



# Low-cost aluminum and iron oxides supported on dioctahedral and trioctahedral smectites: A comparative study of the effectiveness on the heavy metal adsorption from water



F. Franco <sup>a,\*</sup>, M. Benítez-Guerrero <sup>b</sup>, I. Gonzalez-Triviño <sup>b</sup>, R. Pérez-Recuerda <sup>c</sup>, C. Assiego <sup>c</sup>, J. Cifuentes-Melchor <sup>b</sup>, J. Pascual-Cosp <sup>b</sup>

<sup>a</sup> Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n, 29071 Málaga, Spain

<sup>b</sup> Departamento de Ingeniería Civil, de Materiales y Fabricación, E.T.S.I. Industrial, Universidad de Málaga, C. Dr. Ortiz Ramos s/n, 29071 Málaga, Spain

<sup>c</sup> Empresa Municipal de Aguas de Málaga, S.A., Plaza general Torrijos, no 2, Edif. Hospital Noble, 29016 Málaga, Spain

## ARTICLE INFO

### Article history:

Received 22 July 2015

Received in revised form 26 October 2015

Accepted 27 October 2015

Available online 11 November 2015

### Keywords:

Montmorillonite

Saponite

PILC

Porosity

Adsorption properties

Heavy metals

## ABSTRACT

Montmorillonite and saponite were used as raw material for a series of aluminum and iron oxides modified smectites. The structure and texture of adsorbents were characterized by XRF, XRD, ATR-FTIR, SEM and nitrogen adsorption, whereas sorption properties were characterized for As(III), Cd(II), Cr(III), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II), focusing our interest in a reasonable concentration range for the conditioning of drinking water (10–100 ppb). Carbon, commonly used for this purpose, has been used as reference material. Except for Hg(II), we found that the obtained materials show notably higher sorption capacities than carbon. Fe-modified smectites exhibit the best metal adsorption properties, followed by the natural ones, while Al-pillared clay minerals showed the lowest adsorption properties.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

A large number of physical properties and applications of the smectite-group minerals depend on the extent and nature of both external and internal surfaces. Thus, in the last decades many researches have been focused in developing treatments to modify appropriately these characteristics. Acid and pillaring treatments have been the most studied, and montmorillonite was the most used mineral of the smectite group in these works, due to its abundance in the nature (Murray, 2000).

Researches related to the synthesis of pillared clay minerals have increased in recent decades in order to obtain materials with catalytic activity, and with application in oxidizing and petrochemical reactions, and selective NO<sub>x</sub> reduction (Ding et al., 2001). Moreover, in the last years the pillared clay minerals have been received considerable attention due to their ability for organic contaminants removal by catalytic treatment (Molina et al., 2011), and also for heavy metal adsorption (Bhattacharyya and Gupta, 2008) in wastewater depuration processes. Specifically, modified clay minerals with aluminum and iron species are object of study for contaminants removal in water treatment, due to their coagulant and adsorbent properties (Cooper et al., 2002;

Faghihian and Bahramian, 2014), and so are the corresponding calcined pillars of aluminum and iron oxides, with great interest due to their chemical and thermal stability and ease of synthesis (Karamanis and Assimakopoulos, 2007; Ararema et al., 2011). Furthermore, iron oxyhydroxides, both isolated and supported on other materials, such as clay minerals, have been effectively used for the adsorption of different heavy metal cations (Xu and Axe, 2005; Hua et al., 2012). However, the use of these materials for drinking water depuration is scarce, since the economic cost of their synthesis is not profitable from a commercial point of view.

Pillaring treatments consist of exchanging interlayer cations of smectite, mainly Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>, with large inorganic metal hydroxycations, which apparently aggregate to form cationic oligomers in the reactive solutions (Baes and Mesmer, 1976). After the calcination of the intercalated smectite, the metal polyhydroxocation is transformed into an oxide pillar strongly fixed to smectite and exposing their internal surface expanding the 2:1 layers (Vaughan, 1988; Ding et al., 2001). The introduction of pillars, besides increasing the resistance and stability of the clay mineral, provides porosity, a higher surface area, access to acid areas existing in natural smectite, and the presence of potentially active species for a specific reaction (Ding et al., 2001; Vicente et al., 2013). The final size of the internal pores of pillared clay minerals seems to be controlled with the size of the oligomers.

\* Corresponding author.

E-mail address: [ffranco@uma.es](mailto:ffranco@uma.es) (F. Franco).

Several species have been studied as pillaring agents, as alkyl ammonium cations (de Paivia et al., 2008), metallic cluster cations, metallic oxide sol and polyoxocations of different nature (Al, Ni, Zr, Fe, Cr, Bi, Be, B, Nb, Ta, Mo, Ti y Cu) (Bergaya, 1990; Klopogge, 1998), being pillarization through intercalation of  $Al_{13}$  polyoxocation between 2:1 smectite layers the most widely studied (Cool and Vansant, 2004; Bergaya et al., 2006).

Factors as the nature of the starting smectite, the nature of metallic cation, the hydrolysis conditions, the reaction time, even the washing conditions influence the effectiveness of the pillaring process (Valverde et al., 2005). Thus, it is very difficult to compare the results obtained by different authors. The high cost of the synthesis of these materials and the implementation on an industrial scale results in their low commercial use in water purification. Therefore, it is necessary to optimize the synthesis parameters in order to obtain a low-cost PILC able to be efficiently used in the conditioning processes of drinking water.

Since there are very few studies of drinking water conditioning comparing the efficacy of natural clay minerals and their corresponding Fe- or Al-PILC, the aim of this study is to evaluate the effectiveness of adsorption of heavy metals at low concentrations by dioctahedral and trioctahedral smectites and the obtained materials after low-cost Fe- and Al-pillaring treatments, focusing our interest in the reasonable concentration range for the conditioning of drinking water (10–100 ppb).

## 2. Materials and methods

The selected trioctahedral smectite was a saponite supplied by Minas de Gador SA, Süd-Chemie delegation, Spain S.L., from Cabo de Gata–Níjar, Almería, Spain. On the other hand, the selected dioctahedral smectite was a montmorillonite supplied by Castiglioni, Pes & Co. from Lago Pellegrini, Black River, Argentina. In the present work they are referred as S (saponite) and M (montmorillonite) respectively. Moreover, activated carbon powder (Panreac) was used as comparative adsorbent material.

The chemical reagents used were NaOH, HCl (37%),  $FeCl_3 \cdot 6H_2O$ ,  $AlCl_3 \cdot 6H_2O$  (Panreac) and polyaluminium chloride solution (PAC, 18%  $Al_2O_3$ , Kimsa S.L. company). All dispersions and solutions were prepared with distilled water (pH 5, conductivity  $K < 3 \mu S/cm$ ).

Adsorption analysis were performed for As(III), Cd(II), Cu(II), Cr(III), Hg(II), Ni(II), Pb(II) and Zn(II) employing the following inorganic salts:  $Cd(NO_3)_2 \cdot H_2O$  (Alfa Aesar),  $CrCl_3 \cdot 6H_2O$  (VWR Chemicals),  $CuSO_4 \cdot 5H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $Pb(NO_3)_2$  and  $ZnSO_4 \cdot 7H_2O$  (Panreac), from which were prepared stock solutions of 1000 mg/L in distilled water, and two commercial standard solutions (1000 mg/L) for As (III) ( $As_2O_3$  in 2–5%  $HNO_3$ , Panreac) and Hg(II) ( $Hg(NO_3)_2$  in 10%  $HNO_3$ ). Working solutions of 10 mg/L were prepared by diluting each stock solution to obtain the desired concentration.

### 2.1. Preparation of modified clay minerals

Several variables as conditioning the starting smectite, volume of reactive solution vs amount of starting smectite, and water consumption in the elimination of the excess of reactants control the synthesis cost of PILC. In order to obtain low-cost PILC, starting smectites were used without preconditioning, reactive solutions were added with a slight excess to avoid using large amounts of washing water, and after the intercalation the excess of reactive was washed by dialysis.

Different pillaring solutions were generated for the synthesis of aluminum and iron oxides modified smectites. Smectite dispersions at 5% (w/w) were used in all synthetic processes described below.

#### 2.1.1. Iron oxide pillared clay minerals (Fe-PILC)

Following a similar methodology to that proposed by Valverde et al. (2005), the pillaring solution was synthesized through the hydrolysis of 0.2 M  $FeCl_3 \cdot 6H_2O$  solution with 0.4 M NaOH maintaining a molar ratio

(OH/Al) = 2. In order to avoid the precipitation of iron oxyhydroxides, the pH was carefully controlled between 1.6–1.7 by addition of HCl. Intercalation of montmorillonite and saponite was carried out with a proportion of 2 meq of  $Fe^{3+}/g$  of starting smectite stirred for 72 h at room temperature. After decantation, the intercalated smectites were washed by dialysis until to eliminate chloride ions ( $AgNO_3$  test). Finally, samples were calcined at 300 °C for 2 h. These samples were denoted S–Fe–PILC and M–Fe–PILC for saponite and montmorillonite respectively.

#### 2.1.2. Iron oxide supported clay minerals

Fe(III)-homoionic smectite was prepared through the slow addition of a 0.2 M  $FeCl_3 \cdot 6H_2O$  solution on the clay mineral dispersion in a proportion of 2 meq/g of the starting smectites, stirring for 4 h at room temperature. Washing, drying and calcination steps were performed as explained in previous synthetic processes, and the iron oxide supported clay minerals were designated S–Fe and M–Fe for saponite and montmorillonite respectively.

#### 2.1.3. Aluminum oxide pillared clay minerals (Al-PILC)

The synthesis of Al-PILC were performed following an analogous method as proposed by Ge et al. (1994). The hydrolyzed pillaring solution was generated through the slow addition of 0.4 M NaOH to 0.2 M  $AlCl_3 \cdot 6H_2O$  solution, maintaining a molar ratio of (OH/Al) = 2, with a 150 rpm stirring for 2 h at 60 °C. Since with lower amount of  $Al^{3+}$  Al-PILC formation was not observed, the generated dispersions with 20 meq  $Al^{3+}/g$  of starting smectites were maintained during 24 h under vigorous stirring at room temperature. By decantation the supernatant was removed, and then the slurry was washed by dialysis until elimination of chloride ions ( $AgNO_3$  test). Once dried, it was calcined at 400 °C for 2 h. The samples S–Al-PILC and M–Al-PILC were synthesized from saponite and montmorillonite respectively.

### 2.2. Characterization methods

The starting smectites and resulting materials were characterized by X-ray fluorescence (XRF), powder X-ray diffraction (XRD), attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR), scanning electron microscopy (SEM) and nitrogen adsorption–desorption.

The chemical analysis (major elements) of untreated samples and obtained products were performed by means of the WDXRF Thermo ARL Advant XP<sup>+</sup>, sequential XRF. Samples were prepared as beads, melting a mixture of the sample (10%) and  $Li_2B_4O_7$  (90% w/w) to ensure homogeneity in the results.

XRD powder patterns for the samples were collected on a X'Pert Pro MPD automated diffractometer (PANalytical B.V.) equipped with a Ge(111) primary monochromator (strictly monochromatic  $CuK\alpha_1$  radiation) and an X'Celerator detector. The overall measurement time was 33 min per pattern in order to obtain good statistic over the  $2\theta$  range of 2–65° with 0.017° step size.

Infrared analyses were carried out in attenuated total reflection mode (ATR–FTIR) using a Specac's Golden Gate™ ATR Accessory coupled to a VERTEX 70 Fourier transform spectrometer. FTIR spectra were recorded, after 200 scans, with a spectral range between 4000 and 500  $cm^{-1}$  and 4  $cm^{-1}$  resolution.

The morphology of the starting smectites and the obtained materials were examined by scanning electron microscope (SEM) using a JEOL SM-6490 LV. The samples for SEM observation were previously gold-sputtered (10 nm thick) in order to avoid charging of the surface.

Nitrogen adsorption–desorption isotherms were measured at –196 °C using a Micromeritic ASAP 2020 apparatus. The total specific surface areas ( $S_{BET}$ ) were determined through the BET equation (Brunauer et al., 1938). The specific mesopore pore volumes ( $V_{BH}$ ) were calculated from Barret–Joyner–Halenda method (Barrett et al., 1951). The average pore size ( $W_p$ ) were determined approximating the pore geometry to a

Download English Version:

<https://daneshyari.com/en/article/1694225>

Download Persian Version:

<https://daneshyari.com/article/1694225>

[Daneshyari.com](https://daneshyari.com)