



Amitriptyline removal using palygorskite clay



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HIGHLIGHTS

- Palygorskite (PFI-1) is effective for the removal of amitriptyline (AMI).
- Uptake of AMI on PFI-1 is restricted to the external surfaces with fast rate.
- Cation exchange was the dominant mechanism for AMI uptake on PFI-1.
- Minor component smectite in PFI-1 contributed significantly to AMI uptake.

ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form

1 April 2016

Accepted 18 April 2016

Available online 28 April 2016

Handling Editor: Shane Snyder

Keywords:

Amitriptyline

Cation exchange

Palygorskite clay

Mechanism

Removal

Uptake

ABSTRACT

With the increased detections of commonly used pharmaceuticals in surface water and wastewater, extensive attentions were paid recently to the fate and transport of these pharmaceuticals in the environment. Amitriptyline (AMI) is a tricyclic antidepressant widely applied to treat patients with anxiety and depression. In this study, the removal of AMI with palygorskite clay (PFI-1) was investigated under different physico-chemical conditions and supplemented by instrumental analyses. The uptake of AMI on PFI-1 was well fitted by the Langmuir isotherm with an adsorption capacity of $0.168 \text{ mmol g}^{-1}$ at pH 6–7. The AMI uptake was fast and reached equilibrium in 15 min. The X-ray diffraction patterns showed no shift of the (110) peak position of palygorskite after AMI uptake. However, the (001) peak position of the minor component smectite (about 10%) shifted to lower angle as the amounts of AMI input increased. These results suggested surface uptake of AMI on palygorskite and interlayer uptake of AMI in smectite. As smectite is a common component of palygorskite clays, its role in assessing the properties and performances of palygorskite clays for the uptake and removal of contaminants should not be neglected. Overall, the high affinity of AMI for PFI-1 and strong retention of AMI on PFI-1 suggested that it could be a good adsorbent to remove AMI from wastewater. Palygorskite clays can also be a sink for many cationic pharmaceuticals in the environmental of the arid regions.

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1. Introduction

Amitriptyline (AMI) is a tricyclic antidepressant widely applied to treat patients with anxiety and depression (Lee et al., 2005). Just in England alone, the annual consumption of AMI was 5.9 metric tons in 2000 (Sebastine and Wakeman, 2003). The extensive use of

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AMI and its persistence in ambient temperature resulted in its frequent detection in wastewater, surface runoff, and effluents from sewage treatment plants (Li et al., 2013) with concentrations in the ranges of $0.5\text{--}21 \text{ ng l}^{-1}$ (Calisto and Esteves, 2009). Although about 98% AMI removal could be achieved using a membrane bioreactor (Tadkaew et al., 2011), it was listed as non-biodegradable (Richardson and Bowran, 1985) and a 100% detection of AMI was still reported at the effluent of Cilfynydd wastewater treatment plant after treatment (Kasprzyk-Hordern et al., 2009). In addition, there was a considerable lack of knowledge about the environmental fate of a large number of psychiatric pharmaceuticals, including AMI, and further research about this topic was in great

need (Calisto and Esteves, 2009). Moreover, as their persistence and accumulation in the environment were very likely to occur, additional high quality sorption data for structurally diverse compounds, specifically ionic compounds, would be needed for the development of robust assessment techniques used in complex systems such as sewage sludge (Stevens-Garmon et al., 2011; Hörsing et al., 2011; Hyland et al., 2012).

Clay minerals have large surface areas and high cation exchange capacities and thus are commonly studied for their sorptive removal of contaminants. Interactions between AMI and clay minerals were focused on montmorillonite and kaolinite, as these are the common soil minerals found in most regions (Lv et al., 2013; Chang et al., 2014). In comparison to these platy clay minerals, palygorskite is a magnesium-aluminum phyllosilicate with a fibrous form. It has been commonly found in soils and sediments of arid regions and is often used in anti-diarrheal medications. It is estimated that 1,300,000 tons were produced annually with the United States as the largest producer (Murray et al., 2011). Because of periodic reversal of the tetrahedral sheets (every two tetrahedra for palygorskite and every three tetrahedra for sepiolite), it has a periodic array of octahedral ribbons and forms a chain-like structure parallel to the fiber stretch (Galan, 1996). The space inside each channel is large enough to accommodate exchangeable cations and water molecules. As an adsorbent, most studies on palygorskite were conducted for the removal of heavy metals and dyes (Galan, 1996; Sanchez et al., 1999; Taha et al., 2013).

The chain-like structure rendered its expandability, thus, restricted the entrance of larger organic cations into the channels. For this reason, it is anticipated that its behavior for the uptake of cationic drugs would be different from other platy clay minerals and be different from its uptake of small inorganic cations as well. As smectite is a common component in palygorskite clays (Galan, 1996), an evaluation of the possible contribution of smectite component to the adsorption of cationic drugs onto palygorskite clays is particularly of great interest. The goal of this research was to study the interactions between AMI and palygorskite in order to decipher the mechanisms of AMI removal by palygorskite, and to contrast the differences in the uptake of cationic drugs between fibrous clay minerals and platy clay minerals, so that its use in wastewater treatment could be extended.

2. Materials and methods

2.1. Materials

The AMI used was in an HCl form with a molecular weight of 313.9 g mol⁻¹ and a pK_a value of 9.4 (Green, 1967) or 9.45 (Manzo et al., 2006) (Fig. 1a). It is freely soluble in water, while its basic form was virtually insoluble in water (Manzo et al., 2006). It was purchased from Sigma–Aldrich, USA. The PFI-1 palygorskite clay was obtained from the Source Clay Minerals Repository. It contained ~80% palygorskite, 10% smectite, 7% quartz, 2% feldspar, and 1% other (Chiper and Bish, 2001). It had a reported cation exchange capacity (CEC) of 0.175 mmol_c g⁻¹ (Borden and Giese, 2001) and a specific surface area (SSA) of 173 m² g⁻¹ (Dogan et al., 2006).

As the sample contained 10% smectite and it was difficult to find pure palygorskite, to evaluate the relative contribution of palygorskite and smectite in PFI-1, a sepiolite (SepSp-1) acquired from the Source Clay Minerals Repository was used as a replacement for pure palygorskite to test its adsorption capacity of AMI. X-ray diffraction analyses identified sepiolite as the only mineral phase (Gehring et al., 1995). It has a reported CEC of 0.17 mmol_c g⁻¹, similar to that of the PFI-1 (Table 1), and an SSA of 317 m² g⁻¹ (Jaynes et al., 2005).

2.2. Batch AMI adsorption experiments

To each 50 mL centrifuge tube, 0.1 g of palygorskite clay and 20 mL AMI solution at concentrations of 0.16–1.91 mM were combined for the isotherm experiment. An initial concentration of 1.59 mg L⁻¹ was used for studies conducted under different contact times, solution pHs, ionic strengths, and temperatures. The mixtures were shaken on a reciprocal shaker at 150 rpm at room temperature for 24 h, except the kinetic study. The centrifuge tubes were wrapped with aluminum foils to prevent possible photo-degradation of AMI. After mixing, samples were centrifuged at 8000 rpm for 10 min and the supernatants were passed through 0.22 μm filters before being analyzed for equilibrium AMI concentrations by a UV–Vis method. For the kinetic study, the mixtures were shaken for 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, 16, and 24 h. For the pH adsorption edge experiment, the equilibrium solution pH varied between 2 and 11 and was adjusted by adding minute amounts of 2 M NaOH or 2 M HCl gradually and checked every 6 h. For the ionic strength experiment, NaCl was used as the ionic strength adjuster with concentrations of 0.001, 0.01, 0.1, and 1.0 M. For temperature effect study, the temperature was maintained at 303, 313, and 323 K. All experiments were conducted in duplicate.

2.3. Methods of analysis

The AMI concentration was measured using a UV–Vis spectrophotometer (SmartSpec 3000, Bio-Rad Corp.) at the detection wavelength of 240 nm with a detection limit of 0.3 mg L⁻¹ and a linear response range of 1–125 mg L⁻¹. Under the experimental conditions AMI existed as a cation and cation exchange may play a significant role in AMI uptake. Thus, the amounts of Na⁺, K⁺, Mg²⁺, and Ca²⁺ released from PFI-1 were analyzed by ion chromatography (IC) (Dionex 100) with a mobile phase made of 20 mM methanesulfonic acid. The equilibrium concentrations were in the respective ranges of 0.03–0.05, 0.01–0.03, 0.03–0.18, and 0.18–0.51 mM for Na⁺, K⁺, Mg²⁺, and Ca²⁺ desorption under different initial AMI concentrations.

The FTIR spectra were acquired on a Jasco FT/IR-4100 spectrometer equipped with a ZnSe attenuated total reflection accessory. The spectra were acquired from 600 to 4000 cm⁻¹ by accumulating 256 scans at a resolution of 4 cm⁻¹. Powder XRD analyses were performed on a Bruker D8 Advance diffractometer utilizing CuKα radiation at 30 kV and 40 mA and samples were scanned from 2° to 26° 2θ at 1° min⁻¹ with a scanning step of 0.02°. For SEM observation, PFI-1 powder taken from a blank sample was dried at room temperature and coated with Pt. An FEI Quanta 250 FEG SEM operated at an accelerating voltage of 7 kV was used.

3. Results and discussion

3.1. Influence of initial concentration on AMI removal

The data of AMI uptake on PFI-1 under different initial concentrations at pH = 6–7 were fitted using the Langmuir and Freundlich adsorption models and the former fitted to the experimental data better (Fig. 1b). The Langmuir model assumed monolayer adsorption on the adsorbent with limited capacity, while the Freundlich model could be used for heterogeneous multilayer adsorption (Banu et al., 2015). The Langmuir model can be described as:

$$C_s = \frac{K_L C_m C_L}{1 + K_L C_L} \quad (1)$$

where C_s is the amount of AMI adsorbed on solid at equilibrium

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