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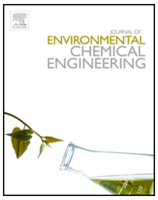

Pendant chains containing thiopropanamide groups inside talc-like phyllosilicate galleries as thermodynamically favorable agents for cation removal

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ABSTRACT

A lamellar inorganic–organic talc-like magnesium phyllosilicate has been synthesized through a single step sol–gel route under mild conditions, using a newly synthesized [3-(3-trimethoxysilylpropyl) thiopropanamide] silylating agent, obtained from acrylamine and 3-mercaptopropyltrimethoxysilane. Elemental analysis data based on the sulfur atom showed an incorporation of 3.66 mmol g^{-1} of the thiopropanamide group inside the galleries of the hybrid. Infrared spectroscopy and nuclear magnetic resonance (NMR) in the solid state for the ^{13}C nucleus confirmed the thiopropanamide moiety covalently bonded inside the lamellar structural galleries. Solid state ^{29}Si NMR showed the presence of T^n silicon species in the backbone in agreement to the hydrolysis and condensation reactions during the sol–gel process. X-ray diffractions gave a basal distance of 1.854 nm, near twice that of the natural talc and the 060 reflection confirmed a structure similar to natural talc. The basic centers on pendant chain coordinate divalent nickel, cadmium and lead cations from aqueous solution at the solid/liquid interface. Based on the Langmuir model, the maximum sorption capacity of the hybrid for these cations was 0.70, 1.10 and 2.71 mmol g^{-1}, respectively. The thermodynamic data for cation/basic center interactions were determined through calorimetric titration, demonstrating spontaneous interactions, ΔG, exothermic enthalpic ΔH and positive entropy ΔS values. These favorable results for removal these toxic cations in a heterogeneous system may be useful for remove ions from wastewaters.

Introduction

Since the emergence of industrial era, a scientific goal is to combine both inorganic and organic properties in a single unique material. These kinds of materials have emerged from different areas of chemistry; however, the concept of hybrids exploded with the birth of soft inorganic chemistry processes, using the so-called "Chimie Douce" procedure. From this advanced methodology, mild synthetic conditions have opened a versatile access to chemically designed inorganic–organic hybrid materials, to improve facilities in the insertion of organic molecules inside an inorganic network. Consequently, great progress has also come from the wide use of the sol–gel process for the syntheses [1]. Thus, the inorganic phase is mostly obtained from alkoxides via hydrolysis and condensation reactions, in which tetraalkoxysilane or trialkoxysilylating agents are commonly used as precursors for the silica network [2].

Nowadays, much attention has been paid to layered inorganic–organic hybrid materials not only due to their applications, but also related to the versatility in their synthesis from a variety of compounds. Such hybrids can be synthesized either by intercalation of various organic species into the interlamellar galleries of the naturally occurring layered compounds or by cation exchanging into the interlamellar spaces. In addition, some relevant organoclays can also be obtained by post-synthesis treatment in the presence of an organoalkoxysilane [3]. A significant improvement in these syntheses is associated with the copolymerization of organoalkoxysilanes in the presence of metallic ions through the sol-gel process, in which the organic molecules can be covalently inserted into the inorganic matrix. The phyllosilicates originating from these synthetic routes have some advantages over the natural ones, due to the high degree of purity that increase applications related to species removal from aqueous solutions [4–10].

The synthesis of phyllosilicates having organic pendant chains with the desired functions can be designed in order to embrace properties with significant practical advantages, to gain structural and thermal stability, resistance to swelling effects, insolubility in organic and aqueous solvents and the possibility to obtain a

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sequence of reactions to immobilize other organic molecules [4,6–10]. The pendant chains inside the galleries have normally active centers that are useful for toxic metal and dye sorptions, drugs delivery and catalysis [6–14]. In addition, the synthesized magnesium, nickel, copper or zinc phyllosilicate structures with covalent pendant chains having attached nitrogen and sulfur basic centers have the ability to remove heavy cations [4,15–18].

Human health and the environment are threatened to get worse due to the increasing levels of heavy metals in water. Generally, some metals abundantly found in water sources are significantly toxic to human beings and the ecological environment due to their persistence and undesirable bioaccumulative capacities, resulting from concentrations in wastewater effluents that are higher than permissible discharge levels. Taking into account all these reasons and some definite regulations and precautions, it becomes necessary to remove these heavy metals from wastewater by appropriate treatment before releasing the wastewater into the environment [19,20].

Numerous processes are available for removing heavy metals, such as precipitation, ultrafiltration, reverse osmosis or electrodialysis, etc. [21], but many of these procedures are expensive or present some difficulties in the course of implementation. On the contrary, sorption is a potential alternative treatment for such removal from wastewaters [22–24]. In this context, inexpensive naturally occurring lignocellulose materials, such as wheat straw, peanut shells, peat moss, bagasse fly ash, tree ferns, grain husks, coconut coir pith, sawdust and the epicarp of babassu coconut have been explored [25–30]. These materials are naturally enriched with cellulose, followed by lignin, tannin and pectin, which contain phenolic and aliphatic hydroxyl and also carboxylic groups. However, the main disadvantages of these materials, in contrast with phyllosilicates, are related to their low resistance to abrasive forces in batch or column applications, leading to leaching of some organic components during the aqueous sorption process [28].

The aim of the present investigation is focused on thermodynamic evaluations of cation removal by layered talc-like magnesium phyllosilicates, obtained by the reaction of a newly synthesized trialkoxysilane and magnesium nitrate in a single step sol–gel process. The hybrid belongs to a 2:1 trioctahedral phyllosilicate family formed by an octahedral layer occupied by a hexagonal magnesium atom sandwiched between two tetrahedral silicate layers [31]. The organic pendant chains are covalently bonded to the inorganic structure with attached basic centers with ability to sorb cations at the solid/liquid interface.

Experimental

Reagents

All the chemicals, magnesium nitrate hexahydrate (Carlo Erba), methanol (Synth), sodium hydroxide (Merck), acrylamide (Aldrich), N,N-methylenebisacrylamide (Acros), triethylamine (Aldrich) 3-mercapopropyltrimethoxysilane (Aldrich), nickel, cadmium and lead nitrates (Vetec) were reagent grade and used as received. The solution of metal ions was prepared in doubly distilled water (ultra-pure Milli-Q Millipore, 18.2 MΩ cm).

Silylating agent

The silylating agent was synthesized under anhydrous conditions, using 3.0 g (37.33 mmol) of acrylamide dissolved in 75 cm^3 of methanol in a 250 cm^3 three necked flask by stirring for 5 min at room temperature. To this solution, 7.0 cm^3 (37.30 mmol) of 3-mercaptopropyltrimethoxysilane was added in the presence of 0.40 mmol of triethylamine as a catalyst. The reaction mixture was stirred for 24 h at 318 K under a nitrogen atmosphere. After completion of the reaction, one third of the methanol was removed under vacuum, to yield a methanolic solution of the corresponding silylating agents [3-(3-(trimethoxysilylpropyl)thiopropanamide)] that was immediately used, to avoid any hydrolysis, for the sol–gel synthesis of the hybrid material in the next step.

Synthesis of phyllosilicate

The talc-like hybrid phyllosilicates of magnesium were synthesized by mixing the methanolic solution of synthesized silylating agent with a methanolic solution of magnesium nitrate, keeping the Si/Mg molar ratio equal to 1.33. Thus, magnesium nitrate hexahydrate (27.0 mmol) was dissolved in 75 cm^3 of methanol in a polyethylene flask. To this methanolic solution the silylating agent (37.30 mmol) also dissolved in methanol was added dropwise under vigorous magnetic stirring at room temperature. The white suspension was precipitated by the slow addition of 0.50 mol dm^{-3} sodium hydroxide [10], until the pH reached 11.5. The white precipitate left in stand-by without stirring for 24 h at 318 K, followed by twice washing with 200 cm^3 of doubly distilled water to yield the solid named MgAA that was dried under vacuum for 24 h at 323 K.

Sorption and calorimetry

The maximum sorption capacity was determined through batchwise methodology, by using a series of flasks containing about 20 mg of hybrid phyllosilicate (MgAA) sample, suspended in 25.0 cm^3 of divalent cationic solutions of lead, cadmium, or nickel, varying from 7.0×10^{-4} to 8.0×10^{-3} mol dm^{-3} in concentration, at 298 ± 1 K. Based on the time to reach equilibrium, which was previously established as 14 h for all experiments, 16 h was chosen to ensure maximum sorption. In any case, after reaching equilibrium, the solid was filtered and the remaining amount of cation was quantified in the supernatant using inductively coupled plasma optical emission spectroscopy (ICP-OES). For each experimental point, the repeatability was checked by at least one duplicate run.

The thermal effects evolved from the interaction of cations with sulfur, nitrogen and oxygen basic centers attached to the phyllosilicate pendant chains at the solid/liquid interface were acquired by the calorimetric titration technique, using an LKB 2277 microcalorimeter [6–8,10]. In this titration, a known amount of about 20 mg of MgAA in 2.0 cm^3 of water was suspended inside the calorimetric vessel with vigorous stirring at 298.15 ± 0.20 K. A microsyringe with a corresponding cationic solution of known concentration of 0.10 mol dm^3 was coupled to the calorimetric vessel. The incremental additions of cation solution to the calorimetric vessel were performed by injections of a series of fixed volumes of 10 mm^3 in a programmed procedure at intervals of 2 h, with an auxiliary pumping system. From this process, the decrease in thermal effects was obtained as the reaction reached the plateau in the corresponding isotherms [6–8,10].

Characterizations

The amount of organic chains attached to the inorganic network inside the galleries of the new hybrid phyllosilicates were calculated on the basis of carbon, hydrogen, nitrogen and sulfur percentages, determined through elemental analysis on a PerkinElmer model 2400 elemental analyzer.

The infrared spectra of the samples in KBr pellets were recorded on a Bomem spectrophotometer, MB series, in the 4000–400 cm^{-1} range with 4 cm^{-1} of resolution from 32 scans.

^{29}Si NMR spectra in the solid state were performed on a Varian INOVA 500 spectrometer at room temperature. The spectra were