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New insights into surface-functionalized swelling high charged micas: Their adsorption performance for non-ionic organic pollutants

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ABSTRACT

The major components of the wastewater from the petroleum refineries are benzene, toluene and phenol and one of the techniques applied to the treatment of effluents is sorption using organo-functionalized clay. The materials exploited in the present study are a family of surface-functionalized synthetic micas and their sorption capacities for non-ionic organic pollutants are analyzed. The organo-functionalization of their surface provides them the capacity to sorb effectively non-ionic pollutants in the interface. Their adsorption performance is a function of the alkylammonium properties such as the chain length, the mass fraction and the organization of the organic cation in the interlayer space of the micas.

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Introduction

Effluents from petrochemical industries and oil refineries are the major sources of hazardous wastes. Among the organic pollutants present in these effluents, phenol stands out; however, there are also other lighter non-ionic hydrocarbons (NOCs) such as benzene, toluene, ethylbenzene and xylene (BTEX) that have higher solubility in water. In fact, volatile organic compounds, VOCs, are known to be among the major contributors to risk for health damage and serious environmental problems [1].

Activated carbon and hydrophobic zeolites are the most widespread alternative to eliminate the VOCs due to its developed microporosity that ensures good sorption capacities [2–4]. However, its application is limited: activated carbon is thermal and chemical instable, causing significant safety problems. Hydrophobic zeolites are ten times more expensive and sensitive to the presence of humidity [5]. Hence, different alternative sorbents are desirable to overcome these kinds of problems [6].

One of the techniques applied to the treatment of contaminated effluents is sorption using clays, and a wide number of studies have been focused on sorption using calcined or surface modified clays [7] and more specifically organoclays [8–12]. The advantage of using these sorbents is mainly their easy availability, with relatively low cost and large surface area [1]. The sorption of NOCs by organoclays depends on the following factors [13,14]: the structure and size of alkylammonium ions, the type of clay, the cation exchange capacity, the density and orientation of the alkyl chains on the surface, and, features solute size, shape and relative solubility/hydrophobicity. Therefore, the favorable factors would be able to tune thorough the synthesis of design phyllosilicates. In this sense, synthetic organo-functionalized clays are replacing natural smectites and vermiculites [15,16]. However, all of those synthetic clays have a low cation exchange capacity (CEC).

The materials examined in the present study are a family of synthetic swelling high-charged micas, which has been organo-functionalized with long chain alkylammonium cations. Therefore, the main objective of this work is to analyze the sorption capacity of NOCs by this novel organomica family that allows a methodical analysis of the parameters that influence this procedure. Benzene, toluene and phenol were selected for the study of NOCs sorption

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since they are known to be the major components of the wastewater from the petroleum refineries.

Experimental

Materials

Na-Mica- n ($n=3$ and 4) were synthesized using the NaCl-melt as described by Alba et al. [17]. Their structural formulae are $\text{Na}_n[\text{Si}_{8-n}\text{Al}_n]\text{Mg}_6\text{O}_{20}\text{F}_4$, where n represent the layer charge ($n=3$ and 4). The starting materials employed were SiO_2 (Sigma; CAS no. 112945-52-5, 99.8% purity), $\text{Al}(\text{OH})_3$ (Riedel-de Haën; CAS no. 21645-51-2, 99% purity), MgF_2 (Aldrich; CAS no. 20831-0, 98% purity), and NaCl (Panreac; CAS no. 131659, 99.5% purity). Stoichiometric proportions of reactants were weighed and mixed in an agate mortar. The molar ratio between the reactants were $(8-n)\text{SiO}_2:(n/2)\text{Al}_2\text{O}_3:6\text{MgF}_2:(2n)\text{NaCl}$ [18]. The optimal amount of mixture reaction was up to 2 g that were grinded in an agate mortar during 30 min. They were calcined in a closed Pt crucibles at 900°C during 15 h using at $10^\circ\text{C min}^{-1}$. The product was washed with distilled water, filtered and dried at room temperature.

Organo-functionalization of micas

The organomicas were prepared by a cation-exchange reaction between the micas and concentration of alkylammonium salt to satisfy the 2 times the CEC of Na-Mica- n . Thus, the primary amine was dissolved in an equivalent amount of HCl (0.1 M) and the resulting mixture stirred for 3 h at 80°C . The alkylammonium dispersion was then mixed with 0.6 g of Na-Mica- n and stirred for 3 h at 80°C . After adding hot deionized water, the mixture was stirred for 30 min at 50°C and then the dispersion was centrifuged at 10,000 rpm for 20 minutes. The product was dissolved in a hot ethanol-water mixture (1:1) and stirred for 1 h at 50°C and then centrifuged [19,20]. The precipitate was dried at room temperature. The sample will be named as C_m -Mica- n ; where n is the layer charge 3 or 4 and m is carbon chain length of the alkylammonium salt ($m=12, 14, 16$, and 18).

Table 1 shows some properties of the alkylammonium-micas that will be used for the discussion of the results.

Sorption of non-ionic organic pollutants

Each batch sorption test was prepared in a 250 mL glass bottle, with 0.1 g of organomica and 100 mL of NOCs (phenol, benzene or toluene) solution in water:ethanol (9:1) at different concentration, 0.2–2.0 mmol of NOCs per gram of organomica. The samples were equilibrated for 12 h in an orbitals shaker (Unimax-2010) at 260 rpm.

The suspensions were centrifuged at 8000 r.p.m. at 8°C for 40 min. The supernatants were withdrawn for NOCs analysis; the difference in the amount before and after sorption reveals the amount of sorbed NOCs (C_s)

$$C_s = (C_i - C_{eq}) \frac{V}{m} \quad (1)$$

Table 1
Chemical and structural properties of organomicas.

C_m -Mica- n	OC	% CEC satisfied by alkylammonium	f_{om}
C_{12} -Mica-4	0.45	90.75	1.29
C_{14} -Mica-4	0.53	99.25	1.27
C_{16} -Mica-4	0.54	97.50	1.26
C_{18} -Mica-4	0.70	119.5	1.25
C_{18} -Mica-3	0.60	116.0	1.25

where the V (L) is the volume of the solution, m is the weight of the mica (kg), C_i (g/L) and C_{eq} (g/L) are the concentration of the organic compounds in initial and final solution, respectively.

Control experiments were performed without organomica and indicated the negligible loss of NOCs by volatilization or by sorption on the glass tubes.

The sorption percentage and the distribution ratio (K_d , L/kg), were calculated as follows:

$$\% \text{Sorption} = \frac{C_i - C_{eq}}{C_i} \cdot 100 \quad (2)$$

$$K_d = \frac{C_s}{C_{eq}} \quad (3)$$

Normalized K_d value by organic content present in each organomica, arise organic content corrected coefficient, K_{om} (L/kg of carbon), calculated according to:

$$K_{om} = K_d \frac{f_{om}}{OC} \quad (4)$$

$$f_{om} = \frac{w_{Cm}}{w_C} \quad (5)$$

where OC is the organic carbon (g alkylammonium/g organomica), it is calculated from the weight loss in the temperature range between 170°C and 900°C , w_{Cm} is the weight of the alkylammonium cation and w_C is the weight of carbon in the alkylammonium cation. Thus, f_{om} is the weight of the alkylammonium cation normalized to the weight of carbon in the alkylammonium cation. Those parameters have been calculated for all organomicas and summarized in Table 1.

Techniques

The organic contaminant concentration in the initial and final solutions was measured with an UV-vis spectrometer (Shimadzu UV-2101PC) at the wavelength of 254 nm (benzene) [21], 261 nm (toluene) [22] and 270 nm (phenol) [22].

Simultaneous thermogravimetric and thermal measurements (TG/DTA) were performed at the Departamento de Cristalografía, Mineralogía y Química Agrícola (University of Seville, Spain) using a NETZSCH (STA 409 PC/PG) instrument which is equipped with a Pt/Pt-Rh thermocouple for direct measurement of the temperature from RT up to 900°C at 10°C/min in an N_2 atmosphere. The DTA reference was pure aluminum oxide.

X-ray diffraction (XRD) patterns were obtained at the CITIUS X-ray laboratory (University of Seville, Spain) on a Bruker D8 Advance instrument equipped with a $\text{Cu K}\alpha$ radiation source operating at 40 kV and 40 mA. Diffractograms were obtained in the 2θ range of $1\text{--}70^\circ$ with a step size of 0.05° and a step time of 3.0 s.

Infrared spectra (FTIR) were recorded in the range $4000\text{--}300\text{ cm}^{-1}$ by the Spectroscopy Service of the ICMS (CSIC-US, Seville, Spain), as KBr pellets, using a Nicolet spectrometer (model 510P) with a nominal resolution of 4 cm^{-1} .

Results and discussions

Influence of the alkylammonium chain length on the phenol sorption by C_m -Mica-4 ($m=12, 14, 16$ y 18 , number of C on the alkyl chain)

The dependence of phenol sorption by C_m -Mica-4 with the equilibrium concentration (Fig. 1a) is characterized by a non-linear behavior and present two regions. In the first region, at low equilibrium concentrations of phenol, a continuous increase of the

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