



Research article

Novel synthetic clays for the adsorption of surfactants from aqueous media



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ABSTRACT

The aim of this work was to assess for the first time the use of two high-charge swelling micas (Na-Mica-4 and C₁₈-Mica-4) for the removal of four linear alkylbenzene sulfonates (LAS) from aqueous samples. To this end, Na-Mica-4 was synthesized and organically functionalized with cations of octadecylamine to obtain C₁₈-Mica-4. Na-Mica-4 and C₁₈-Mica-4 were characterized by X-Ray diffraction, Zeta potential, specific surface area and thermogravimetric analysis before and after the adsorption experiments.

LAS removal studies were carried out in water samples spiked with a LAS mixture (10 mg L⁻¹). Removal rates with C₁₈-Mica-4 were between 94% and 97% at pH = 2, and between 98% and 99% at pH = 5 after 1 h. For the same amount of Na-Mica-4, removal rates were between 54% and 81% at pH = 2, and between 24% and 66% at pH = 5 after seven days.

No significant effects on the removal rates of C₁₈-Mica-4 were observed for pH values between 0.5 and 9. The experimental equilibrium data were fitted to 30 min, with removal rates of up to 98% in all the experiments. C₁₈-Mica-4 characterization tests indicate that LAS adsorption occurs in the interlayer space. Finally, C₁₈-Mica-4 was applied successfully to the removal of the target compounds from influent and effluent wastewater, surface water and tap water samples.

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1. Introduction

The preservation of aquatic ecosystems is driving the search for new alternatives to remove organic priority pollutants. Some strategies reported in the literature include advanced oxidation processes, nanofiltration, reverse osmosis, or adsorption (Martins et al., 2017; Rashed, 2013; Liu et al., 2009). Adsorption is widely used due to its efficiency, selectivity, affordability, simplicity and the reusability of the adsorbent (Martins et al., 2017; Park et al., 2011). In general, adsorbents should have relatively large surface areas, mechanical stability, and must be recyclable and biodegradable. Clay minerals have attracted the attention of researchers owing to their high cation exchange capacity, swelling properties, and high surface areas. For example, phyllosilicates have proven very effective in enhancing the adsorption process (Lee and Tiwari, 2012; Pazos et al., 2012; Alba et al., 2009). Previous studies have

reported on the use of layered clay minerals such as smectites or bentonites (Lagaly, 2001) for the removal of cations and polar organic compounds (alcohols, amines, and ketones) from water samples (Sánchez-Martín et al., 2008; Zadaka et al., 2007; Alba et al., 2006; Yapar and Yilmaz, 2005; Polubesova et al., 2005). However, clay minerals have a greater tendency to adsorb inorganic cations in wastes than the organic constituents. This is due to the usually larger molecular size of organics and to the hydrophilic nature of clays. Nonetheless, several studies have indicated that the modification of clays may increase their organophilicity and therefore the adsorption efficiency for the removal of several types of organic pollutants including pharmaceuticals, dyes and related organic compounds, aromatic organic compounds, pesticides and herbicides (Sun et al., 2017; Lingya et al., 2016; Gámiz et al., 2015; Runliang et al., 2014; Zhou et al., 2012; Lee and Tiwari, 2012; Park et al., 2011; Hocine et al., 2004).

In order to obtain clays with improved adsorption properties (Park et al., 2002), highly charged expandable micas have been developed. Their charge is similar to that of highly charged natural

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micaceous, but unlike them these synthetic micaceous show a high expansion capacity. Additionally, the incorporation of long-chain alkylammonium ions into the interlayer space of high-charge micaceous increases their expansion capacity which also improves the adsorption capacity of the resulting organomica (Pazos et al., 2017, 2012; Alba et al., 2011a). Additional advantages of synthetic micaceous are their ready availability, low cost, controllable composition and purity.

In this study, the adsorption capacity of Na-Mica-4 and C₁₈-Mica-4 for the removal of four LAS from aqueous samples is compared. LAS are especially troubling organic pollutants because of their impact on aquatic and terrestrial ecosystems and their wide use (Sakai et al., 2017a, b; Camacho-Muñoz et al., 2014; Mungray and Kumar, 2009). To our knowledge, this is the first time that these micaceous are used for the adsorption of LAS.

2. Experimental

2.1. Materials and reagents

SiO₂ (CAS no. 112945-52-5, 99.8% purity), Al(OH)₃ (CAS no. 21645-51-2), MgF₂ (CAS no. 7783-40-6), and NaCl (CAS no. 7647-14-5, ≥99.5% purity) used for Na-Mica-4 synthesis were purchased from Sigma-Aldrich (Madrid, Spain). Dodecylamine salt (CAS no. 124-30-1, ≥99.0% purity) used for organic functionalization of Na-mica-4 was also purchased from Sigma Aldrich.

HPLC-grade water, acetonitrile and methanol used for the liquid chromatography–tandem mass spectrometry assays were supplied by Romil (Barcelona, Spain). Analytical-grade hydrochloric acid and ammonium acetate 98% were obtained from Panreac (Barcelona, Spain). A commercial LAS homologue mixture, containing C₁₀ (12.3%), C₁₁ (32.1%), C₁₂ (30.8%) and C₁₃ (23.4%), was kindly supplied by Petroquímica Española (PETRESA, Spain). The physical and chemical properties of LAS are shown in Table 1.

2.2. Synthesis of high-charge swelling micaceous

Na-Mica-4 was synthesized by NaCl melt method following the procedure described by Alba et al. (2006). Na-Mica-4 cation exchange capacity (CEC) is 468 mequiv/100 g and its structural formula is Na₄[Si₄Al₄]Mg₆O₂₀F₄ · nH₂O. The reactants (SiO₂, Al(OH)₃, MgF₂, and NaCl) were weighed and mixed in an agate mortar until the mixture became homogeneous.

Heat treatments were carried out in a platinum crucible at 900 °C for 15 h using a heating rate of 10 °C · min⁻¹. The solid was separated by filtration, washed with distilled water, dried at room temperature, and then ground in an agate mortar.

2.3. Organic functionalization of Na-mica-4

C₁₈-Mica-4 was prepared by a cation-exchange reaction between Na-mica-4 and excess primary alkylammonium salt dodecylamine (2 CEC of Na-Mica-4) (Alba et al., 2011a). The primary amines were dissolved in an equivalent amount of HCl (0.1 M) and the resulting mixture was stirred for 3 h at 80 °C. The alkylammonium solution was then mixed with 0.6 g of Na-Mica-4 and stirred for 3 h at 80 °C. Subsequently, hot deionized water was added and the mixture was stirred for 30 min at 50 °C and centrifuged at 8000 rpm for 30 min at 5 °C. The product was dissolved in a hot ethanol:water mixture (1:1), stirred for 1 h and centrifuged at 8000 rpm for 30 min at 5 °C. The precipitate was finally dried at room temperature.

2.4. Sample collection

Influent and effluent wastewater samples were collected in September 2016 from a waste water treatment plant (WWTP) located in Sevilla (South of Spain). Six daily composite samples were prepared by mixing sample volumes that were collected every hour over a 24-h period by an automatic sampler. Surface water and tap water samples were collected during the same period from the Guadalquivir river and the city of Sevilla, respectively. Prior to the experiments, samples were filtered through a 1.2 μm glass-fiber membrane filter (Whatman, Maidstone, UK) in order to remove suspended matter.

2.5. Adsorption experiments

Each filtered sample (8 mL) was placed in a 25 mL flask containing 50 mg of either Na-Mica-4 or C₁₈-Mica-4 and spiked with a LAS mixture (10 μg mL⁻¹). After stirring at 800 rpm for 1 h, the supernatants were filtered through a 0.22 μm nylon filter. A 20-μL aliquot of the supernatants was injected into the chromatographic system. The parameters affecting LAS adsorption such as the type of synthetic mica, sample pH and extraction time were optimized. All experiments were carried out in triplicate. Removal rates were calculated from the equation:

$$\text{LAS Removal (\%)} = ((C_{\text{spiked}} - C_{\text{blank}})/C_{\text{standard}})$$

where C_{spiked} is the concentration of LAS measured in spiked samples; C_{blank} is the concentration obtained from a blank sample (samples without standard solution addition); and C_{standard} is the concentration obtained by direct injection of the standard solutions at the same concentration level as the spiked samples. The linearity of the method was evaluated from the standard solutions in triplicate at concentrations in the range 0.01–10 μg mL⁻¹.

2.6. Techniques

X-ray diffraction data were obtained using a Bruker D8 Advance A25 diffractometer (Bruker, Germany) aligned in Bragg-Brentano geometry. A Lynxeye PSD detector (Bruker, Germany) and copper Kα radiation (λ = 0.15405 nm) were also used. The data points were collected over a 2θ 1°–70° range with a step size of 0.03° and step time of 0.1 s, a tube voltage of 40 kV, and current of 30 mA.

Z-potential was calculated using the Smoluchowski equation (Smoluchowski, 1941). C₁₈-Mica-Na was suspended in water (1 g L⁻¹) before and after the adsorption experiment and the zeta potentials were measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA). The pH of the solution was measured using a Crison GLP 21 pH meter.

Surface area analyses were performed on an ASAP 2420 system (Micromeritics, USA) that uses N₂ sorption and the BET method (Brunauer et al., 1938).

Simultaneous differential scanning calorimetry and thermal gravimetric analysis were performed on a Q600 STD system (TA instruments, USA). The samples were heated from 20 °C to 700 °C at a rate of 10 °C min⁻¹ in nitrogen atmosphere.

Liquid chromatography–tandem mass spectrometry analyses were performed on an Agilent 1200 series LC system (Agilent, USA) equipped with a vacuum degasser, a binary pump, an autosampler and a thermostated column compartment. Separation was carried out using a Zorbax Eclipse XDB–C₁₈ Rapid Resolution HT column (4.6 mm × 50 mm i.d.; 1.8 μm particle size) (Agilent, USA). Separation was performed by gradient elution with methanol (solvent A) and a 10 mM aqueous solution of ammonium acetate (solvent B). The gradient profile elution conditions were 0–2 min: linear

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