Adsorption of Diclofenac onto Organoclays: Effects of surfactant and environmental (pH and temperature) conditions

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Abstract

Among pharmaceutical products (PPs) recalcitrant to water treatments, diclofenac shows a high toxicity and remains at high concentration in natural aquatic environments. The aim of this study concerns the understanding of the adsorption mechanism of this anionic PP onto two organoclays prepared with two long-alkyl chains cationic surfactants showing different chemical nature for various experimental pH and temperature conditions. The experimental data obtained by a set of complementary techniques (X-ray diffraction, elemental analyses, gas chromatography coupled with mass spectrometry, and Fourier transform infrared spectroscopy) and the use of Langmuir, Freundlich and Dubinin-Radushkevish equation models, reveal that organoclays show a good affinity to diclofenac which is enhanced as the temperature is under 35°C and for pH above 4.5 (i.e. > pKa of diclofenac) while the chemical nature of surfactant appears to play a minor role. The thermodynamic parameters derived from the fitting procedure point out the strong electrostatic interaction with organic cations adsorbed within the interlayer space in the organoclays for the adsorption of diclofenac. This study stress out the application

of organoclays for the adsorption of a recalcitrant PPs in numerous aquatic compartments that can be used as a complement with activated carbon for waste water treatment.

1. Introduction

Despite the presence of inorganic pollutants such as trace elements and their well-known toxic effects, the priority of the water contaminants has turned recently to emerging micro-pollutants such as pharmaceutical products (PPs) which are more and more frequently found in various aquatic compartments. Among PPs that are non-biodegradable and recalcitrant to conventional wastewater treatments, diclofenac, a non-steroidal anti-inflammatory drug, is one of the few compounds that show harmless actions on both aquatic and terrestrial ecosystems [1-4]. The occurrence of diclofenac in surface, groundwater and even drinking water results to its high consumption in modern countries that stands to 200-2300 μg^{-1} day^{-1} $habitant^{-1}$ [5-6] which leads thus to discharge with concentration up to 1000 ng L^{-1} in wastewater plants influents [4].

Adsorption represents an effective and simple technique to remove both inorganic and organic micro-pollutants. Clay minerals were for a long time known for their outstanding adsorption properties. However, although being used in drinking water treatment, these layered materials turn out to be ineffective for the sequestration of persistent nonpolar hydrophobic contaminants and/or negatively charged organic species such as diclofenac. The chemical modification of clay mineral through the use of cationic surfactant generates organoclay adsorbents that combine both properties of the inorganic layered material and hydrophobic environment with the intercalation of the organic cation. Thus, these materials have shown particular properties for the adsorption of many emerging pollutants and were found to be more effective in some cases than activated carbon. Recent studies have highlighted an improvement of the adsorption capacity using organoclays as adsorbents that can potentially be an alternative for the remediation of micro-pollutants [7-17]. Indeed, these materials adsorb a large range of pollutants, such as pesticides [18-19], herbicides [20], phenolic compounds [21-22] and various pharmaceutical products [23-24]. The adsorption efficiency of organoclays mainly depends on both the chemical nature and the structural organization of the intercalated surfactants [25-26]. Thus, surfactants showing a long alkyl chains such as hexadecyltrimethylammonium (HDTMA) create an appropriate

organic environment within the inorganic frame for the adsorption of alkanes whereas modifiers such as benzyl decyltrimethylammonium (BDTA) or benzyltrimethylammonium (BTMA) owing aromatic rings show an excellent affinity with aromatic compounds [25-26]. Numerous works focused on the improvement of the adsorption of organic contaminants by using cationic organoclays where the the density of surfactant reached an amount of maximum of 1 time that of the cation exchange capacity (CEC) of clay mineral allowing one to create a hydrophobic environment without any strong steric effect that may restrict the sequestration of pollutants. Thus, such organoclays with 1 CEC surfactant density are revealed to be an appropriate sorbent and were proposed as realistic material for the treatment of water. While the incorporation of surfactant at high concentration (i.e. > 1CEC) generates a large hydrophobic network with an arrangement of the organic cations in bilayer within the interlayer space that may enhance or reduce the adsorption properties, rare studies focused on the sorption of organic compounds onto organoclays prepared at such high surfactant density.

Thus, this work stresses out the adsorption of diclofenac onto two organoclays prepared with two different long alkyl tail cationic surfactants: the BDTA and the HDTMA. These two organic cations showing different chemical groups, the BDTA displaying an aromatic ring that may contribute to the adsorption driving forces, were adsorbed at a concentration of 4 times that of the cation exchange capacity (CEC) of the clay mineral where adsorbents display a large interlayer space and a consequent organic environment, which may favor the further adsorption of diclofenac. The extent of the adsorption and the identification of the main interactional mechanisms were determined through the combined information obtained by a set of complementary techniques, including X-ray diffraction (XRD), elemental analyses (CHNS), gas chromatography coupled with mass spectrometry (GC/MS) and Fourier transform infrared spectroscopy (FTIR). The latter spectroscopic technique gives critical information of possible re-arrangement of surfactants and allows us to corroborate the adsorption data, but also to follow, through an original way, the density of both diclofenac and the organic cations. In addition to the discussion of the nature of the cationic surfactant for the adsorption of diclofenac and its characterization with the use of FTIR, this study also aimed to evaluate the removal of diclofenac for

different pH and temperature experimental conditions for a proper determination of the adsorption isotherms and thermodynamics of this micro-pollutant onto the organoclay adsorbents.

2. Materials and Methods

2.1. Adsorbents

Wyoming sodium montmorillonite (Mt), obtained from the Source Clay Minerals Repository, University of Missouri (Columbia, MO) was used in this study as a starting material. The structural formula can be expressed as: $(Ca_{0.12}Na_{0.32}K_{0.05})[Al_{3.01}Fe(III)_{0.41}Mn_{0.01}Mg_{0.54}Ti_{0.02}][Si_{7,98}Al_{0.02}]O_{20}(OH)_4$. Mt was fractioned to < 2 μm by gravity sedimentation, purified and Na^+ exchanged [14]. This Mt clay mineral shows a cation exchange capacity (CEC) of 76.4 meq per 100 g clay.

Both benzyldimethyltetradecyl ammonium (BDTA) and hexadecyltrimethylammonium (HDTMA) cationic surfactants were supplied from Sigma Aldrich Chemical. Aqueous solutions of BDTA and HDTMA with Millipore deionized water were prepared at ambient temperature for concentration at 4 times the cation exchange capacity (CEC) of Mt clay. These surfactant solutions were poured in aqueous Mt dispersions before being stirred at 300 rpm for 24 h. At the end of this procedure, the solutions were centrifuged at 3000 rpm for 20 min and the supernatants were removed. The resulting organoclays are dried at 100°C for 24 h before analysis.

2.2. Experimental techniques

The concentration diclofenac before and after being in contact with the adsorbents was obtained by GC/MS analysis using Trace GC Ultra chromatograph and TSQ Quantum XLS mass spectrometer (Thermo Scientific). Moreover, elemental analyses (Carbon, Nitrogen) on powder form samples were performed by using a Thermo Scientific flash 2000 analyzer. The concentration diclofenac before and after being in contact with the adsorbents was obtained by GC/MS analysis after a derivatisation of diclofenac with a mixture of MTBSTFA/pyridine (2:1, v/v). Analyses were performed on a Trace GC Ultra gas chromatograph (GC) fitted with a Thermo Trace Gold TG-5 MS capillary column (60 m, 0.25 mm i.d., 0.25 μm film thickness) and coupled to a TSQ Quantum XLS mass spectrometer equipped with an AS 3000 autosampler (both from Thermo Scientific) with the same methods as described by elsewhere [31]: the temperature of the column was held at 50°C for 3 min, increased from 50 to 120°C

at 30°C.min^{-1}, and from 120 to 310°C at 3°C.min^{-1} with a final isothermal hold at 310°C for 21 min. 2 µL of sample was injected in splitless mode at 280°C. Helium was the carrier gas (1 mL.min^{-1}). The mass spectrometer was operated in EI mode at 70eV, from m/z 50 to 500.

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

The d_{001} spacing's of the layered materials (organoclays and diclofenac/organoclay complexes) were determined by the first *00l* reflection from the X-rays patterns which were recorded in a conventional θ-θ Bragg-Brentano configuration by using a Thermo Electron ARL'XTRA diffractometer equipped with a Cu anode (CuK_α = 1.5418 Å) coupled with a Si(Li) solid detector. The diffractograms on dry samples (100°C for 24 h) were performed between 1 and 24° (2θ) with an angular and time steps of 0.04° and 10 s, respectively.

2.3. Adsorption of diclofenac

Diclofenac (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid of which pKa is 4.1) purchased from Sigma Aldrich Chemical, and assumed to have a purity > 98 % was used under sodium salt form which shows a solubility better than 10 g L^{-1}. Batch adsorption experiments of diclofenac onto organoclays were conducted in duplicate using at least 10 initial aqueous solutions ranging from 10 mg L^{-1} to 2 g L^{-1}. The solid to liquid ratio was kept constant, where 100 mg of organoclays were used for 50 mL of diclofenac aqueous solutions in centrifuge tubes and the pH was adjusted by a mix of HCl acidic and NaOH basic solutions. Samples were shaken on a rotary shaker at 50 rpm during 24 h in order to reach the equilibrium final concentrations and the centrifuged at 5000 rpm for 25 min. Both supernatants and sorbents after contact with the diclofenac were removed and analyzed through GC/MS. The amount of

adsorbed diclofenac was calculated by the difference between the initial and equilibrium final concentrations that allowed us to determine the adsorption isotherms which were corroborated with CHNS analyses. Before their XRD and FTIR characterizations, the entire resulting organoclays and Mt after adsorption of diclofenac were dried at 100°C for 48 h for CHNS, XRD and FTIR sorbents characterizations.

2.4 Adsorption isotherm

The resulting adsorption isotherms of the diclofenac onto organoclays and Mt were fitted using Langmuir model expressed as (1) [32]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the equilibrium diclofenac amount adsorbed on organoclays (mol g^{-1}), C_e the equilibrium diclofenac concentration in the resulting solution (mol L^{-1}), q_{max} the maximun adsorption capacity of the sorbents (mol g^{-1}) and K_L the Langmuir adsorption constant which is related to the thermodynamic equation of Gibbs free energy by relation (2):

$$\Delta G° = -RT \ln K_L \quad (2)$$

where R is the universal gas constant (8.214 J mol^{-1} K^{-1}).However, the adsorption of both surfactants and diclofenac contributes to a change of the chemical nature of the surface as well as a heterogeneity in the distribution of the adsorption sites, and therefore Freundlich and Dubinin-Radushkevish (D-R) model isotherm equations were used. The Freundlich isotherm is an empirical equation to describe heterogeneous systems of which the linear form is (3) [32-33]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where K_F (L g^{-1}) and n are both adsorption Freundlich parameters which respectively indicate the adsorption efficiency and the non-linearity degree between diclofenac and sorbents. The Freundlich parameter n suggest when 1/ n is between 0.1 and 1 a favorable adsorption process [34]. The D-R

isotherm allow to acquire complementary thermodynamic parameters. The equation is expressed as (4) [35-36]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

where ε is the Polayi potential, q_m the theoretical saturation capacity of the sorbent and β the constant related to the activity coefficient ($mol^2\ J^{-2}$) connected to the free energy E of adsorption ($kJ\ mol^{-1}$) with equation (5):

$$E = \frac{1}{\sqrt{2\beta}} \quad (5)$$

The latter parameter gives information about adsorption mechanism. Indeed, if E < 8 $kJ.mol^{-1}$, the adsorption process follows preferentially molecular interactional mechanism, while for E > 8 $kJ.mol^{-1}$ ion-exchange is envisaged [37].

3. Results and Discussion

3.1. BDTA-Mt and HDTMA-Mt organoclays properties

The BDTA-Mt and HDTMA-Mt organoclays were characterized by both XRD (Fig. 1a) and FTIR (Fig. 1b) analyses. The *00l* diffraction patterns of both cationic organoclays shift to lower of 2θ angular values underlining the intercalation of surfactant within the interlayer space of the layered starting clay mineral. Indeed, the dehydrated sodium exchanged clay mineral shows a *00l* reflection at 9.2 ° (2θ) leading to an interlayer spacing of 9.7 Å which is in agreement with previous works [10, 38]. As expected, with a concentration of 4 times the CEC for the cationic surfactants, the expansion of the interlayer space reaches 34.5 Å for BDTA-Mt and for HDTMA-Mt organoclays, that matches an organization of the organic cations in normal bilayer or paraffin structure. Indeed, FTIR spectra confirm such surfactant organization and show typical features characteristics of the organic compounds, such as the absorption bands at 2840-2920 cm^{-1} relative to the symmetric and antisymmetric CH_2 stretching vibrations of the surfactant alkyl chains (Fig. 1b) [10, 13].

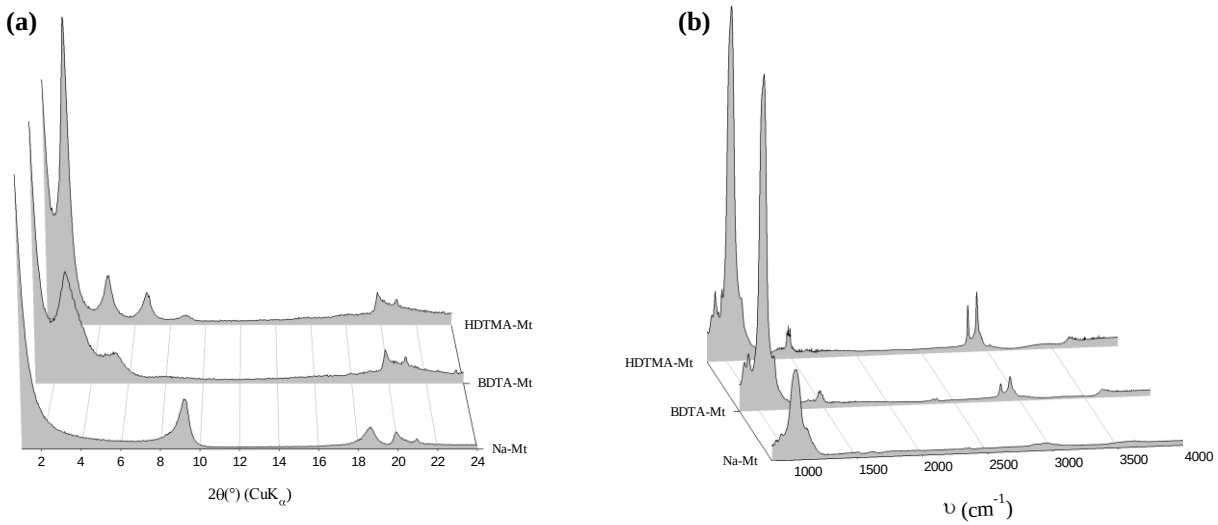


Fig. 1. (a) XRD patterns for dehydrated Na-Mt, BDTA-Mt and HDTMA-Mt organoclays. **(b)** FTIR spectra of Na-Mt, BDTA-Mt and HDTMA-Mt organoclays. The proper intercalation of both surfactants is confirmed by the shift of the first *00l* reflection at low angle values (XRD data) and with the CH_2 scissoring and stretching bands of the alkyl tails of the organic cations.

It is well established that the wavenumbers of the CH_2 stretching bands of hydrocarbon chains are extremely sensitive to the conformational ordering and change in the gauche-trans conformer ratio of the chains which can be used as probe, in correlation with the d_{001} spacing variation, for the surfactant arrangement within the silicate layers. Here, the wavenumbers of both symmetric and antisymmetric CH_2 stretching vibrations indicate that the organic cations located in the internal structure show an all-trans conformation [13, 14].

3.2. Effect of the surfactant

The final adsorption properties of organoclay materials mainly depend on the chemical nature of the adsorbed surfactant. The intercalation of cationic surfactants, through ion exchange with the inorganic cations, switches the chemical nature of the starting layered material from hydrophilic to hydrophobic while expands at a wide opening the interlayer space in order to the adsorption of organic compounds. Nevertheless, the improvement of the sequestration mainly depends on both the chemical nature and the structural organization of the intercalated surfactants. Thus, surfactants showing a long alkyl chains

such as HDTMA create an appropriate organic environment within the inorganic frame for the adsorption of alkanes whereas modifiers, such as BDTA show an excellent affinity with aromatic compounds [14].

Here, since diclofenac consists of two aromatic rings and display a negative charge in aqueous solution for pH above its pKa, thus it is expected the nature of the intercalated surfactant plays on the magnitude of the adsorption. The equilibrium adsorption isotherms of this PP onto both HDTMA-Mt and BDTA-Mt organoclays performed at room temperature and for a free pH (i.e. pH above the pKa of the diclofenac) display similar lineshapes with two main regimes: (i) a gradual growth of the adsorbed amount of diclofenac as its equilibrium concentration is increased; and (ii) a steady state at high concentration (Fig. 2).

The use of Langmuir equation model allows one to quantify the degree of affinity between the diclofenac and the two adsorbents, which here appears to be identical. Nevertheless, at high concentration of diclofenac, BDTA-Mt organoclay seems to be more efficient with a maximum adsorbed amount 1.9 x 10^{-4} mol g^{-1} whereas HDTMA-Mt shows a plateau with a maximum adsorbed amount of 1.55 x 10^{-4} mol g^{-1}. This slight difference (15%) of adsorbed amount may result to the nature of surfactant where BDTA could interact through molecular interactions (π-π) with diclofenac leading to enhancement of the adsorption. Nevertheless, while the adsorption and intercalation of surfactant give a hydrophobic surface, it decreases the specific surface area of the starting clay mineral. The contribution to the reduction of the accessible surface mainly depends on the nature of the inserted surfactant. This also has to be taken into account and may be another cause for the difference of maximum adsorbed amount of diclofenac onto organoclays.

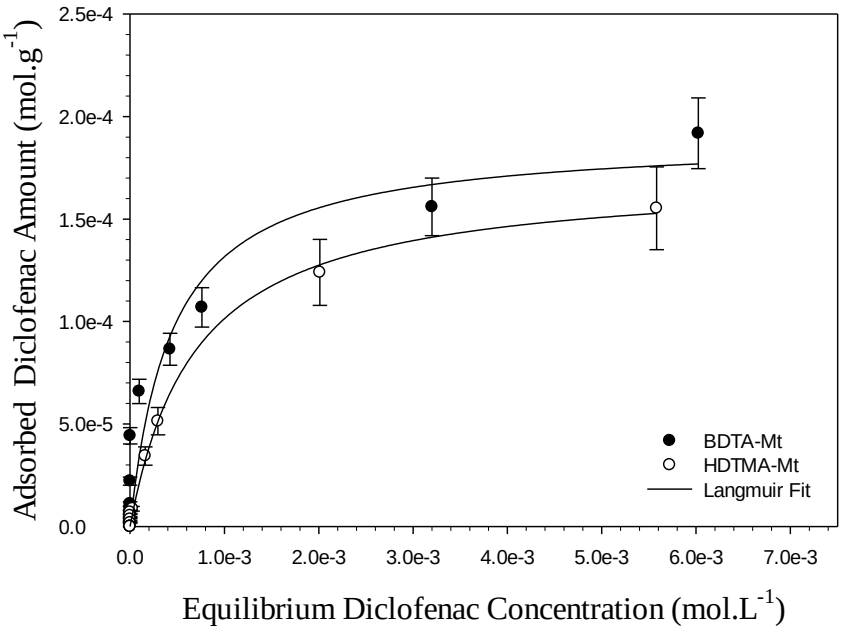


Fig. 2. Effect of the chemical nature of cationic surfactant (BDTA-Mt and HDTMA-Mt) on adsorption of diclofenac at ambient temperature (25°C) and using starting concentration of diclofenac ranging from 10 mg L^{-1} to 2 g L^{-1}.

The equilibrium adsorption isotherms highlight the proper affinity of diclofenac to both organoclays. XRD patterns of the organoclays (Fig.S1 in supplementary information) after being in contact with diclofenac do not show any difference with d_{001} spacing's remaining at the same openings. However, the value of adsorbed diclofenac in the steady state regime reaches an amount that exceeds the maximum possible adsorbed onto the external surface of organoclay platelets, stressing out that diclofenac is intercalated within the interlayer space of both organoclays and should disrupt the arrangement of the organic cations. FTIR spectroscopy gives us important information on the conformation of organic cations by focusing on the CH_2 stretching bands wavenumbers windows in the range 2800-3000 cm^{-1} (Fig. 3).

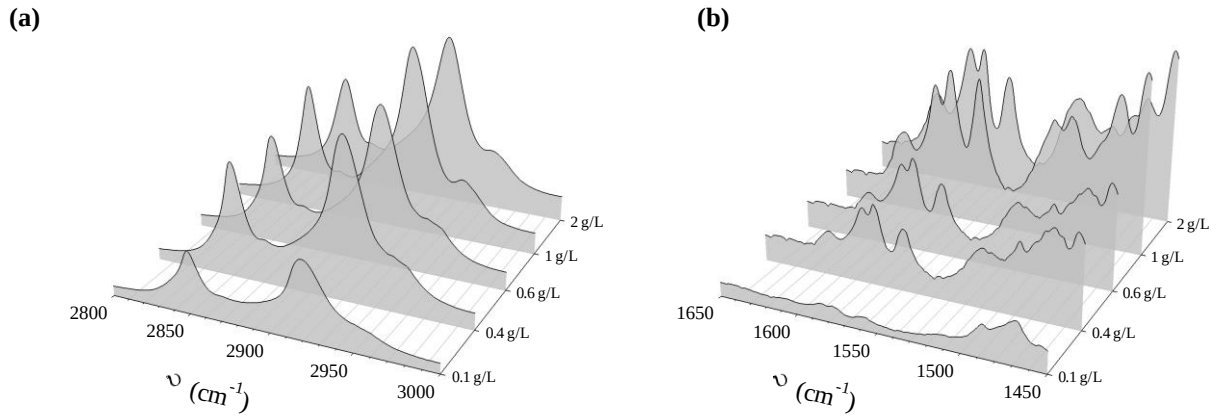


Fig. 3. 3D evolution of the FTIR spectra in the wavenumbers window of CH_2 stretching bands for **(a)** HDTMA-Mt organoclay in the range 2800-3000 cm^{-1} and the **(b)** CO_2^- stretching bands of diclofenac in the range 1450-1650 cm^{-1} for different starting diclofenac concentrations (0.1, 0.4, 0.6, 1 and 2 g L^{-1}).

In addition to determining any conformational change, this quantitative technique (in transmission mode) allows one to follow the evolution of both surfactants and diclofenac amount. Thus, FTIR data allows one to extract similar information as adsorption isotherms obtained through GC/MS, but also to analyze the fate of surfactants. Indeed, the integrated intensity of the CH_2 stretching bands is based on the density of surfactants as well as that of the CO_2^- stretching in the range of 1450-1650 cm^{-1} follows that of diclofenac. The evolution of the integrated intensity CO_2^- stretching bands related to the diclofenac density shows a lineshape similar to that of the resulting GC/MS adsorption isotherms, confirming the proper adsorption of the PP onto both organoclays (Fig. 4 shows the results for HDTMA-Mt, but similar behavior is obtained for BDTA-Mt, see Fig.S2 in supplementary information). In contrast, the decrease of the integrated intensity of both CH_2 stretching bands for the organic cations in organoclay as the concentration of diclofenac is increased reveals a reorganization of the surfactant within the interlayer space due to the adsorption of PP which is highlighted with the shift to high frequencies of both symmetric and antisymmetric CH_2 stretching bands (Fig. 5).

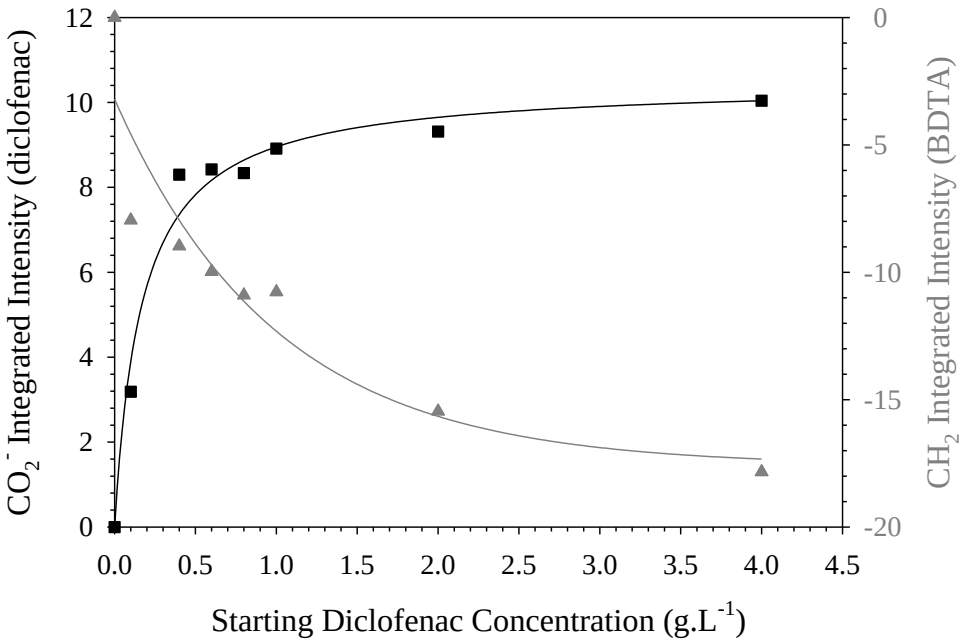


Fig. 4. Evolution of normalized integrated FTIR intensity of both CO_2^- bands (diclofenac) and CH_2 bands (surfactants) as a function of the starting diclofenac concentration. The lines are guides for the eyes.

Nevertheless, the reorganization of the surfactant aggregates depends on the adsorbed amount of diclofenac. In low concentration regime, diclofenac may be adsorbed onto the external surface of organoclay platelets and thus does not or slightly perturb the all-trans conformation and paraffin structure of the organic cations within the interlayer space. Once the starting concentration of diclofenac reaches 0.5 g L^{-1}, the organic cations undergo a deep rearrangement in lateral layers where the alkyl chains show more gauche conformer (i.e. disorder) and are less packed together within the interlayer space.

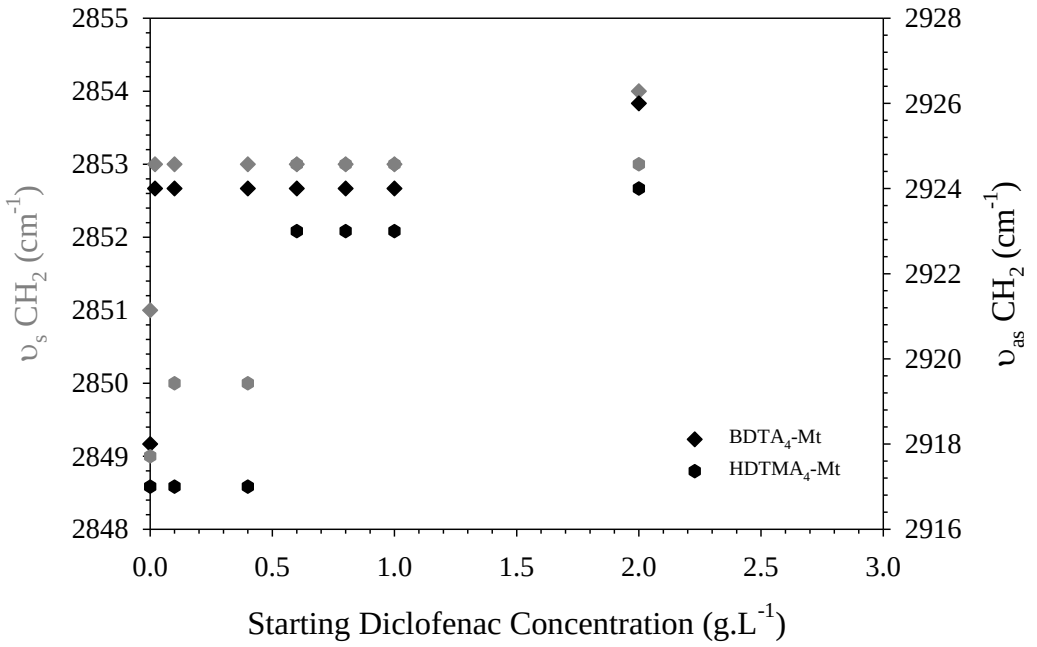


Fig. 5. Representation of the change in frequency of the symmetric and asymmetric CH_2 stretching bands of the HDTMA-Mt and BDTA-Mt organoclays as a function of the starting diclofenac concentration.

3.3. Thermodynamics

The temperature may drive to antagonist situations. Indeed, while temperature increases mobility of organic (i.e. reduction of mean free path) compounds making the adsorption or contact with a surface easier, it also reduces the energy of activation of numerous processes. Nevertheless, several experimental studies on the adsorption of different types of pollutants onto clay minerals or soils pointed out an increase of temperature reduces the percentage of adsorption [24]. The equilibrium isotherms at 5, 25, 35 and 50 °C resulting of the adsorption of diclofenac onto BDTA-Mt and HDTMA-Mt organoclays were fitted with Langmuir, Freundlich and D-R model equations. The whole adsorption parameters derived from and quality of the fitting procedure (R^2) are listed in Table 1.

Moreover, we used an error function (F_{error}) in order to evaluate which equation models was best suited to describe these processes. A lower result from the error function indicated a smaller difference between adsorption capacity calculated by the model (q_{cal}) and the experimental (q_{exp}). F_{error} can be expressed according to the following equation (6):

$$F_{error} = \sum_{i}^{p} \left(\frac{q_{i\,cal} - q_{i\,exp}}{q_{i\,exp}}\right)^2 \quad (6)$$

where $q_{i\,cal}$ is the value of adsorbed diclofenac amount predicted by the fitted model, $q_{i\,exp}$ is the value of adsorbed diclofenac amount measured experimentally, i indicated the initial diclofenac concentration of the experiment and p is the number of experiments performed.

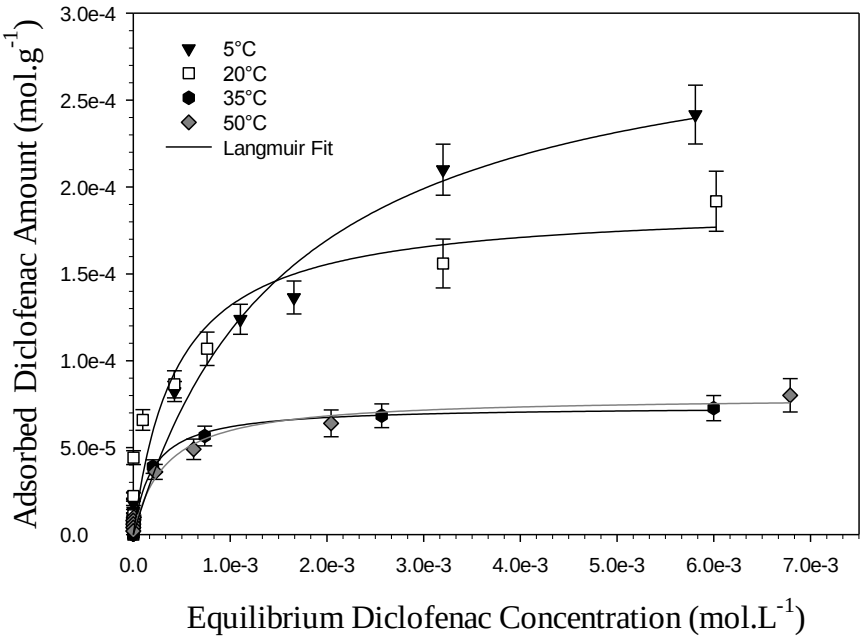


Fig. 6. Equilibrium adsorption isotherms of diclofenac onto BDTA-Mt organoclay (prepared at a concentration of 4 times the CEC of the starting Mt) for 4 different temperatures: 5, 25, 35, 50°C. The efficiency of the adsorption is greater at low temperature.

Table 1 Adsorption isotherm constants determined with Langmuir, Freundlich, and Dubinin-Radushkevich model fit for the adsorption of diclofenac onto BDTA-Mt and HDTMA-Mt organoclays for different temperatures and pH experimental conditions.

Adsorbant			Langmuir					Freundlich				Dubinin-Radushkevich				
	T (°C)	pH	q_{max} (mol.g^{-1})	K_L (L.mol^{-1})	$\Delta G°$ (kJ.mol^{-1})	R^2	F_{error}	K_F (L.g^{-1})	n	R^2	F_{error}	q_m (mol.g^{-1})	β (mol^2.J^{-2})	E (kJ.mol^{-1})	R^2	F_{error}
BDTA-Mt	5	6.5	3.06×10^{-4}	617	-15.9	0.986	0.065	2.26×10^{-3}	2.34	0.983	1.4×10^{-5}	5.80×10^{-4}	6.18×10^{-9}	8.99	0.978	1.2×10^{-4}
	25	6.5	1.88×10^{-4}	2298	-19.1	0.912	0.271	8.73×10^{-4}	3.35	0.989	3.5×10^{-5}	3.39×10^{-4}	3.69×10^{-9}	11.6	0.996	2.5×10^{-5}
	35	6.5	7.37×10^{-5}	5263	-21.2	0.985	0.002	4.48×10^{-4}	3.49	0.941	2.1×10^{-5}	1.08×10^{-4}	2.07×10^{-9}	15.5	0.980	6.8×10^{-5}
	50	6.5	7.94×10^{-5}	3058	-19.8	0.963	0.016	3.23×10^{-4}	3.87	0.995	4.3×10^{-4}	1.22×10^{-4}	2.34×10^{-9}	14.6	0.999	4.1×10^{-5}
HDTMA-Mt	5	6.5	3.16×10^{-4}	425	-14.9	0.981	0.263	6.67×10^{-3}	1.60	0.971	1.5×10^{-5}	6.48×10^{-4}	7.46×10^{-9}	8.18	0.982	3.0×10^{-4}
	25	6.5	1.71×10^{-4}	1439	-18.1	0.996	0.011	3.11×10^{-3}	1.87	0.962	3.1×10^{-5}	4.48×10^{-4}	6.45×10^{-9}	8.81	0.991	1.3×10^{-4}
	35	6.5	1.26×10^{-4}	1858	-18.6	0.983	0.056	1.47×10^{-3}	2.25	0.972	2.3×10^{-5}	2.54×10^{-4}	4.88×10^{-9}	10.1	0.962	3.9×10^{-4}
	50	6.5	1.10×10^{-4}	2379	-19.3	0.992	0.008	1.28×10^{-3}	2.23	0.914	3.9×10^{-4}	2.67×10^{-4}	5.60×10^{-9}	9.45	0.966	7.4×10^{-4}
BDTA-Mt	25	4	1.41×10^{-4}	3062	-19.8	0.917	0.065	5.72×10^{-4}	3.72	0.988	7.7×10^{-4}	1.24×10^{-4}	1.14×10^{-9}	20.9	0.859	2.4×10^{-4}
	25	11	1.98×10^{-4}	2187	-19.1	0.912	0.071	7.33×10^{-4}	3.81	0.989	6.9×10^{-4}	1.77×10^{-4}	1.20×10^{-9}	20.4	0.911	5.1×10^{-4}
HDTMA-Mt	25	4	1.37×10^{-4}	1976	-18.8	0.949	0.003	1.31×10^{-3}	2.47	0.995	2.9×10^{-4}	2.54×10^{-4}	3.94×10^{-9}	11.2	0.994	6.8×10^{-4}
	25	11	1.76×10^{-4}	5681	-21.4	0.994	0.003	3.26×10^{-3}	2.03	0.980	2.4×10^{-4}	4.31×10^{-4}	4.70×10^{-9}	10.3	0.994	1.1×10^{-5}

Langmuir model is based on the assumption of monolayer adsorption on a structurally homogenous adsorbent, where all sorption sites are identical and energy equivalent whereas the empirical Freundlich equation is applicable to adsorption on heterogeneous surfaces, where the interaction between the adsorbed molecules is not limited to the formation of a monolayer. Finally, the D-R equation isotherm represents a more general model for adsorption, since it assumes a heterogeneous surface and variability for the adsorption potential and was applied successfully for fitting the adsorption of organic species onto organoclays. Here, the diclofenac adsorption isotherms are properly fitted by the three equation models used as R^2 values show with a magnitude comprised between 0.859 and 0.999 and F_{error} values are between 6.8 x 10^{-5} and 0.271 (Table 1). Based on R^2 values, experimental data seem to be better adjusted to the Langmuir model, however its F_{error} are higher than 0.002 and to those for both Freundlich and D-R equations, ranging from 6.8 x 10^{-5} to 7.7 x 10^{-4}. Although Langmuir equation properly fitted experimental data, the two latter equations appear to be more suitable for modeling the adsorption of diclofenac onto both organoclays surface. Indeed, organoclays shows a heterogeneous surface with a reorganization of the organic cations once diclofenac is adsorbed leading to a distribution of several adsorption sites that are taken into account in both Freundlich and D-R equation models (Fig.S3-4 in supplementary information).

Nevertheless, the quality of the fits obtained by using a Langmuir equation is far enough to work on their parameters (Fig. 6). The whole ΔG° values derived from the Langmuir fitting procedure are negative for both organoclays and decrease when temperature rises ranging from -15.9 kJ mol^{-1} for BDTA-Mt at 5°C to -19.8 kJ mol^{-1} at 50°C, suggesting that the adsorption is spontaneous and more favorable at low temperature [39]. In addition, since the thermodynamics parameter derived from the fitting procedure show similar values for both organoclays, it thus reinforces the idea that the nature of surfactant appears to play a minor

role in the adsorption of the anionic PP here. The preparation of the organoclays was achieved at a concentration of 4 times the CEC where organic cations, after 1 CEC, are adsorbed through molecular hydrophobic interaction leading to a positive charge of the surfactant aggregates within the interlayer space. Thus, instead of the nature of surfactant it is much more the positive charge of the surfactant and the proportion of accessible mobilized organic cations that can form ionic organic complexes with diclofenac in a first step, which can be adsorbed in a second step onto organoclays, suggesting a chemisorption process. Indeed, if the adsorbed amount increases as the temperature increases, it corresponds to physisorption whereas the opposite trend generally underlines a chemisorption process [40]. Here, the adsorbed amount q_m decreases as the temperature increases excluding *de facto* any physisorption mechanism. The increase in temperature enhances the dynamics of the whole organic compounds making easier adsorption but also the mobility of the alkyl-chains of the surfactant cations. Indeed, it is well known that temperature affects alkyl chains with the introduction of gauche conformer or disorder leading to a perturbation of the adsorption sites in the hydrophobic environment grafted onto the clay mineral. If temperature may favor the probability of contact between diclofenac and the accessible organic cations where the driving force involves a chemisorption mechanism, it also disrupts the hydrophobic adsorption sites generated by the grafted surfactant cations onto the clay surface and here it appears that the balance between these two antagonist effects tips in favor of a decrease of the adsorption efficiency at high temperature. Both $\Delta G°$ and the estimated adsorbed amount q_{max} as well as the adsorption efficiency more generally decrease as the temperature rises indicating a chemical adsorption of diclofenac onto organoclays. Moreover, the enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) can be calculated with the van't Hoff equation (7):

$$\Delta G° = \Delta H° - T\Delta S° \quad (7)$$

The ΔH° values for BDTA-Mt and HDTMA-Mt are positive and, respectively, equal to 10.4 kJ mol^{-1} and 11.8 kJ mol^{-1}, reflecting the endothermic process of the adsorption of diclofenac onto the adsorbents. The positive ΔS° values (97.3 J mol^{-1} K^{-1} and 97.9 J mol^{-1} K^{-1} for BDTA-Mt and HDTMA-Mt, respectively) suggest an adsorption of diclofenac leads to the randomness in the solid/liquid interface.

The Freundlich constant K_F is related to the adsorption capacity of the organoclays and is enhanced with the decrease in temperature, which is coherent with the Langmuir analysis. Further, the empirical parameter of Freundlich 1/n is between 0.1 and 1 confirming also that the adsorption process is favorable for both organoclays. The efficiency decrease of organoclay to adsorb diclofenac at high temperature may also be understood by the theoretical saturation capacity q_m determined with the D-R equation model. Indeed, for BDTA-Mt (but similar feature is observed for HDTMA-Mt), q_m exhibits a drastic diminution from 5.80 x 10^{-4} mol g^{-1} to 1.22 x 10^{-4} mol g^{-1} if one changes the temperature from 5°C to 50°C. D-R model stresses out with E > 8 kJ mol^{-1} (Table 1) in the whole studied pH and temperature range, chemisorption mechanism mainly ensures the adsorption of diclofenac, involving strong electrostatic interactions with the mobilized organic cations whatever their chemical nature giving a certain stability of the resulting composite materials as well as a credit to use organoclays as geosorbent for the adsorption of diclofenac and more generally PPs.

3.4. Effect of pH on the adsorption of diclofenac onto BDTA-Mt and HDTMA-Mt organoclays

The efficiency of the adsorption and the magnitude of the parameters derived from the fitting procedure by using Langmuir, Freundlich and D-R equation models depend on numerous parameters, such as the temperature, ionic strength, pH, and both the chemical nature and molecular size of the organic cations. The effect of pH modifies both the density of charge of the chemical form of the diclofenac, but also those of the clay surface and its organoclay derivatives as well as its structure. Indeed, it is well known that low pH leads to an attack of

the octahedral sheets with a release of Al^{3+} or Mg^{2+} cations that can substitute to the sodium cations, thus to a complete destructuration of the layered structure of the clay mineral. However, our observations (not shown) indicate that the adsorption of surfactant prevents any degradation of the layered structure of the organoclays nor any release of surface by keeping a similar arrangement of surfactant aggregates within the interlayer space. In other words, while conferring a hydrophobic behavior, the adsorption/intercalation of surfactant acts as a coating of the silicate surface buffering it from any acidic attacks. This means that whatever the pH conditions used here in this study, both HDTMA-Mt and BDTA-Mt organoclays exhibit similar structure and surface and a change in pH only drives to a modification of the charge of diclofenac.

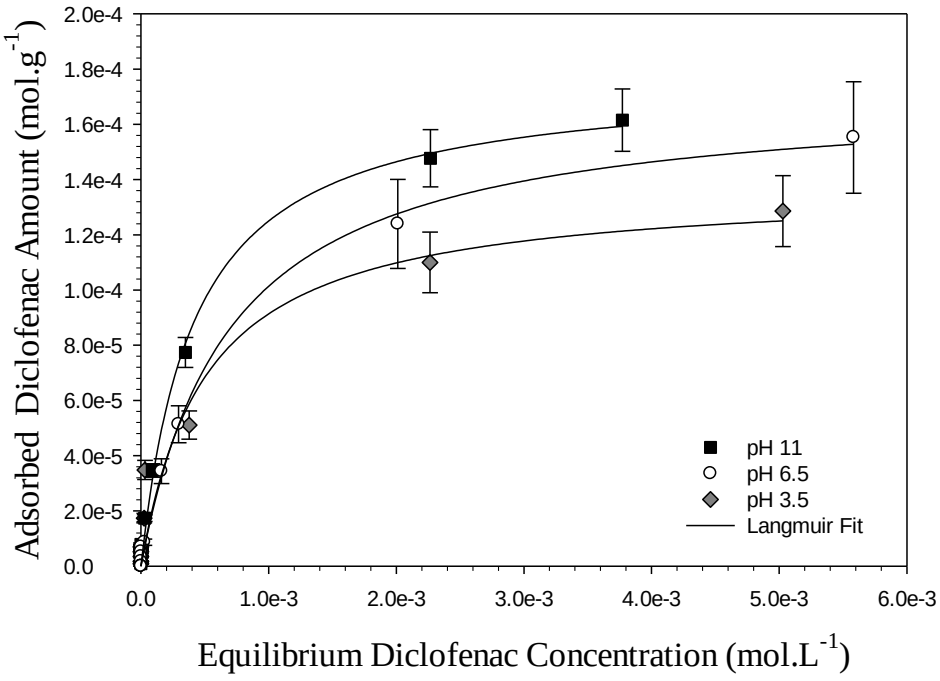


Fig. 7. Equilibrium adsorption isotherms of diclofenac (pKa=4.51) onto HDTMA-Mt organoclay (prepared at a concentration of 4 times the CEC of the starting Mt) for three different pH values of 3.5, 6.0-6.5, and 11.0. The efficiency of the adsorption is enhanced at high pH.

Here, three values of pH were tested where the diclofenac mainly displays a protonated form at the lowest pH value of 3.5 although negative diclofenac are also present in solution whereas for the two other pH > pKa, diclofenac is negative. Interestingly, at a pH of 3.5 where it was expected to get a low adsorption, the equilibrium adsorption isotherm show a lineshape similar to those at high pH (Fig. 7). Moreover, the parameters derived (with $\Delta G° < 9$ kJ mol^{-1}) from the Langmuir fit underline that the adsorption thermodynamically spontaneous and favorable. It is likely the proportion of the diclofenac in anions is associated organic cations and follows a similar adsorption mechanism as it was previously explained but it cannot exclude that further protonated molecules could be adsorbed as well onto the adsorbents surface. Nevertheless, the adsorption efficiency is particularly enhanced at high pH value where the fraction of diclofenac is preponderant. Indeed, the K_L values for HDTMA-Mt vary from 1.97×10^3 to 5.68×10^3 L mol^{-1} for low and high pH respectively confirming the better affinity of diclofenac with adsorbent at high pH values. The same trend is supported with the K_F values which varies from 1.31×10^{-3} L.g^{-1} (acidic pH) to 3.26×10^{-3} L g^{-1} (basic pH) and the theoretical saturation capacity q_m of D-R model. Their coherent evolutions point out the importance of the pH value mainly playing on the charge of diclofenac on the adsorption efficiency of the two organoclays.

4. Conclusion

The use of both BDTA and HDTMA cationic surfactants with a Na^+ exchanged Mt for the preparation of organoclays display favorable adsorption for diclofenac defined as an emerging micro-pollutant due to its presence at significant concentrations in numerous natural water environments. Thermodynamics parameters derived from Langmuir, Freundlich and D-R equation fitting procedure suggest that the adsorption onto the two sorbents is mainly driven by strong electrostatic interaction between diclofenac and both surfactants. It appears that the nature of surfactant plays a minor role but is rather the mobilized organic cations, which are main vectors for the adsorption of diclofenac. The association of hydrophobic complexes between diclofenac and surfactant in solution leads to their adsorption/intercalation onto organoclays implying a rearrangement of the surfactant as FTIR spectra stressed out. The magnitude of the adsorption is somehow controlled by the experimental temperature and pH conditions. Indeed, as it was expected, a rise in temperature involves a decrease in the adsorbed amount of diclofenac. The grafting of surfactant prevents any deterioration of the organoclay structure while keeping the arrangement of the surfactant aggregates. In acidic conditions, the proportion of diclofenac showing a negative charge decreases, thus reduces the adsorbed amount onto organoclays. Finally, the prepared organoclays show an adequate surface for the adsorption of diclofenac for various experimental conditions that it is possible to get in analogous natural environments, and thus are revealed as interesting materials in complement to activated carbon for water remediation. However, before any potential application or use as treatment method, further research works need to be undertaken, in particular the desorption of diclofenac with organic solvent and the quantification the adsorption efficiency with reuse organoclays.

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