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1 **Monitoring diclofenac adsorption by organophilic alkylpyridinium**
2 **bentonites**

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26 **Abstract**

27 Organoclays have been applied as efficient adsorbents for pharmaceutical pollutants from
28 aqueous solution. In this work, dodecylpyridinium chloride (C₁₂pyCl) and
29 hexadecylpyridinium chloride (C₁₆pyCl) cationic surfactants were used for the preparation of
30 organobentonites destined for diclofenac sodium (DFNa) adsorption, an anionic drug widely
31 detected in wastewater. The organofunctionalization of the clay samples was performed under
32 microwave irradiation at 50 °C for 5 min with surfactant amounts of 100% and 200% in
33 relation to the cation exchange capacity (CEC) of the pristine bentonite. The amount of
34 incorporated ammonium salts based on CHN elemental analysis was higher for all samples
35 prepared with 200% of the CEC. The basal spacings of the organoclays ranged from 1.54-
36 2.13 nm, indicating the entrance of organic cations into the interlayer spacing of the clay
37 samples, and the spacing depended on the size of the alkyl organic chain. The hydrophobic
38 character of the organobentonites was verified by thermogravimetry and infrared
39 spectroscopy (FTIR). The adsorption isotherms showed that the drug capacity adsorption was
40 influenced by the amount of surfactant incorporated into the bentonite, the packing density
41 and the arrangement of the surfactants in the interlayer spacing. Zeta potential measurements
42 of the organobentonites and FTIR analysis after drug adsorption suggested that electrostatic
43 and nonelectrostatic interactions contributed to the mechanism of adsorption.

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46

47 **Keywords:** Organobentonite; microwave heating; adsorption; anti-inflammatory drug;
48 diclofenac

49 **1. Introduction**

50 The presence of pharmaceutical compounds in the environment has become a major
51 concern, particularly due to the consequences related to long exposure, which are still
52 unknown (Lonappan et al., 2016). Diclofenac (2- [2,6-dichlorophenylamino] phenylethanoic
53 acid) is among the main drugs studied in recent years. Diclofenac is a nonsteroidal anti-
54 inflammatory drug often prescribed in human and veterinary medicine and used to reduce
55 inflammation and pains (Acuña et al., 2015; He et al., 2017). As a consequence of its high
56 production and consumption worldwide, both diclofenac and its metabolites have been
57 detected in aquatic bodies in several countries at concentrations of 0.7-4400 ng L⁻¹ in surface
58 waters and up to 8.5 µg L⁻¹ in wastewater (Lonappan et al., 2016; Scheurell et al., 2009);
59 concentrations of its transformation products are in the range of 0.08 to 1.80 µg L⁻¹ (Scheurell
60 et al., 2009). In Brazil, diclofenac was also observed in water in the range of 3.3-785 ng L⁻¹
61 (Starling et al., 2019). Therefore, diclofenac is among the main drugs studied in recent years
62 regarding its identification/detection in aquatic bodies (Biel-Maeso et al., 2018; Starling et al.,
63 2019), removal/degradation (Maia et al., 2019; Mugunthan et al., 2018), and environmental
64 impacts (Klaudia et al., 2019; Moreno-González et al., 2016; Oaks et al., 2004).

65 Both toxicity and bioaccumulation of diclofenac have been observed for various living
66 aquatic organisms, even at low concentrations (Klaudia et al., 2019; Moreno-González et al.,
67 2016), and diclofenac was identified as the cause of mortality and decline of the vulture
68 population in Pakistan (Oaks et al., 2004). Some studies have observed that diclofenac
69 metabolites can be generated through biotransformation in living organisms or through
70 exposure to sunlight, and some of them are even more toxic than pure diclofenac (Bonnefille
71 et al., 2018; Klaudia et al., 2019).

72 Due to the environmental problems, several diclofenac removal methods have been
73 evaluated, such as coagulation, flocculation and activated sludge treatment (Carballa et al.,

74 2005; Vieno and Sillanpää, 2014); adsorption based on natural or synthetic materials (Andrew
75 Lin et al., 2015; Maia et al., 2019); and degradation through advanced oxidative processes,
76 such as ozonation (Beltrán et al., 2009), photo-Fenton (Pérez-Estrada et al., 2005) and
77 photocatalysis (Mugunthan et al., 2018).

78 In this context, adsorption is highlighted because of the ease of operation and
79 avoidance of subproducts. Organophilic clay minerals have been applied as efficient
80 adsorbents for drug removal from aquatic bodies (Ghemit et al., 2019; Karaman et al., 2012;
81 Maia et al., 2019; Martinez-Costa et al., 2018; Oliveira et al., 2017; Oliveira and Guégan,
82 2016; Sun et al., 2017a; Thanhmingliana, 2015). The performance of organophilic clays was
83 attributed to a better compatibility with organic pollutants thanks to their hydrophobic nature
84 and to the presence of new sites for adsorption (Oliveira and Guégan, 2016; Zhuang et al.,
85 2019, 2018). Therefore, modified clays with surfactants containing an aromatic ring in their
86 structure have been applied for the adsorption of different pollutants, such as phenolic
87 compounds (Luo et al., 2015), aniline (Gu et al., 2014), bisphenol A (Yang et al., 2016),
88 naphthalene and phenanthrene (Changchaivong and Khaodhiar, 2009). The mechanism of
89 interaction involves both π - π interactions between aromatic rings of the surfactant and the
90 rings of the pollutant and other organic interactions (hydrogen bonding, London forces, etc),
91 making these modified clays better adsorbents (Oliveira et al., 2017; Oliveira and Guégan,
92 2016). Indeed, hexadecylpyridinium chloride was used, commonly applied as an antibacterial
93 agent widely in antiseptic solutions and some personal care products, as well as a preservative
94 in pharmaceutical preparations and in the meat industry as a spray for the control of microbial
95 growth (Herrera et al., 2004; Özdemir et al., 2013).

96 Furthermore, the adsorption of organic pollutants is improved when the incorporated
97 amount of surfactant is higher than the cationic exchange capacity (CEC) of the clay mineral
98 (Brito et al., 2018; Luo et al., 2018).

99 In the present study, organoclays were obtained by the organofunctionalization of
100 bentonite, a mineral constituted predominantly by $\geq 50\%$ smectite, most commonly
101 montmorillonite (Mt). Mt is a 2:1 phyllosilicate with a general structure of $(M^{x+}, nH_2O)(Al^{3+}_{2-}$
102 $_yMg^{2+}_ySi^{4+}_4O_{10}(OH)_2$, where Si^{4+} ions are coordinated to four oxygens in tetrahedral sites and
103 Mg^{2+}/Al^{3+} ions are octahedrally coordinated to six oxygens. The hydrated interlayer cations
104 M^{x+} (commonly Na^+ or Ca^{2+}) balance the negative layer charge due to the isomorphic
105 substitution of Mg^{2+} for Al^{3+} in the octahedral sheet. These interlayer cations can be
106 exchanged by organic cations in water solution, resulting in organophilic bentonite derivatives
107 (Lagaly et al., 2013).

108 Therefore, in this case, organobentonites were synthesized through microwave (MW)
109 heating in a very short time (5 min) by reaction with two alkyipyridinium surfactants that
110 have aromatic rings in their structure. The influences of the chain length and composition of
111 both molecules on the synthesis of organobentonites, and diclofenac adsorption on modified
112 clay samples was evaluated. The synthesized samples were used for the first time for
113 diclofenac adsorption. The tests of drug adsorption were conducted under different
114 experimental conditions, and the influence of adsorbent dosage, pH, time and initial
115 diclofenac concentration were investigated. New insights in the mechanism of drug/solid
116 adsorption were also suggested based on characterization of the adsorbents after drug
117 adsorption.

118 **2. Experimental**

119 **2.1 Materials**

120 A sodium bentonite sample (BentNa), CEC 74.64 cmol(+)/kg, was supplied by
121 Bentonise Bentonita Company, Brazil. The chemical composition of the bentonite was as
122 follows: SiO_2 (52.98%), Al_2O_3 (18.35%), Fe_2O_3 (3.96%), TiO_2 (0.18%), CaO (0.01%), MgO

123 (2.47%), Na₂O (2.56%), K₂O (0.22%) and fire loss 18.59% (Cavalcanti et al., 2019). 1-
124 Dodecylpyridinium chloride hydrate (C₁₂pyCl) and hexadecylpyridinium chloride
125 monohydrate (C₁₆pyCl) with purity grades of 98% and 99%, respectively, were supplied by
126 Sigma-Aldrich and used as received. Diclofenac sodium salt (CAS number 15307-79-6, MM
127 = 318.13 g mol⁻¹ and pKa 4.1) was purchased from Sigma-Aldrich.

128 **2.2 Preparation of the alkylpyridinium bentonites**

129 Organobentonites were synthesized based on a previous procedure (Brito et al., 2018).
130 Initially, two solutions of the salts were prepared in concentrations corresponding to 100 and
131 200% of the CEC of the bentonite. A sample of 4.0 g of BentNa was suspended in 100 mL of
132 each surfactant solution in a Teflon vessel reactor and heated in a microwave reactor (IS-TEC
133 MW reactor model RMW-1, Brazil, with a power of 1100 W and 2.45 GHz) for 5 min at 50
134 °C. The obtained solids were recovered by centrifugation at 10000 rpm, washed with distilled
135 water until testing negative for chlorite with 0.01 mol L⁻¹ AgNO₃ and dried in an oven for at
136 least 24 h at 50 °C.

137 **2.3 Diclofenac sorption**

138 The test of diclofenac adsorption followed a previous method (Brito et al., 2018;
139 França et al., 2019), by which the influences of the medium pH (6.0-10.0), dosage of the solid
140 (25-400 mg), time (0.5 – 120 min) and drug initial concentration (1-500 mg L⁻¹) were
141 evaluated.

142 Batch tests were performed at 30 °C by using samples of organobentonites dispersed
143 in 20 mL of diclofenac solution. This temperature is the medium temperature found for
144 Brazilian aquatic bodies. After each test, the solids were recovered by centrifugation, and the
145 diclofenac concentrations were monitored by UV-Vis molecular spectrometry (Shimadzu

146 spectrometer model TCC-240 240) at 276 nm (Ghemit et al., 2019). The amount of adsorbed
147 drug (q) was calculated as established in Eq. 1:

$$148 \quad q = \frac{(C_i - C_e)V}{m} \quad (1)$$

149
150 where C_i and C_e are the drug concentrations before and after adsorption (mg L^{-1}),
151 respectively, V is the total volume of drug solution (L) and m is the mass of the solid (g).

152 To investigate pH, 50 mg of solids was reacted with 20 mL of 100 mg L^{-1} diclofenac
153 solution for 24 h. The pH was adjusted with 0.05 mol L^{-1} NaOH or HNO_3 solutions.

154 Tests for the dosage of solids were monitored at optimum pH under the same
155 conditions described.

156 Tests for different times of interaction were conducted with the fixed mass obtained in
157 the solid dosage tests and at optimum pH for times in the range of 0.5-120 min.

158 Finally, the initial diclofenac concentrations were evaluated in the range of 1-500 mg
159 L^{-1} at the optimized pH, dosage of solids and time of contact.

160 All experiments were performed in triplicate.

161 **2.4 Kinetic and equilibrium models**

162 The experimental data were adjusted to fit the following kinetic models: pseudo-first-
163 order (Lagergren, 1898), pseudo-second-order (Ho and McKay, 1999) and simplified Elovich
164 equation (Chien and Clayton, 1984), assuming $\alpha\beta t \gg 1$, (see Eqs. 1 to 3 in Supplementary
165 Material SII).

166 The equilibrium isotherms were analyzed with the Langmuir (Langmuir, 1918),
167 Freundlich (Freundlich, 1906) and Temkin (Temkin and Pyzhev, 1940) models (see Eqs. 4-6
168 in Supplementary Material SII).

169 The standard deviation (SD-root mean square error), Eq. 2, was used to verify which
170 equation models were best suited to describe the experimental data (Lima et al., 2015).

171

$$172 \quad SD = \sqrt{\frac{1}{n_p - p} \sum_i^n (q_{i,exp} - q_{i,model})^2} \quad (2)$$

173

174 where $q_{i,exp}$ and $q_{i,model}$ are the experimental adsorbed drug amount and theoretical
175 amount obtained by the kinetic models, n_p is the number of performed experiments, and p is
176 the number of parameters of the fitted model.

177 2.5 Characterizations

178 X-ray diffraction (XRD) analyses were conducted on a Shimadzu XD3A model
179 diffractometer with $CuK\alpha$ radiation and a fixed power source (40 kV and 30 mA). FTIR
180 spectra were recorded in the 4000-400 cm^{-1} region by a Shimadzu IR Prestige-21 model; the
181 samples were dispersed in KBr pellets, and a resolution of 4 cm^{-1} and accumulation of 20
182 scans were used for each run. Thermogravimetry data for the solids were obtained using an
183 SDT Q600 V20.9 Build 20 thermal analyzer with a heating rate of 10 $^{\circ}C \text{ min}^{-1}$ under 100 mL
184 min^{-1} of argon flow in the range of 30 to 900 $^{\circ}C$. CHN elemental analysis was obtained by
185 using a Perkin-Elmer PE-2400 microelemental analyzer. Chloride was analyzed by titration:
186 samples of 100 mg in triplicate was suspended in 0.01 mol L^{-1} $NaNO_3$ for 24 h at 25 $^{\circ}C$. The
187 dispersions were centrifuged and the procedure was repeated 3 times to ensure the exchange
188 of Cl^{-} by NO_3^{-} . After centrifugation, aliquots of 10 mL of supernatant were titrated with
189 standard $AgNO_3$ solution (Skoog et al., 2012). Zeta potential (ζ) was measured using a
190 Zetasizer Nano Zs (Malvern Instruments) for isoelectric titration through pH titration. The pH
191 of the solutions was adjusted with 0.100 mol L^{-1} $NaOH$ or 0.500 mol L^{-1} HNO_3 .

192 3. Results and discussion

193 3.1 X-ray diffraction

194

195 The XRD pattern of BentNa (Figure SM1a) showed smectite with sodium
196 montmorillonite (Mt) as the predominant phase and impurities of quartz (Q) and muscovite
197 (M), in agreement with ICDD cards 00.029.1498, 00.058.2036 and 01.070.8055 and previous
198 studies (Cavalcanti et al., 2019; Queiroga et al., 2019). Characteristic reflections of Mt at $2\theta =$
199 7.37° suggested a basal spacing (d_{001}) of 1.12 nm, as further indicated by additional
200 reflections at 2θ values of 19.6° , 28.3° , 35.0° and 61.8° .

201 The intercalation of alkylpyridinium cations was confirmed by the increase in basal
202 spacings to 1.56, 1.74, 1.66 and 2.13 nm for Bent-C₁₂py-100%, Bent-C₁₆py-100%, Bent-
203 C₁₂py-200% and Bent-C₁₆py-200% (Figure SM1), respectively. The results indicated that
204 higher values were observed for solids prepared with 200% of the CEC and a longer organic
205 chain of the salt (Changchaivong and Khaodhiar, 2009; Greenland and Quirk, 1962; Muñoz-
206 Shugulí et al., 2019).

207 Studies have established that the size of the organic chain and the intercalated amount
208 determine the arrangement of surfactants in the interlayer spacing. For example, C₁₆py⁺
209 monolayer ($d_{001} = 1.32\sim 1.47$ nm), bilayer ($d_{001} = 1.68\sim 1.78$ nm) and pseudotrilayer ($d_{001} =$
210 $2.14\sim 2.20$ nm) arrangements in the gallery spacing of montmorillonite have been proposed
211 (Meleshyn and Bunnenberg, 2006). Based on the size of the surfactant molecules and the final
212 basal spacings (Chen et al., 2005; Luo et al., 2018), monolayer arrangement occurred for
213 Bent-C₁₂py-100%, bilayer arrangement occurred for Bent-C₁₂py-200% and Bent-C₁₆py-
214 100%, and pseudotrilayer arrangement occurred for Bent-C₁₆py-200%, as illustrated in Figure
215 SM2.

216 The XRD results were compared with previous studies that considered the synthesis of
217 organobentonites by using conventional and microwave heating with the same proportion of
218 surfactant adopted in the present work (Table SM1). The obtained values for Bent-C₁₆py are
219 close to those obtained by (Schampera and Dultz, 2009) and Muñoz-Shugulí et al. (2019)
220 using conventional heating at times of 20 and 1 h at 60 °C, respectively. However, divergent
221 values were also observed and were associated with the different CECs of the pristine
222 bentonites used (He et al., 2014) different conditions of synthesis. Therefore, the studies
223 showed that aspects such as washing and drying (Luo et al., 2016) and the nature of the
224 interlayer cations (Volzone et al., 2002) can influence the final basal spacing and the amount
225 of intercalated surfactant.

226

227 **3.2 CHNCl elemental analysis**

228

229 The amount of incorporated surfactant in the bentonite was determined based on C and
230 N elemental analysis (Table 1); the values were close to the CEC (~ 90% of the initial salt
231 concentration) for Bent-C₁₂py-100% and Bent-C₁₆py-100% and were near that for
232 montmorillonites modified with C₁₆py⁺ using 100% of the CEC by conventional heating
233 (Schampera and Dultz, 2009).

234 For the organobentonites obtained using 200% of the CEC of BentNa, only Bent-
235 C₁₆py-200% exhibited a value higher than the CEC (112.4%), while C₁₂py-200% exhibited a
236 value of 93.3%. The excess of surfactant in Bent-C₁₆py-200% was incorporated as the ion
237 pair C₁₆pyCl through hydrophobic interactions between the alkyl tails of the organic chain
238 (Luo et al., 2018; Meleshyn and Bunnenberg, 2006), and was further verified by the presence
239 of the chloride in the organoclays (Table 1). No Cl⁻ ions were detected in other
240 organobentonites (Bent-C₁₂py-100%, Bent-C₁₆py-100% and Bent-C₁₂py-200%).

241 The better affinity of bentonite for surfactants with longer organic chains was related
242 to an increase in the contribution of Van der Waals interactions and a decrease in the
243 hydration enthalpy of the organic salt, favoring intercalation (Teppen and Aggarwal, 2007).

244 This result suggested that the packing densities of the groups in the solids can be
245 influenced by the amount of intercalated molecules.

246

247 **3.3 Infrared spectroscopy**

248

249 Infrared spectra were used to monitor the organofunctionalization of the bentonite;
250 therefore, the spectra of the pristine and modified solids are shown in Figure SM3. For
251 sodium bentonite, typical bands were detected at 3632 cm^{-1} and 3440 cm^{-1} , assigned to the
252 hydroxyl stretching of structural M-OH ($M = \text{Al}^{3+}$, Mg^{2+} or Fe^{3+}) and silanol. The bending of
253 water molecules was also observed at 1638 cm^{-1} (Slaný et al., 2019).

254 For the region below 1200 cm^{-1} , bands at 1115 and 1042 cm^{-1} were related to Si-O
255 stretching, and bands at $915\text{-}847\text{ cm}^{-1}$ were due to AlMOH deformation ($M = \text{Al}$, Fe or Mg)
256 (Slaný et al., 2019). The presence of quartz impurities was confirmed by the Si-O deformation
257 at 798 cm^{-1} . Other bands at 620 , 519 and 465 cm^{-1} were assigned to Al-O/Si-O, Al-O-Si and
258 Si-O-Si deformations, respectively, and are characteristic of montmorillonite (Slaný et al.,
259 2019).

260 The intercalation of the surfactants in the clay minerals was accompanied by the
261 appearance of new bands in the range of $3136\text{-}3096\text{ cm}^{-1}$, attributed to the aromatic CH
262 stretching of pyridine rings, and from $2928\text{-}2851\text{ cm}^{-1}$, related to CH_2 antisymmetric and
263 symmetrical stretching vibrations (Lin-Vien et al., 1991; Luo et al., 2018). The location of the
264 $\nu_{\text{as}}(\text{CH}_2)$ band at wavelengths higher than those of free surfactants (Table SM2) suggests the

265 existence of structures with a disordered arrangement of organic cations (gauche conformers)
266 in the interlayer region of the montmorillonite (Chen et al., 2005; Slaný et al., 2019).

267 The spectra also exhibited a low-intensity band at 1502 cm^{-1} associated with C=C
268 vibrations of aromatic rings, bands at 1486 and 1469 cm^{-1} , associated with CH_3 and CH_2
269 deformations, respectively and a band at 729 cm^{-1} , related to $(\text{CH}_2)_n$ in-phase rocking,
270 characteristic of alkyl chains of surfactants (Lin-Vien et al., 1991; Slaný et al., 2019). The
271 absorptions at 777 and 679 cm^{-1} were assigned to deformation of the pyridine ring (Lin-Vien
272 et al., 1991).

273 **3.4 Thermogravimetry**

274

275 Thermogravimetry is a useful tool to quantify the amount of organic content in a solid
276 but is also associated with other techniques, such as XRD and FTIR, to characterize how
277 surfactants are confined in the interlayer region (Chen et al., 2005). TG curves (Figure SM4)
278 and the associated mass losses are summarized in Table SM3.

279 The TG curve of pristine bentonite exhibited two steps of mass loss, the first step at
280 $30\text{-}200\text{ }^\circ\text{C}$, attributed to the elimination of the interlayer water and water adsorbed on the
281 surface, and the second from $200\text{-}900\text{ }^\circ\text{C}$, associated with the condensation of structural OH
282 (Muñoz-Shugulí et al., 2019).

283 The organobentonites showed four and five events of mass loss. For all samples, the
284 first event associated with the elimination of water was $\leq 1.2\%$, suggesting the hydrophobic
285 nature of the organoclays (Muñoz-Shugulí et al., 2019). Additionally, the sum of mass losses
286 of the other events was higher than in the pristine clay and are associated to an exothermal
287 event (Heat flow not presented), which was an indication of the presence of organic moieties
288 in the solids.

289 The initial temperature associated with the degradation of the organic part decreased
290 as the incorporated amount of surfactant increased and was observed at 182, 175, 174 and 118
291 °C for the Bent-C12py-100%, Bent-C16py-100% Bent-C12py-200% and Bent-C16py-200%
292 solids, respectively; this degradation finished at 513-520 °C; therefore, the number of
293 decomposition events exhibited within this range depended on the types of interactions (Chen
294 et al., 2005; Muñoz-Shugulí et al., 2019).

295 Meleshyn and Bunnenberg, (2006) suggested that a lower temperature for the exit of
296 surfactants occurs due to the different arrangements of organic chains in the interlayer spacing
297 of clay samples and is an indication of weaker interactions (lower energy) between the
298 organic cations and the mineral surface. In other words, as the organic cation content
299 increases, the configurations change from monolayer and bilayer to pseudotrilyer, in
300 accordance with the observed results.

301 Above 520 °C, mass loss was attributed to dehydroxylation (Luo et al., 2018; Muñoz-
302 Shugulí et al., 2019).

303

304 **3.5 Zeta potential**

305

306 Zeta potential measurements (Figure SM5) suggested that the point of zero charge
307 (pH_{PZC}) occurred at pH 3.4, 2.5, 4.1 and 8.1 for Bent-C₁₂-100%, Bent-C₁₆-100%, Bent-C₁₂-
308 200% and Bent-C₁₆-200%, respectively. BentNa is negatively charged in all pH ranges. The
309 modification of clay minerals with cationic surfactants promotes a total or partial variation in
310 surface charge, depending on the amount of organic cations incorporated (Brito et al., 2018;
311 Schampera and Dultz, 2009). Therefore, the values of pH_{PZC} observed for Bent-C₁₂-100%,
312 Bent-C₁₆-100% and Bent-C₁₂-200% are probably related to the low amount of surfactant
313 incorporated (~ 90% of the CEC), while the higher value of pH_{PZC} for Bent-C₁₆-200% is

314 consistent with the excess surfactant adsorbed probably on the basal surface of the bentonite
315 sample, as indicated by the CHNCl and thermogravimetry results.

316

317 **3.7 Adsorption of diclofenac on the solids**

318 **3.7.1 Influence of pH**

319 The effect of pH on the adsorption process has often been evaluated according to the
320 different behaviors presented by drugs and solids in aqueous media (Ghemit et al., 2019;
321 Oliveira et al., 2017). This parameter was analyzed considering the speciation of the
322 diclofenac molecule at different pH values (Figure SM6i) and zeta potential measurements (ζ)
323 (Figure SM5). The results showed that the adsorption depended slightly on the pH (Figure
324 SM6ii); the maximum values were 12.87, 18.19, 25.30 and 39.40 mg g⁻¹ for Bent-C₁₂-100%,
325 Bent-C₁₆-100%, Bent-C₁₂-200% and Bent-C₁₆-200%, respectively, at pH 6.0 and were better
326 than those at pH 8 and 10.

327 Based on the pKa (4.1) of diclofenac, at pH \geq 6, the anionic form dominates, and the
328 decreased adsorption with increased pH (6-10) for Bent-C₁₂-100%, Bent-C₁₆-100% and Bent-
329 C₁₂-200% can be associated with the repulsion between deprotonated diclofenac and
330 organobentonites (Luo et al., 2015), considering the pH_{PZC} value; at pH < pH_{PZC}, the surface
331 is positively charged, and the surface is negatively charged for pH values above the pH_{PZC}.
332 These results suggested that non-electrostatic interactions contributed to the mechanism of
333 adsorption.

334

335 **3.7.2 Dosage of the adsorbent**

336 The dosage of the adsorbent (Figure SM7) is important for establishing the best
337 adsorption efficiency of the drug from solution. The adsorption percentages increase

338 gradually with increased organobentonite mass due to the increase of interaction sites amount
339 (Brito et al., 2018; Ghemit et al., 2019).

340 The best performance was observed for 300, 200, 150 and 50 mg of Bent-C₁₂-100%,
341 Bent-C₁₆-100%, Bent-C₁₂-200% and Bent-C₁₆-200%, respectively and these dosages were
342 associated with adsorption efficiencies of 88.3, 97.1, 93.5 and 99.5%. The adsorbed amounts
343 per gram of adsorbent (q) were 5.9 mg g⁻¹ for Bent-C₁₂py-100%, 9.3 mg g⁻¹ for Bent-C₁₆py-
344 100%, 13.0 mg g⁻¹ for Bent-C₁₂py-200% and 38.7 mg g⁻¹ para Bent-C₁₆py-200% (Figure
345 SM7ii).

346

347 **3.7.3 Kinetic studies**

348 Adsorption kinetic studies of diclofenac (Figure SM8) were carried out using the
349 masses corresponding to the maximum percentages of diclofenac adsorption obtained in the
350 evaluation of the adsorbent dosage effect at pH 6.0. The isotherms showed rapid adsorption of
351 the drug by the organophilic clays at 60 and 10 min for the solids obtained with 100% and
352 200% of the CEC, respectively. These results were close to those observed for other
353 organophilic clays used for diclofenac adsorption (Ghemit et al., 2019; Sun et al., 2017a).

354 The adsorption kinetics were analyzed by nonlinear regression of the isotherms to the
355 pseudo-first-order, pseudo-second-order and Elovich models, whose parameters are
356 summarized in Table 2. In addition to R², the fit of the isotherms to the models was also
357 evaluated using the standard deviation (SD) (Lima et al., 2015), which showed a better fit to
358 the Elovich equation for Bent-C₁₂py-100% and Bent-C₁₆py-100% and a better fit to the
359 pseudo-second-order model for Bent-C₁₂py-200% and Bent-C₁₆py-200%. The Elovich model
360 describes the process as chemisorption and considers the heterogeneity of the surface of the
361 adsorbent (Lima et al., 2015).

362

363 3.7.4 Adsorption isotherms

364 The equilibrium isotherms were evaluated at 1-500 mg L⁻¹ diclofenac (Figure 1), pH 6
365 and 60 min. The isotherms for the organobentonites initially showed an increase in adsorbed
366 amount (q_e) with increased drug concentration, reaching almost constant values at initial
367 concentrations (C_i) of 350 mg L⁻¹ for Bent-C₁₆py-100% and Bent-C₁₂py-200%, 300 mg L⁻¹
368 for Bent-C₁₆py-200% and 450 mg L⁻¹ for Bent-C₁₂py-100%.

369 The maximum adsorption capacities (q_{max}) were 13.02, 19.30, 25.50 and 91.13 mg g⁻¹
370 on Bent-C₁₂py-100%, Bent-C₁₆py-100%, Bent-C₁₂py-200% and Bent-C₁₆py-200%,
371 respectively. The result for pristine bentonite was less than 5% of the reported values (< 5 mg
372 g⁻¹) under the same conditions. These results were also compared with the diclofenac
373 adsorption capacity on other organoclays samples obtained from conventional procedure at
374 time of 15-72 h (Table SM4), and illustrated the good performance of the organobentonites
375 obtained in this study in only 5 min by microwave irradiation. Long time reactions is a
376 limitation for use of organoclays industrial scale (Yapar, 2009), however, the use of
377 microwave irradiation behaved as good alternative for rapid and reproductive preparation of
378 modified clay minerals.

379 Beyond the low-cost and good efficiency of the organobentonites, the choice of
380 adsorbent depends of other factors such biocompatibility with the ecosystem and their
381 regeneration and recycle (Biswas et al., 2019; Momina et al., 2018), that were not studied in this
382 present case.

383 Some organoclays exhibited high toxicity (Sarkar et al., 2013; Witthuhn et al., 2005) while
384 others did not showed any toxicity for the original community of soil microorganisms responsible
385 for biodegradation (Abbate et al., 2013), therefore, the toxicity of alkylpyridium bentonites remains
386 still unknown. The antibacterial activities of hexadecylpyridinium-montmorillonites was verified
387 only against some bacteria responsible for infections in humans and animals and food

388 contamination (Herrera et al., 2000; Malachová et al., 2009; Özdemir et al., 2013), and when
389 added to the diet of weaned pigs was proposed as an alternative to antibiotic chlortetracycline
390 for improving growth performance, mucosal architecture and modifying intestinal microflora
391 (Ke et al., 2014). Moreover, some studies observed that these solids can be used as precursor
392 to obtain new materials such as porous clay heterostructures (Zhu et al., 2005) or carbon-clay
393 composites (Jović-Jovičić et al., 2019).

394 Comparing the results for solids modified with the same surfactant, better adsorption
395 was observed for adsorbents with a higher organic content and basal spacing, for example
396 organobentonite prepared with 100 and 200% of the CEC. Similar results were observed in
397 previous studies for organobentonites prepared with hexadecyltrimethylammonium (Ghemit
398 et al., 2019; Sun et al., 2017a).

399 In addition, the nature of the surfactant, packing density, amount incorporated and
400 organization of the organic cations in the interlayer region can influence drug adsorption in
401 aqueous media (Oliveira et al., 2017; Oliveira and Guégan, 2016). Organic pollutant
402 adsorption on organophilic pyridinium montmorillonites is dependent on these cited effects
403 (Chen et al., 2005; Gu et al., 2014; Luo et al., 2015), as has also been observed for inorganic
404 pollutants (Luo et al., 2017). The cited studies demonstrate that the different characteristics of
405 organoclays influence their affinity for pollutants and, in some cases, their interaction
406 mechanisms.

407 In this present case, the obtained q_e values for diclofenac adsorption on Bent-C₁₂py-
408 100%, Bent-C₁₆py-100% and Bent-C₁₂py-100% were also influenced by the packing density
409 and the organization of alkylpyridinium cations inside the interlayer spacing since these
410 adsorbents presented lower amounts of incorporated surfactants (close to the CEC) but
411 different d_{001} and cation sizes.

412 The data were evaluated according to the Langmuir, Freundlich and Temkin
413 adsorption models, and the parameters obtained are summarized in Table 3. From the values
414 of R^2 and SD, the experimental data were better fit by the Langmuir model for all
415 organobentonitas, indicating that chemisorption can be the preponderant mechanism involved
416 in the diclofenac adsorption. Langmuir model is based on the existence of homogenous
417 adsorption sites. The adjustment was better for Bent-C₁₂py-100% sample (higher R^2 and
418 lower SD), which is an indication of more uniformed distribution of the adsorptions sites of
419 the same nature.

420

421 **3.7.5 Characterization of the drug/clay mineral hybrids**

422 **3.7.5.1 X-ray diffraction**

423 XRD patterns of the drug/clay mineral hybrids (Figure 2) obtained with 10, 100 and
424 500 mg L⁻¹ of initial drug concentrations did not present alterations in the basal spacing, as
425 observed in the literature for organophilic montmorillonites (Oliveira et al., 2017; Oliveira
426 and Guégan, 2016; Sun et al., 2017a).

427 The adsorption of a drug in the interlayer region of a clay mineral can drive the
428 rearrangement of the surfactant molecules without changes in the value of the basal spacing
429 (Meleshyn and Bunnenberg, 2006; Oliveira et al., 2017; Oliveira and Guégan, 2016; Sun et
430 al., 2017a). For the sample Bent-C₁₂py-200% ($d_{001} = 1.66$ nm), the packaging density was
431 higher than that for Bent-C₁₂py-100% ($d_{001} = 1.56$ nm). Consequently, the entrance of the
432 drug would be more difficult for Bent-C₁₂py-200%, however the adsorption was higher for
433 this sample. It more reasonable that the drug did not access more internal adsorption sites.

434 For Bent-C₁₆py-200%, the behavior was different once the basal spacing was 2.13 nm,
435 the amount of organic salt in the solid was higher than the CEC (0.84 mmol g⁻¹) associated

436 with the presence of the C₁₆pyCl ionic pair. Therefore, the presence of chloride in the
437 equilibrium solution after drug adsorption was a strong indication of another mechanism for
438 adsorption, such as anion exchange between the Cl⁻ ions and anionic drug. Similar results
439 have also been described previously in perchlorate adsorption (Chitrakar et al., 2012; Luo et
440 al., 2016). The literature shows that Cl⁻ ions in C₁₆py⁺-modified montmorillonite were located
441 near the mid plane of the interlayer space (Meleshyn and Bunnenberg, 2006) and are therefore
442 accessible adsorption sites for anionic species, such as diclofenac.

443

444 **3.7.5.2 Infrared spectroscopy**

445

446 For better analysis of the results, the infrared spectra of the free drug and drug/solid
447 hybrids prepared at 10, 100 and 500 mg L⁻¹ diclofenac were divided into three regions,
448 (Figures 3 and SM9). Therefore, infrared spectra in the region of 4000-2750 cm⁻¹ showed
449 diclofenac bands at 3388 and 2357 cm⁻¹ assigned to free and bound N-H stretching,
450 respectively, the latter through intramolecular hydrogen bonds (N-H^{···}O) (Kovala-Demertzi et
451 al., 1993; Lin-Vien et al., 1991). The bands at 3080 and 3036 cm⁻¹ were attributed to $\nu(\text{C-}$
452 $\text{H})_{\text{aromatic}}$, and those at 2971 and 2897 cm⁻¹ were due antisymmetric and symmetric aliphatic
453 CH₂ stretching (Lin-Vien et al., 1991). For the drug/Bent-C₁₆-200% hybrid, the initial band of
454 OH stretching of water at 3410 cm⁻¹ was shifted to 3430-3422 cm⁻¹ for solids with 3.71 mg g⁻¹
455 (C_i = 10 mg L⁻¹) and 91.13 mg g⁻¹ (C_i = 500 mg L⁻¹). For the other solids with diclofenac, no
456 alteration was observed in this region.

457 For region 2 (1750-1250 cm⁻¹), diclofenac presents typical bands associated with
458 aromatic ring stretching at 1603 and 1556 cm⁻¹, a band at 1507 and 1500 cm⁻¹ assigned to C-
459 N-H bending of the secondary amine and C-H rock of aromatic rings, band at 1468 cm⁻¹ due
460 to C-N stretching and C-H rock (aromatic ring), and bands at 1452 and 1305 cm⁻¹ attributed to

461 CH₂ bending (Iliescu et al., 2004; Lin-Vien et al., 1991). The samples with adsorbed
462 diclofenac showed broader bands of aromatic ring stretching at 1558 cm⁻¹ and CH₂ bending at
463 1455 cm⁻¹.

464 The diclofenac infrared spectrum also presents bands at 1575 and 1400 cm⁻¹, assigned
465 to antisymmetric and symmetrical stretching of carboxylate group, respectively. The observed
466 wavenumber variation $\Delta\nu(\text{COO}^-)$ of 175 cm⁻¹ is characteristic of the drug in ionic form
467 (Kovala-Demertzi et al., 1993). Therefore, both bands were detected at 1580~1584 cm⁻¹ and
468 1378~1370 cm⁻¹ for all organobentonite/drug solid samples, suggesting that -COO⁻ groups
469 were also involved, possibly through electrostatic interaction (Sun et al., 2017b, 2017c).

470 The occurrence of electrostatic interactions between diclofenac and Bent-C₁₂-100%,
471 Bent-C₁₆-100% and Bent-C₁₂-200% is not probable due to the negative charges of the
472 surfaces at pH 6.0. Similar behavior was observed for an organophilic montmorillonite
473 obtained using a concentration of C₁₆pyCl at 92% of the CEC (Luo et al., 2017). Although the
474 surface was negatively charged and the amount was lower than the CEC, ReO₄⁻ was adsorbed.
475 The proposed interaction was associated with the desorption of the surfactant weakly bound
476 to montmorillonite, capturing of anions in solution and subsequent adsorption of C₁₆py⁺ReO₄⁻
477 on the external surface by hydrophobic interactions. This same mechanism was also
478 suggested for the adsorption of ClO₄⁻ anions on C₁₆py⁺.montmorillonite (Luo et al., 2016).

479 Finally, region 3 of the FTIR spectrum for free diclofenac presented bands at 766, 746
480 and 714 cm⁻¹ assigned to C-H deformation (Kovala-Demertzi et al., 1993) and characteristic
481 of 1,2-disubstituted and 1,2,3-trisubstituted aromatic rings (Iliescu et al., 2004), and the band
482 at 635 cm⁻¹ is characteristic of ring deformation modes (Lin-Vien et al., 1991). For this
483 region, only Bent-C₁₆-200% exhibited a shoulder at 746 cm⁻¹ when a high initial drug
484 concentration was used.

485

486 3.7.6 Mechanism of drug interaction

487 The new properties of the organophilic clays were attributed to a change in character
488 from hydrophilic to hydrophobic, anion exchange as a consequence of the incorporation of
489 excess surfactant and different packing densities and arrangements of the organic cations in
490 the interlayer region, which favor interactions with pollutants (Oliveira et al., 2017; Oliveira
491 and Guégan, 2016). Thus, the different characteristics presented by each solid contributed in
492 several forms to diclofenac adsorption due to the different affinities, as observed in the values
493 of q_{\max} .

494 A theoretical study realized by Meleshyn and Bunnenberg (2006) indicated that
495 interlayer anion sorption on montmorillonite modified with $C_{16}pyCl$ occurs only for higher
496 surfactant contents and basal spacings (2.1~2.2 nm) and consequently when a
497 pseudotrimolecular form is obtained. In this condition, chloride can be accommodated
498 between the layers as a counter ion of $C_{16}py^+$ or sodium cations. Several works have shown
499 that some of the interlayer cations of pristine bentonite remain in the bentonite structure even
500 when the amount of $C_{16}py^+$ incorporated is equal to or higher than the CEC and act as cation
501 or anion exchange sites (Chitrakar et al., 2012; Luo et al., 2016), in agreement with the
502 theoretical study (Meleshyn and Bunnenberg, 2006).

503 Based on the CHNCl results, the amount of surfactant higher than the CEC and the
504 presence of chloride ions ($0.154 \text{ mmol g}^{-1}$) were observed only for Bent- $C_{16}py$ -200%. In this
505 case, $0.145 \text{ mmol g}^{-1} Cl^-$ was detected in the equilibrium solution after diclofenac adsorption,
506 which was half of the maximum diclofenac adsorbed ($0.291 \text{ mmol g}^{-1}$).

507 For the other solids, although the amount of alkyipyridinium cation incorporated was
508 lower than the CEC of the pristine bentonite, the FTIR results also suggested electrostatic
509 between the incorporated surfactant (pyridinium) and the carboxylate groups of diclofenac.

510 However, the influence of the pH on drug adsorption is not electrostatic in nature and
511 contributes to organophilic (alkyl groups of the salt and ring of the drug) and π - π interactions,
512 the latter between the pyridine rings and the aromatic rings of the pollutant. In particular,
513 interactions involving π electrons have often been described in the adsorption of aromatic
514 compounds by pyridinium organophilic clays (Changchaivong and Khaodhiar, 2009; Gu et
515 al., 2014; Luo et al., 2015; Yang et al., 2016), and for diclofenac adsorption by
516 benzyltrimethyltetradecylammonium-montmorillonite (Oliveira et al., 2017; Oliveira and
517 Guégan, 2016). A general scheme of the proposed interaction mechanisms of drug adsorption
518 on organobentonites was based on obtained results and also in the literature. Depending of the
519 sample, at least four different contributions were involved in the diclofenac adsorption as
520 illustrated in Figure 4.

521 **4. Conclusion**

522 The organic modification of bentonite with alkylpyridinium cations through
523 microwave heating resulted in organophilic clays with different characteristics, which were
524 dependent on the amount of surfactant and the size of the organic chain, as shown in the CHN
525 and XRD results. The use of microwave for organophilization of bentonites with both
526 surfactants at time of 5 min at 50 °C was a promising technique.

527 As a consequence, the organobentonites exhibited different diclofenac adsorption
528 capacity from aqueous solution, which were probably influenced by the amount of
529 incorporated surfactant, the packing density and different arrangements of the organic
530 moieties in the interlayer region. The differences between these factors determine the degree
531 of affinity of the hybrids for the anionic drug on the surface due to the different adsorption
532 sites.

533 The drug/organoclay interaction consisted of electrostatic, organophilic and, possibly,
534 π - π interactions for all functionalized bentonites. The best performance for diclofenac
535 adsorption was 91.13 mg g⁻¹ for Bent-C₁₆py-200% due to the excess of surfactant
536 incorporated. This present study demonstrated the versatility of these solids for anionic
537 species or even neutral species, considering the presence of different interaction sites.

538

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789 **Figure captions**

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791 Figure 1 - Equilibrium isotherms and their fitting to the Langmuir, Freundlich and Temkin
792 models for sodium diclofenac adsorption on a) Bent-C₁₂py-100%, (b) Bent-C₁₆py-100%, (c)
793 Bent-C₁₂py-200% and (d) Bent-C₁₆py-200% at 25 °C and pH 6.0.

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795 Figure 2 – XRD patterns of organobentonites for (i) Bent-C₁₂py-100%, (ii) Bent-C₁₆py-100%,
796 (iii) Bent-C₁₂py-200% and (iv) Bent-C₁₆py-200% (a) before and after diclofenac adsorption
797 for hybrids prepared with initial drug concentrations of (b) 10 mg L⁻¹, (c) 100 mg L⁻¹ and (d)
798 500 mg L⁻¹.

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800 Figure 3 – FTIR results for a) Bent-C₁₆py-200% before and after diclofenac sorption using
801 initial concentrations of b) 10 mg L⁻¹, c) 100 mg L⁻¹ and d) 500 mg L⁻¹; and e) free diclofenac
802 sodium.

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804 Figure 4 - Proposed scheme for diclofenac/organobentonite interaction, M = mechanism.

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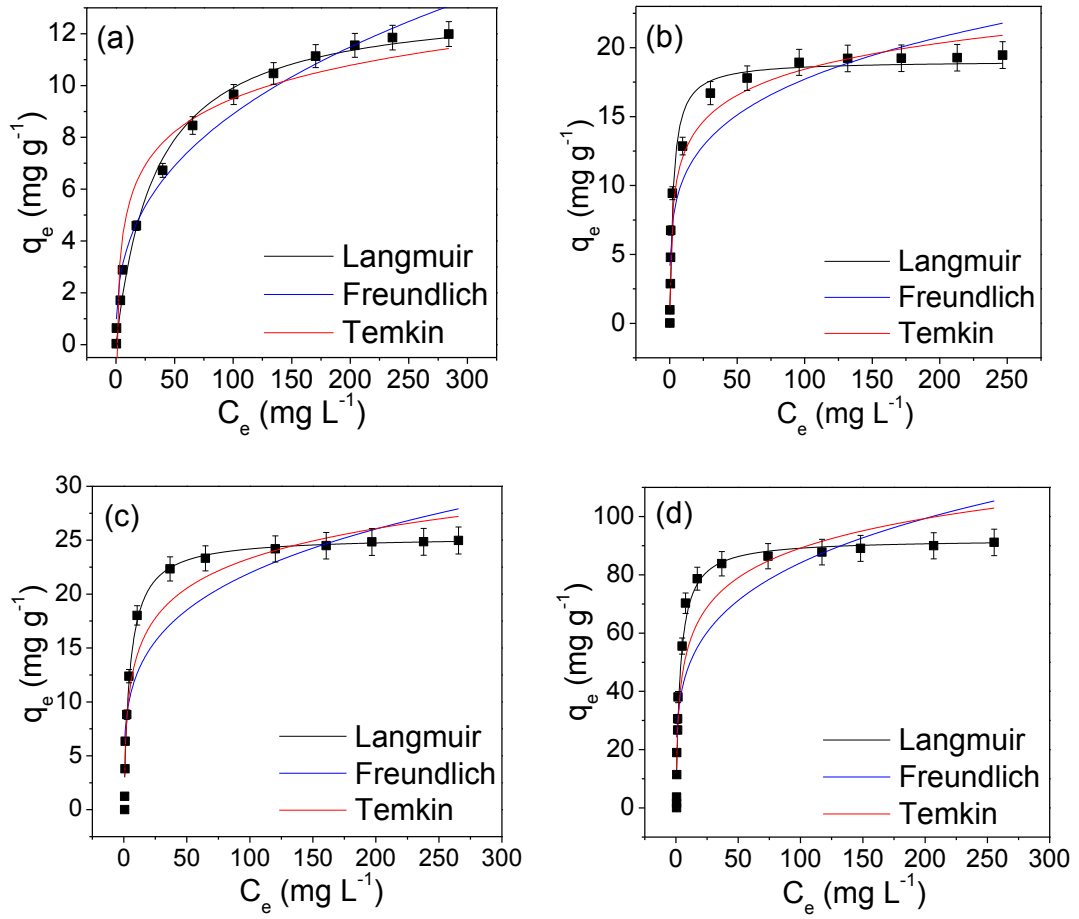
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814 Figure 1

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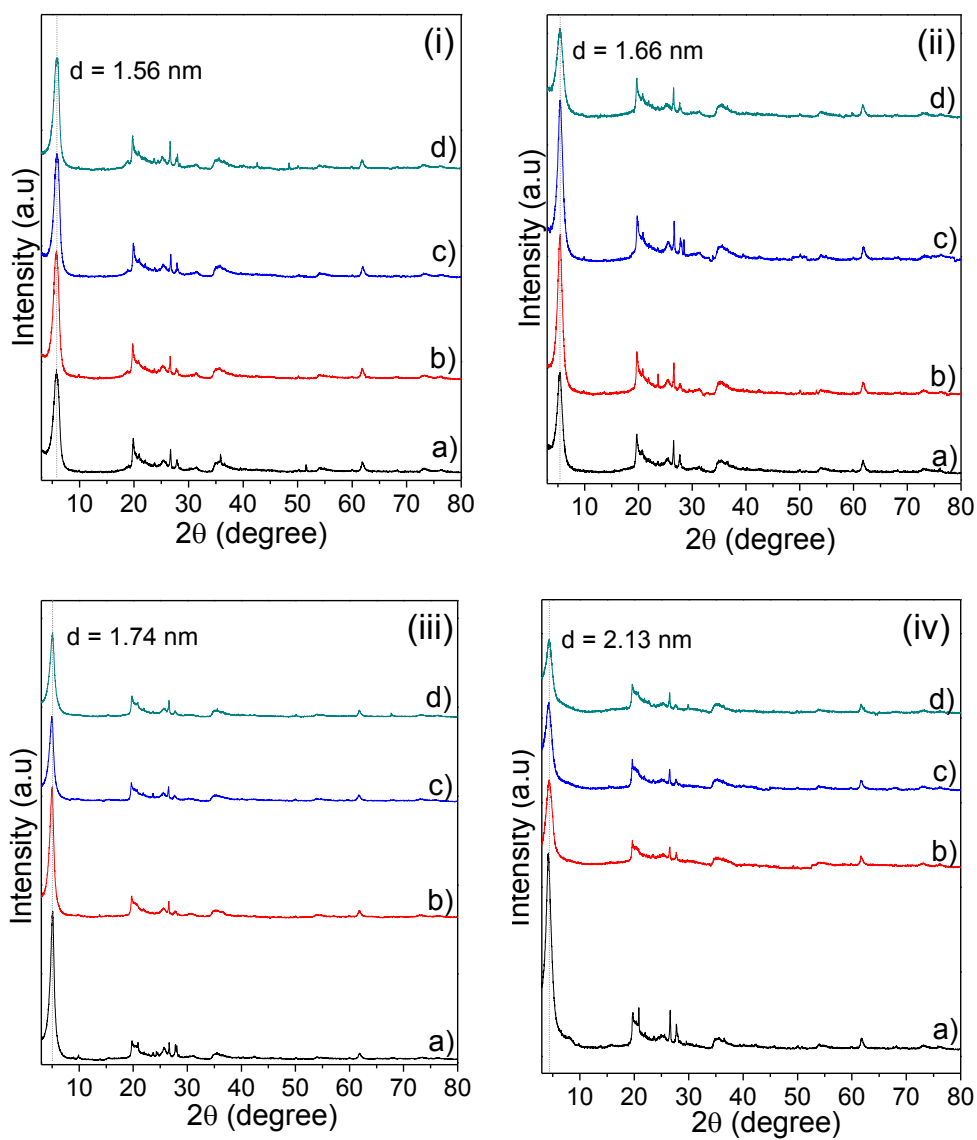
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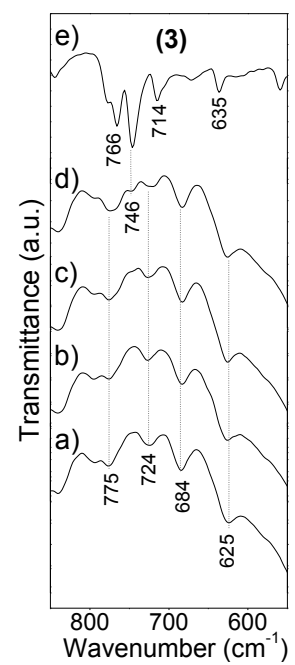
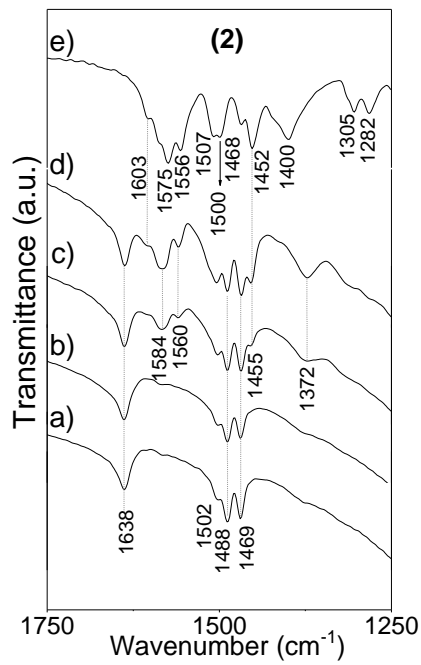
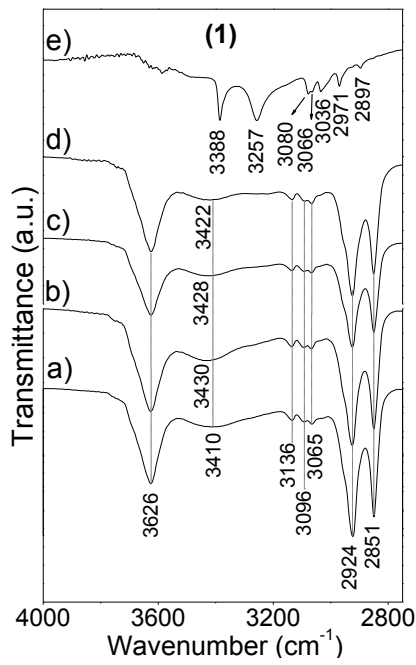
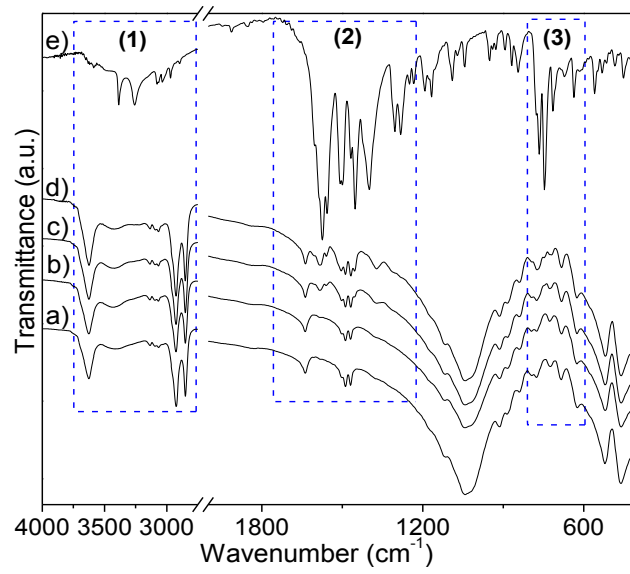
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832 **Figure 3**

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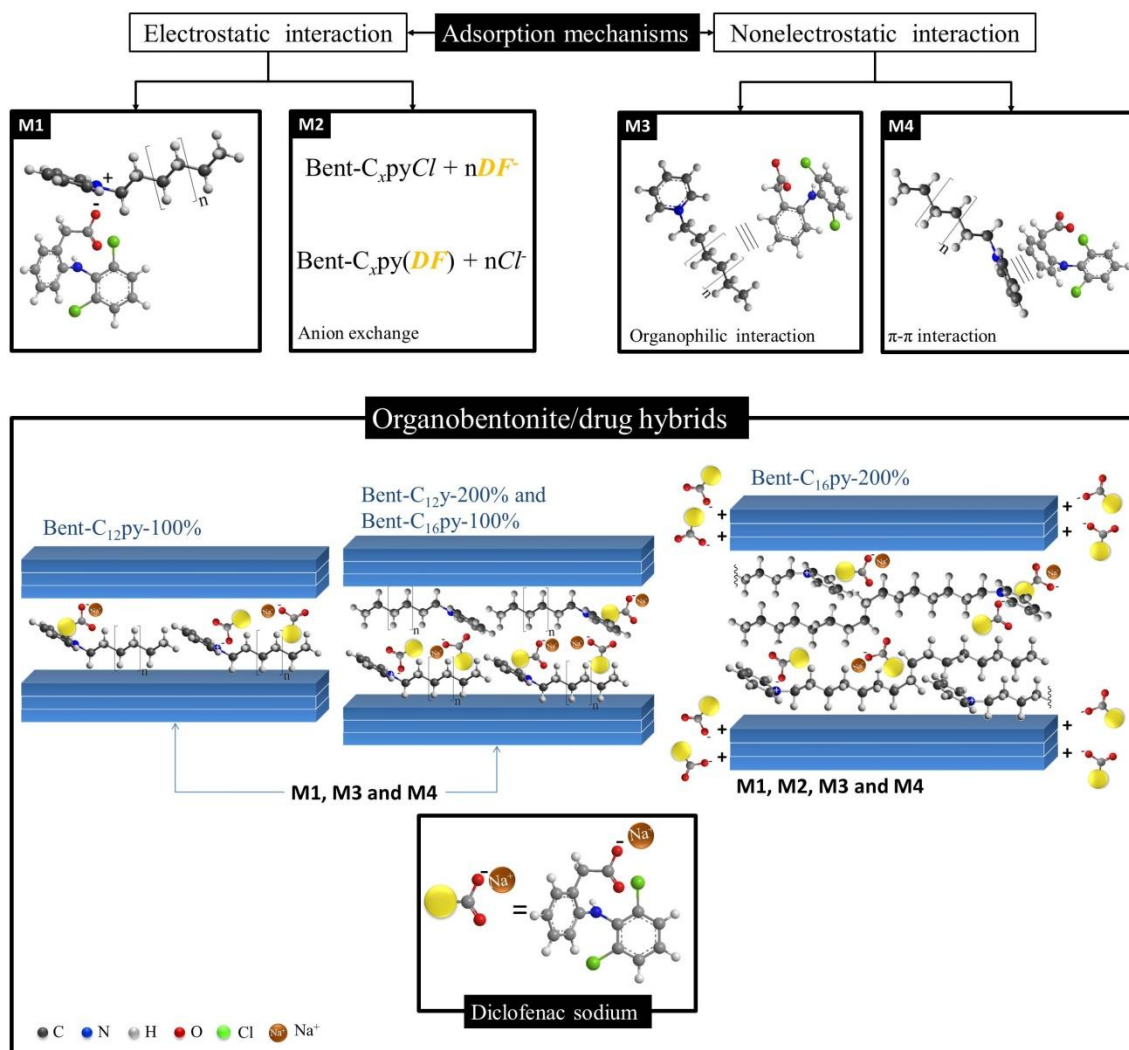
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840 Figure 4

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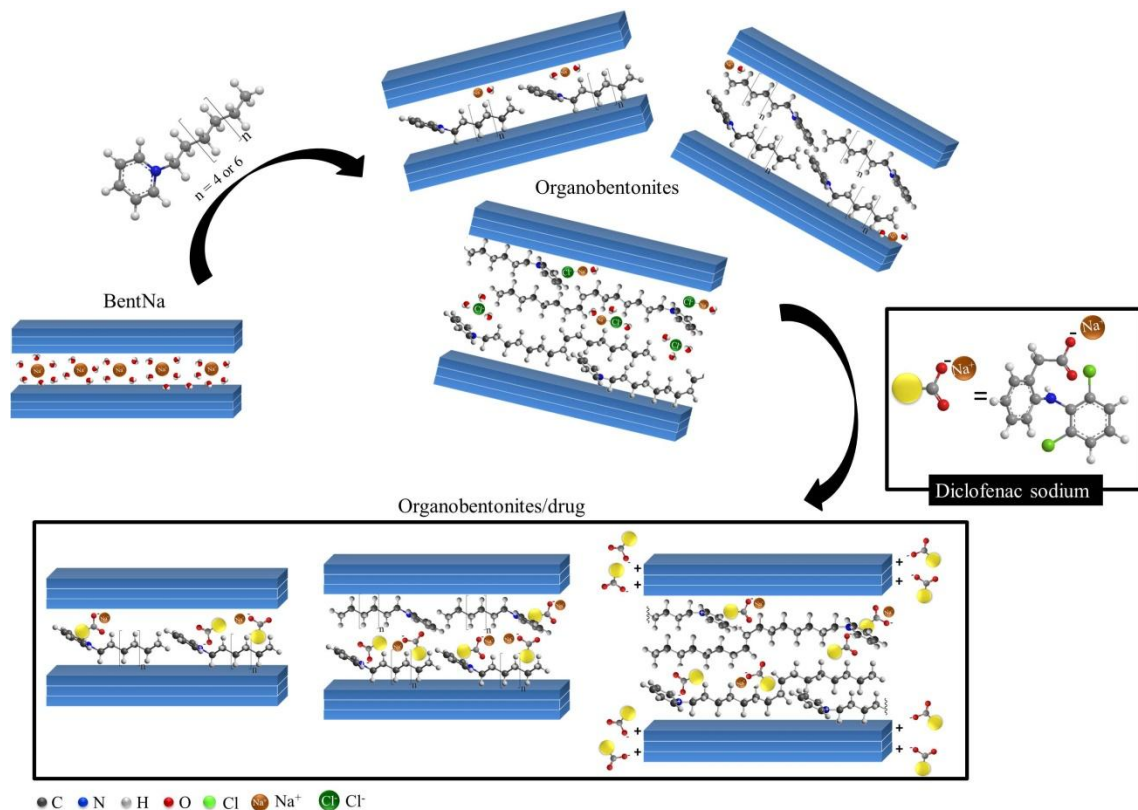
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850 **Graphical abstract**



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861 Table 1 – C, N and Cl elemental analysis of organobentonites and percentage of incorporated
 862 surfactant in relation to the CEC of BentNa (σ_f).

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Sample	C		N		σ_f	Cl ⁻
	%	mmol g ⁻¹	%	mmol g ⁻¹	%	mmol g ⁻¹
Bent-C ₁₂ py-100%	12.30	10.25	0.93	0.66	89.0	*
Bent-C ₁₆ py-100%	15.75	13.13	0.97	0.69	92.8	*
Bent-C ₁₂ py-200%	14.85	12.38	0.98	0.70	93.3	*
Bent-C ₁₆ py-200%	20.85	17.37	1.18	0.84	112.4	0.15 ± 0.01

864 *null for all

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881 Table 2 – Kinetic parameters obtained from the pseudo-first-order, pseudo-second-order and
 882 Elovich equations in nonlinear fitting of diclofenac adsorption on organophilic bentonites
 883 (Experimental conditions: 25 °C, pH 6.0 and 100 mg L⁻¹ diclofenac solution).

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Pseudo-first-order					
Solid	q _{e(exp)} (mg g ⁻¹)	k ₁ (min ⁻¹)	q _{e(cal)} (mg g ⁻¹)	R ²	SD (mg g ⁻¹)
Bent-C ₁₂ py-100%	5.50 ± 0.10	2.84 ± 0.65	5.01 ± 0.13	0.9242	0.410
Bent-C ₁₆ py-100%	8.98 ± 0.27	3.54 ± 0.82	8.36 ± 0.20	0.9573	0.554
Bent-C ₁₂ py-200%	12.98 ± 0.05	2.18 ± 0.12	12.80 ± 0.09	0.9938	0.293
Bent-C ₁₆ py-200%	38.71 ± 0.04	4.06 ± 0.33	38.53 ± 0.27	0.9950	0.814
Pseudo-second-order					
Solid	q _{e(exp)} (mg g ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	q _{e(cal)} (mg g ⁻¹)	R ²	SD (mg g ⁻¹)
Bent-C ₁₂ py-100%	5.50 ± 0.10	0.99 ± 0.25	5.18 ± 0.11	0.9641	0.282
Bent-C ₁₆ py-100%	8.98 ± 0.27	0.81 ± 0.25	8.54 ± 0.16	0.9752	0.422
Bent-C ₁₂ py-200%	12.98 ± 0.05	0.35 ± 0.01	13.06 ± 0.05	0.9985	0.141
Bent-C ₁₆ py-200%	38.71 ± 0.04	0.33 ± 0.02	38.95 ± 0.11	0.9993	0.308
Elovich					
Solid	α (10 ⁶ mg g ⁻¹ min ⁻¹)	β (g mg ⁻¹)	R ²	SD (mg g ⁻¹)	
Bent-C ₁₂ py-100%	1.07 ± 0.66	3.56 ± 0.13	0.9983	0.061	
Bent-C ₁₆ py-100%	44.5 ± 33.4	2.57 ± 0.09	0.9992	0.076	
Bent-C ₁₂ py-200%	84.97 ± 377.04	1.73 ± 0.38	0.9622	0.727	
Bent-C ₁₆ py-200%	9.48 10 ¹⁵ ± 133.78 10 ¹⁵	1.40 ± 0.37	0.9915	1.061	

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886

887 Table 3 – Adsorption parameters of diclofenac on organophilic bentonites at 25 °C and pH 6.0
 888 according to the Langmuir, Freundlich and Temkin models.
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Langmuir					
Solid	q_e (exp)	q_{max}	K_L	R^2	SD
	($mg\ g^{-1}$)	($mg\ g^{-1}$)	($10^{-1}\ L\ mg^{-1}$)		($mg\ g^{-1}$)
Bent-C ₁₂ py-100%	13.02 ± 0.65	13.26 ± 0.35	0.30 ± 0.03	0.9917	0.41
Bent-C ₁₆ py-100%	19.30 ± 0.96	19.05 ± 0.43	4.00 ± 0.56	0.9806	1.05
Bent-C ₁₂ py-200%	25.50 ± 1.02	25.33 ± 0.53	2.11 ± 0.24	0.9843	1.23
Bent-C ₁₆ py-200%	91.13 ± 1.82	92.20 ± 2.68	2.91 ± 0.39	0.9704	6.15
Freundlich					
Solid	n	K_f	R^2	SD	
		($mg\ g^{-1})(mg\ L^{-1})^{-1/n}$)		(mg g ⁻¹)	
Bent-C ₁₂ py-100%	2.71 ± 0.21	1.63 ± 0.23	0.9767	0.70	
Bent-C ₁₆ py-100%	4.37 ± 0.60	6.17 ± 0.91	0.8943	2.47	
Bent-C ₁₂ py-200%	4.10 ± 0.65	7.10 ± 1.33	0.8533	3.76	
Bent-C ₁₆ py-200%	4.16 ± 0.67	27.82 ± 4.81	0.7961	16.14	
Temkin					
Solid	b_T	A_T	R^2	SD	
	($10^2\ J\ mol^{-1}$)	($L\ mg^{-1}$)		(mg g ⁻¹)	
Bent-C ₁₂ py-100%	13.61 ± 1.02	1.70 ± 0.56	0.9366	1.31	
Bent-C ₁₆ py-100%	9.22 ± 0.40	8.60 ± 1.90	0.9766	1.16	
Bent-C ₁₂ py-200%	6.20 ± 0.40	3.43 ± 0.99	0.9498	2.20	
Bent-C ₁₆ py-200%	1.70 ± 0.13	4.41 ± 1.38	0.9156	10.38	

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