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# 1 Coupled Organoclay/micelle action for the adsorption of diclofenac

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## 11 **Abstract**

12 A Na-smectite clay mineral (Na-Mt) was exchanged with various amounts of  
13 benzyltrimethyltetradecyl ammonium chloride cationic surfactant (BDTAC) up to four times  
14 the cation exchange capacity (CEC). The adsorption properties of these organoclays as well as  
15 a coupled micelle/organoclay process were evaluated to remove an anionic pharmaceutical  
16 product: the diclofenac (DFC), recognized as a recalcitrant compound to conventional water  
17 treatments and to be poorly adsorbed onto untreated clay mineral. The DFC affinity appears to  
18 depend on the lipophilic character of organoclays in correlation to the density of intercalated  
19 BDTA and is particularly enhanced for sorbent systems with free surfactant or micelle in  
20 solution. The combination of both organoclay and BDTA in excess or micelle as one pot  
21 adsorption system appears to be the most efficient material for the sequestration of DFC and  
22 other pharmaceutical product (PP) with a  $K_F$  Freundlich constant of  $1.7 \text{ L g}^{-1}$  and no restriction  
23 of the adsorbed DFC amount as the linear adsorption isotherm shows. BDTA hydrophobic core  
24 micelle coupled with a positive electric charge forms organic complex with DFC that are  
25 properly intercalated within the interlayer space of BDTA-Mt organoclays as both Fourier  
26 transform infrared (FTIR) and X-ray diffraction (XRD) data supported.

## 27 **1. Introduction**

28 Current water treatments consist in three successive steps where the latter one known as  
29 ternary operation, aiming at the elimination of the whole organic products included viruses or  
30 bacteria, is based on different chemical processes such as: UV irradiation, ozonation, advanced  
31 oxidation. Nevertheless, it somehow appears difficult to apply them at an industrial scale and  
32 often generates unwanted products showing a toxicity that can be worse than those of actual  
33 emerging organic pollutants such as pharmaceutical products (PPs).<sup>1-3</sup> If the coupling  
34 ozonation/adsorption on granular activated carbon (GAC) for instance seems to be an  
35 alternative<sup>4-6</sup>, its use still requests to be optimized since GAC surface shows a strong alteration  
36 of its structure and the employment of GAC as adsorbent alone implies a frequent recycling  
37 (thermal, and chemical activation) due to its easy saturation of its porous network with both  
38 organic matter and inorganic salts or mineral phases.<sup>7-9</sup> Thus, beyond the question related to the  
39 efficiency or improvement of both wastewater and drinking water treatments, current research  
40 works shift towards the development of novel materials based on adsorption for the removal of  
41 organic pollutants.<sup>10-19</sup>

42 Adsorption represents a simple and easy process avoiding degraded molecules. Among the  
43 materials matching the criteria for adsorption: a large specific surface area and a possibility of  
44 recycling; clay minerals and other layered materials analogous (layered double hydroxides,  
45 organoclays...) display particular interests for adsorption and were proposed as potential  
46 solution in water treatments.<sup>16, 19</sup> Indeed, moreover to develop numerous accessible adsorption  
47 sites, these layered materials show ion exchange capacities and outstanding hydration  
48 properties with an exfoliation of the nanosheets that can self-assembled in liquid crystalline  
49 phases.<sup>14,20</sup> Ion exchange with surfactants allows a modification of the chemical surface of  
50 layered materials with the intercalation of ionic surfactants within their interlayer space for the  
51 preparation of organo-clays/LDHs. Surfactants used as chemical modifier and/or in association

52 with clay mineral in solution generate a hydrophobic environment improving and enlarging the  
53 spectrum of adsorbed organic compounds. While zeolites and clay minerals were proposed as  
54 potential friendly drug delivery systems<sup>21-22</sup>, their uses were restricted to the adsorption of  
55 cationic and/or polar organic compounds and show some limits to hydrophobic and anionic  
56 organic compounds such as PPs.<sup>1-3, 13</sup> In contrast, with a hydrophobic environment conferring  
57 by surfactants, organoclays show advanced adsorption properties for numerous compounds.<sup>19,</sup>  
58 <sup>23</sup>

59 With concentrations reaching up to mg L<sup>-1</sup> in wastewater, detergents or surfactants represent  
60 an underhand contamination as pharmaceuticals do. However, the presence of these detergents  
61 represents a blessing in disguise where the addition of clay mineral may form organoclays  
62 driving to an efficient remediation system. Indeed, uptake of PPs was particularly enhanced  
63 with the combination of clay mineral and micelle surfactant or surfactant in excess that  
64 represents an efficient remediation system, where hydrophobic core micelle act as solvent to  
65 organic contaminants driving to molecular complexes that can be adsorbed onto both inorganic  
66 and hybrid layered materials.<sup>7-9, 24</sup>

67 Thus, this study is inscribed in that frame research work with a particular attention to a better  
68 understanding of the interactional mechanisms between a pharmaceutical: the diclofenac (DFC)  
69 and a cationic organoclay with different surfactant arrangement and density, as well as with a  
70 coupled organoclay/micelle action. A long alkyl tail with an aromatic ring cationic surfactant:  
71 the benzyldimethyltetradecylammonium (BDTA), recognized to show certain versatility to  
72 interact with numerous organic compounds through different interactional processes was  
73 chosen as a chemical modifier.<sup>1, 19</sup> Since the arrangement plays on the adsorption properties,  
74 three organoclays were prepared at a concentration of 0.4, 1 and 4 times that of the cation  
75 exchange capacity (CEC) of the clay mineral where adsorbents display an increase of the  
76 interlayer space with the confinement of a lateral monolayer, bilayer and paraffin organization

77 while showing an organic environment, which may favor *a priori* the further adsorption of  
78 DFC.<sup>1,16,19</sup> DFC was selected here since it is a PP commonly found in aquatic environments  
79 due to its large consumption as well as its low biodegradability and is one of the few  
80 pharmaceutical compounds showing a high ecotoxicity affecting both aquatic and terrestrial  
81 ecosystems.<sup>25-27</sup>

82

83

## 84        2. Materials and Methods

### 85        2.1. Adsorbents

86        Wyoming sodium montmorillonite (Mt), obtained from the Source Clay Minerals Repository,  
87        University of Missouri (Columbia, MO) was used in this study as a starting material. The  
88        structural            formula            can            be            expressed            as:

89         $(\text{Ca}_{0.12}\text{Na}_{0.32}\text{K}_{0.05})[\text{Al}_{3.01}\text{Fe(III)}_{0.41}\text{Mn}_{0.01}\text{Mg}_{0.54}\text{Ti}_{0.02}][\text{Si}_{7.98}\text{Al}_{0.02}]\text{O}_{20}(\text{OH})_4$ . Mt was fractioned  
90        to  $< 2 \mu\text{m}$  by gravity sedimentation, purified and  $\text{Na}^+$  exchanged. This Mt clay mineral shows  
91        a cation exchange capacity (CEC) of 76.4 meq per 100 g clay.

92        Benzyltrimethyltetradecyl ammonium (BDTA) cationic surfactant was supplied from Sigma  
93        Aldrich Chemical that exhibits a critical micelle concentration (cmc) of  $2 \times 10^{-3} \text{ mol L}^{-1}$ .  
94        Aqueous solutions of BDTA with Millipore deionized water were prepared at ambient  
95        temperature at concentrations of 0.4, 1 and 4 times the cation exchange capacity (CEC) of Mt  
96        clay leading to three different surfactant organizations within the interlayer space: lateral  
97        monolayer, bilayer and a paraffin structure that drive on the magnitude of adsorption of the  
98        organoclays. These surfactant solutions were poured in aqueous Mt dispersions at a  
99        concentration of 3% (in weight) before being stirred at 300 rpm for 24 h. At the end of this  
100        procedure, the solutions were centrifuged at 3000 rpm for 20 min and the supernatants were  
101        removed. The resulting organoclays were dried at  $100^\circ\text{C}$  for 24 h before analysis and used as  
102        sorbents ensuring us to have dehydrated materials without any degradation or change of the  
103        surfactants organization as it was previously measured elsewhere.

104

### 105        2.2. Experimental techniques

106        The concentration of DFC before and after being in contact with the adsorbents was obtained  
107        by GC/MS analysis using Trace GC Ultra chromatograph and TSQ Quantum XLS mass  
108        spectrometer (Thermo Scientific).

109 Fourier transform infrared (FTIR) measurements in the range  $650\text{-}4000\text{ cm}^{-1}$ , were recorded  
110 using a Thermo Nicolet 6700 FT spectrometer equipped with a Deuterated Triglycine Sulfate  
111 (DTGS) detector and a Nicolet Continuum microscope. The powder samples were spread over  
112 a NaCl window of the microscope. The analyzed sample area was a square of side  $100\text{ }\mu\text{m}$   
113 chosen under the microscope 15X Infinity Reflectomat objective. The analyses were  
114 performed in transmission mode and each spectrum corresponded to the average of 256 scans  
115 collected at  $2\text{ cm}^{-1}$  resolution.

116 The structural changes of the layered materials (organoclays and diclofenac/organoclay  
117 complexes) were determined by X-ray diffraction. X-ray diffraction patterns were recorded in  
118 a conventional  $\theta\text{-}\theta$  Bragg-Brentano configuration by using a Thermo Electron ARL'XTRA  
119 diffractometer equipped with a Cu anode ( $\text{CuK}\alpha = 1.5418\text{ \AA}$ ) coupled with a Si(Li) solid  
120 detector. The diffractograms on dry samples ( $100^\circ\text{C}$  for 24 h) were performed between  $1$  and  
121  $24^\circ$  ( $2\theta$ ) with an angular and time steps of  $0.04^\circ$  and 10 s, respectively.

122

### 123 *2.3. Adsorption of diclofenac*

124 DFC (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid of which pKa is 4.1 and has a log  $K_{ow}$   
125 of 4.51 where  $K_{ow}$  represents the octanol/water partition coefficient) purchased from Sigma  
126 Aldrich Chemical, and assumed to have a purity  $> 98\%$  was used in its sodium salt form which  
127 shows a solubility better than  $10\text{ g L}^{-1}$ . Batch adsorption experiments of DFC onto organoclays  
128 were conducted in duplicate using at least 10 initial aqueous solutions ranging from  $10\text{ mg L}^{-1}$   
129 to  $2\text{ g L}^{-1}$ . The solid to liquid ratio was kept constant, where 100 mg of organoclays were used  
130 for 50 mL of diclofenac aqueous solutions in centrifuge tubes and the pH was adjusted at a  
131 value of 6.5 by a mix of both HCl acidic and NaOH basic solutions. Samples were shaken on a  
132 rotary shaker at 50 rpm during 24 h in order to reach the equilibrium final concentrations and  
133 were centrifuged at 5000 rpm for 25 min. Both supernatants and sorbents after contact with

134 DFC were removed and analyzed through GC/MS. The amount of adsorbed DFC was  
135 calculated by the difference between the initial and equilibrium final concentrations that  
136 allowed us to determine the equilibrium adsorption isotherms. Before their XRD and FTIR  
137 characterizations, the entire resulting organoclays and Mt after adsorption of DFC were dried  
138 at 100°C for 48 h.



### 139        **3. Results and discussion**

#### 140    *3.1. Enhancement of the adsorption properties*

141        Due to its negative charge, DFC (Supplement information SI, Figure 1) is poorly adsorbed on  
142        clay minerals<sup>2</sup>, in contrast to their anionic analogous, i.e. layered double hydroxides (LDHs)  
143        which proved their particular affinity to numerous anionic compounds: ibuprofen, ketoprofen  
144        pharmaceutical ingredients; and thus were proposed as release systems for biomedical  
145        applications.<sup>28</sup> Indeed, moreover to control the PPs release by limiting their amounts and  
146        potential water contamination, the confinement of PPs within the interlayer space of layered  
147        materials drives to an amorphization or a glassy state that enhances their therapeutic actions.<sup>3</sup>  
148        Nevertheless, since their LDHs structure cannot be kept at low pH, their uses are restricted  
149        pH>8 (except those with particular chemical composition) limiting their removal properties for  
150        waste or drinking (potable) waters.<sup>19</sup>

151        The adsorption of both ionic and nonionic surfactants onto porous materials switches their  
152        chemical surface from hydrophilic to hydrophobic.<sup>1, 16,19</sup> Moreover to protect both the surface  
153        and the layered structure from any chemical attack, the grafting of surfactants offers new  
154        adsorption sites with the generation of a hydrophobic environment that enhances the adsorption  
155        properties for numerous pollutants.<sup>1</sup> The optimization of the adsorption efficiency mainly  
156        depends on the nature, density and organization of the adsorbed surfactants. Here, in this work,  
157        organoclays were prepared, with a long alkyl tail cationic surfactant: the BDTA, to first verify  
158        these previous observations. X-ray diffraction patterns (Figure SI-2) show the intercalation of  
159        BDTA at the concentration of 0.4, 1, and 4 times the CEC, with a shift of the *00l* reflection to  
160        low angular value. By corroborating the CH<sub>2</sub> stretching vibrations frequencies of the BDTA  
161        hydrocarbon chains (Figure SI-3) and the values of the *d*<sub>001</sub> interlayer space estimated though  
162        the angular position of the *00l* reflection, the surfactant/organoclay arrangement can be drawn

163 and is summarized as follows in Figure 1: a lateral monolayer (BDTA<sub>0.4</sub>-Mt); lateral bilayers  
164 (BDTA-Mt), and normal bilayer or paraffin organization (BDTA<sub>4</sub>-Mt).<sup>1,16</sup>

165 As expected and previously observed for numerous organoclay/organic product couples,  
166 equilibrium adsorption isotherms confirm the improvement of the adsorption properties of  
167 composite layered materials compared to raw clay mineral (Figure 2). The GC/MS results point  
168 out the poor adsorption of diclofenac, organic compound showing two aromatic rings and being  
169 mainly anionic at pH > pK<sub>A</sub>, onto raw clay mineral. Although the isotherm lineshapes differ, the  
170 adsorbed amount of diclofenac onto Na-Mt estimated at the plateau of reaches that one of  
171 BDTA<sub>0.4</sub>-Mt, organoclay showing a dual hydrophilic/hydrophobic since 60% of the  
172 compensating cations are kept. This somehow surprising result underlines the complexity and  
173 richness of the interactional mechanisms involved in the DFC adsorption.

174 Apart from the BDTA<sub>0.4</sub>-Mt isotherm which exhibits a linear behavior, other isotherms show  
175 similar lineshapes with two main regimes: (i) a gradual growing of the adsorbed amounts  
176 following the equilibrium concentration, and (ii) a plateau or steady state at high concentration.  
177 Adsorption isotherms allow one to precisely quantify the degree of affinity between the DFC  
178 and the four adsorbents, which mainly depends on the density of BDTA. Indeed, BDTA<sub>4</sub>-Mt  
179 organoclay seems to be more efficient with a maximum adsorbed amount  $1.9 \times 10^{-4} \text{ mol g}^{-1}$   
180 whereas BDTA-Mt shows a plateau with a maximum adsorbed amount of  $1.19 \times 10^{-4} \text{ mol g}^{-1}$   
181 and a maximum amount of  $5.05 \times 10^{-5} \text{ mol g}^{-1}$  for BDTA<sub>0.4</sub>-Mt. In contrast to the maximal  
182 adsorbed amount onto Na-Mt ( $4.05 \times 10^{-5} \text{ mol g}^{-1}$ ), one order of magnitude detaches to those  
183 of organoclays, stressing out here the importance of the organophilic character of the  
184 organoclay surface where molecular hydrophobic and  $\pi$ - $\pi$  interactions efficiently allow the  
185 adsorption of DFC, as it was expected with  $K_{ow}$  coefficient of the diclofenac. If it is tempting  
186 to try a direct correlation between the density of surfactant and DFC adsorbed amounts, this  
187 could not be done here since the adsorption depends on the BDTA organization and the

188 diversity of the driving adsorption forces as the results of Na-Mt display and BDTA<sub>0.4</sub>-Mt.  
189 Indeed, in the latter case, the BDTA<sub>0.4</sub>-Mt organoclay shows a reasonable increase of its  
190 interlayer space while almost 50% of its whole surface displays a lipophilic behavior that may  
191 restrict the possibility of adsorption of DCF and thus explains a linear lineshape for the  
192 adsorption. In contrast, the improvement of the DFC removal is meaningful for BDTA density  
193 > 1CEC with a adsorption capacity greater than 260 and about 380 % for BDTA-Mt and  
194 BDTA<sub>4</sub>-Mt respectively compared to those of both BDTA<sub>0.4</sub>-Mt and Na-Mt.

195 By comparing the maximum amounts at the plateau to the theoretical ones that can be  
196 adsorbed onto the layered materials showing a specific surface area of 750 m<sup>2</sup> g<sup>-1</sup> and a mean  
197 molecular radius of 3 Å for DFC<sup>29,30</sup>, the experimental adsorbed values represent about 20%,  
198 52%, et 76% of the whole accessible surface, exceeding that of the external surface (with the  
199 hypothesis of a monolayer adsorption). If the adsorption of DFC leads to a shift of the *00l*  
200 reflection to low angular value (Figure SI-4), attesting a possible intercalation within the  
201 interlayer space; the diffractograms of the whole organoclays after being in contact with  
202 diclofenac do not show any structural changes (i.e. no shift to low angle of the 00l reflection  
203 was observed), nor any crystallization of diclofenac onto the external surface (Figure SI-5).  
204 Nevertheless, in regards to the adsorbed amount, the adsorption leads to the intercalation of  
205 diclofenac where free spots are available within the interlayer space and/or between the  
206 hydrocarbon chains implying a possible re-organization of BDTA.

207

208

209 *3.2. Confirmation of the proper adsorption through FTIR analyses*

210 FTIR spectroscopy gives us important information on the conformation of both organic  
211 cations by focusing on the CH<sub>2</sub> stretching bands wavenumbers windows in the range 2800–  
212 3000 cm<sup>-1</sup> (Figure 3A) and DFC amount, in particular the CO<sub>2</sub><sup>-</sup> stretching in the range of 1450–  
213 1650 cm<sup>-1</sup> (Figure 3B).<sup>1, 16, 21</sup> In addition to determining any conformational change, this  
214 quantitative technique (in transmission mode) allows one to appreciate the evolution of both  
215 surfactants and adsorbed PP. Indeed, the spectral feedbacks of the CO<sub>2</sub><sup>-</sup> stretching bands follow  
216 the DFC concentration. Thus, FTIR data allows one to extract similar information as adsorption  
217 isotherms obtained by GC/MS and stress out the originality of the method to follow the  
218 adsorption of an organic compound onto a surface, but also to analyze the fate of surfactants.  
219 Indeed, the integrated intensity of the CH<sub>2</sub> stretching bands is based on the density of surfactants  
220 as well as that of CO<sub>2</sub><sup>-</sup> stretching bands for DFC.

221 The deconvolution operation of these vibrational bands (SI Figures 6 & 7) allows one to  
222 follow the evolution of the amounts related to both DFC and BDTA (Figures 4 & 5). The  
223 evolution of the integrated intensity CO<sub>2</sub><sup>-</sup> stretching bands related to the diclofenac density that  
224 shows a line-shape similar to that of the resulting GC/MS adsorption isotherms, confirming the  
225 proper adsorption of the PP onto the whole adsorbents (Figure 4). The deconvolution of the  
226 CH<sub>2</sub> stretching bands stresses out the stability of the organization of BDTA within the interlayer  
227 space of BDTA<sub>0.4</sub>-Mt and BDTA-Mt as both FTIR and XRD analyses showed. In contrast, the  
228 decrease of the integrated intensity of both CH<sub>2</sub> stretching bands for BDTA<sub>4</sub>-Mt as the  
229 concentration of DFC is increased reveals a reorganization of the surfactant within the interlayer  
230 space due to the adsorption of PP due to the release of BDTA (Figure 5). Since the d<sub>001</sub> spacing  
231 remains at a constant value with the adsorption of diclofenac while both symmetric and  
232 antisymmetric CH<sub>2</sub> stretching bands appear to shift at high frequencies, it indicates a  
233 reorganization of BDTA from an all-trans to a gauche conformation (Figure 5).<sup>16, 21</sup> It is

234 important to mention that the preparation of the BDTA<sub>4</sub>-Mt was achieved at a concentration of  
235 4 times the CEC where organic cations, after 1CEC, are adsorbed through molecular  
236 hydrophobic interaction leading to a positive charge of the surfactant aggregates within the  
237 interlayer space. Since hydrophobic interaction could be easily disrupted with temperature or by  
238 stirring, one can doubt on the stability of organoclay. Nevertheless, the previous tests by  
239 dissolved organic carbon of BDTA<sub>4</sub>-Mt suspensions under stirring revealed no release of  
240 surfactant, nor reorganization of the BDTA that showed an all-trans conformation keeping a  
241  $d_{001}$  spacing at 34.5 Å.<sup>16,19</sup> Thus, moreover to the contribution of the hydrophobic character, it  
242 appears that the positive charge of organoclay and the proportion of accessible mobilized or  
243 free BDTA organic cations play as vectors for the adsorption of diclofenac in important  
244 amounts.

245

### 246 *3.3. Free surfactant as a path for adsorption*

247 In regards to the efficiency of the adsorption for BDTA<sub>4</sub>-Mt where free organic cations in  
248 organoclay seem to interact with diclofenac favoring its adsorption, a one-pot adsorption  
249 experiment based on this assumption was tested. By adding both BDTA-Mt organoclay (lateral  
250 bilayer organization) and BDTA surfactant in excess (micelle or monomer) in DFC solutions;  
251 it was expected a direct combination between organic cations and PP via electrostatic  
252 interaction, leading to the formation of organic complexes that can be adsorbed onto BDTA-  
253 Mt enhancing considerably the efficiency of DFC removal. Such mixture makes sense since  
254 wastewater is frequently contaminated with detergents (surfactants) at concentrations up to mg  
255 L<sup>-1</sup>, and thus can be used as vector for the adsorption of organic contaminants if one injects  
256 organoclays or clay minerals in effluents or wastewaters.

257 Equilibrium adsorption isotherm onto BDTA-Mt in BDTA solution displays a linear trend  
258 with huge adsorbed DFC amount (Figure 2), suggesting a total adsorption without any  
259 saturation of the system even at high concentration. The infrared spectra confirm the proper

260 adsorption of diclofenac and show with a gradual growing of absorption bands of both DFC  
261 and BDTA onto BDTA-Mt (Figure 4) confirming that free BDTA molecules favor and  
262 contribute to the adsorption. Indeed, since BDTA is an organic cation whereas DFC an anion,  
263 it is obvious that the compounds in solution could easily form organic complexes interacting  
264 through electrostatic interaction. These complexes can be intercalated/adsorbed at high amount  
265 due to the hydrophobic nature of BDTA-Mt.<sup>7-9</sup> Since BDTA in solution was at high  
266 concentration, it was possible to think that BDTA was first adsorbed onto BDTA-Mt with the  
267 possibility to generate a BDTA<sub>4</sub>-Mt organoclay as the main actor for PP adsorption. This could  
268 be valid if CH<sub>2</sub> stretching bands of the resulting complexes show a shift in frequency, which  
269 was not observed here and moreover, the adsorbed amount would have been similar to that of  
270 the experiment led onto BDTA<sub>4</sub>-Mt. X-ray diffractograms of BDTA-Mt with both diclofenac  
271 and BDTA in excess (Figure 6) clearly show a shift to low angle with a *00l* reflection observed  
272 at about 3° (*d*<sub>001</sub> > 34 Å) for the highest concentration of diclofenac confirming thus the  
273 intercalation, in confrontation with FTIR data, of both DFC and BDTA (Figure 7).

274

### 275 3.4. Environmental applications

276 The adsorption data were fit using a Freundlich equation, model applicable to the adsorption  
277 on heterogeneous surfaces where the interaction between the adsorbed molecules is not limited  
278 to the formation of a monolayer:

$$279 \quad q_e = K_F C_e^{1/n}$$

280 where *q<sub>e</sub>* is the mol of diclofenac per g of adsorbents (mol g<sup>-1</sup>), *K<sub>F</sub>* (L g<sup>-1</sup>) and *n* are both  
281 adsorption Freundlich parameters which respectively indicate the adsorption efficiency and the  
282 non-linearity degree between DFC and sorbents. As expected, the adsorption capacity of the  
283 systems depends on their lipophilic character as well as their ability to provide free BDTA  
284 organic cations (i.e. BDTA<sub>4</sub>-Mt and BDTA-Mt with the surfactant in excess in solution).

285 Indeed,  $K_F$  constants, derived from the fitting procedure where  $R^2 > 0.936$  attesting the good  
286 agreement of the experimental data with Freundlich model, reflects the adsorption capacity of  
287 the studied sorbents. Interestingly, although showing a hydrophobic character, BDTA<sub>0.4</sub>-Mt  
288 shows a lower  $K_F$  value ( $4.2 \times 10^{-3} \text{ L g}^{-1}$ ) comparatively to Na-Mt of which  $K_F$  is one order of  
289 magnitude higher (Table 1). The adsorption of diclofenac is achieved in solution with an  
290 equilibrium between its protonated and acidic forms (with a preponderance of its acidic form  
291 at the studied  $\text{pH} \approx 6.5$ ) where clay platelets are fully exfoliated giving to a total access of the  
292 whole adsorption sites. While the intercalation of BDTA at a concentration of 40% leads to a  
293 lipophilic behavior of about 50% of the whole surface and opens the interlayer space, it restricts  
294 the possibility of adsorption of DFC. In contrast,  $K_F$  constants are significantly greater for  
295 BDTA<sub>4</sub>-Mt and BDTA-Mt underlining the importance of the lipophilic character of the sorbent.  
296 Of the sorbent systems evaluated here, the combination of both BDTA-Mt and BDTA micelle  
297 in solution (one pot adsorption) shows the highest affinity for diclofenac with 1.0 g of this  
298 system allows approximately 1.76 L of effluent to be treated. In comparison to other systems  
299 such as granular activated carbon (GAC) with  $K_F = 141 \text{ L g L}^{-1}$  and  $n = 0.19$ , the diclofenac  
300 removal efficiency is quite high and similar to values reported in the literature (15–50%) for  
301 other systems like the grape bagasse.<sup>4, 10</sup> It is important also to mention that the time required  
302 to reach equilibrium was much shorter using organoclay or a combined organoclay/surfactant  
303 in excess (less than 24 h) compared to GAC (48 h). Moreover, this latter material has an  
304 intrinsically high affinity for hydrophobic compounds without implying a partitioning process.  
305 Indeed, its high affinity for organic compounds with van der Waals forces combined with pore-  
306 filling processes occurs in macro-, meso- and micro-pores. In a context of wastewater  
307 remediation, several effects drastically reduce GAC uptake: (i) blocking of the pores with  
308 colloids, humic acids, and oils, and (ii) competition between pollutants.<sup>23</sup>

309 The enhance uptake of diclofenac by BDTA-Mt/BDTA in excess verifies it use as potential  
310 solution for wastewater process since it shows an efficiency equivalent to grape bagasse  
311 material of which adsorption removal is far greater than other conventional treatments, such as  
312 biological filtration (removal of 9%) and coagulation–flocculation processes (removal of less  
313 than 1%).<sup>4,5,10</sup> However, before any application in wastewater or drinking water treatments,  
314 further investigations concerning the desorption of both diclofenac and BDTA with organic and  
315 water solvent need to be undertaken.

316



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## Table

Table 1. Equilibrium Adsorption isotherm constants determined with Freundlich model fit for the adsorption of diclofenac onto several BDTA-Mt organoclays showing different surfactant arrangements and BDTA-Mt organoclay with BDTA micelles.

	Na-Mt	BDTA <sub>0.4</sub> -Mt	BDTA-Mt	BDTA-Mt/ BDTA in excess	BDTA <sub>4</sub> -Mt
<b>K<sub>F</sub> (L g<sup>-1</sup>)</b>	3.87 x 10 <sup>-2</sup>	4.20 x 10 <sup>-3</sup>	0.09	1.76	0.1
<b>n</b>	4.95	0.90	5.40	2.38	6.71
<b>R<sup>2</sup></b>	0.997	0.988	0.992	0.997	0.936

## Figures

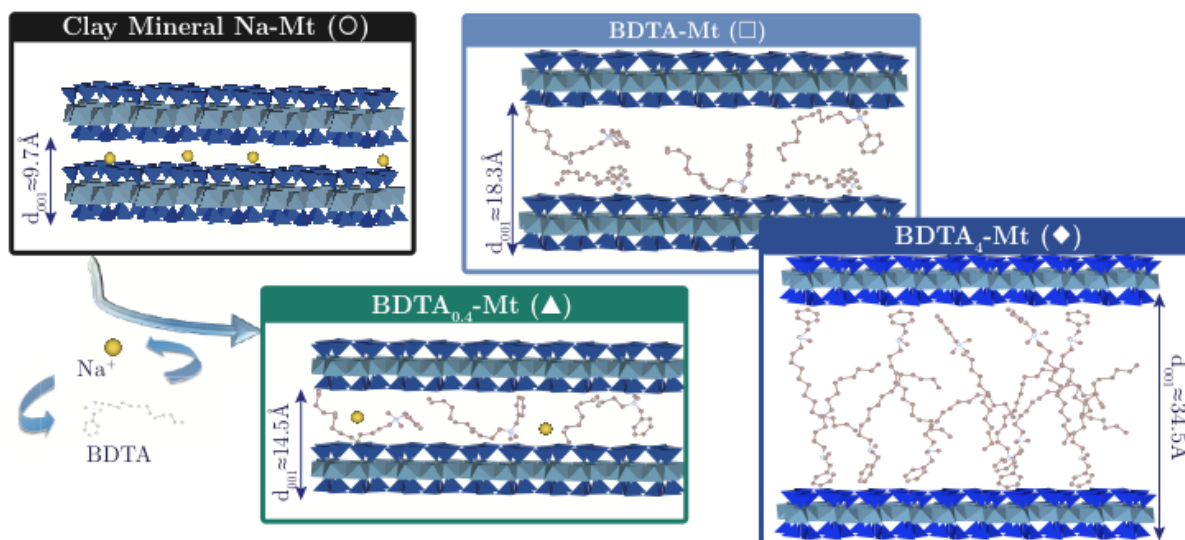


Figure 1: Schematic representation of the whole geo-sorbents used in this study: Na-Mt clay mineral, BDTA<sub>0.4</sub>-Mt (60% of the compensating cations are preserved) showing a lateral monolayer arrangement, BDTA-Mt (100% of the compensations cations are substituted to BDTA) with a lateral bilayer organization, and BDTA<sub>4</sub>-Mt (prepared at 4 times the value of the cation exchange capacity where extra BDTA cations are intercalated expanding the interlayer space at spacing's close to 35 Å) with a paraffin organization of the surfactant.

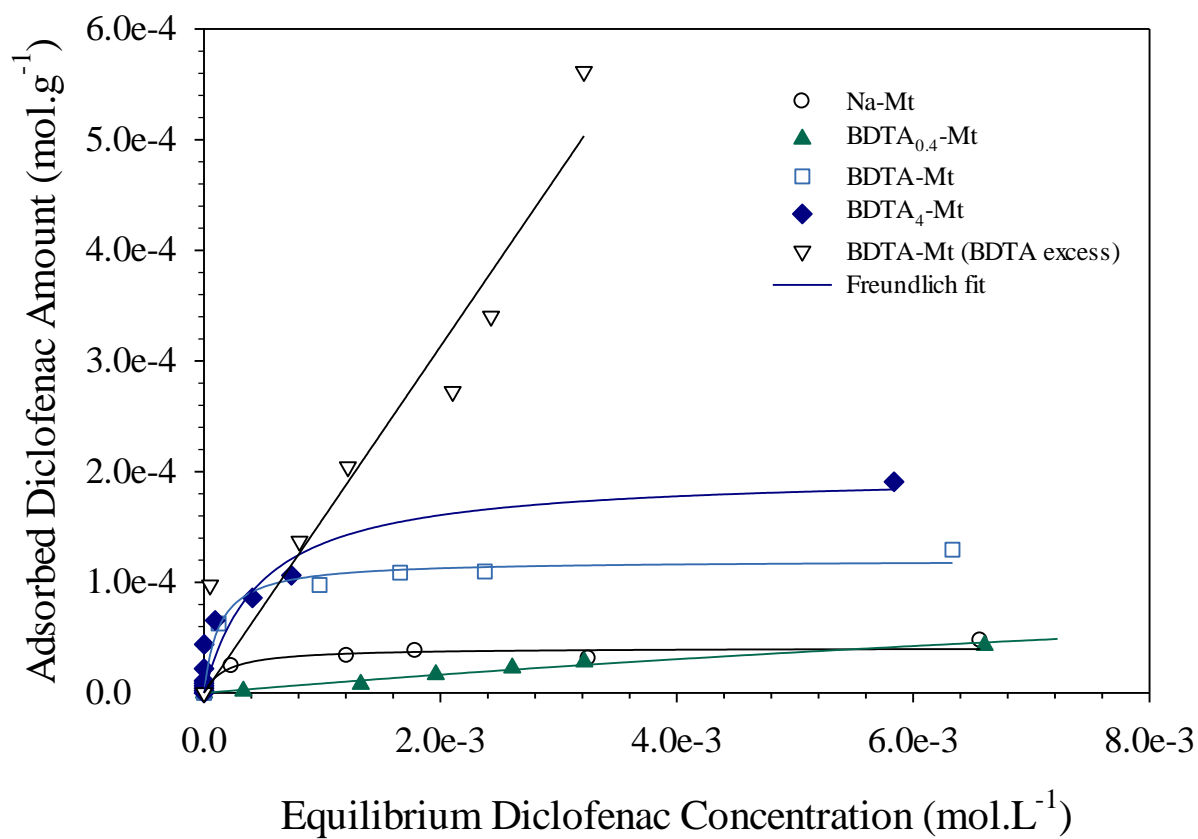
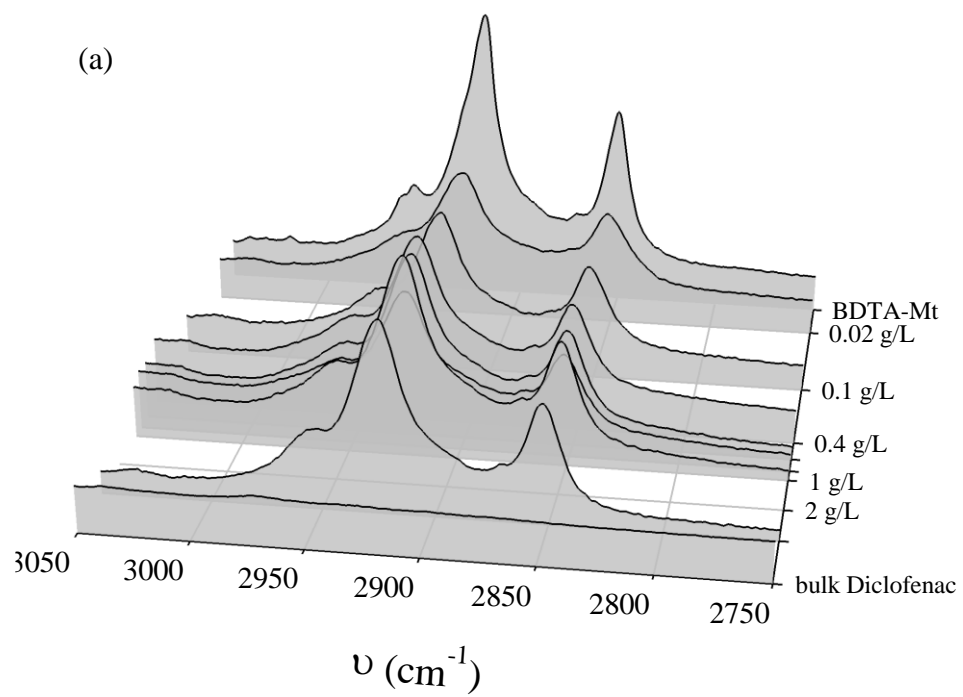


Figure 2: Equilibrium adsorption isotherms of diclofenac onto an untreated Na exchanged montmorillonite: Na-Mt (white circle), a BDTA<sub>0.4</sub>-Mt organoclay (green triangle top), a BDTA-Mt organoclay (white filled light blue square), a BDTA<sub>4</sub>-Mt organoclay (dark blue diamond), and coupled BDTA-Mt with an excess of surfactant in solution (white triangle down). The solid lines represent the fits by using the Freundlich equation model.



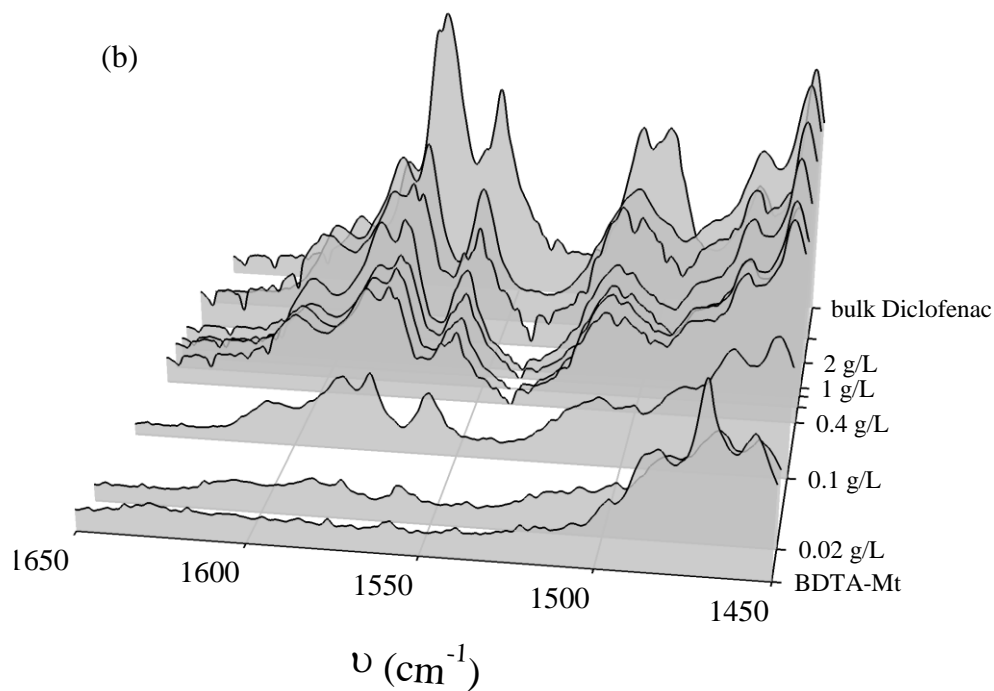


Figure 3: (a) 3D evolution of the FTIR spectra in the 2750-3050  $\text{cm}^{-1}$  wavenumbers range (probing the  $\text{CH}_2$  stretching bands of the BDTA hydrocarbon chains) of the BDTA<sub>4</sub>-Mt organoclays as a function of the starting diclofenac concentration ( $\text{g L}^{-1}$ ); (b) 3D evolution of the FTIR spectra in the 1450-1650  $\text{cm}^{-1}$  wavenumbers range (probing the  $\text{COO}^-$  absorption bands) of the BDTA<sub>4</sub>-Mt organoclays as a function of the starting diclofenac concentration (selected series but a similar evolution for the other adsorbents was observed).

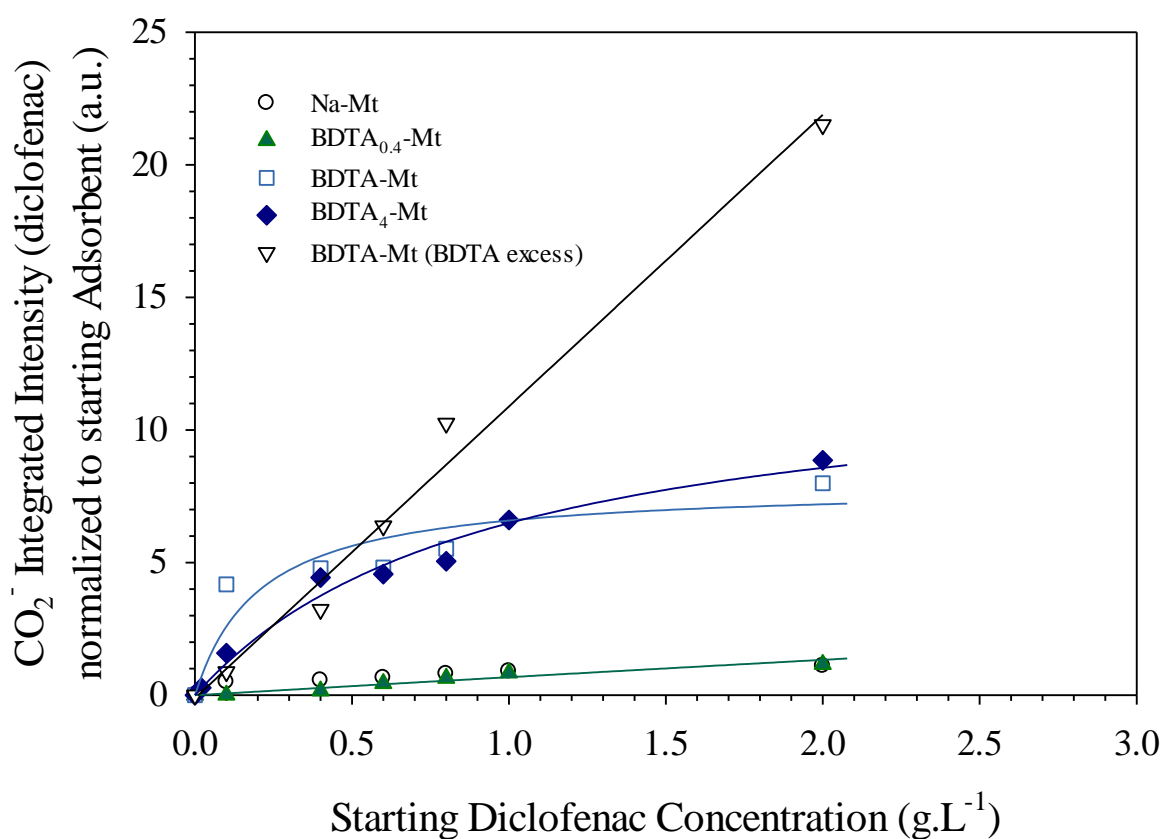


Figure 4: Integrated intensity of the diclofenac ( $\text{COO}^-$ ) as a function of the starting diclofenac concentration ( $\text{g L}^{-1}$ ) for an untreated Na exchanged montmorillonite: Na-Mt (white circle), a  $\text{BDTA}_{0.4}$ -Mt organoclay (green triangle top), a BDTA-Mt organoclay (white filled light blue square), a  $\text{BDTA}_4$ -Mt organoclay (dark blue diamond), and coupled BDTA-Mt with an excess of surfactant in solution (white triangle down). The solid lines represent a guide for the eyes.



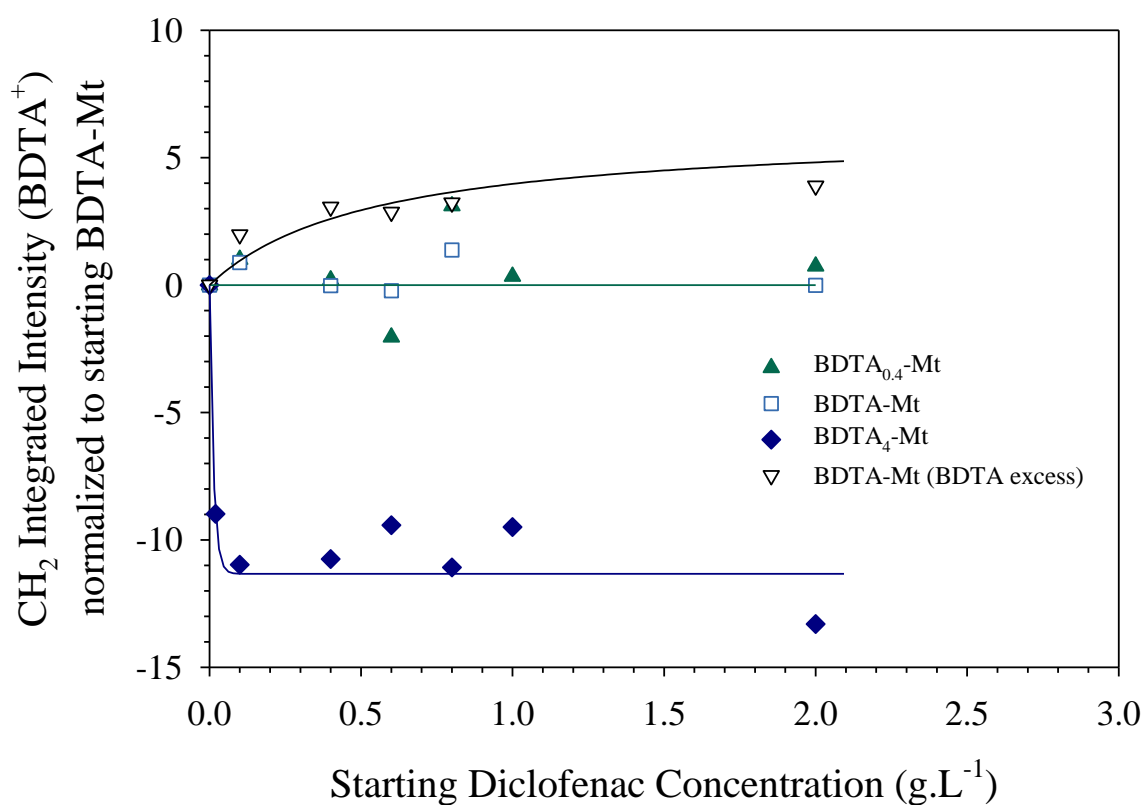


Figure 5: Integrated intensity of the BDTA (CH<sub>2</sub>) absorption bands as a function of the starting diclofenac concentration (g L<sup>-1</sup>) for a BDTA<sub>0.4</sub>-Mt organoclay (green triangle top), a BDTA-Mt organoclay (white filled light blue square), a BDTA<sub>4</sub>-Mt organoclay (dark blue diamond), and coupled BDTA-Mt with an excess of surfactant in solution (white triangle down). The solid lines represent a guide for the eyes.

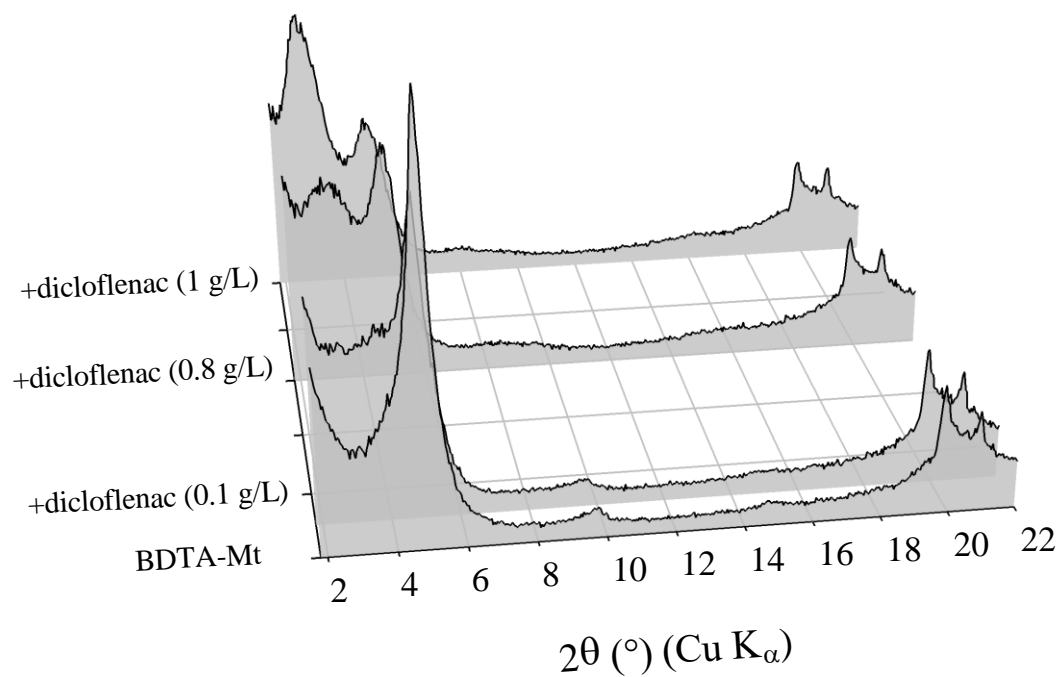


Figure 6: 3D evolution of the X-ray diffraction patterns of the dehydrated diclofenac-BDTA-Mt with BDTA in excess composite layered materials for selected concentration of diclofenac ( $\text{g L}^{-1}$ ).

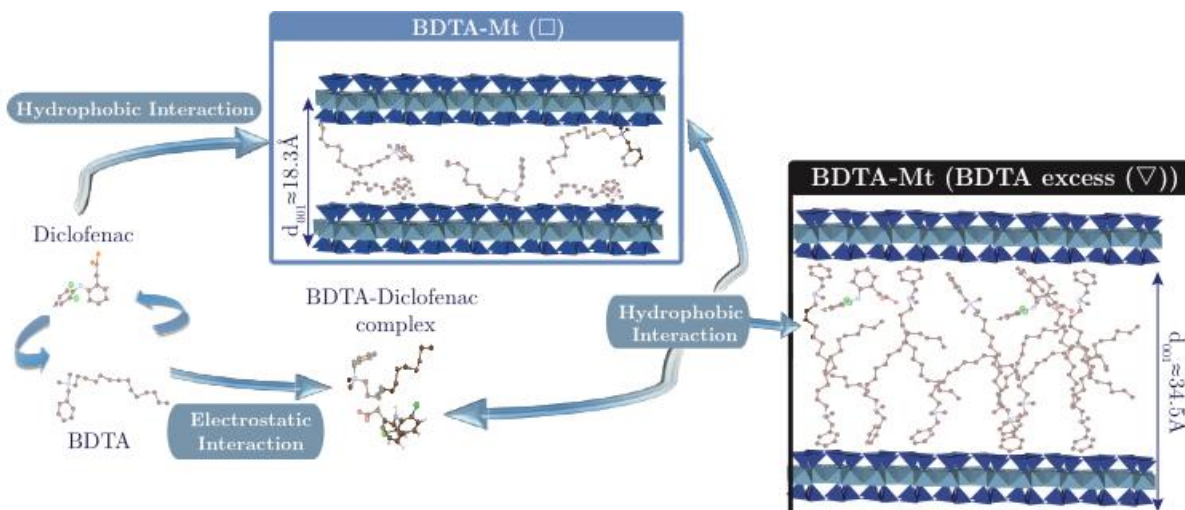


Figure 7: Schematic representation of the possible adsorption mechanisms for diclofenac onto BDTA-Mt (hydrophobic interaction) and with BDTA in excess (micelle) forming BDTA-Diclofenac complex that could be intercalated through hydrophobic interaction within the interlayer space of a BDTA-Mt organoclay.