



Grafting of organosilane derived from 3-glycidoxypropyltrimethoxysilane and thiourea onto magnesium phyllosilicate by sol–gel process and investigation of metal adsorption properties

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ABSTRACT

A layered inorganic–organic magnesium silicate (Mg-GTPS-TU) has been successfully synthesized by using sol–gel based precursor under mild temperature conditions and a new silylating agent (GTPS-TU) derived from 3-glycidoxypropyltrimethoxysilane (GTPS) and thiourea (TU) as the silicon source. The hybrid material was characterized through elemental analysis, infrared spectroscopy, X-ray diffractometry, thermogravimetry, and carbon and silicon solid-state nuclear magnetic resonance spectroscopy. The result confirmed the attachment of organic functionality to the inorganic silicon network. The inter-lamellar distance for the hybrid material was found to be 18.8 Å. Metal adsorption characteristics follows Cr(III) > Mn(II) > Zn(II) with more affinity towards Cr(III) in dilute aqueous solution. Evaluation of thermodynamic parameters ΔH and ΔS for Cr(III) were found to be 25.44 J mol⁻¹ and 79.9 J mol⁻¹ K⁻¹, respectively, indicating adsorption process to be endothermic in nature. The negative value of ΔG indicated the feasibility and spontaneity of ongoing adsorption process at relatively higher temperature. The presence of multiple coordination sites in the attached organic functionality expresses the potentiality of the hybrid material containing new silylating agent for heavy cation removal from ecosystem.

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1. Introduction

Synthesis of organic modified metal containing phyllosilicates through sol–gel process gains importance for various new applications in the areas of catalysis, adsorption, chromatographic techniques, and biomaterials [1–7]. Such kind of hybrid materials are synthesized by intercalating various organic species into two-dimensional galleries of layered materials such as smectites [8–10], and thus immobilizing organic molecules following a sol–gel process [11]. The one-step synthesis of layered inorganic–organic crystalline compounds at room temperature produce an ordered self-assembled structure in which the covalent bond is established between organic and inorganic sides of the formed layer. A series of new layered materials using commercial as well synthetic new silylating agents and containing various metals such as magnesium, nickel [12–20], aluminum [21,22], copper [18], zinc [1], and calcium [23] in the lamellar structure has been reported by various researchers. Normally, the chosen metallic divalent cation is located in an octahedrally arrangement in the

layer forming 1:1 or 2:1 families [6]. Although, applications using hybrid materials are quite wide spread depending on the observed properties [24,25], presence of organic moiety in the structural matrix limits its use for high-temperature application purposes. Usefulness of organic–inorganic hybrid materials in metal adsorption studies from dilute aqueous solutions have also been widely investigated due to the available scope for introducing functional variations in organic moieties that is responsible for metal adsorption behavior within the layered structure [1,12–17,22].

Synthesis of organic modified magnesium phyllosilicates through sol–gel processes, in which the magnesium ions are incorporated in the inorganic framework formed by alkoxy silanes in a basic medium [18,26], resulted in an inorganic talc like structure in which organic moiety is attached to the inorganic network. The hybrid material so formed contains the organic chains of alkylalkoxysilanes precursor distributed inside the interlayer region [27]. For example, Lagadic et al. [2] prepared a thiol-functionalized layered magnesium phyllosilicate from mercaptopropyltrimethoxysilane and MgCl₂ under basic conditions using a rapid, environmentally friendly co-condensation process in order to achieve high loading of SH functionalities. The high metal-loading capacities of the hybrid material were explained by

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high content of SH-binding groups and their easy accessibility due to the expansion capability of the flexible framework structure. On the basis of the results obtained by various researchers, it may be anticipated that silicate materials with a more open framework structure would show higher loading as well as better affinity towards metal ions.

In the present investigation, we are reporting the synthesis of a new covalently linked inorganic–organic lamellar hybrid material containing silicon and magnesium. A new silylating agent was prepared from thiourea (TU) and 3-glycidoxypropyltrimethoxysilane (GTPS) under suitable reaction conditions. The synthesis of magnesium phyllosilicates was carried out *in situ* in an alkaline condition. Basic media favors the hydrolysis of the alkoxy groups of organosilane to form silanol groups, which is negatively charged due to pH approximately being 12. The negatively charged species could be aggregated into an ordered molecular array. The negatively charged micelles may also function as templates and can attract magnesium cations from solution to form a layered hybrid structure with an inorganic phase constituting Si–O–Mg bond. The novelty of designing such kind of new synthetic hybrid is associated with high purity, homogeneity and the organofunctional alkoxysilane containing donor centers such as nitrogen and sulfur attached on pendant chain. The chosen donor centers are expected to show certain selective characteristics for binding and extraction of metal ions from aqueous and non-aqueous solutions based on established phenomenon [28–30]. Moreover, this important ligand has so far not been incorporated in the phyllosilicate structure. A simple low-temperature route was adopted for the synthesis of the hybrid material in contrast to other available chemical methods such as heat treatment and reaction with catalyst [31]. The usability of the adsorbent was studied to evaluate the potentiality of such materials in heavy metal removal and environmental clean up technologies. One of the most important future applications of new organosilane is that a great variety of composition can also be obtained by considering not only the metallic cation employed but specific organosilane used as precursor agent [32].

2. Experimental

2.1. Reagents

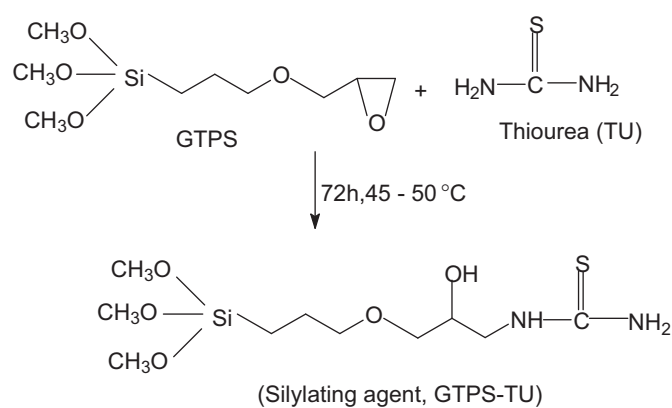
The reagents 3-glycidoxypropyltrimethoxysilane and thiourea (Aldrich) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used without any further purification. Ethanol was dried before use. For the metal adsorption studies, metal salts of Mn(II), Zn(II), and Cr(III) were dissolved in doubly distilled water obtained from an ultra-pure Milli-Q Millipore 18.2 M Ω cm system.

2.2. Synthesis of silylating agent

The silylating agent (GTPS-TU), as shown in the reaction Scheme 1, was synthesized in a nitrogen atmosphere to ensure anhydrous condition during preparation process. Thus, 14.1 cm³ (0.0638 mol) of GTPS was added to TU (4.9 g, 0.064 mol) dissolved in 150 cm³ of ethanol under stirring condition at $(50 \pm 3)^\circ\text{C}$, and the same reaction condition was maintained for 72 h, after which the solvent quantity was reduced to one third of its added volume.

2.3. Synthesis of functionalized magnesium phyllosilicate

The functionalized layered magnesium phyllosilicate material was synthesized following a previously described procedure [14]. In a typical synthesis, to a polyethylene flask containing 12.28 g



Scheme 1. Synthesis of silylating agent (GTPS-TU).

(0.0479 mol) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 100 cm³ of ethanol, a freshly prepared ethanolic solution of synthesized silylating agent GTPS-TU (0.064 mol) was added in a drop-wise manner using addition funnel, while maintaining the system temperature at $40(\pm 2)^\circ\text{C}$. The molar ratio of Si/Mg was calculated to be 1.33. The suspension was slowly stirred at approximately 30 rpm for 1 h, and then a solution of 192 cm³ of sodium hydroxide (0.50 mol dm⁻³), prepared in deionized water, was added drop-wise with continuation of slow stirring rate during the total addition process. The resultant suspension was kept for 24 h at 40°C , and then at room temperature for 7 days. The obtained gel material was isolated by centrifugation process, then thoroughly washed with ethanol (3 times) and subsequently with deionized water for several times till the pH of the solution reached neutral value. The material was dried under vacuum for 72 h at 50°C and finally grinded to yield a white powdered material, which was named as Mg-GTPS-TU.

2.4. Characterization

The amount of organic pendant chains, attached onto the inorganic layers formed were calculated based on carbon, hydrogen, and nitrogen and sulfur percentages determined through elemental analysis on a Perkin Elmer, model 2400, elemental analyzer. The infrared spectra of the solid samples in KBr pellets were performed by diffuse reflectance by accumulating 35 scans on a Bomem spectrophotometer, MB-Series, in the range of $4000\text{--}400\text{cm}^{-1}$, with 4cm^{-1} of resolution. Nuclear magnetic resonance spectra, of the solid samples of phyllosilicate material, were obtained on a Bruker AC 300/P spectrometer at room temperature. For each run, approximately one gram of each solid sample was compacted into 7 mm zirconium oxide rotor. The measurements were obtained at frequencies of 59.63 and 75.47 MHz, for silicon and carbon, respectively, with a magic angle spinning of 4 Hz. In order to increase the signal-to-noise ratio of the solid-state spectra, the CP/MAS technique was used. ²⁹Si and ¹³C CP/MAS spectra were obtained with pulse repetitions of 3 s for both nuclei and contact times of 1 and 3 ms, respectively. The X-ray diffraction (XRD) patterns for the synthesized phyllosilicate sample was obtained on a Shimadzu model XD3A diffractometer (40 kV/30 mA), in the range of $2\theta = 1.5\text{--}70^\circ$ with a nickel-filtered $\text{CuK}\alpha$ radiation, with wavelength of 1.54 Å. From these data, the interlayer spacing of the compounds was calculated. The scanning electron micrograph (SEM) of the sample was obtained in a JSM 6360 LV apparatus with sub-vacuum condition and particle acceleration at 20 kV. The thermogravimetric analysis was performed on a TA instrument in an argon atmosphere, coupled to a model 1090B thermobalance, by using a

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