



## Research articles

## Synthesis and characterization of magnetic-montmorillonite and magnetic-organo-montmorillonite: Surface sites involved on cobalt sorption



Facundo Barraqué<sup>a</sup>, Maria L. Montes<sup>b,\*</sup>, Mariela A. Fernández<sup>a</sup>, Roberto C. Mercader<sup>b</sup>, Roberto J. Candal<sup>c</sup>, Rosa M. Torres Sánchez<sup>a</sup>

<sup>a</sup> CETMIC, Camino Centenario y 506, B1897ZCA M. B. Gonnet, Argentina

<sup>b</sup> IFLP, Instituto de Física La Plata - CONICET CCT-La Plata, Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

<sup>c</sup> Instituto de Investigación e Ingeniería Ambiental, CONICET, Universidad Nacional de San Martín, Av. 25 de Mayo y Francia, San Martín 1650, Argentina

## ARTICLE INFO

## Keywords:

Magnetic composite synthesis  
Magnetite  
Montmorillonite  
Organo-montmorillonite cobalt sorption

## ABSTRACT

Montmorillonite magnetic-clay nanoparticles (MtMag) and its exchanged product with hexadecyltrimethylammonium (O100MtMag) were synthesized by alkaline oxidation of ferrous sulfate, characterized by diverse techniques (XRD, Mössbauer spectroscopy, VSM, SEM, Zeta Potential, total specific surface area, TOC) and used as  $\text{Co}^{2+}$  sorbents. The magnetic characteristic of these materials allows them to be used in cases of decontamination of water polluted with dangerous materials, such as radioactive ones, reducing the risk to health due to indirect manipulation by means of external magnetic fields. For comparison, samples without magnetic material (O100Mt) and in absence of clay (Mag) were also synthesized. The synthesis of magnetic materials disclosed the presence of magnetite and goethite nanoparticles, while the saturation magnetization displayed by O100MtMag was higher than that obtained for MtMag, indicating the existence of a higher amount of magnetite particles in the first one. This suggests that O100MtMag could be manipulated easier than MtMag through external magnetic fields. Moreover, the surface electric charge of MtMag sample can be described as a mixture of Magnetite and montmorillonite, with ratios related to the surface of both components.  $\text{Co}^{2+}$  sorption percentages, using an initial  $\text{Co}^{2+}$  concentration of 85 mg/L, resulted similar for the different materials while the  $\text{Co}^{2+}$  sorption was ascribed to interactions with the montmorillonite interlayer and external surface. The current results indicate that O100MtMag is a more appropriate material than MtMag for  $\text{Co}^{2+}$  removal by external magnets.

### 1. Introduction

In the last decades a significant interest has been devoted to search ecofriendly, sustainable and low-cost technologies for pollutants removal from wastewater. Among these, sorption has excelled as an effective and economical technique, generating the need to obtain new sorbent materials with higher retention capacity or different manipulation possibilities.

Magnetic nano-materials have attracted scientific interest due to its adsorbent ability and isolation capacity by application of external magnetic fields. These features allow them to be used in many applications. For example, in medicine, anticancer drugs are loaded with magnetic materials to be directed to particular sites thus reducing the dose required in several therapies and minimizing side-effects [1,2]; in effluent treatments, for the removal of dyes, heavy metals, and biologically active compounds with high separation efficiency and

reusability [3–6], etc.

Moreover, montmorillonite (Mt) has been largely used as sorbent materials for a wide range of pollutants, like heavy metals [7–9] and organic compounds [10–13] because of its relatively large surface area, cation-exchange capacity (CEC), swell-ability, great abundance and low cost. One of the strategies to extend and/or enhance the montmorillonites adsorption spectrum of contaminants was to tailor the clay structures. Particularly, the attachment of long chain alkyl groups of quaternary amino compounds (QAC) to different clays generate the so called organoclays, which improves not only the adsorption of organic pollutants [14,15] by increasing the number of non-polar sites thus generating more effective interactions with organic molecules, but also promotes a better separation of the suspension by increasing its particle size [16].

Combination of magnetic nanoparticles with clays has been applied even in enzymatic immobilization [17], as bactericide materials [18],

\* Corresponding author.

E-mail address: [lmontes@fisica.unlp.edu.ar](mailto:lmontes@fisica.unlp.edu.ar) (M.L. Montes).

<https://doi.org/10.1016/j.jmmm.2018.07.052>

Received 14 March 2018; Received in revised form 8 June 2018; Accepted 15 July 2018

Available online 17 July 2018

0304-8853/ © 2018 Elsevier B.V. All rights reserved.

in catalytic activity [19,20], environmental remediation and biocompatible materials [21–24].

Furthermore, the development of magnetic Mt or organo-Mt systems would allow to dangerous pollutant removal in continuous process, promoting the sorbent separation advantage by an external magnetic field and reducing the risk to health due to indirect manipulation.

There are several methods to synthesize  $\text{Fe}_3\text{O}_4$  nanoparticles: oxidative hydrolysis of iron (II) sulfate in alkaline media, alkaline hydrolysis of iron (II) and iron (III) chloride solutions, controlled alkaline oxidation in nitrate presence and precipitation from iron (II) and iron (III) chloride solutions by hydrolysis of urea. Among them, the controlled alkaline oxidation of iron (II) sulfate produce high-size magnetite particles, with the advantage of being an easy, efficient, and economical preparation process [21,23,25–27].

In this work  $\text{Fe}_3\text{O}_4$  nanoparticles have been synthesized by controlled alkaline oxidation of iron (II) sulfate in absence (Mag) and presence (MtMag) of montmorillonite clay. In addition, hexadecyltrimethylammonium bromide (HDTMABr) has been used to attain the organo-Mt (O100Mt) exchanged 100% of CEC and to further synthesize  $\text{Fe}_3\text{O}_4$  nanoparticles in the sample (O100MtMag). A deep characterization of all these materials has been performed by X-ray diffraction (XRD), Mössbauer spectroscopy, vibrating sample magnetometer (VSM), scanning electron microscopy (SEM), and zeta potential determination.

Cobalt is a heavy metal that can be released for diverse industries, including the nuclear one. The development of sorbent materials to optimize the nuclear wastewater treatment is crucial for human health and environmental quality and the magnetic materials will allow reducing its manipulation, diminishing the radioactivity exposition and the health risk. With this fact in mind, the ability of the different synthesized materials was analyzed performing Co sorption experiments in batch condition, and determining the surface sites involved.

## 2. Materials and methods

The raw material, previously characterized, was commercial Argentine bentonite (Castiglioni Pes and Co.) from *Río Negro* Province. The chemical analysis performed on a sample of purified montmorillonite (Mt), yielded the structural formula  $[(\text{Si}_{3.89}\text{Al}_{0.11})(\text{Al}_{1.43}\text{Fe}_{0.26}\text{Mg}_{0.30})]\text{Na}_{0.30}\text{Ca}_{0.09}\text{K}_{0.01}$ , isoelectric point (IEP<sub>pH</sub> = 2.7), external surface area (determined by  $\text{N}_2$  adsorption) of  $34.0\text{ m}^2/\text{g}$  [28] and cation exchange capacity (CEC) equal to  $0.825\text{ mmol g}^{-1}$  [29].

The magnetic samples were synthesized using  $\text{KNO}_3$  and KOH (99% purity) purchased from Biopack and  $\text{Fe}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$  (analytical degree) bought from Cicarelli Lab.

The hexadecyltrimethylammonium bromide (HDTMABr) ( $\geq 97\%$ ), MW =  $364.45\text{ g/mol}$  and critical micelle concentrations (CMC),  $0.9\text{ mM}$  [30], was delivered by Fluka (Buchs, Switzerland) and used as received.  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (99%) was provided by Sigma.

The procedure indicated previously by Gamba et al. [29] was carried out to obtain organic-montmorillonite. Briefly, an amount of the HDTMABr equivalent to 100% CEC value of Mt was dissolved in 1 L of distilled water and 15 g of Mt was slowly added and stirred (400 rpm) for 24 h. The product attained was washed with distilled water to free them of bromide anions (tested by  $\text{AgNO}_3$ ), lyophilized, ground in an agate mortar and labeled as O100Mt.

The preparation of magnetic montmorillonite (MtMag) was performed following the method described by Bartonkova et al. [27]. Briefly, 25 mL of  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$  (0.3 M) was added to an aqueous Mt suspension (2.5 g/425 mL water). After stirring for 2 h, 25 mL of  $\text{KNO}_3$  (0.49 M) and 25 mL of KOH (1.25 M) were added, and the temperature of the suspension was raised to  $90^\circ\text{C}$ . The magnetite formation was followed by the change of the color suspension to dark brown [31]. The dispersion was cooled at room temperature and washed twice with distilled water. The solid was recovered by magnetic separation and lyophilized.

Pure magnetic material (Mag) was also obtained by mixing the corresponding reagents and following the same procedure described previously without the clay mineral.

Organic-magnetic montmorillonite (O100MtMag) was obtained following the Bartonkova et al. [27] procedure using as starting clay material O100Mt sample.

In order to compare some MtMag sample properties, 1 g of mechanical mixture of Mt and Mag 70:30 (w/w) was dissolved in 100 mL  $\text{KCl } 10^{-3}\text{ M}$  stirred 10 min and used for XRD analysis and zeta potential determination.

X-ray diffraction (XRD) patterns were collected using a Philips PW 1710 diffractometer with  $\text{CuK}\alpha$  radiation, operated at 40 kV and 30 mA, with counting time 10 s/step and  $0.02^\circ$  ( $2\theta$ ) step size. Samples were scanned on oriented samples maintained at constant relative humidity of 0.47 for 48 h in order to improve the precision of the peak values [32].

Mössbauer spectroscopy (MS) spectra of all materials were collected at RT using a constant-acceleration spectrometer in transmission geometry with a  $^{57}\text{Co/Rh}$  source (nominal activity 5 mCi) and a multi-channel scaler of 512 channels. Velocity calibration was performed using a  $12\ \mu\text{m}$  thick  $\alpha\text{-Fe}$  foil. Hyperfine parameters are referred to this standard. Mt Mössbauer spectrum was collected between  $-4.0$  and  $4.0\text{ mm/s}$ , due to the absence of magnetic compounds, while the magnetic samples spectra were measured from  $-11$  to  $11\text{ mm/s}$ . All the spectra were numerically analyzed using a computer code that takes into account hyperfine magnetic fields and quadrupole splitting distributions [33].

The high-field susceptibility ( $\chi_{\text{hifi}}$ ), saturation magnetization ( $M_s$ ) and remnant magnetization ( $M_r$ ) were determined from the hysteresis loops acquired in a VSM magnetometer LakeShore 7404 using external magnetic fields between  $-1.9\text{ T}$  and  $1.9\text{ T}$ . Samples were supported in a diamagnetic sample holder with negligible magnetic response.

Scanning electron microphotographs (SEM) were performed in a JEOL, JCM-6000 with combined energy dispersive X-ray spectroscopy (EDS) analyzer. Samples were fixed to 10 mm metal mounts using carbon tape, and spit coated with gold under vacuum in argon atmosphere.

Electrokinetic potentials were determined using Brookhaven 90Plus/Bi-MAS. The electrophoretic mobility was converted automatically into zeta potential values using the Smoluchowski equation. To generate zeta potential versus pH curves, 40 mg of sample were dispersed in 40 mL  $\text{KCl } 1\text{ mM}$ , used as inert electrolyte. The slurry was continuously stirred and the suspension pH was adjusted adding HCl or KOH.

The total specific surface area (TSSA) values of some samples were determined by water vapor adsorption at a relative humidity (rh) of 0.48 as described previously [34]. Also external specific surface area, of Mag sample, was measured by nitrogen adsorption ( $S_{\text{N}_2}$ ) at 77 K, previously dried at  $100^\circ\text{C}$  for 6 h under high vacuum, using a Micromeritics Accusorb 2100 E instrument

Total organic carbon (TOC) of some samples was determined by TOC-VCPH (Shimadzu) equipment. The unit of solid samples combustion (SSM-5000A) allows determining TOC by difference between total and inorganic carbon. Previous to analyses, samples were dried at  $60^\circ\text{C}$  for 48 h.

A stock solution of  $1.7\text{ mM Co}^{2+}$  was prepared by adding the correspondent amount of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  to distilled water. Additional concentrations were obtained by dilution in distilled water. The  $\text{Co}^{2+}$  sorption experiments were performed in batch conditions (8 mL, pH = 6.5, contact time 24 h,  $T = 25^\circ\text{C}$ , solid/liquid ratio:  $1\text{ g L}^{-1}$ ) varying the initial  $\text{Co}^{2+}$  concentration (30, 50 and  $85\text{ mg L}^{-1}$ ) and the sorbent materials were: Mt, MtMag, O100Mt and O100MtMag. For Mt and O100Mt samples, after the indicated contact time, suspensions were centrifuged for 15 min at 15,000 rpm, while for MtMag, and O100MtMag samples a magnetic separation was utilized.

The supernatants were collected and  $\text{Co}^{2+}$  concentration was

Download English Version:

<https://daneshyari.com/en/article/8152679>

Download Persian Version:

<https://daneshyari.com/article/8152679>

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