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Mechanisms of removal of three widespread pharmaceuticals by two clay materials

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HIGHLIGHTS

- LECA efficiently removes gemfibrozil, mefenamic acid and naproxen from water.
- Vermiculite has faster adsorption kinetics than LECA (non-stirring conditions).
- Gemfibrozil and mefenamic acid attain a partition equilibrium onto vermiculite.
- Adsorption of naproxen onto vermiculite follows a Langmuir isotherm.
- The three drugs all bind to vermiculite in a similar way through the surface's Mg^{2+}.

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ABSTRACT

Pharmaceutical residues presence in the environment is among nowadays top emergent environmental issues. For removal of such pollutants, adsorption is a generally efficient process that can be complementary to conventional treatment. Research of cheap, widely available adsorbents may make this process economically attractive. The aim of the present work was to evaluate the capacity of two clay materials (exfoliated vermiculite, LECA) to adsorb gemfibrozil, mefenamic acid and naproxen in lab-scale batch assays. Results show that both adsorbents are able to remove the pharmaceuticals from aqueous medium. Although vermiculite exhibited higher adsorption capacities per unit mass of adsorbent, LECA yielded higher absolute removals of the pharmaceuticals due to the larger mass of adsorbent. Quantum chemistry calculations predicted that the forms of binding of the three molecules to the vermiculite surface are essentially identical, but the adsorption isotherm of naproxen differs substantially from the other two's. The linear forms of the latter impose limits at lower concentrations to the removal efficiencies of these pharmaceuticals by vermiculite, thereby electing LECA as more efficient. Notwithstanding, vermiculite's high specific adsorption capacity and also its much faster adsorption kinetics suggest that there may be some benefits in combining both materials as a composite adsorbent solution.

1. Introduction

Contamination of water resources with pharmaceuticals has been one of the top concerns of environmental science in the latest years [1–6]. The widespread use of pharmaceuticals and the generally inefficient removal of such contaminants by most wastewater treatment plants (WWTPs) are the main reasons for their frequent detection in many water quality monitoring studies [1–4,7]. In fact, most conventional wastewater treatment plants are inefficient for the removal of micropollutants in general (and especially of persistent organic xenobiotics) as these conventional systems were mainly designed for removing bulk pollutants [1–3,8].

Several advanced technologies have been evaluated as options to treat these contaminants (e.g. advanced oxidation processes or membrane processes) [1–3,8]. However, despite the sometimes high removal efficiencies attained, most of these technologies are too expensive to be considered as viable solutions on a large scale [2,3,9,10]. Moreover, if not properly operated, some of these treatments, such as advanced oxidation processes, may originate

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transformation products which may be more persistent or toxic than the parent compounds if complete mineralization is not attained [2,7,8,11,12].

Adsorption processes have been regarded as a potentially interesting option to complement existing water and wastewater treatment systems aiming to improve the removal of many organic xenobiotic pollutants, including pharmaceuticals [10,13–19]. However, the selection of the adsorbent materials is crucial, not solely from the perspective of the pollutants removal efficiency but also in regard to its cost.

Among some of the adsorbents studied, clay-based materials have received some attention [18–21] due to their interesting properties such as the high cation exchange capacity, swelling properties providing increased specific surface areas (although swelling may also negatively impact their hydraulic conductivity in filtration applications), as well as their wide availability. Some of the most common types of clay minerals (kaolinite, illite, montmorillonite, vermiculite, sepiolite, bentonite) have already been tested for the removal of a variety of organic micropollutants [16,21–25]. In addition to the naturally occurring non-processed clay materials, modifications of some clay minerals have also been studied to improve their sorption properties. Among the most common processing of clay minerals are chemical modifications (e.g. yielding apolar organo-clays) or the production of lightweight clay materials through thermal treatment (e.g. light expanded clay aggregates (LECA), expanded shale, expanded slate and exfoliated vermiculite) [19,20,25–28]. Among thermally processed clay materials, LECA and exfoliated vermiculite have been increasingly used over the latest years for water and wastewater treatment, performing several possible roles, such as filters or as support matrix in constructed wetlands systems [19,29–38]. Both materials have exhibited good adsorbent qualities for the removal of several organic pollutants [25,28,39,40].

Although adsorption assays targeting pharmaceuticals are less abundant than for other classes of organic pollutants (such as pesticides, PAHs, dyes or phenolic compounds), there is a general perception from the available literature that many clay materials may be effective for the removal of most pharmaceuticals from water [16,21–24,41–46]. However, not much data is currently available on the use of these two materials, LECA and exfoliated vermiculite in particular, for the latter type of application.

A better understanding of the interactions of organic molecules with clay minerals may provide guidance for a more judicious selection of materials to be applied in water/wastewater treatment systems, with enhanced removal of emerging organic pollutants such as pharmaceuticals. However, the behaviors of different compounds may vary substantially and be difficult to predict. There is a variety of mechanisms that can be involved in the adsorption of organic molecules to mineral surfaces, namely electrostatic (ionic) interactions, cation-bridging links, hydrogen-bonding, van der Waals (dispersion) interactions or chemisorption phenomena (with the establishment of chemical bond-like, highly energetic interactions). In many cases such behavior is controlled by specific interactions with certain functional groups and, in addition, both the material's surface and the molecules may exhibit acid-base properties which result in complex pH-dependences. Notwithstanding, those facts should not dissuade from attempting to characterize fundamental features of the behavior of certain functional groups and even to describe a common behavior of certain chemical families.

There are still many details of the adsorption phenomena over clay mineral surfaces that are not yet sufficiently known, which points to the need for further studies to be carried out and suggesting that there are ample opportunities to enhance the effectiveness of this type of processes.

In this work, an evaluation is presented of two clay materials, namely exfoliated vermiculite and LECA, which have already been tested with success to remove some organic xenobiotics including some pharmaceutical compounds. These materials will be evaluated in regard to their ability to adsorb three pharmaceuticals which are very commonly detected in water quality monitoring studies (naproxen, gemfibrozil and mefenamic acid) through a set of lab-scale batch assays. As complement to the experimental work, and in order to provide some molecular-level insight into the adsorption processes, electronic structure calculations of adsorbed molecules to a slab surface of vermiculite were carried out. A discussion of the preferred adsorption sites and the type of interactions established between pharmaceuticals molecules and the vermiculite surface is included.

2. Materials and methods

2.1. Chemicals and materials

The assays were performed on aqueous solutions of the following pure pharmaceutical compounds: Gemfibrozil (GB) (Sigma Aldrich, ≥99% purity), Mefenamic Acid (MA) (Sigma Aldrich, ≥98% purity) and Naproxen sodium salt (NP) (Sigma Aldrich, ≥98% purity). Some of the most relevant physical and chemical properties of these substances are listed in Table 1.

In this study two different natural processed materials were tested: exfoliated vermiculite of granulometric grade 3 (Aguiar & Mello, Lda, Portugal) and LECA of granulometric grade 2/4 (Maxit-Group Portugal). Prior to use, vermiculite and LECA were washed several times with Millipore water (Simplicity® UV, Millipore Corp., France) in order to remove fine particles and suspended solids, and were subsequently air dried.

2.2. Physical and chemical characterization of the tested media

The particle-size distributions on a weight basis were analyzed in triplicate by the conventional dry-sieving technique [47]. Grain-size distribution plots were used to estimate d_{10} (effective grain size) and d_{60}, and the uniformities of the particle size distributions (the uniformity coefficients, U) were calculated as the ratio between d_{60} and d_{10}. The apparent porosities (void space) of the media were determined from the amount of water needed to saturate a known volume of the solid (number of replicates $n = 5$) [31]. Bulk densities were determined based on the ratios between the dry weight and the bulk volume of the media ($n = 5$) [31]. The pH of water in contact with the media was determined ($n = 5$) by stirring for 30 min 10 g of powdered LECA or 1.5 g of exfoliated vermiculite in 25 mL of Millipore water and then conducting the potentiometric measurement of pH. The point of zero charge (PZC) was determined ($n = 5$) using the mass titration method [48,49].

2.3. Pharmaceutical removal assays

Two sets of batch adsorption studies were performed on GB, MA and NP solutions prepared with Millipore water using the two different clay material adsorbents, namely exfoliated vermiculite and LECA.

The adsorptive media were previously sterilized by dry-heat sterilization at 160 °C overnight. The experiments were conducted in the dark to avoid photodegradation, and without stirring to provide a better approximation to low flow rate conditions commonly used in real scenarios such as slow filtration under gravity or in constructed wetlands beds. Experiments were done in triplicate and at a controlled room temperature of 20 °C.

For the determination of the amounts of pharmaceuticals adsorbed in the different assays, aliquots were collected from each

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