Applied Surface Science 346 (2015) 232–239

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis and characterization of magnetic palygorskite nanoparticles and their application on methylene blue remotion from water

Antonieta Middea [a,b], Luciana S. Spinelli [b,*], Fernando G. Souza Junior [b], Reiner Neumann [a,d], Otavio da F.M. Gomes [a,d], Thais L.A.P. Fernandes [a], Luiz C. de Lima [a], Vitoria M.T.S. Barthem [c], Fernanda V. de Carvalho [a]

[a] Centre for Mineral Technology (CETEM), Av. Pedro Calmon, 900, Cidade Universitária, Rio de Janeiro 21941908, Brazil
[b] Federal University of Rio de Janeiro, Institute of Macromolecules, Av. Horácio Macedo, 2030, Cidade Universitária, Rio de Janeiro 21941598, Brazil
[c] Federal University of Rio de Janeiro, Physics Institute, Av. Athos da Silveira Ramos, 149, Cidade Universitária, Rio de Janeiro 21941972, Brazil
[d] Federal University of Rio de Janeiro, National Museum of Brazil, Postgraduate Program in Geosciences, Av. Quinta da Boa Vista, S/N Bairro Imperial de São Cristóvão, Rio de Janeiro 20940040, Brazil

ARTICLE INFO

Article history:
Received 13 November 2014
Received in revised form 1 March 2015
Accepted 14 March 2015
Available online 7 April 2015

Keywords:
Magnetic nanoparticles
Palygorskite
Methylene blue
Adsorption
Magnetic adsorbents
Magnetic separation

ABSTRACT

Recently there has been considerable interest in magnetic sorbents materials, which is added excellent capabilities such as sorption and magnetic response to an applied field. Accordingly, palygorskite nanoparticles were covered by magnetite using a co-precipitation technique and characterized by: X-ray fluorescence (XRF), X-ray diffraction (XRD), surface analysing and scanning electron microscopy (SEM) with element analysis and mapping, particle size, pore surface area (BET), density, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and zeta potential. Additionally, magnetic properties were studied by SQUID magnetometer, magnetic force microscopy (MFM) and also using a simple experimental setup. Magnetic nanoparticles produced had average diameters in a nanometric range. The amount of iron present in the nanoparticles increased by six times after the magnetization and a superparamagnetic behavior was exhibited with high saturation magnetization, from 4.0×10^{-4} Am^2/kg to about 20 Am^2/kg. A weight loss was also observed around 277 °C–339 °C by TGA, indicating a structural change from magnetite to maghemite, which confirms the magnetization of palygorskite. Batch adsorption experiments were carried out for the removal of methylene blue cationic dye from aqueous solution using pure and covered by magnetite palygorskite nanoparticles as adsorbents. Furthermore, about 90% of methylene blue was removed within 3 min using magnetized palygorskite.

1. Introduction

The development of magnetic nanotechnology has grown intensely in recent years, leading to innovative methods for use in biochemistry, microbiology, cell biology, analytical chemistry, ore mining and environmental technology. Nanoscale magnetic particles are highly effective in separation processes due to their high specific surface area and the absence of internal diffusion resistance, besides being easily recovered with an external magnetic field [1,2].

Magnetic nanoparticles can be used to remove contaminants from wastewaters by applying a magnetic field after they adsorb the contaminant, making them a good option for removing organic and inorganic contaminants at low cost [3]. In general, natural clays are excellent cation exchangers due to their high surface area and negative surface charge. In some mineralogy, depending on the extent of exposed interlayer surface and in relation to palygorskite, the BET surface area of about 150 m^2/g is found in the literature [4]. They are often used to adsorb metallic contaminants. These physical–chemical properties, in the case of palygorskite, are due to its structure that when compared to other industrial clays such as bentonite, montmorillonite, kaolinite, *etc.* [5]: palygorskite is a complex silicate (2:1 layer silicate) of magnesium, with an open-channel structure, that forms long crystals. The water in these channels is called zeolitic water and is expelled at a lower temperature than the dehydroxylation temperature. The tetrahedral sheets are linked infinitely in two dimensions which confer a structural difference between the other clay minerals in that the octahedral sheets are continuous in only one

* Corresponding author. Tel.: +55 2139387033; fax: +55 2122701317.
E-mail addresses: amiddea@cetem.gov.br, amiddea@ima.ufrj.br (A. Middea), spinelli@ima.ufrj.br (L.S. Spinelli).

http://dx.doi.org/10.1016/j.apsusc.2015.03.080
0169-4332/

dimension and divided into ribbons. The formula of the crystal unit cell is $Mg_{10}Si_{16}O_{40}(OH)_4{\cdot}(OH_2)_8{\cdot}8H_2O$, where (OH_2) represents the structural water and (H_2O) is the water that fills the fibrous channels present in the clay mineral [6].

The specialized literature contains few studies about magnetization of palygorskites [4,6–8]. Among the possible uses of magnetized palygorskite is for removal of U(VI) from aqueous solutions.

Methylene blue is a cationic and aromatic stain that is soluble in water and alcohol. When heated it can generate sulphur oxide and nitric oxide. It deteriorates water quality by reducing the dissolved oxygen, which modifies the properties and characteristics of aqueous fluids and causes toxic effects on aquatic organisms, among other problems [9]. Methylene blue is discharged by various industries (makers of textiles, paper, polyester and nylon), directly influencing the water color and turbidity. More importantly, the water contaminated with this substance is harmful to human and animal health, causing breathing difficulties, nausea, vomiting and sudoresis [10].

In this context, the goal of our work was to combine the adsorption properties of palygorskite and the magnetic properties of magnetite to produce a magnetic adsorbent, by means of interaction with the cation Fe^{3+}, for use to remove methylene blue from aqueous solutions.

2. Experimental

The palygorskite sample used in this study was provided by Colorminas-Colorífico e Mineração S.A., obtained from Piaui state, northeastern Brazil. The reagents ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) were analytical grade, obtained from Merck Co., and were used as received. Distilled water was used throughout.

2.1. Sample preparation

The palygorskite magnetization was performed using co-precipitation of ferric and ferrous chloride [11,12] in an alkaline medium, as shown in Eq. (1):

$$2FeCl_3 + FeCl_2 + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O \qquad (1)$$

A solution with 1% (w/v), palygorskite nanoparticles with adsorbed Fe (III), previously prepared with $FeCl_3{\cdot}6H_2O$ [10], was dispersed in an ultrasonic bath for 30 min, yielding a stable suspension. The ratio of ferrous and ferric chloride in the reaction is 2:1, so 2500 mg/L of $FeCl_2{\cdot}4H_2O$ was added to the suspension with vigorous stirring at 750 rpm. The system temperature was increased to 70 °C and 10 mL of NH_4OH (25%, v/v) was added drop by drop under further stirring. The conditions were maintained for 30 min. The black precipitate obtained was washed repeatedly with distilled water until the pH declined to 7, then the magnetic nanoparticles were dried in a vacuum and stored. The diagram in Fig. 1 exemplifies this synthesis.

2.2. Chemical characterization

The chemical characterization was done using the X-ray fluorescence, X-ray diffraction and FT-IR, according to the literature [11].

2.3. Structural and physical–chemical characterization

The systems used in this work were also characterized regarding their structures (morphology and porosity), density, size, zeta potential and thermal behavior, using the methods described below.

2.3.1. SEM/EDX

An FEI Quanta 400 scanning electron microscope with integrated energy dispersive X-ray analyzer was used for morphological studies. The samples were coated with Au (for SEM analysis), at 25 kV with small spot size as described before [11] and for EDX, the samples were not coated.

2.3.2. Size

The nanoparticles' size was evaluated with a Malvern Mastersizer 2000 particle size analyzer. The nanoparticles were dispersed in water for 30 min at 1700 rpm.

2.3.3. Zeta potential

The surface charge of the nanoparticles was evaluated by a Malvern Nano Zetasizer instrument. A suspension of palygorskite nanoparticles and the magnetized ones in molar KCl 10^{-3} (indifferent electrolyte) were prepared. The pH was adjusted using NaOH and HCl in the range between 2.0 and 11.0 [11].

2.3.4. TGA/DTA

The TGA/DTA analysis of the nanoparticles was performed with a Mettler Toledo TGA/DSC1 Star System, at a heating rate of 10 °C/min, under air atmosphere with a flow rate of 50 mL/min.

2.4. Magnetic characterization

Since the function of the nanoparticles produced is related with their magnetic properties, determination of magnetic force [13], SQUID (superconducting quantum interference device) analysis and AFM/MFM were used to investigate these properties.

2.4.1. Magnetic force determination

The magnetic force curves were obtained using the methodology described by Souza Jr. et al. [13] which relates the mass of the sample weighed directly into a magnetometer attached to an analytical balance. The magnetic potential varies when the sample is magnetic, attracting the magnetic particles and consequently reducing their weight on the scale.

2.4.2. SQUID

The magnetization measurements were obtained with a magnetometer system based on a physical effect and quantification of the magnetic flux in a closed superconductor circuit, which is highly sensitive to small magnetic flux variations. For these measurements, we used a clear plastic straw as the sample holder, because of the negligible magnetic signal in relation to that of the various samples tested.

2.4.3. AFM/MFM

To map the magnetic domains at the surface of the nanoparticles before and after magnetization, we acquired phase and magnetic topographic images of these surfaces with a JPK magnetic force microscope (MFM) operating in non-contact mode with a Micromasch Co-Cr tip, with frequency and resonance of 175 kHz and radius <10 nm. This tip was magnetized in perpendicular direction to the surface at distances of 30, 50, 70 and 100 nm. A variety of images with different tips of the same series were obtained at random sites on the films' surfaces, to assure reproducibility of the results.

2.5. Methylene blue removal from aqueous media

We first conducted a preliminary evaluation of the application of the palygorskite nanoparticles produced to remove methylene blue from an aqueous solution. For this purpose, we used 2 g of original