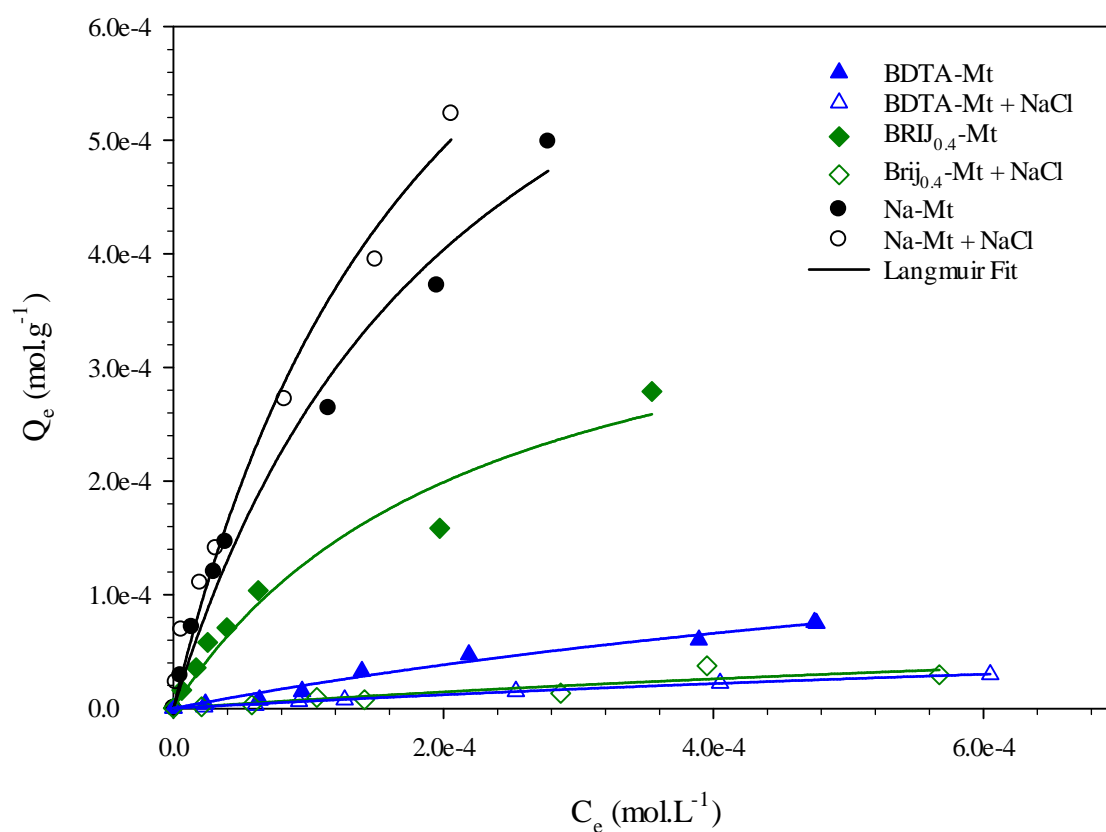


Figure 2e: Effect of the ionic strength with the addition of NaCl electrolytes ( $10^{-2}$  M) on the equilibrium adsorption isotherms of Norfloxacin (NFX) onto untreated Na exchanged montmorillonite: Na-Mt (circle), BDTA-Mt (triangle top) and Brij<sub>0.4</sub>-Mt (diamond).  $Q_e$  represents the adsorbed amount of pharmaceutical while  $C_e$  is the equilibrium pharmaceutical concentration. The solid lines represent the fits by using the Langmuir equation model.

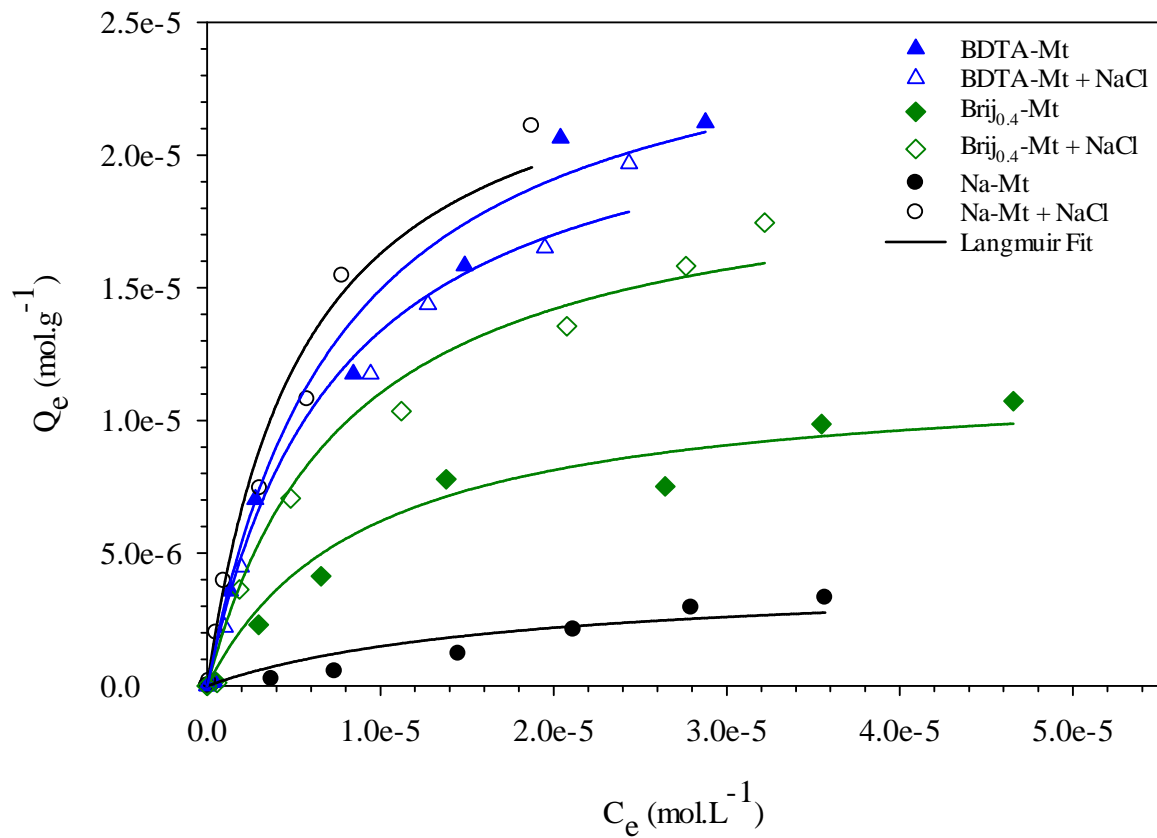


Figure 2f: Effect of the ionic strength with the addition of NaCl electrolytes ( $10^{-2}$  M) on the equilibrium adsorption isotherms of Carbamazepine (CBZ) onto untreated Na exchanged montmorillonite: Na-Mt (circle), BDTA-Mt (triangle top) and Brij<sub>0.4</sub>-Mt (diamond).  $Q_e$  represents the adsorbed amount of pharmaceutical while  $C_e$  is the equilibrium pharmaceutical concentration. The solid lines represent the fits by using the Langmuir equation model.

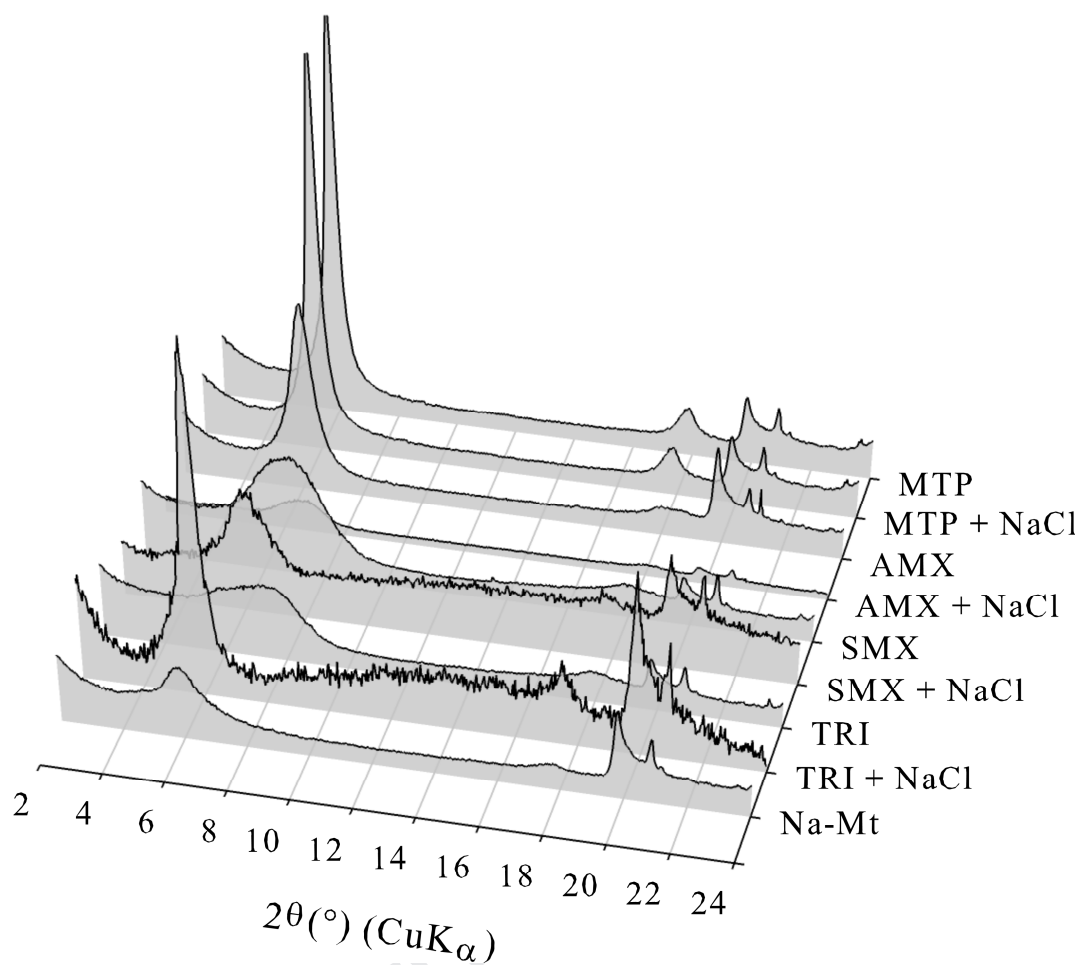
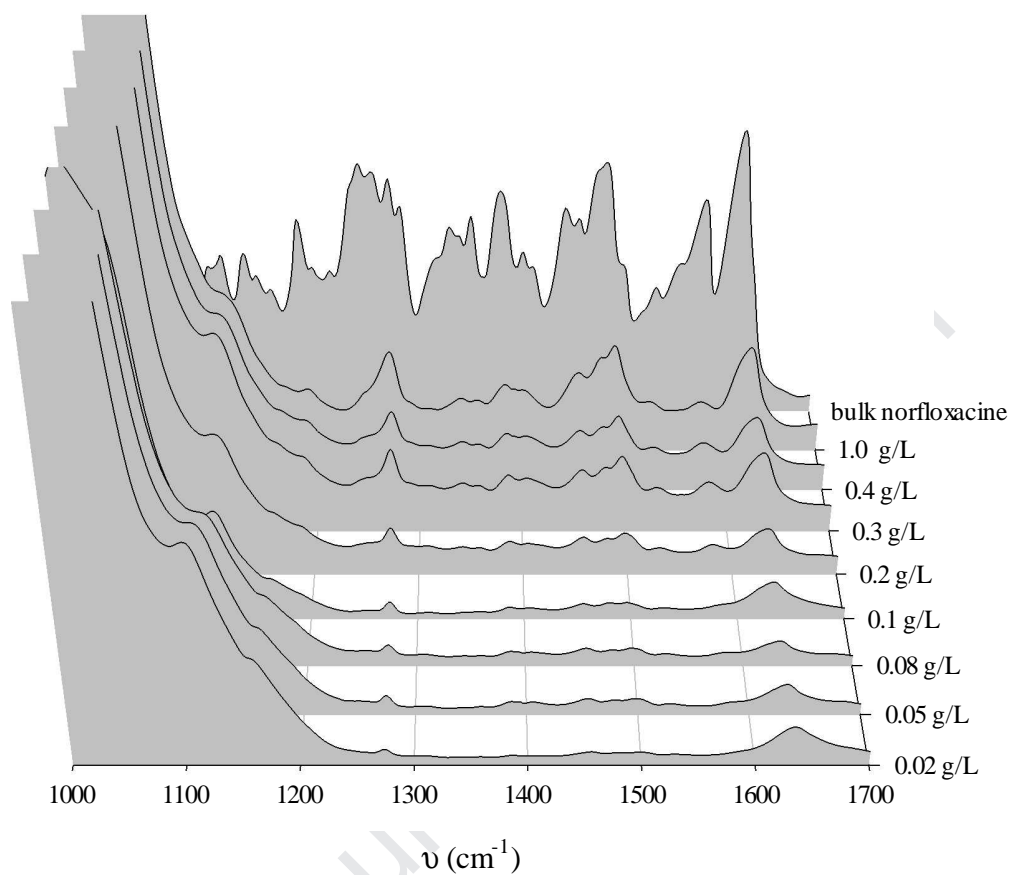


Figure 3: 3D evolution of the X-ray diffraction patterns (selected data) of Na-Mt after the adsorption of Trimethoprim (TRI), Sulfamethoxazole (SMX), Amoxicillin (AMX) and Metoprolol (MTP) with and without any electrolytes (NaCl at a concentration of  $10^{-2}$  M). With an interlayer distance ( $d_{001}$  spacing) of about 18 Å, and an average molecular size of 5 Å for the pharmaceuticals, no structural changes in the evolution of the organoclays are observed.

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4 Figure 4: 3D evolution of the FTIR spectra in the 1000-1700  $\text{cm}^{-1}$  wavenumbers range  
5 (probing the  $\text{COO}^-$  absorption bands of the norfloxacin among others) of Na-Mt (selected  
6 series but a similar evolution for the other adsorbents was observed) as a function of the  
7 starting norfloxacin concentration ( $\text{g L}^{-1}$ ).

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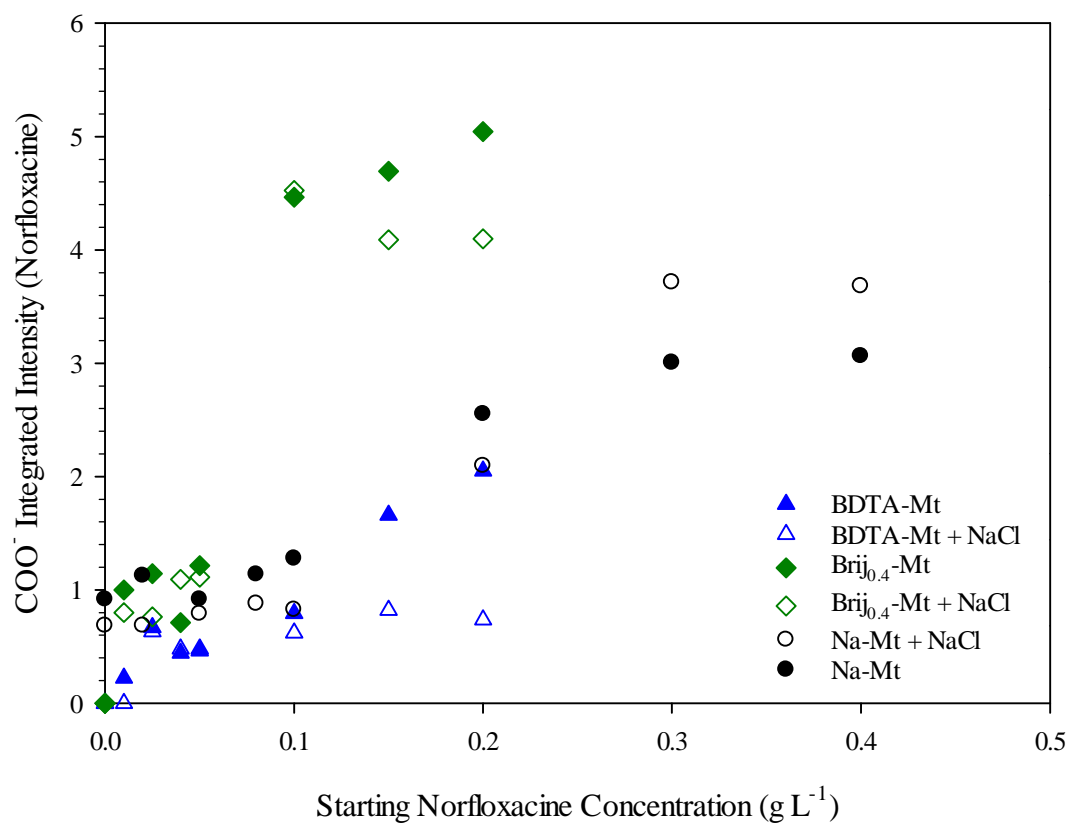
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11 (selected data).

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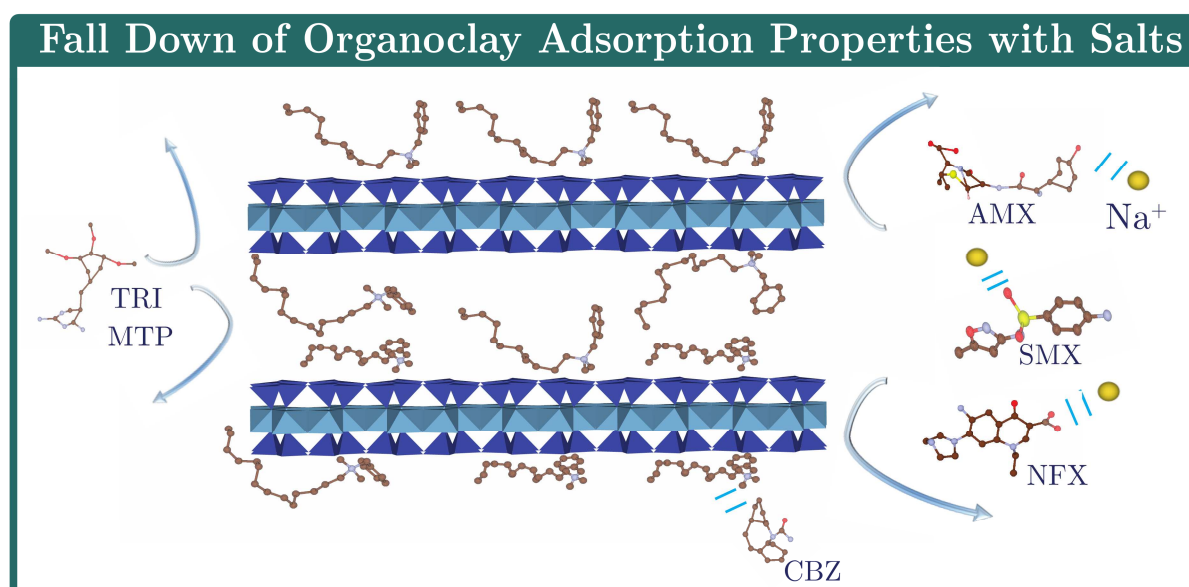
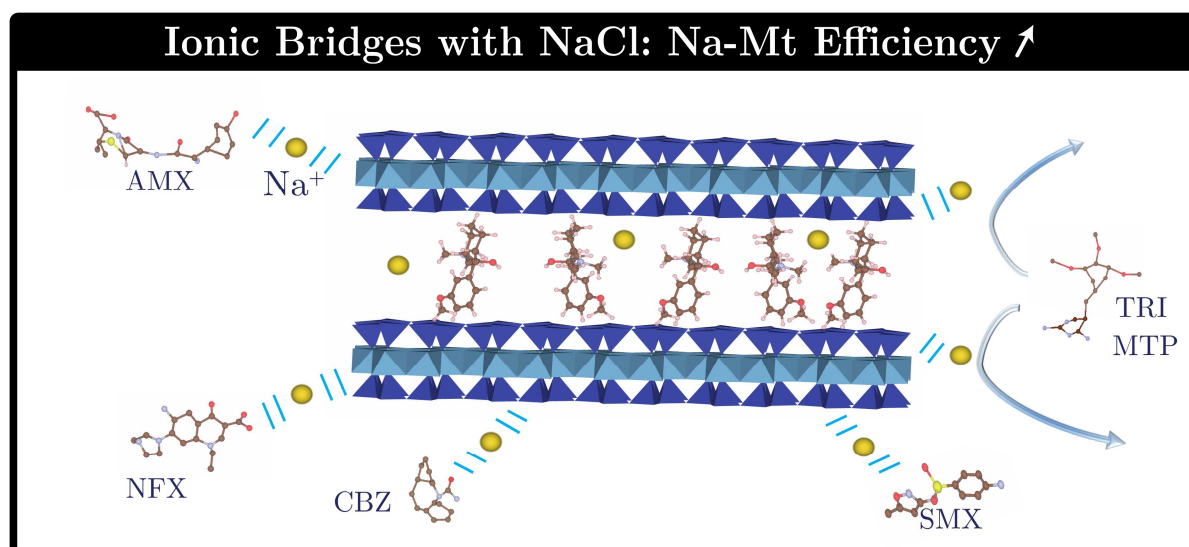
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17 Figure 5: Integrated intensity of the COO<sup>-</sup> stretching bands of norfloxacin as a function of the  
 18 its starting concentration (g L<sup>-1</sup>) for Na-Mt (black and white filled circles), BDTA-Mt (navy  
 19 blue and white filled triangle top) cationic organoclay, and Brij<sub>0.4</sub>-Mt (green and white filled  
 20 diamond) nonionic organoclay with (symbols filled with a color) and without NaCl  
 21 electrolytes.

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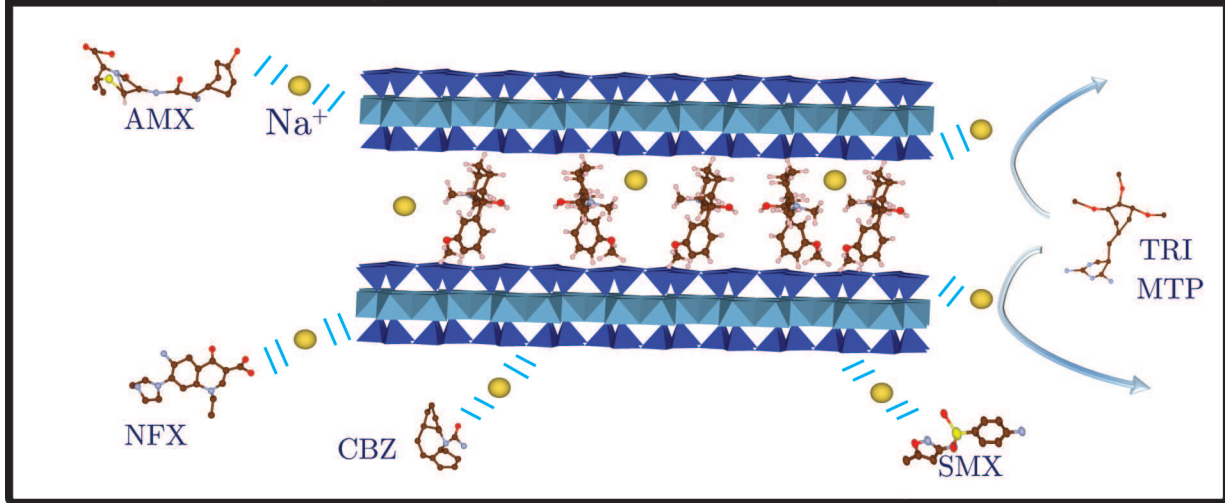
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27 Figure 6: Schematic representation of the impact of the salts on the adsorption/desorption of  
 28 the pharmaceuticals onto Na-Mt, Brij<sub>0.4</sub>-Mt, and BDTA-Mt. The presence of electrolytes  
 29 favors the adsorption with the creation of ionic bridges to Na-Mt while it backwards the  
 30 adsorption/desorption equilibrium of pharmaceuticals onto both nonionic and cationic  
 31 organoclays showing a poor efficiency in experimental conditions close to that of effluents.

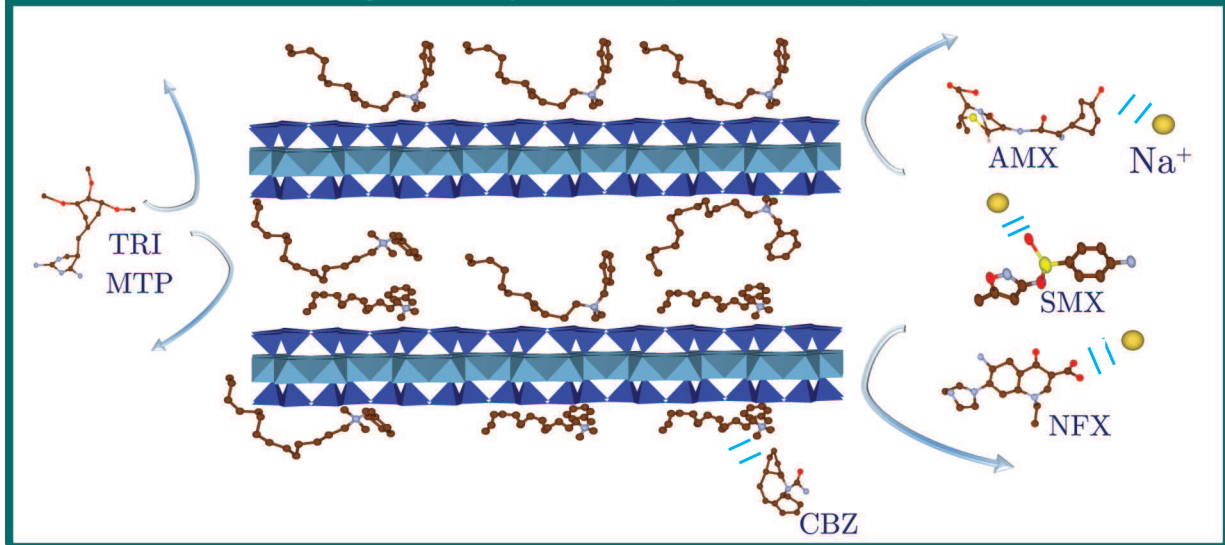
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### Ionic Bridges with NaCl: Na-Mt Efficiency ↑



### Fall Down of Organoclay Adsorption Properties with Salts



### **Research Highlights**

The electric charge of pharmaceuticals (PPs) governs their adsorption

Organoclays improve the adsorption of PPs due to their hydrophobic nature

Without any salts, organoclays show a certain efficiency in the adsorption of PPs

The adsorption is enhanced onto Na-Mt in presence of an electrolyte

Organoclays appear as poor sorbent materials in presence of salts