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Nanohybrids of Mg/Al layered double hydroxide and long-chain (C18) unsaturated fatty acid anions: Structure and sorptive properties

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ABSTRACT

Long-chain (C18) unsaturated fatty acid anions, elaidate (ELA), oleate (OLE), linoleate (LINO), and linolenate (LINOLEN), were intercalated into Mg/Al (3:1) layered double hydroxide (LDH) and the resultant organo-LDH nanohybrid materials were characterized and subsequently evaluated as sorbents of six pesticides (clopyralid, imazethapyr, diuron, atrazine, alachlor, and terbuthylazine). The effect of the degree (18:1, 18:2, 18:3) and type (*cis*/*trans*) of unsaturation in the fatty acid alkyl chain on both the structure and sorptive properties of the LDH-unsaturated fatty acid nanohybrids was determined. All fatty acid anions were readily intercalated into the LDH, yielding structures with basal spacing values ranging between 32 Å (LDH-LINOLEN) and 40 Å (LDH-ELA). The bend imposed by the *cis* geometry of the double bonds present in OLE, LINO and LINOLEN was identified as a major factor determining the arrangement of these anions in the LDH interlayer space. Intercalation of *cis*-unsaturated fatty acid anions led to less densely packed structures and reduced the interlayer distance of the resultant nanohybrid compared to the structures resulting from intercalation of the linear, *trans*-unsaturated elaidate anion. All organo-LDHs displayed higher affinity to uncharged pesticides as compared to unmodified LDH, but double bonds in the fatty acid alkyl chain, particularly when present in *cis* configuration, reduced the affinity of the organo-LDHs to all pesticides, presumably because they led to structures with reduced hydrophobicity as compared to those resulting from the incorporation of linear organic anions.

1. Introduction

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds, are a special group of layered materials. Their structure consists of positively charged brucite-type layers of mixed divalent (M^{II}) and trivalent (M^{III}) metal hydroxide, $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$, where the positive charge is balanced by exchangeable hydrated anions ($A^{n-}_{x/n} \cdot mH_2O$) located in the interlayer space (Cavani et al., 1991; Rives, 2001). LDHs have recently gained much attention because of their broad applications as sorbents, anionic exchangers, base catalysts, polymer additives, etc. (Cavani et al., 1991; Paek et al., 2011; Rives, 2001). In particular, the great interest in LDHs as sorbent materials is related to their anionic exchange properties, the large specific surface areas associated with their layered nanostructure, the ease with which they are synthesized, and the possibility of modifying their surfaces to increase their affinity for specific sorbates (Cornejo et al., 2008; Lagaly, 2001).

Because of their anion exchange properties, LDHs often display a high affinity for anionic contaminants. Furthermore, the calcination product of various LDHs (e.g., 500 °C) is a mixed oxide, which has the peculiarity that it can rehydrate from water containing anions to reconstruct the original LDH layered structure (Miyata, 1980), a property known as "memory effect" (Cavani et al., 1991; Chibwe and Jones, 1989; Narita et al., 1991). Accordingly, both LDHs and their calcined products have been proposed as sorbents to remove anionic pollutants from aqueous solutions, either by an anionic exchange mechanism or by a reconstruction mechanism or memory effect (Cardoso and Valim, 2006; Hermosín et al., 1993; Inacio et al., 2001; Sato and Okuwaki, 1991).

The anionic exchange properties of LDHs also allow the intercalation of a wide variety of organic anions in the LDH interlayer space to yield the so-called organo-LDHs (Ayala-Luis et al., 2010; Clearfield et al., 1991; Costantino et al., 2009; Meyn et al., 1990; Miyata and Kumura, 1973). Many short and long-chain alkyl carboxylates, alkyl sulfates, and alkyl sulfonates have been intercalated into LDHs, expanding the interlayer and rendering the LDH surfaces hydrophobic (Costa et al., 2008; Meyn et al., 1990; Newman and Jones, 1998; Pavlovic et al., 1997; Xu et al., 2004). Combination at the nanometric scale of the expansive surface areas, anisotropic shape and reactive surfaces of LDHs with the functional and/or hydrophobic behavior of organic anions has been pointed out as an attractive way to develop organic–inorganic nanohybrid materials with properties that are inherent to both types

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of components (Paek et al., 2011). How organic anions are intercalated and packed in the interlayer is the theme of much current research (Xu and Braterman, 2010). In an environmental context, the study of organo-LDHs as sorbents for the removal or immobilization of organic pollutants is also a current research goal (Ayala-Luis et al., 2010; Bruna et al., 2012; Celis et al., 1999; Cornejo et al., 2008; Villa et al., 1999; Zhao and Nagy, 2004).

As for long-chain alkyl carboxylates, the structures resulting from the intercalation of saturated fatty acids, such as lauric, myristic, palmitic and stearic acids, into LDHs have extensively been characterized (Ayala-Luis et al., 2010; Borja and Dutta, 1992; Carlino, 1997; Costantino et al., 2005; Iyi et al., 2009; Kuehn and Pollmann, 2010); however, little is known about the structure of organo-LDHs prepared by intercalation of unsaturated fatty acids and even less about their sorptive properties (Inomata and Ogawa, 2006; Kameshima et al., 2006). Most previous studies have focused on the structural characterization of LDH-oleate nanohybrids (Donato et al., 2012; Inomata and Ogawa, 2006; Kameshima et al., 2006; Xu et al., 2004). We found only one comparative study on the intercalation of elaidate and oleate anions (Xu et al., 2004), and none on the intercalation of polyunsaturated analogues such as linoleate or linolenate.

The presence of one or more double bonds in the alkyl chain is expected to affect significantly the packing mode of the intercalated surfactant (Kanicky and Shah, 2002). In particular, for fatty acids containing *cis*-unsaturated chains, the *cis* geometry imposes a bend in the alkyl chain which can disrupt the arrangement of the organic anions in the LDH interlayers. Thus, the structure and properties of organo-LDHs are expected to vary depending on the number, position, and configuration of the double bonds within the alkyl chain. Lagaly et al. (1977) stressed the importance of the effect of unsaturation on the structures resulting after intercalation of alkylammonium ions into smectite; however, as for LDHs, the intercalation of unsaturated anionic surfactants has scarcely been investigated (Inomata and Ogawa, 2006). *cis*-Unsaturated fats are natural compounds conventionally regarded as healthier than saturated fats. Consequently, the use of unsaturated fatty acid anions for LDH modification would reduce concern about the incorporation of the resulting materials into soil and aquatic environments for practical applications compared to the use of their saturated analogues and other anionic surfactants (Cruz-Guzmán et al., 2004).

In the present study, four long-chain (C18) unsaturated fatty acid anions (elaidate, oleate, linoleate, and linolenate) (Fig. 1) were intercalated into a Mg/Al (3:1) LDH using the reconstruction method (memory effect). The resultant organo-LDHs were characterized and subsequently evaluated as sorbents of six pesticides with different chemical structures. By using different unsaturated fatty acids with the same chain length (C18), we aimed at assessing whether the degree and type of unsaturation in the fatty acid affected the structure and sorptive properties of the resultant nanohybrids. Dodecylsulfate-intercalated LDH was also prepared, characterized, and assayed as a pesticide sorbent for comparative purposes.

2. Materials and methods

2.1. Sample preparation

The starting carbonate-Mg:Al (3:1) LDH was prepared by the conventional coprecipitation method (Reichle, 1986). An aqueous solution (100 mL) containing 0.3 mol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.1 mol of $Al(NO_3)_3 \cdot 9H_2O$ was added dropwise to an alkaline solution (500 mL) containing 1.6 mol of NaOH and 0.37 mol of Na_2CO_3. The precipitate obtained was hydrothermally treated at 80 °C for 24 h, washed with deionized water, and then freeze-dried.

Elaidate (ELA)-, oleate (OLE)-, linoleate (LINO)-, and α-linolenate (LINOLEN)-intercalated LDH samples were prepared by the reconstruction method from calcined-LDH, i.e. the product resulting from heating the LDH sample at 500 °C for 3 h, following a procedure similar to that described by Chibwe and Jones (1989). For the synthesis, 500 mg of calcined-LDH (containing 2.6 mmol of Al) was added to 110 mL of aqueous solutions containing 3 mmol of elaidic, oleic, linoleic, or α-linolenic acid (Sigma-Aldrich, Spain) plus 3.3 mmol of NaOH, which was added to

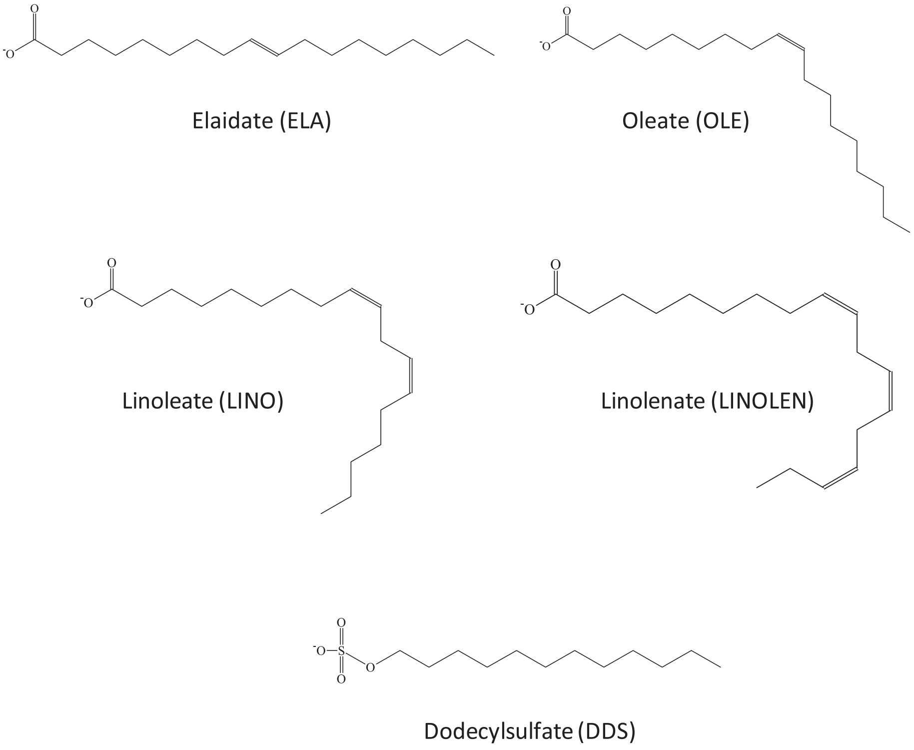

Fig. 1. Chemical structures of the organic anions used to prepare the organo-LDHs.