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Adsorption of Diclofenac Pharmaceutical onto a Cationic Organoclay and an Untreated Montmorillonite

Tiago De Oliveira[1], Régis Guégan[1, 2]

[1]Institut des Sciences de la Terre d'Orléans, UMR 7327, CNRS-Université d'Orléans, 1A Rue de la Férollerie, 45071 Orléans Cedex 2, France
[2]Faculty of Science and Engineering, (Global Center for Science and Engineering), Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

regis.guegan@univ-orleans.fr, regis.guegan@aoni.waseda.jp

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 an organoclay prepared with a long-alkyl chains cationic surfactant 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 while the chemical nature of surfactant appears to play a minor role. This study stresses out the application of organoclays for the adsorption of a recalcitrant PP in numerous aquatic compartments that can be used as a complement with activated carbon for waste water treatment for instance.

1. Introduction

Pharmaceutical products (PPs) are non-biodegraded substances which are more and more commonly found in sewage and surface water [1]. Although being present at low concentration, these substances have been recognized to drive to toxic effects on several ecosystems. Among PPs recalcitrant to water treatments, diclofenac, a nonsteroidal anti-inflammatory substance, shows a high toxicity [2] and remains at high concentration in the environment [3] due to its particular resistance to the current treatment [4]. For this purpose, new techniques including adsorbents have to be developed for the adsorption of PPs [5-12]. Adsorption represents an effective and easy way to remove both inorganic and organic micro-pollutants limiting the formation of pharmaceutical residues with unknown effect in the environment. Clay minerals were for a long time known for their outstanding adsorption properties. However, although being used in water treatment factory, 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 via the use of cationic surfactants, like the benzyl dimethyl tetradecyl ammonium (BDTA), for the preparation of organoclays generate a hydrophobic environment which enhance the adsorption for emerging micro-pollutants [5-12]. Indeed, the intercalation of cationic surfactants switches the chemical nature of the starting layered material from hydrophilic to hydrophobic. Moreover, the resulting organoclay composite layered materials show an opening of their interlayer space that significantly improve the

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adsorption of numerous organic compounds [7]. The aim of this research work was to study the adsorption of diclofenac onto a cationic organoclay for water remediation.

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. This Mt clay mineral shows a cation exchange capacity (CEC) of 92.4 meq per 100 g clay. The benzyl dimethyl tetradecyl ammonium (BDTA) cationic surfactant was supplied from Sigma Aldrich Chemical. Aqueous solutions of BDTA with Millipore deionized water were prepared at ambient temperature for concentration at 4 times the cation exchange capacity (CEC) of Mt clay. The surfactant solution was poured in aqueous Mt dispersions before being stirred at 300 rpm for 24 h. At the end of this procedure, the solution was centrifuged at 3000 rpm for 20 min and the supernatant was removed. The resulting organoclay was dried at 100°C for 24 h before analysis and used as sorbents.

2.2. Experimental Techniques

The concentration of diclofenac before and after being in contact with the organoclay was obtained by GC/MS analysis using Trace GC Ultra chromatograph and TSQ Quantum XLS mass spectrometer (Thermo Scientific). 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} resolutions.

The structural changes of the layered materials (organoclays and diclofenac/organoclay complexes) were determined by X-ray diffraction. X-ray diffraction patterns 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) purchased from Sigma Aldrich Chemical, and assumed to have a purity > 98 % was used in its sodium salt form which shows a solubility better than 10 g L^{-1}. A batch adsorption experiment of diclofenac onto organoclays was conducted with a solution at 1 g L^{-1}. The solid to liquid ratio was kept constant, where 100 mg of organoclays was used for 50 mL of diclofenac aqueous solutions in centrifuge tubes. Sample was shaken on a rotary shaker at 50 rpm during 24 h in order to reach the equilibrium final concentrations and was centrifuged at 5000 rpm for 25 min. Both supernatants and $BDTA_4$-Mt organoclay after contact with the diclofenac were removed and analysed through GC/MS. The amount of adsorbed diclofenac was calculated by the difference between the initial and equilibrium final concentrations. Before their XRD and FTIR characterizations, the entire resulting organoclay and Mt after adsorption of diclofenac were dried at 100°C for 48 h for both XRD and FTIR characterizations.

3. Results and Discussion

3.1. Adsorbent properties

X-Ray diffraction patterns of the Na-montmorillonite (Na-Mt) and $BDTA_4$-Mt organoclay are shown in figure 1. The X-ray diffraction patterns of the Na-Mt displays a broad (*00l*) reflection located

around 9° (2θ) leading to an interlayer spacing close to 10 Å which underlines the dehydration of the clay mineral according to previous observations and numerical simulations on natural montmorillonites [13, 14]. Na-Mt is also characterized by several diffraction peaks at 20° (2θ) corresponding to a (*02.11*) reflection, and despite the purification process, contains quartz impurity, identified with Bragg peaks located at 21° (2θ). The X-ray diffraction patterns of $BDTA_4$-Mt shows several diffraction peaks at the 3° and 6° (2θ), corresponding to (*001*) and (*002*) reflections which reflect the existence of a well ordering in the silicate layers. This demonstrates that the intercalation of BDTA is stable and forms an ordered structure within the silicate layers. The insertion of BDTA expands the distance between the layers, giving a d_{001} spacing of ~35 Å. This value implies that inserted surfactant may adopt a perpendicular position between the clay platelets [7], which was confirmed through FTIR analysis.

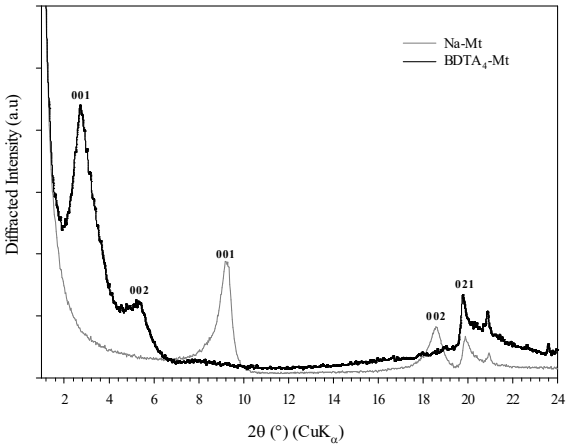

Figure 1. X-ray diffractograms of Na-Mt and $BDTA_4$-Mt organoclay.
The intercalation of BDTA is confirmed by the shift to low angle value of the *00l* reflections, expanding the d_{001} spacing from 1 (dehydrated Na-Mt) to 3.5 nm ($BDTA_4$-Mt).

Infrared spectroscopy gives a qualitative idea on the adsorption process. Figure 2 shows the infrared spectra between 650 and 4000 cm^{-1} of the dehydrated Na-montmorillonite, $BDTA_4$-Mt organoclays before and after being in contact with diclofenac which show similar feature: an intense absorption band corresponding to the Si-O stretching mode at 1030 cm^{-1} and the shoulder at 1117 cm^{-1}, several bands at 840, 890, and 918 cm^{-1} assigned to the AlMgOH, AlFeOH and AlAlOH deformations respectively, OH angular deformation observed at 1635 cm-1, whereas the OH stretching of water spreads out on a wide range of wavenumbers between 3200 and 3600 cm^{-1}. The last broad band at 3626 cm^{-1} is assigned to the OH stretching of structural hydroxyl groups. Moreover, to the assignment of the bands related to the clay mineral, the spectra reveal bands characterizing another crystalline or amorphous phases. Indeed, the weak band at 800 cm^{-1} is assigned to the Si-O stretching of quartz and/or amorpheous silica.

The spectrum of $BDTA_4$-Mt reveals expected bands of the Na-Mt with two additional bands related to the adsorption of BDTA onto the clay mineral surface. Indeed, the broad infrared absorption band at 1470 cm^{-1} is relative to the CH_2 scissoring mode whereas the intense absorption bands at 2920 and 2850 cm^{-1} correspond to the antisymmetric and symmetric CH_2 stretching mode of the hydrocarbon chains, respectively. These two CH_2 stretching bands are recognized to strongly depend on the density of confined surfactant within the interlayer space [12]. In addition to give an idea of the density of confined BDTA, the wavenumbers of CH_2 stretching bands stress out the conformational order of surfactant. The wavenumbers of both symmetric and antisymmetric absorption bands for the confined surfactant indicate that BDTA adopt an all-trans conformation within the interlayer space of the clay mineral.

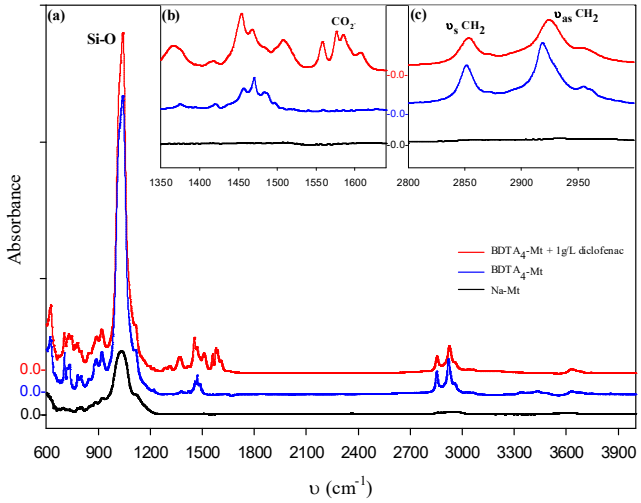

Figure 2. FTIR spectra of Na-Mt (black line), $BDTA_4$-Mt (blue line) and $BDTA_4$-Mt after interaction with a solution of diclofenac at 1 g L^{-1} (red line) **(a)** in the range 600-3900 cm^{-1}. **(b)** in the wavenumbers window of CO_2^- stretching bands of diclofenac in the range 1450-1650 cm^{-1}. **(c)** in the wavenumbers window of CH_2 symmetric (s) and asymmetric (as) stretching bands of BDTA surfactant in the range 2800-3000 cm^{-1}.

3.2. Environmental properties of $BDTA_4$-Mt: Diclofenac adsorption

Analytical GC/MS chromatogram results of solutions after interaction between the organoclay and the diclofenac (figure 3) shows the relative abundance of the different compounds in the supernatant. The picks in the range 15-24 minutes show the MTBSTFA compounds used for the sialylation of the sample before GC/MS analysis which allows a better thermal stability and a higher volatility for molecules. The chlorinated compound pick, visible at a retention time of 45 minutes, may correspond to a residue of diclofenac degradation during the process. The specific diclofenac pick is situated at a retention time of 54 minutes. The quantification of resulting diclofenac molecules after interaction in the supernatant requires the use of a standard. The 5-alpha-cholestan standard, at a concentration of 10.4 mg L^{-1}, has a retention time of 62 minutes. Area ratio between diclofenac and 5-alpha-cholestan picks provides the quantification of the diclofenac molecule present on the resulting solution. The analysis confirms a diminution of diclofenac amount, due to the adsorption onto organoclay.

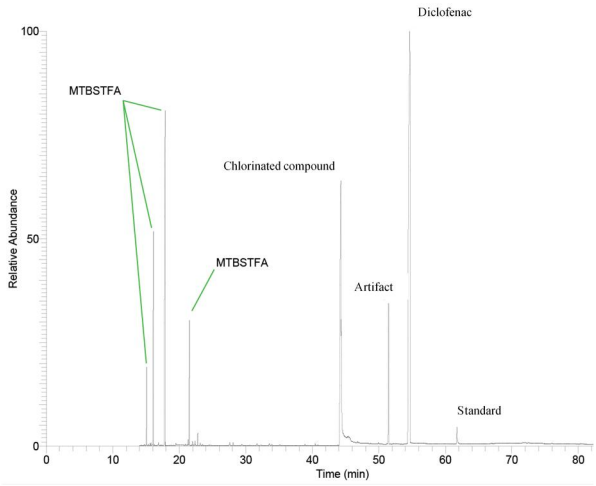

Figure 3. Total ion chromatogram obtained by GC/MS analysis after interaction between $BDTA_4$-Mt and 1 g L^{-1} solution of diclofenac at 25°C. The artefact pick, visible at a retention time of 52 minutes, is related to the GC/MS detector.

The spectrum of BDTA4-Mt after interaction with diclofenac at 1 g L^{-1} (insert in figure 2) reveals, new bands corresponding to the CO_2^- stretching bands of diclofenac in the range 1500-1600 cm^{-1} (in addition to organoclay absorption bands). The presence of CO_2^- stretching bands specific to the diclofenac, onto the resulting organoclay powder confirms the proper adsorption of diclofenac molecule within the organoclay determined through GC/MS analysis.

4. Conclusions

The use of BDTA cationic surfactant with a Na^+ exchanged clay for the preparation of organoclay contributes to enhance the adsorption of diclofenac defined as a micro-pollutant. The intercalation of surfactant at 4 times the CEC leads to an expansion of the interlayer space allowing a better access to diclofenac. Regarding the efficiency of these composite materials, the prepared organoclays in this study displayed some particular interests for the sequestration of diclofenac in wastewater or natural effluents.

Acknowledgments

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