

Synthesized layered inorganic–organic magnesium organosilicate containing a disulfide moiety as a promising sorbent for cations removal

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ABSTRACT

A new-layered inorganic–organic magnesium organosilicate was synthesized through a single step template sol–gel route under mild conditions, using a new alkoxy silane, containing a 2-aminophenyl disulfide molecule. Elemental analysis data based on the nitrogen atom showed an incorporation of 1.97 mmol of organic pendant groups for each gram of the hybrid formed. The X-ray diffraction patterns demonstrated that this nanocompound exhibited lamellar structure, in agreement with that found for natural inorganic silicates. Infrared spectroscopy and nuclear magnetic resonance for the ^{29}Si nucleus in the solid state are in agreement with the success of the proposed synthetic method. The presence of nitrogen and sulfur basic centers attached to the pendant groups inside the lamellar structure is used as basic centers to coordinate cations from aqueous solution at the solid/liquid interface. The isotherms were fitted to Langmuir and Freundlich models. The maxima adsorption capacities for copper, lead and cadmium, calculated from Langmuir model, were 3.28, 1.42 and 0.35 mmol g $^{-1}$, respectively. These values are comparable to other adsorbing nanomaterials. This behavior suggested that this new inorganic–organic hybrid could be employed as a promising adsorbent for cation removal from polluted systems.

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1. Introduction

Waste streams containing low-to-medium levels of heavy metals and their compounds are widely encountered due to diverse activities of mankind, such as metallurgy and chemistry, and fertilizer, electronic device, battery, paper and paint manufacturing. The majority of heavy metals is highly toxic and non-biodegradable, and should be removed from polluted streams to improve human life in the ecosystem, as a result of environmental quality standards. Nowadays, many of the pollutants are due to the increase in industrial development and cause aquatic system damage, presenting as undesirable and dangerous agents to waters, including potable water in many communities [1].

Conventional methods for heavy metal removal from wastewaters include chemical precipitation, ion-exchange processes, membrane separation, reverse osmosis, evaporation, electrochemical treatment and some other techniques. However, the effectiveness of these methodologies when these metals are found at low concentrations is, in fact, deficient. One of the most important alternatives available to solve such problems is the use of adsorption processes. These techniques can be widely used with a variety of solid sorbents to remove certain classes of chemical pol-

lutants from waters. The success of this adsorption process depends directly on the sorbent properties, which could be expected to be inexpensive and not require any additional pre-treatment step before its application [2]. A variety of inorganic and organic adsorbents, both naturally occurring and synthetic materials, including zeolites [3], phyllosilicates [4,5] chitosan [6], clay minerals [7], chemically modified silicas [8–10], polymers [11] and biosorbents [12,13] are currently used.

With the objective of advancing the use of new efficient materials for adsorbing undesirable species from a given medium, there has been renewed interest in synthesizing nanostructured inorganic–organic hybrids [14] through one-step sol–gel template reactions under mild conditions, to obtain self-organized layered hybrid materials [15–18]. The general goal for such operations is to couple simultaneously two properties in a unique solid, one contributed by the organic part covalently bonded to a well-established inorganic framework. One class of such materials are the phyllosilicates, which could be designed through apparently simple synthetic procedures, by attaching chemical modification on the phyllosilicate surface, through the best reaction path involving a one-step low-temperature route, which implies the copolymerization of magnesium cations with trialkoxysilanes under alkaline conditions [19]. These hybrid materials are members of a known family of 2:1 trioctahedral phyllo(organo)silicates with approximate compositions of $\text{Si}_8\text{R}_8\text{Mg}_6\text{O}_{16}(\text{OH})_4$, based on the original parent talc structure, represented by $\text{Si}_8\text{Mg}_6\text{O}_{20}(\text{OH})_4$ [20].

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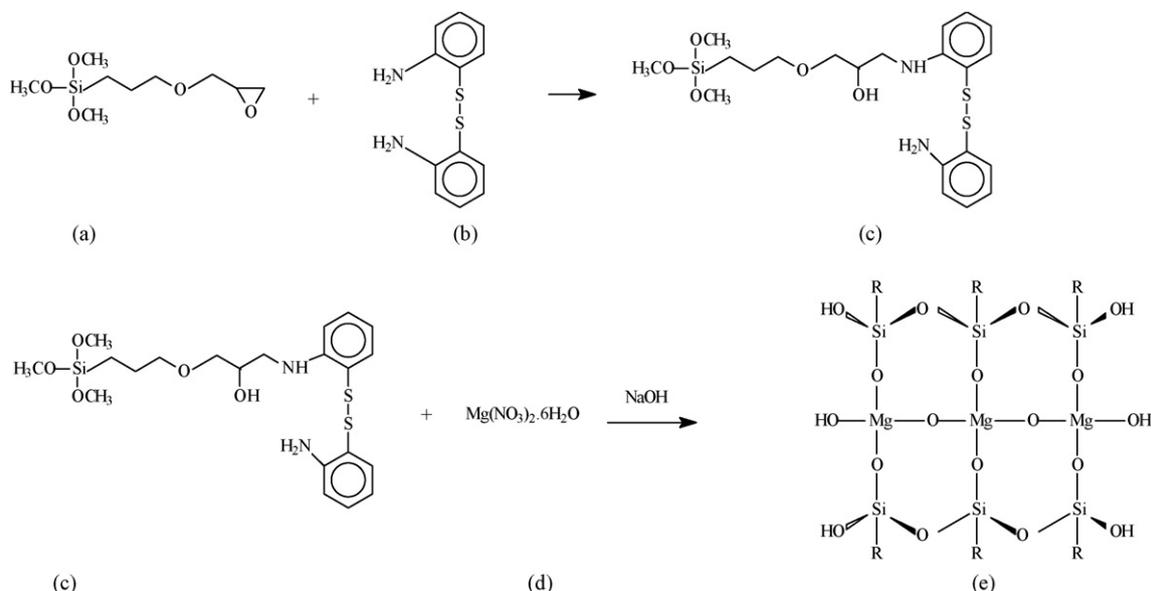


Fig. 1. Reaction of 3-glycidoxypropyltrimethoxysilane (a) with 2-aminophenyldisulfide (b) to yield the new silylating agent (c), and its reaction with magnesium nitrate (d) to yield the new magnesium organosilicate (e), R being the silylating agent attached to the inorganic backbone in interlayer space.

The aim of the present investigation was to synthesize a new-layered inorganic–organic magnesium organosilicate by a single step template sol–gel route under mild conditions, using a new alkoxy silane, containing a 2-aminophenyldisulfide molecule. This procedure permitted the attachment of organic molecules in an inorganic network with a talc-like structure, to give a non-expandible structurally layered phyllosilicate, containing magnesium silicate in a 2:1 layer disposition, whose arrangement can be briefly described as a magnesium sandwich structure. The silicon atom, which is tetrahedrally coordinated by oxygen atoms, bridges with magnesium and the resulting brucite-type layer structure is formed by octahedral magnesium atoms coordinated by oxygen atoms and hydroxyl groups. The organic chains originating from the alkylalkoxysilane precursor are distributed inside the interlayer region [21]. This new organosilicate containing nitrogen and sulfur basic centers was applied for copper, lead and cadmium removal from aqueous solutions and the data were adjusted to the Langmuir and Freundlich adsorption models.

2. Materials and methods

2.1. Chemicals

All chemicals, magnesium nitrate (Carlo Erba), ethanol (Synth), sodium hydroxide (Nuclear), 2-aminophenyldisulfide (Aldrich), 3-glycidoxypropyltrimethoxysilane (Aldrich), lead, cadmium and copper nitrates (Vetec) were reagent grade and used as received. Deionized water was purified using a Milli-Q system (Millipore).

2.2. Synthesis

Due to the enormous facility of the alkoxide moiety to interact with residual humidity, the new silylating agent was synthesized under anhydrous conditions. Thus, 4.97 g (0.020 mol) of 2-aminophenyldisulfide was dissolved in 80 cm³ of dry ethanol, then 4.4 cm³ (0.020 mol) of 3-glycidoxypropyltrimethoxysilane was added [10]. This solution was maintained under reflux in a dry nitrogen atmosphere for 72 h.

For the hybrid, identical precautions with humidity were adopted, the Si/Mg molar ratio was maintained at 1.33, to simulate the same relationship found in the natural talc silicate.

Briefly, the fresh new synthesized silylating agent was added to a stirred solution containing 3.84 g (0.015 mol) of magnesium nitrate hexahydrate dissolved in 75 cm³ of ethanol [22]. Approximately, 60 cm³ of a 0.50 mol dm⁻³ NaOH solution was slowly added to the resulting alcohol mixture with an addition funnel, under magnetic stirring, while the temperature was maintained at 323 K, to give a final pH value of 11.5. The solid formed was aged for 48 h at 323 K and, after that, was filtered, extensively washed with deionized water and dried under vacuum for 8 h.

2.3. Characterization

Carbon, hydrogen and nitrogen percentages for the new hybrid were determined on a PerkinElmer model 2400 analyzer. Infrared spectra were recorded on a Bomem MB-Series FTIR spectrometer, with KBr pressed samples, from 4000 to 400 cm⁻¹ with 4 cm⁻¹ of resolution. X-ray diffraction patterns were collected on a Shimadzu model XRD 7000 diffractometer using Cu K α radiation at 40 kV and 30 mA.

²⁹Si NMR spectra in the solid state were performed on an INOVA 500 spectrometer (Varian), using cross polarization and magic angle spinning (CP/MAS). For this analysis, a contact time of 1 ms and a pulse repetition time of 3 s were employed, with a frequency of 59.61 MHz. The measurements were carried out at room temperature. Thermal analyses were performed on a DuPont model 9900, heating to 1223 K at a rate of 0.17 K s⁻¹. The amount of metallic cations was determined by ICP-OES with a PerkinElmer 3000 DV apparatus.

2.4. Batch adsorption

Adsorption was followed batchwise in aqueous solution for divalent lead, cadmium and copper nitrates at 298 ± 1 K. For these adsorption measurements, samples of about 30 mg of organosilicate were suspended in 10.0 cm³ of aqueous solution containing 1.0 × 10⁻³ to 5.0 × 10⁻² mol dm⁻³ concentrations of each cation in a thermostated orbital shaker for 5 h. These cation solutions were prepared by dissolving the respective nitrate salts in deionized water, to give a final pH 4.5. After equilibrium was established, the suspension was centrifuged, aliquots of the supernatant were

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