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1 Coupled Organoclay/micelle action for the adsorption of diclofenac

2 *Tiago De Oliveira, Régis Guégan**

3 Institut des Sciences de la Terre d'Orléans, UMR 7327, CNRS-Université d'Orléans, 1A Rue
4 de la Férollerie, 45071 Orléans Cedex 2, France

5 tiago.de-oliveira@univ-orleans.fr

6 regis.guegan@univ-orleans.fr

7 **August 9th, 2016**

8 *To whom correspondence should be addressed. E-mail: regis.guegan@univ-orleans.fr. Phone:
9 +33 (0) 2 38 49 25 41. Fax: +33 (0) 2 38 63 64 88

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 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).¹⁻³ If the coupling
34 ozonation/adsorption on granular activated carbon (GAC) for instance seems to be an
35 alternative⁴⁻⁶, 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.⁷⁻⁹ 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.¹⁰⁻¹⁹

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.^{16, 19} 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.^{14,20} 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 systems²¹⁻²², 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.^{1-3, 13} In contrast, with a hydrophobic environment conferring
57 by surfactants, organoclays show advanced adsorption properties for numerous compounds.^{19,}
58 ²³

59 With concentrations reaching up to mg L⁻¹ 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.^{7-9, 24}

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.^{1, 19} 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.^{1,16,19} 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.²⁵⁻²⁷

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 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°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 650-4000 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 μm
113 chosen under the microscope 15X Infinity Reflechromat objective. The analyses were
114 performed in transmission mode and each spectrum corresponded to the average of 256 scans
115 collected at 2 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 θ - θ 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°C for 24 h) were performed between 1 and
121 24° (2θ) with an angular and time steps of 0.04° 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 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 mg L^{-1}
129 to 2 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 minerals², 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.²⁸ 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.³
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.¹⁹

151 The adsorption of both ionic and nonionic surfactants onto porous materials switches their
152 chemical surface from hydrophilic to hydrophobic.^{1, 16,19} 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.¹ 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 CH₂ stretching vibrations frequencies of the BDTA
161 hydrocarbon chains (Figure SI-3) and the values of the *d*₀₀₁ 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_{0.4}-Mt); lateral bilayers
164 (BDTA-Mt), and normal bilayer or paraffin organization (BDTA₄-Mt).^{1,16}

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_A, 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_{0.4}-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_{0.4}-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, BDTA₄-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_{0.4}-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 π - π 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_{0.4}-Mt.
189 Indeed, in the latter case, the BDTA_{0.4}-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 BDTA₄-Mt respectively compared to those of both BDTA_{0.4}-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 m² g⁻¹ and a mean
197 molecular radius of 3 Å for DFC^{29,30}, 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 CH₂ stretching bands wavenumbers windows in the range 2800–
212 3000 cm⁻¹ (Figure 3A) and DFC amount, in particular the CO₂⁻ stretching in the range of 1450–
213 1650 cm⁻¹ (Figure 3B).^{1, 16, 21} 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 CO₂⁻ 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 CH₂ stretching bands is based on the density of surfactants
220 as well as that of CO₂⁻ 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 CO₂⁻ 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 CH₂ stretching bands stresses out the stability of the organization of BDTA within the interlayer
227 space of BDTA_{0.4}-Mt and BDTA-Mt as both FTIR and XRD analyses showed. In contrast, the
228 decrease of the integrated intensity of both CH₂ stretching bands for BDTA₄-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 d₀₀₁ spacing
231 remains at a constant value with the adsorption of diclofenac while both symmetric and
232 antisymmetric CH₂ 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).^{16, 21} It is

234 important to mention that the preparation of the BDTA₄-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 BDTA₄-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.^{16,19} 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 BDTA₄-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⁻¹, and thus can be used as a 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.⁷⁻⁹ 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 BDTA₄-Mt organoclay as the main actor for PP adsorption. This could
268 be valid if CH₂ 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 BDTA₄-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° ($d_{001} > 34 \text{ \AA}$) 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_e is the mol of diclofenac per g of adsorbents (mol g^{-1}), K_F (L g^{-1}) 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. BDTA₄-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_{0.4}-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 BDTA₄-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.^{4, 10} 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.²³

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%).^{4,5,10} 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

References

1. De Oliveira, T.; Guégan, R.; Thiebault, T.; Milbeau, C. L.; Muller, F.; Teixeira, V.; Giovanela, M.; Boussafir, M., Adsorption of diclofenac onto organoclays: Effects of surfactant and environmental (pH and temperature) conditions. *Journal of Hazardous Materials*.
2. Thiebault, T.; Boussafir, M.; Guegan, R.; Le Milbeau, C.; Le Forestier, L., Clayey-sand filter for the removal of pharmaceuticals from wastewater effluent: percolation experiments. *Environmental Science: Water Research & Technology* **2016**, *2*, (3), 529-538.
3. Thiebault, T.; Guégan, R.; Boussafir, M., Adsorption mechanisms of emerging micro-pollutants with a clay mineral: Case of tramadol and doxepine pharmaceutical products. *Journal of Colloid and Interface Science* **2015**, *453*, 1-8.
4. Sotelo, J. L.; Ovejero, G.; Rodríguez, A.; Álvarez, S.; Galán, J.; García, J., Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon. *Chemical Engineering Journal* **2014**, *240*, 443-453.
5. Sotelo, J. L.; Rodríguez, A.; Álvarez, S.; García, J., Removal of caffeine and diclofenac on activated carbon in fixed bed column. *Chemical Engineering Research and Design* **2012**, *90*, (7), 967-974.
6. Rakić, V.; Rac, V.; Krmar, M.; Otman, O.; Auroux, A., The adsorption of pharmaceutically active compounds from aqueous solutions onto activated carbons. *Journal of Hazardous Materials* **2015**, *282*, 141-149.
7. Undabeytia, T.; Nir, S.; Sánchez-Verdejo, T.; Villaverde, J.; Maqueda, C.; Morillo, E., A clay-vesicle system for water purification from organic pollutants. *Water Research* **2008**, *42*, (4-5), 1211-1219.
8. Polubesova, T.; Nir, S.; Zadaka, D.; Rabinovitz, O.; Serban, C.; Groisman, L.; Rubin, B., Water Purification from Organic Pollutants by Optimized Micelle-Clay Systems. *Environmental Science & Technology* **2005**, *39*, (7), 2343-2348.
9. Polubesova, T.; Zadaka, D.; Groisman, L.; Nir, S., Water remediation by micelle-clay system: Case study for tetracycline and sulfonamide antibiotics. *Water Research* **2006**, *40*, (12), 2369-2374.
10. Antunes, M.; Esteves, V. I.; Guégan, R.; Crespo, J. S.; Fernandes, A. N.; Giovanela, M., Removal of diclofenac sodium from aqueous solution by Isabel grape bagasse. *Chemical Engineering Journal* **2012**, *192*, 114-121.
11. Bui, T. X.; Kang, S.-Y.; Lee, S.-H.; Choi, H., Organically functionalized mesoporous SBA-15 as sorbents for removal of selected pharmaceuticals from water. *Journal of Hazardous Materials* **2011**, *193*, 156-163.
12. Gardi, I.; Nir, S.; Mishaël, Y. G., Filtration of triazine herbicides by polymer-clay sorbents: Coupling an experimental mechanistic approach with empirical modeling. *Water Research* **2015**, *70*, 64-73.
13. Guégan, R.; Giovanela, M.; Warmont, F.; Motelica-Heino, M., Nonionic organoclay: A 'Swiss Army knife' for the adsorption of organic micro-pollutants? *Journal of Colloid and Interface Science* **2015**, *437*, 71-79.
14. Guegan, R.; Sueyoshi, K.; Anraku, S.; Yamamoto, S.; Miyamoto, N., Sandwich organization of non-ionic surfactant liquid crystalline phases as induced by large inorganic K4Nb6O17 nanosheets. *Chemical Communications* **2016**, *52*, (8), 1594-1597.
15. Karaman, R.; Khamis, M.; Quried, M.; Halabieh, R.; Makhazeh, I.; Manassra, A.; Abbadi, J.; Qtait, A.; Bufo, S. A.; Nasser, A.; Nir, S., Removal of diclofenac potassium from wastewater using clay-micelle complex. *Environmental Technology* **2012**, *33*, (11), 1279-1287.

16. de Paiva, L. B.; Morales, A. R.; Valenzuela Diaz, F. R., Organoclays: properties, preparation and applications, *Appl. Clay Sci.* **2008**, 42, 8-24
17. Suriyanon, N.; Punyapalakul, P.; Ngamcharussrivichai, C., Mechanistic study of diclofenac and carbamazepine adsorption on functionalized silica-based porous materials. *Chemical Engineering Journal* **2013**, 214, 208-218.
18. Zhao, Q.; Burns, S. E., Modeling Sorption and Diffusion of Organic Sorbate in Hexadecyltrimethylammonium-Modified Clay Nanopores – A Molecular Dynamics Simulation Study. *Environmental Science & Technology* **2013**, 47, (6), 2769-2776.
19. Park, Y.; Ayoko, G. A.; Frost, R. L., Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. *Journal of Colloid and Interface Science* **2011**, 354, (1), 292-305.
20. Guegan, R., Self-assembly of a non-ionic surfactant onto a clay mineral for the preparation of hybrid layered materials. *Soft Matter* **2013**, 9, (45), 10913-10920.
21. Serri, C.; de Gennaro, B.; Catalanotti, L.; Cappelletti, P.; Langella, A.; Mercurio, M.; Mayol, L.; Biondi, M., Surfactant-modified phillipsite and chabazite as novel excipients for pharmaceutical applications? *Microporous and Mesoporous Materials* **2016**, 224, 143-148.
22. Perioli, L.; Posati, T.; Nocchetti, M.; Bellezza, F.; Costantino, U.; Cipiciani, A., Intercalation and release of antiinflammatory drug diclofenac into nanosized ZnAl hydrotalcite-like compound. *Applied Clay Science* **2011**, 53, (3), 374-378.21.
23. Johnston, C. T.; Khan, B.; Barth, E. F.; Chattopadhyay, S.; Boyd, S. A., Nature of the Interlayer Environment in an Organoclay Optimized for the Sequestration of Dibenzo-p-dioxin. *Environmental Science & Technology* **2012**, 46, (17), 9584-9591.
24. Li, Z., Oxyanion Sorption and Surface Anion Exchange by Surfactant-Modified Clay Minerals. *Journal of Environmental Quality* **1999**, 28, (5), 1457-1463.
25. Schwaiger, J.; Ferling, H.; Mallow, U.; Wintermayr, H.; Negele, R. D., Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: Part I: histopathological alterations and bioaccumulation in rainbow trout. *Aquatic Toxicology* **2004**, 68, (2), 141-150.
26. Bradley, P. M.; Journey, C. A.; Button, D. T.; Carlisle, D. M.; Clark, J. M.; Mahler, B. J.; Nakagaki, N.; Qi, S. L.; Waite, I. R.; VanMetre, P. C., Metformin and Other Pharmaceuticals Widespread in Wadeable Streams of the Southeastern United States. *Environmental Science & Technology Letters* **2016**, 3, (6), 243-249.
27. Meng, X.-Z.; Venkatesan, A. K.; Ni, Y.-L.; Steele, J. C.; Wu, L.-L.; Bignert, A.; Bergman, Å.; Halden, R. U., Organic Contaminants in Chinese Sewage Sludge: A Meta-Analysis of the Literature of the Past 30 Years. *Environmental Science & Technology* **2016**, 50, (11), 5454-5466.
28. Del Hoyo, C., Layered double hydroxides and human health: an overview. *Applied Clay Science* **2007**, 36, 103-121.
29. Nabipour, H.; Sadr, M. H., Controlled release of Diclofenac, an anti-inflammatory drug by nanocompositing with layered zinc hydroxide, *J Porous Mater* **2015**, 22, 447-454
30. Maitani Y.; Kugo M.; Nakagaki, M.; Nagai, T.; Ionic size and behavior of diclofenac salts in water and ethanol/water mixtures by conductivity at 25 °C. *Journal of Pharmaceutical Sciences* **1993**, 82 (12), 1245-1249

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 _{0.4} -Mt	BDTA-Mt	BDTA-Mt/ BDTA in excess	BDTA ₄ -Mt
K_F (L g⁻¹)	3.87 x 10 ⁻²	4.20 x 10 ⁻³	0.09	1.76	0.1
n	4.95	0.90	5.40	2.38	6.71
R²	0.997	0.988	0.992	0.997	0.936

Figures

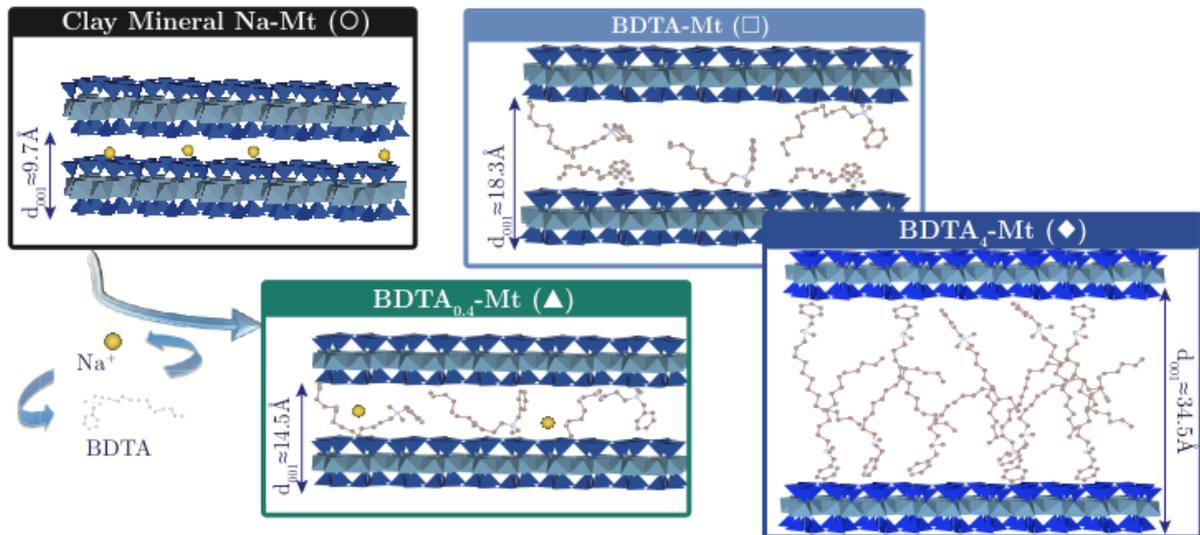


Figure 1: Schematic representation of the whole geo-sorbents used in this study: Na-Mt clay mineral, BDTA_{0.4}-Mt (60% of the compensating cations are preserved) showing a lateral monolayer arrangement, BDTA-Mt (100% of the compensations cations are substituted to BDTA) with a lateral bilayer organization, and BDTA₄-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.

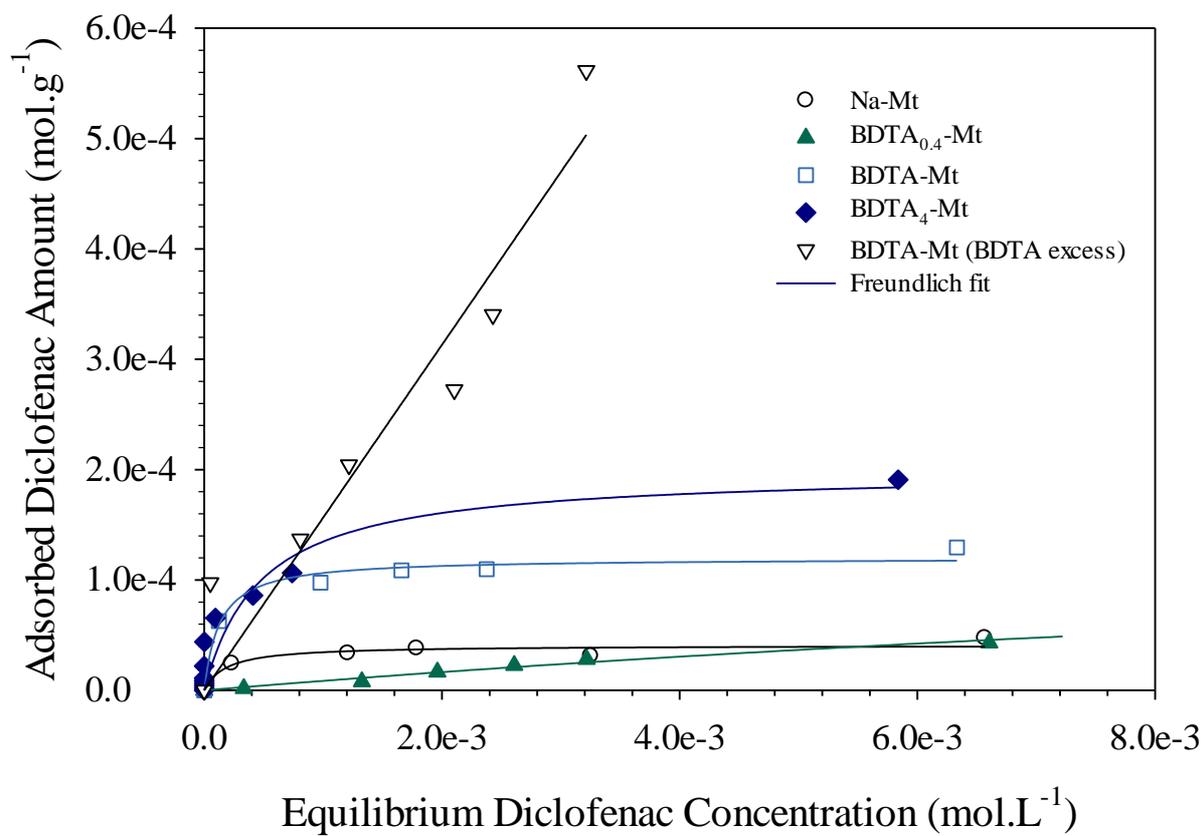
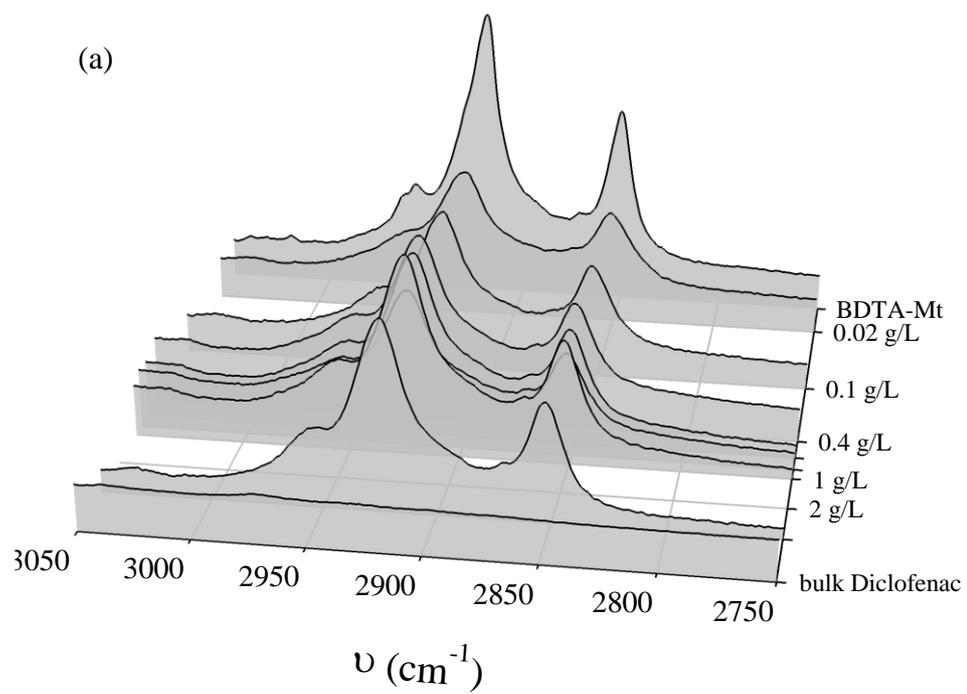


Figure 2: Equilibrium adsorption isotherms of diclofenac onto an untreated Na exchanged montmorillonite: Na-Mt (white circle), a BDTA_{0.4}-Mt organoclay (green triangle top), a BDTA-Mt organoclay (white filled light blue square), a BDTA₄-Mt organoclay (dark blue diamond), and coupled BDTA-Mt with an excess of surfactant in solution (white triangle down). The solid lines represent the fits by using the Freundlich equation model.



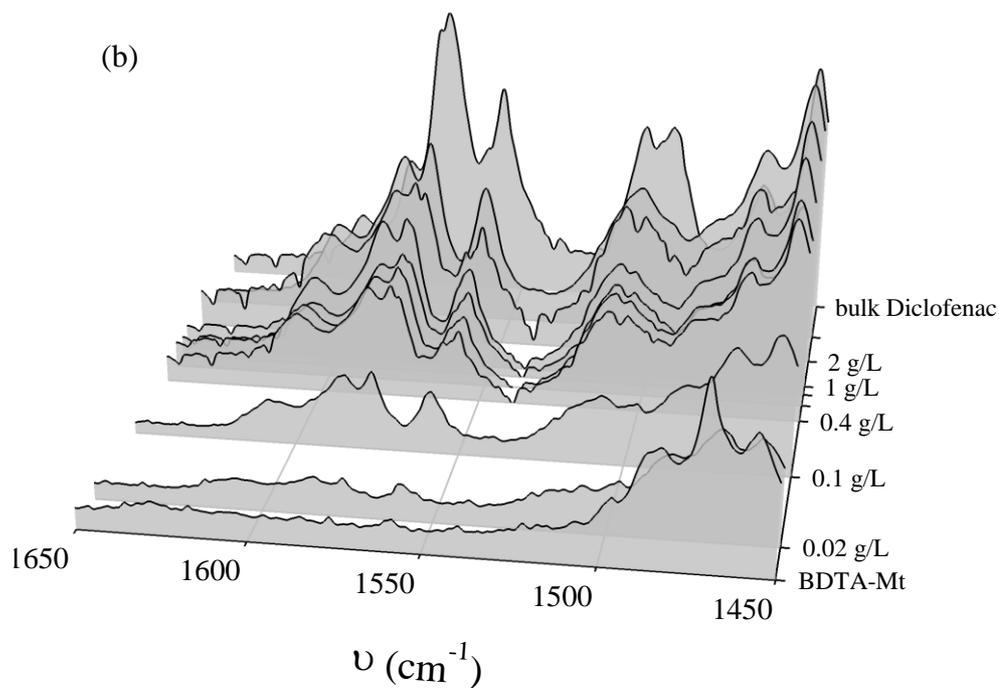


Figure 3: (a) 3D evolution of the FTIR spectra in the 2750-3050 cm^{-1} wavenumbers range (probing the CH_2 stretching bands of the BDTA hydrocarbon chains) of the BDTA₄-Mt organoclays as a function of the starting diclofenac concentration (g L^{-1}); (b) 3D evolution of the FTIR spectra in the 1450-1650 cm^{-1} wavenumbers range (probing the COO^- absorption bands) of the BDTA₄-Mt organoclays as a function of the starting diclofenac concentration (selected series but a similar evolution for the other adsorbents was observed).

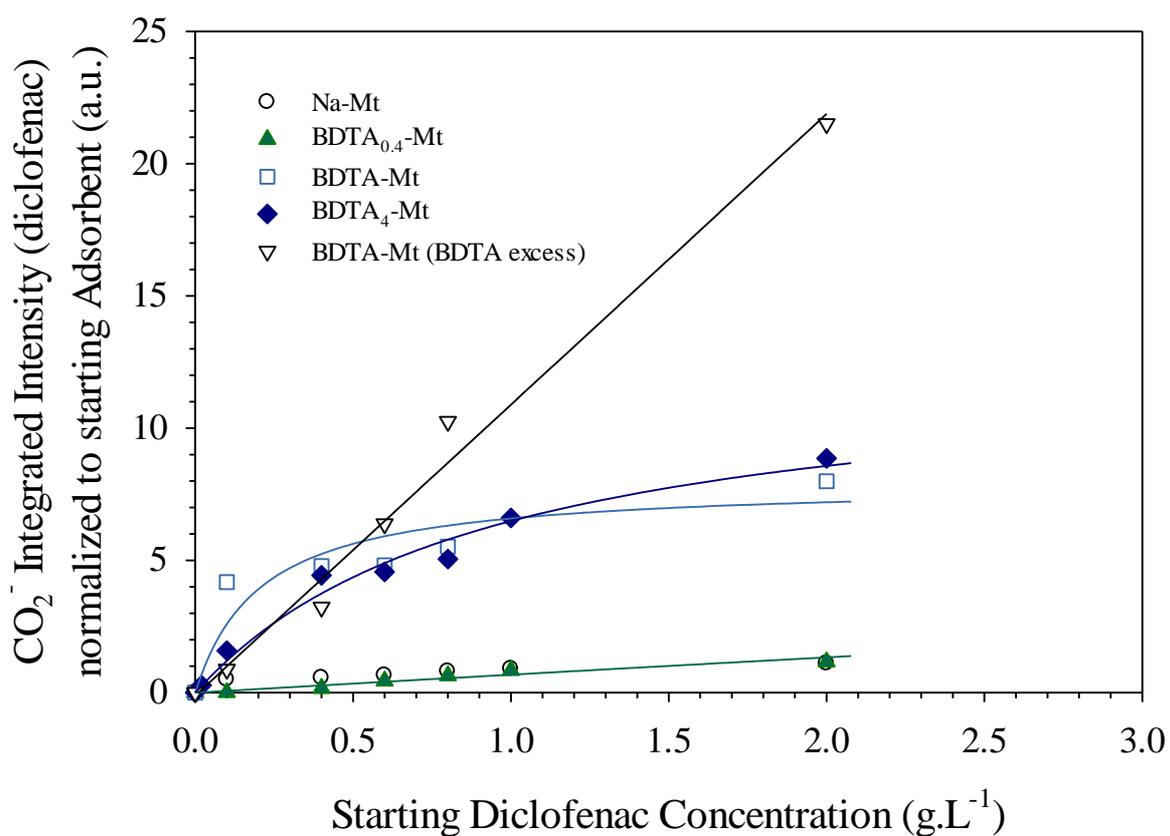


Figure 4: Integrated intensity of the diclofenac (COO^-) as a function of the starting diclofenac concentration (g L^{-1}) for an untreated Na exchanged montmorillonite: Na-Mt (white circle), a $\text{BDTA}_{0.4}$ -Mt organoclay (green triangle top), a BDTA-Mt organoclay (white filled light blue square), a 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.

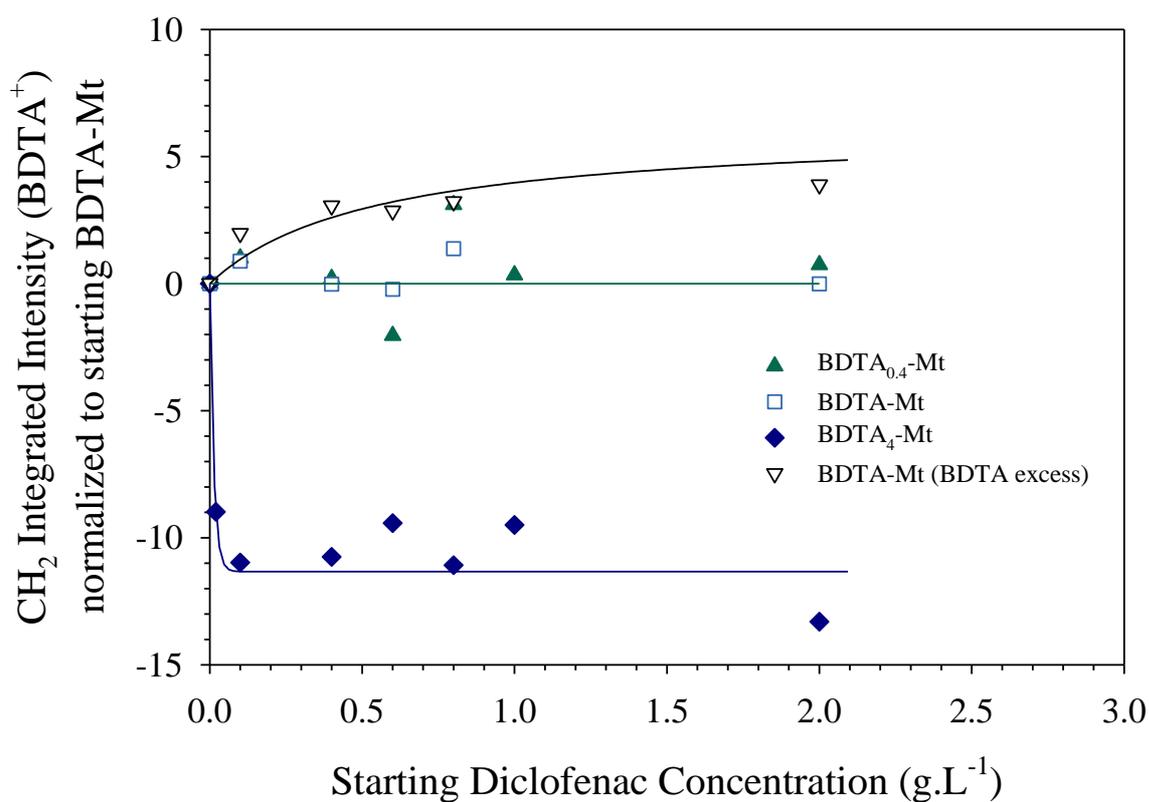


Figure 5: Integrated intensity of the BDTA (CH₂) absorption bands as a function of the starting diclofenac concentration (g L⁻¹) for a BDTA_{0.4}-Mt organoclay (green triangle top), a BDTA-Mt organoclay (white filled light blue square), a BDTA₄-Mt organoclay (dark blue diamond), and coupled BDTA-Mt with an excess of surfactant in solution (white triangle down). The solid lines represent a guide for the eyes.

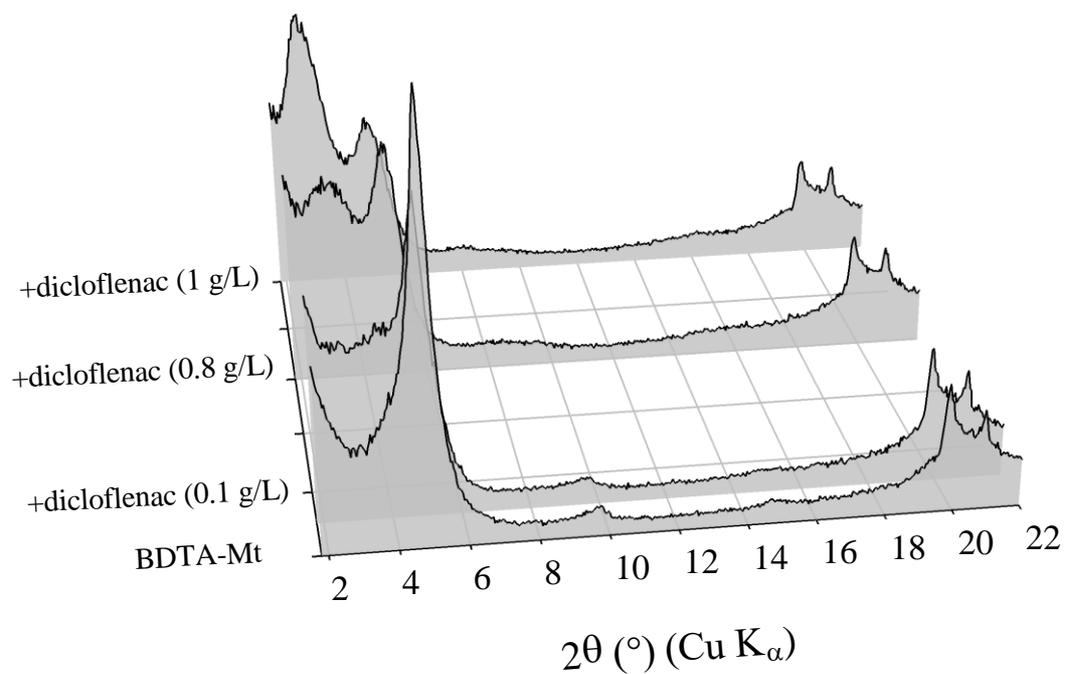


Figure 6: 3D evolution of the X-ray diffraction patterns of the dehydrated diclofenac-BDTA-Mt with BDTA in excess composite layered materials for selected concentration of diclofenac (g L^{-1}).

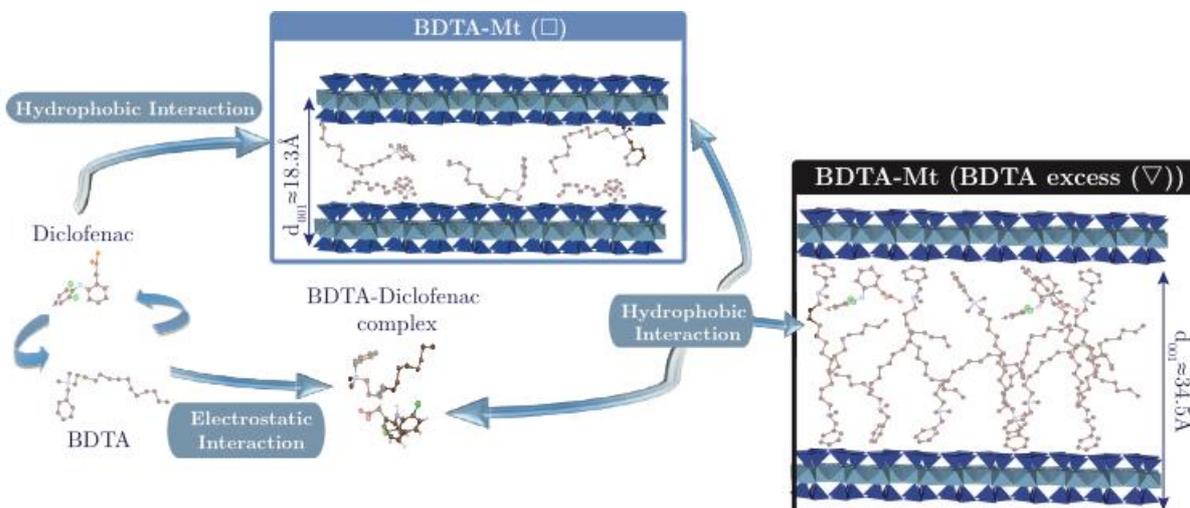


Figure 7: Schematic representation of the possible adsorption mechanisms for diclofenac onto BDTA-Mt (hydrophobic interaction) and with BDTA in excess (micelle) forming BDTA-Diclofenac complex that could be intercalated through hydrophobic interaction within the interlayer space of a BDTA-Mt organoclay.