Preparation and characterization of a single-walled aluminosilicate nanotube-iron oxide composite: Its applications to removal of aqueous arsenate

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ABSTRACT

A chemical method to synthesize a magnetite coating on aluminosilicate nanotubes (imogolite) that can be used as a magnetic adsorptive composite is reported via a new procedure based on impregnation with excess of solvent. This produced a nanocomposite of imogolite and magnetite, retaining at least two of the individual properties of its initial chemical species, which are determinant for some technological applications: large surface area and high saturation magnetization. Comparatively significant differences in terms of electrophoretic and magnetic characteristics were found between the direct solid mixture of the starting materials and the resultant imogolite–magnetite mixture. The adsorption kinetics of arsenate is described adequately by the pseudo-second model and the maximum adsorbed amounts (q_e) of this anion were closed to those obtained experimentally. A high rate of arsenate adsorption on Fe−imogolite was initially observed, suggesting that the formation of new surface sites qualitatively and quantitatively improve the removal of arsenate. The combined use of different characterization techniques (XRD, TEM, Mössbauer spectroscopy, EM, VSM and SQUID) and the kinetic sorption study suggest that Fe−imogolite has a large potential for the treatment of arsenate polluted water or other nanotechnological applications, due to its high chemical reactivity.

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1. Introduction

Imogolite is a single-walled tubular aluminosilicate (SWTA) present in soils of volcanic origin such as the andisols [1,2]. Based on its unique set of properties, such as chemical reactivity (easy functionalization), mechanical resistance, optical and electric properties, and large surface area, imogolite is believed to be of remarkable technological interest [3–6]. The typical chemical formula of imogolite is $(OH)_3Al_2O_3SiOH$, with tubes of average size 2.5 nm outer diameter, 0.9 nm inner diameter, and lengths varying from 100 nm to several micrometers [7–9].

One of the most interesting characteristics of imogolite is its ability to selectively adsorb both cations and anions on its active surface sites. Predominantly, the surface sites are silanols ($\equiv$Si–OH) on the inner surface and aluminols ($\equiv$Al–OH and $\equiv$Al$_2$–OH) on the outer surface [7,9,10]. In addition to its intrinsic reactivity, these groups can easily be functionalized for nanotechnological applications [11–17]. This has been stimulating the development of new chemical processes for its synthesis. Particular efforts are being made in the search for structural and surface modifications to boost their uses in the manufacture of electric and optical devices, in medical therapies involving the transport and administration of drugs, in environmental cleaning by removal of pollutants from water bodies, and in energy storage [3,17–19].

In this context, obtaining a magnetic composite based on imogolite has many more particular interests, taking into account its high potential for industrial applications, which is comparable to only few other nanosized materials [3,20].

The main aims are (1) to develop a simple methodology to prepare a nanocomposite (Fe−imogolite hereafter) formed from imogolite and a magnetic iron oxide, (2) to characterize and

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compare it with a simple solid mixture of imogolite and magnetite (Fe$_{ox}$+imogolite hereafter), and (3) to determine the kinetic sorption behavior of the As(V) on the imogolite, Fe−imogolite and magnetite considering different kinetic models.

2. Experimental

2.1. Materials

The imogolite sample was prepared using tetraethyl orthosilicate, (99.995%, Sigma–Aldrich), NaOH (99.996%, Merck), and AlCl$_3$ (99.998%, Merck). The coating procedure involves the use of KNO$_3$ (99.998%, Merck), FeSO$_4$·7H$_2$O (99.998%, Merck) and NH$_4$OH (99.997%, Sigma–Aldrich). In sorption studies Na$_2$HAsO$_4$·7H$_2$O (99.998%, Merck) and NaCl (99.998%, Merck) were used. When needed, reagent grade solvents were considered.

2.2. Synthesis of single-walled tubular

The imogolite was prepared according to the procedure described by Arancibia-Miranda et al. [9]. Tetraethyl orthosilicate (TEOS) was added to a 5 mM aqueous solution of AlCl$_3$ until an Al:Si ratio of 2:1 was reached. Then a 0.1 M NaOH solution was added at a rate of 1.0 mL min^{-1} until an Al:Si:OH ratio of 2:1:4 was obtained. The mixture was stirred during 60 min and then heated at 368 K for 5 days. Once the aging process was completed, the resultant mixture was allowed to cool down to ambient temperature. A 0.1 M NH$_4$OH solution was added, stirring vigorously, until a pH of about 8.0 was reached. The solid was concentrated by centrifuging the suspension at 9000 rpm for 30 in and was washed with double distilled water until it reached an electric conductivity of less than 0.78 S m^{-1}.

2.3. Synthesis of iron oxide and preparation of the Fe−imogolite composite

Both products were obtained using the procedure given by Cornell and Schwerman, 1996, with few modifications. To get the magnetic iron oxide, 250 mg of FeSO$_4$·7H$_2$O was dissolved in 20.0 mL of double-distilled water previously degassed with N$_2$, together with 33 mg of KNO$_3$, and 0.5 mL of concentrated NH$_4$OH was added to precipitate the iron oxide [21]. To prepare the magnetic composite with imogolite, 620 mg of FeSO$_4$·7H$_2$O was dissolved in 100 mL of double-distilled water at 363 K in a N$_2$ atmosphere, and 250 mg of lyophilized imogolite was then added, to get an imogolite:Fe weight ratio close to 2.0 and a pH 3.3. The mixture was stirred for 4 h at 363 K in a N$_2$ atmosphere. Then 33.0 mg of KNO$_3$ and 0.5 mL of concentrated NH$_4$OH were added to precipitate the Fe oxides [22].

The physical mixture (Fe$_{ox}$+imogolite) was prepared by mixing homogeneously 250 mg of lyophilized imogolite with synthetic nanomagnetite, achieving an imogolite:Fe weight ratio close to 2.0.

2.4. Sorption studies of arsenate

A stock solution of 1000 mg L^{-1} As(V) was prepared by dissolving Na$_2$HAsO$_4$·7H$_2$O in double distilled water. Batch adsorption of As(V) was studied in 40 mL polypropylene centrifuge tubes containing 50 mg of imogolite, nanomagnetite or Fe−imogolite in 20 mL of As(V) stock solution in 0.01 M NaCl. The dependence of As(V) adsorption as a function of time was studied on a solution of As(V) containing 350 mg L^{-1} in equilibrium with 50 mg of imogolite, Fe−imogolite or nanomagnetite. The samples were equilibrated using an orbital shaker during 240 min. The temperature for the experiments was 298 K and the pH conditions were 6.5 ± 0.2 for As(V) [23]. The samples were centrifuged at

10,000 rpm for 30 min, the supernatant was filtered through 0.22 μm Millex-GX membranes, and analyzed by ICP-OES. The amount of adsorbed arsenate was determined from the difference between the initial and final concentrations in solution, according to Eq. (1).

$$q_t = \frac{(C_0 - C_t)V}{(M)} \tag{1}$$

where C_0 and C_t are the initial arsenate concentration in (mg L^{-1}) and that at time t, respectively, V (L) is the volume, and M (g) is the mass of the substrate.

2.5. Characterization

The products were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Mössbauer spectroscopy, electrophoretic mobility (EM), vibrating sample magnetometry (VSM) and superconducting quantum interference devices (SQUID).

XRD data were obtained on a Philips X'Pert diffractometer with graphite-monochromated CuKα radiation, using oriented aggregates preparations obtained by drying water suspensions of the samples on glass slides.

The isoelectric point (IEP) was determined by measuring the electrophoretic mobility of particles on a Zeta Meter ZM-77 apparatus. About 30 mg of each sample was suspended in 200 mL of a solution with ionic strength 1.0 mM (NaCl), and the EM was determined as a function of pH. The IEP was obtained from the EM versus pH graph as the pH at which EM = 0.

The samples were studied on a Zeiss EM 910 transmission electron microscope using 80 kV-acceleration potential, on carbon substrates prepared as follows: A drop of the sample suspended in water was transferred onto the face of a freshly cleaved sheet of mica and the solvent allowed to evaporate. A thin layer of carbon was deposited on the surface by vacuum evaporation. The carbon/product film was separated from the mica sheet by flotation on distilled water and subsequently transferred to a perforated Cu support grid.

The specific surface area (SSA) and the volume and diameter of micropore and mesopore were determined from nitrogen adsorption–desorption isotherms measured on a Micromeritics model ASAP 2010 (Micromeritics, Norcross, GA, USA) and on a Carlo Erba Sorptmatic 900 (Carlo Erba, Milan, Italy), using the static volumetric method. Samples of 500 mg were degassed at 483 K for 24 h, with a residual vacuum of 0.532 Pa. The SSA was calculated from the nitrogen adsorption isotherm at 77 K by the Brunauer–Emmett–Teller (BET) method. Micropore volume was calculated from nitrogen adsorption at 77 K by the t-plot method; the volume and diameter of the mesopores were calculated from the adsorption/desorption nitrogen isotherm by the Barrett–Joyner–Halenda (BJH) method. All samples were analyzed in triplicate.

The ^{57}Fe Mössbauer analysis was carried out at 298 K with a transmission acceleration constant setup with an ∼α30 mCi ^{57}Co/Rh source and α-Fe as reference. The data were stored in a 512-channel MCS memory unit, with a Doppler velocity ranging around ±10 mm s^{-1}. The experimental data were least-squares-fitted with Lorentzian functions using the NORMOS^{TM} program algorithm.

The magnetization of the samples was determined as a function of the external field applied through a vibrating sample magnetometer (VSM) at ambient temperature and at 77 K. Furthermore, the magnetic behavior of the synthesized samples was evaluated under μ$_0$H fields of varying strength up to 1 T and at temperatures set from 50 K to 300 K, with a Cryogenic Ltd. SQUID magnetometer.