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 silylaing 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 interlamellar 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 $MgCl_2$ 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

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 $Mg(NO_3)_2 \cdot 6H_2O$ 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 MΩ 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 cm^3 (0.0638 mol) of GTPS was added to TU (4.9 g, 0.064 mol) dissolved in 150 cm^3 of ethanol under stirring condition at $(50\pm3)\,°C$, 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
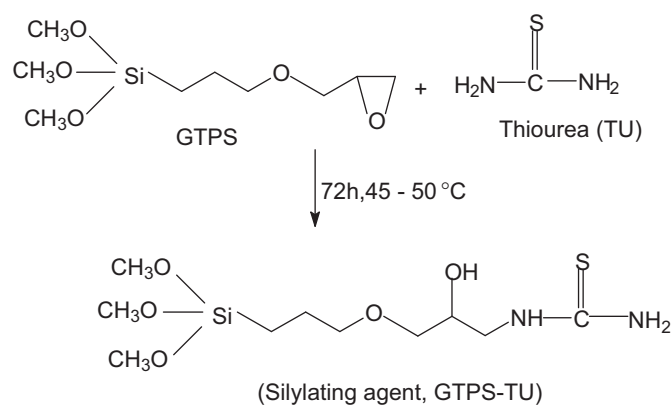
Scheme 1. Synthesis of silylating agent (GTPS-TU).

(0.0479 mol) of $Mg(NO_3)_2 \cdot 6H_2O$ dissolved in 100 cm^3 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 $40(\pm2)\,°C$. 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 cm^3 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 4000–400 cm^{-1}, with 4 cm^{-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. ^{29}Si and ^{13}C 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 $2\theta = 1.5–70°$ with a nickel-filtered CuKα 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
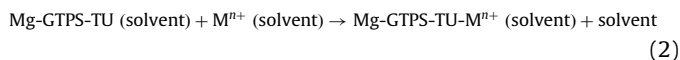
heating rate of $0.167 \, \text{K s}^{-1}$, under a flow of $30 \, \text{cm}^3 \, \text{s}^{-1}$, varying from room temperature up to 1200 K, with an initial mass of approximately 10 mg of solid sample. The amount of metal ion adsorbed was determined by the difference between the initial concentration in aqueous solution and that found in the supernatant, by using ICP-OES Perkin Elmer 3000 DV apparatus. For each experimental point, the reproducibility was checked by at least one duplicate run.

2.5. Analytical studies

Adsorption of metal ions were carried out in batch method [33] in which 50.0 mg of adsorbent material (Mg-GTPS-TU) taken in a conical flask was added with $25.0 \, \text{cm}^3$ aqueous solutions of metal cation. The conical flask was placed in an incubator-shaker at 298 ± 1 K for 24 h. A time period of 24 h was chosen to ensure maximum adsorption of metal ions onto the adsorbent material. After establishing equilibrium, the solid was separated by centrifugation and aliquots of the supernatant were pipette out carefully from the suspension, and the amounts of the cation remaining in the solution was determined. The amount of cation removed during adsorption was calculated using the following expression (Eq. (1)):

$$Q = V(C_o - C_e)/W \tag{1}$$

where Q is the adsorption capacity (mg g^{-1}), C_o and C_e are the initial and equilibrium concentration of sorbed metal ions (mg L^{-1}), and W is the mass of the solid adsorbent (g) used in the adsorption process and V is the volume of metal solution (L). The metal adsorption process by the layered phyllosilicate material can be represented by the following expression (Eq. (2)):

$$\text{Mg-GTPS-TU (solvent)} + \text{M}^{n+} \text{ (solvent)} \rightarrow \text{Mg-GTPS-TU-M}^{n+} \text{ (solvent)} + \text{solvent} \tag{2}$$

The regeneration of Mg-GTPS-TU after metal adsorption was tested using literature procedure [34]. A fully metal saturated sample materials, obtained by mixing 50 mg of Mg-GPTS-TU with $100 \, \text{mg L}^{-1}$ Cr(III) solution in deionized water for 24 h, was stirred in 100 mL of aqueous 1 N HCl. The green colored adsorbent material immediately turned white. The solution was stirred overnight, and then the white powder was collected by filtration, washed with deionized water, and dried in air. The chromium contents of the solid samples were determined before and after acid treatment to evaluate the effectiveness of regeneration process. The reusability of the adsorbent material as a heavy metal adsorbent was assessed by retreating the leached material with chromium solution and the metal content was evaluated.

3. Results and discussion

3.1. Characterizations

A schematic representation of the sol–gel process, employed to prepare the inorganic–organic hybrid layered material in which the organofunctional trialkoxysilane form the silica layer with a covalent silicon–carbon bond containing magnesium sandwiched in the hybrid structure, is presented in Fig. 1. The elemental analysis value for the synthesized material (Mg-GTPS-TU) containing the silylating agent was found to be %C: 32.6; %H: 6.8; %N: 10.75, and %S: 8.03. The presence of nitrogen and sulfur in the hybrid material confirms the presence of organic moiety in the hybrid structure. Based on the analytical data, the density of pendant organic molecule immobilized in the tetrahedral silica layer of the hybrid material can be calculated. Thus, the precursor GTPS-TU grafted onto silica gave an amount of $3.2 \pm 0.1 \, \text{mmol g}^{-1}$.
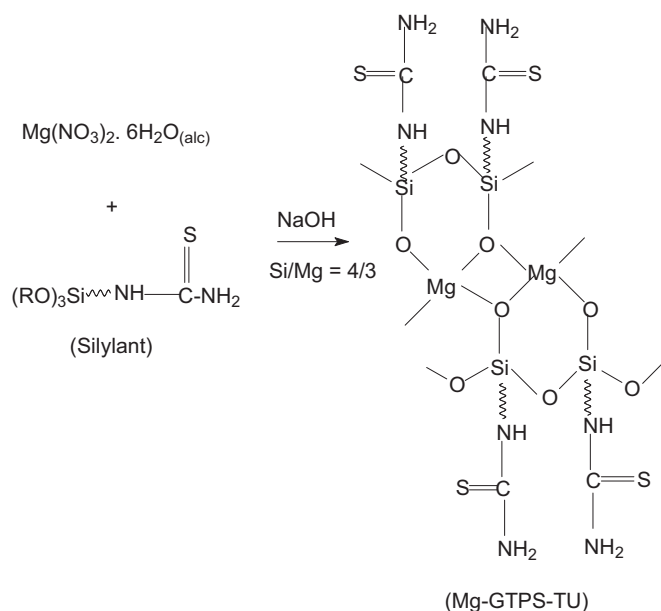

Fig. 1. A schematic representation of the hybrid material containing the silylating agent.

As shown in Fig. 1, the organic pendant chains in the hybrid material contains potentially active centers for coordinating with heavy metal cations for effective removal from dilute aqueous solution. However, infrared spectroscopy of the hybrid material, presented in Fig. 2, strongly supported the presence of organic moiety boned to the layered structure of the material. The hybrid material showed bands at 2930 and $2945 \, \text{cm}^{-1}$ which was assigned to ν(C–H), indicating that the organic group was covalently attached to the layer structure of the material [6]. Other important characteristics bands observed at 1570 and $1323 \, \text{cm}^{-1}$ were assigned to δ(N–H) and ν(C=S), respectively. An intense peak at $1130 \, \text{cm}^{-1}$ was assigned to ν(Si–O–Si) and observation of this peak corresponds to the formation of a tetrahedrical layer in the organophyllosilicate [15,35]. The presence of vibration band at $540 \, \text{cm}^{-1}$ was attributed to the δ(Mg–O) of the hybrid material. Further, the presence of peak at $1190 \, \text{cm}^{-1}$ was attributed to the vibrational stretching frequency of Si–C bond. All these observations strongly supported the presence of organic moiety in the synthesized hybrid material.

The solid-state NMR is an important auxiliary tool to elucidate the structure of the organic moiety present in the hybrid material. The ^{13}C-NMR spectrum of the hybrid material, as shown in Fig. 3, displayed signals in consistent with previously reported data on similar functionalized hybrid material, indicating that the organic chains are incorporated into the layered framework. Additionally, the observed peak intensities and their sharpness suggested that the organic groups remain fairly mobile within the interlayer galleries [36]. The signal at $\delta 9.9 \, \text{ppm}$ was assigned to the carbon (C_1) directly bonded to the silicon. The other peaks observed at $\delta 24.3, 33.3, 47.8, 74.8$, and 137.1 ppm were assigned to the carbons of pendant group as shown in the proposed structure. Thus, the sequence of peaks presented in the spectrum confirms the formation of hybrid material by synthetic procedure adopted for such process [37].

^{29}Si NMR used as an important tool to derive a set of valuable information regarding attachment of pendant organic chains to the silicate formed in the sol–gel process. The spectrum of the lamellar hybrid is shown in Fig. 4 along with the respective peaks assignments. The three distinct signals at −65.7, −55.9, and −48.4, δppm, respectively, attributed to the T^3: [R–Si–(OSi)$_3$], T^2:
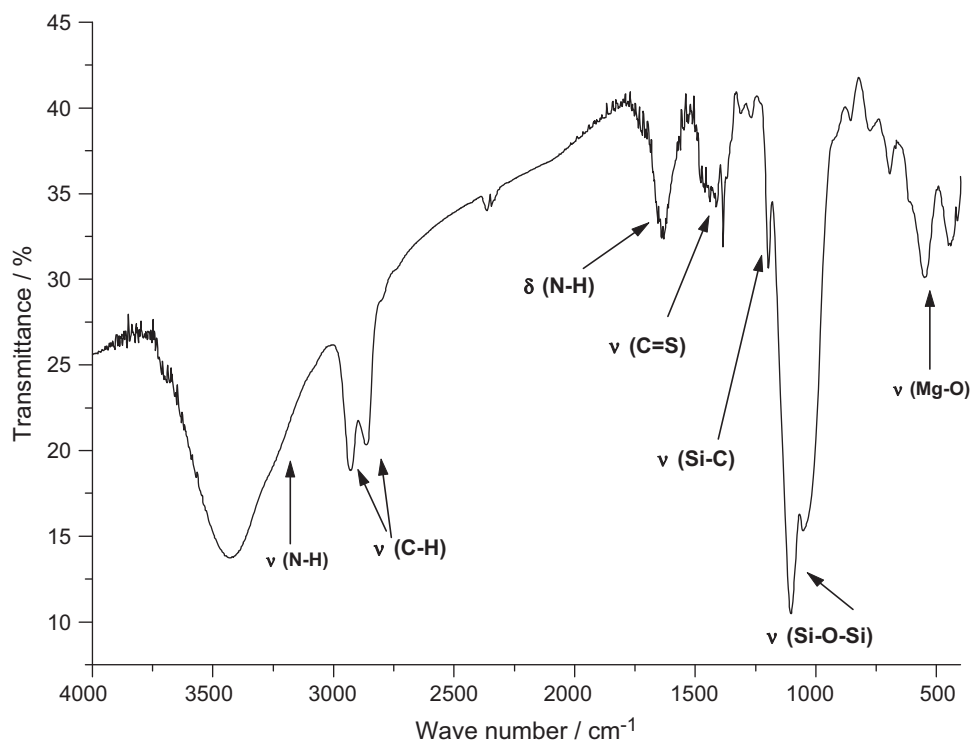
Fig. 2. FTIR spectra of Mg-GTPS-TU hybrid material.
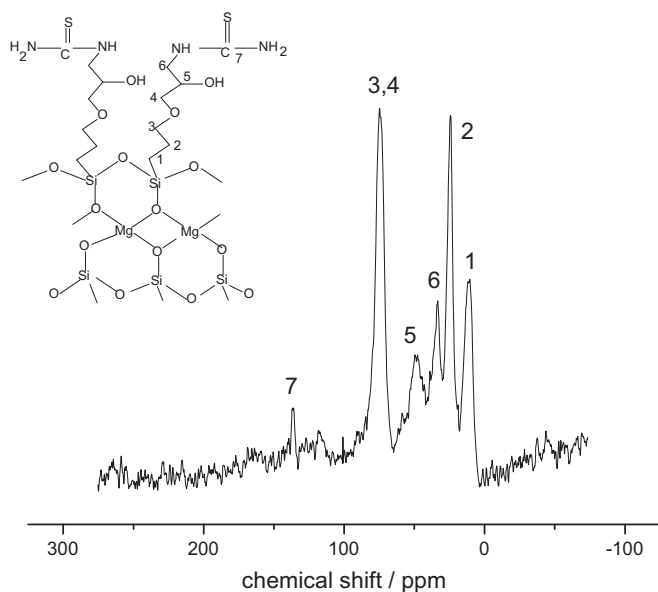
Fig. 3. ^{13}C NMR spectra for the synthesized hybrid material (Mg-GTPS-TU).

Fig. 4. ^{29}Si NMR spectra for Mg-GTPS-TU hybrid material.
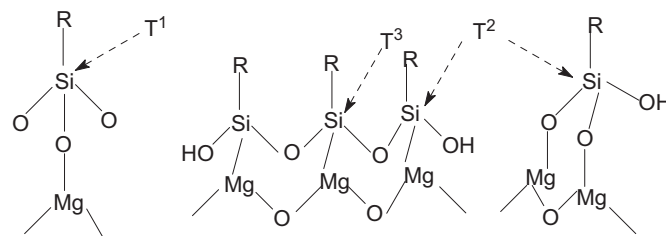
Fig. 5. Peak assignment based on ^{29}Si NMR data.

[R–Si–(OSi)$_2$OH], and T^1: [R–Si(OSi)(OH)$_2$], originating from the bonding of silylating agent to the inorganic backbone. The peak assignments, based on the previous data on analogous system [6] involving modified silicas and other phyllosilicates, are shown in Fig. 5.

The scanning electron micrograph of the sample material (Fig. 6) provides evidence toward the layer structure of the material. The lamellar characteristics of the material were particularly well demonstrated in the given picture and the interlayer spacing was calculated using X-ray diffraction pattern data.

The X-ray diffraction pattern for the hybrid material is shown in Fig. 7, for which the assignment of the diffraction planes were indexed from talc DRX data [38]. The peaks in the 0 0 1 plane at 2θ
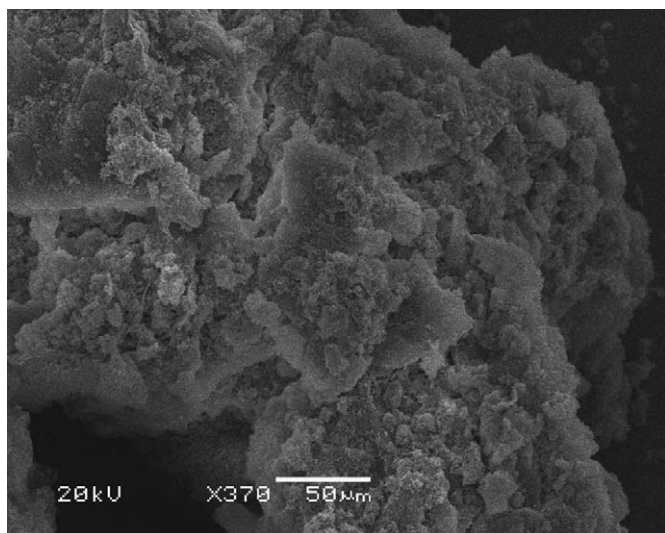
Fig. 6. Scanning electron micrograph of hybrid material showing the layered structure.
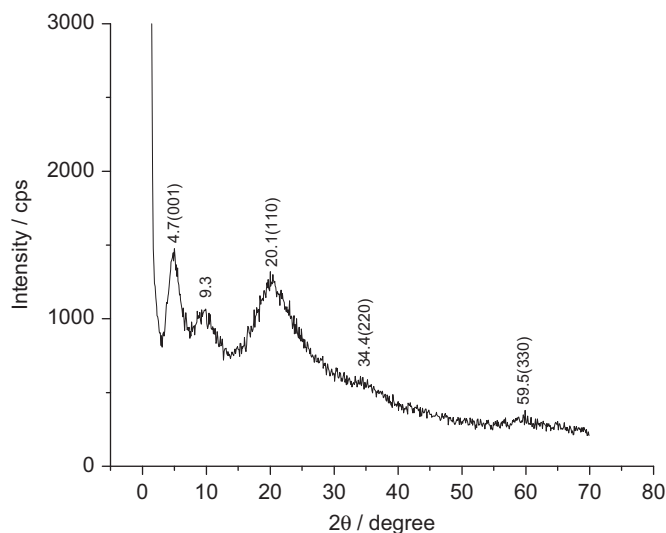

Fig. 7. X-ray diffraction pattern for hybrid material Mg-GTPS-TU.

equal to 4.7, corresponds to a lamellar distance of 18.8 Å for the hybrid material, while in natural talc phyllosilicate this value is reported as 9.34 Å [19]. This phenomenon of expansion of interlayer space as a result of grafting of organic moiety in the region has also been reported by a number of researchers [5]. Such a process is also responsible for observed interlayer disorder, which in the present case is supported by increased intensity of reflection at 1 1 0 plane, which appeared at 20.1° [13,16]. A peak of low intensity at 59.5° corresponds to reflection in the 0 6 0 planes supporting the formation of trioctahedral layer in the synthesized hybrid material [13].

The thermal degradation pattern of the hybrid material is shown in Fig. 8. The various steps of decomposition are demonstrated by derivative curves in the region 250–1100 K. The weight loss observed blow 373 K is ascribed to loss of water/ solvents molecule from the surface in analogy with the presence of grafted hydrophobic interlayer [39]. A significant weight loss amounting 48–51%, observed in the region 473–800 K, was mainly due to the various combustion reactions in addition to the loss of ethanol, which may present in the interlayer space [40]. To

corroborate the evidence, the elemental analysis report showed the presence of considerable amount of carbon, thus confirming the presence of organic moiety in the interlayer structure. A negligible mass loss observed in the region 900–1100 K, which could be due to the presence of remaining silanol groups bonded to the surface that condensed on heating to produce siloxane bonds [1].

3.2. Analytical studies

The hybrid material contains both sulfur and nitrogen as the available ligating sites in the structure and the availability of molecules covalently attached to the tetrahedral silicon atom of the inorganic layer can be useful to coordinate cations in case of presence of basic atoms in these pendant chains present inside the lamellar cavity. The ability of hybrid material in extraction of a number of cations such as Cr(III), Mn(II), and Zn(II) was evaluated in batch experiment. The initial white solid Mg-GTPS-TU changed their original color for green and pink, respectively, after chromium and manganese adsorption. From the contact time variation studies (Fig. 9), the order of sorption of the metal ions was found to be Cr(III) > Mn(II) > Zn(II) which could be attributed to the hardness of cations [41]. The sorption of Cr(III) tends to attend at saturation value in 30 min time period where as adsorption remains almost constant for Mn(II) and Zn(II). With increase in metal concentration (Fig. 10), the amount of adsorption increases. This could be attributed to the fact that with increase in metal concentration, the binding capacity of the adsorbent approaches a saturation value, thus resulting in overall decrease in removal percentage. However, with increasing pH of the medium the metal adsorption increases significantly (Fig. 11). In this case, the absence of a plateau indicated that the basic centers of organic functionalities are not fully saturated. Increasing pH beyond 8 was discouraged due to possibility of hydrolysis of metal ions. Fig. 12 illustrated the possible form of hybrid material–metal ion interaction in which the pendant functional groups present in the hybrid structure are shown to coordinate with available metal ion in solution. Thus, investigation of the adsorption properties suggested the effectiveness of organic functionalities on the pendant chain in coordinating with metal ions.

The effect of variation of temperature of the medium upon adsorption the adsorption process was also evaluated within a temperature range of 30–50 °C (Fig. 13). Increase in solution temperature beyond 45 °C resulted in decrease in metal adsorption, thus indicating the instability of the hybrid material for high-temperature application purposes. The related thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated for Cr(III) adsorption using the following equations (Eqs. (3) and (4)):

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{3}$$

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

where ΔS and ΔH are the changes in entropy and enthalpy of adsorption, respectively. The plot of $\log K_C$ vs. $1/T$ for Cr(III), as shown in Fig. 14, was found to be linear. ΔH and ΔS, evaluated from the slope and intercept of van't Hoff plots, were found to be 25.44 kJ mol^{-1} and 79.9 J mol^{-1} K^{-1}, respectively. ΔH being positive value justified that adsorption of Cr(III) was endothermic process. The negative value of ΔG suggested more adsorption of Cr(III) at higher temperature for which the adsorption process could expect to be spontaneous due to contribution of entropy at higher temperature only.
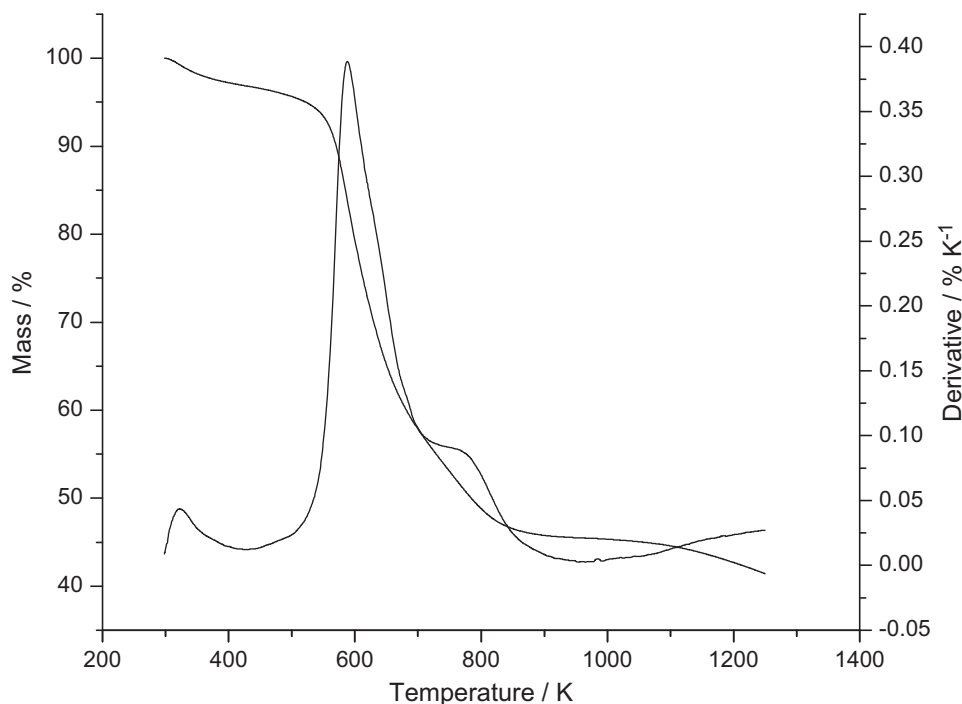
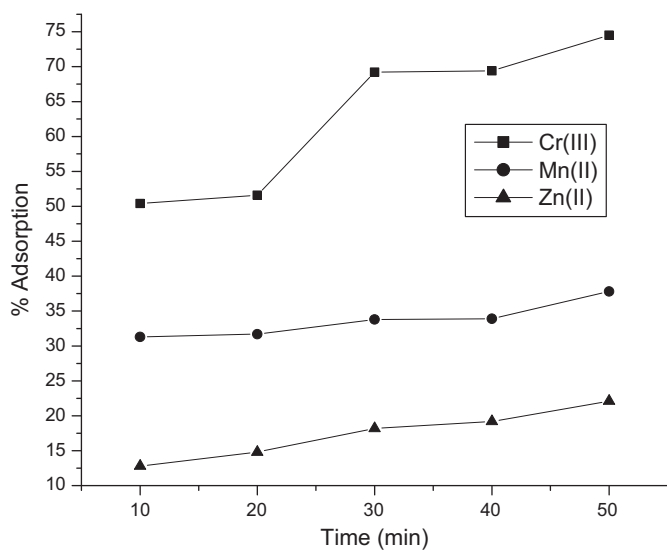**Fig. 8.** Thermogravimetric and derivative curves for the hybrid Mg-GTPS-TU.

Fig. 9. Effect of variation of contact time upon adsorption process.

Fig. 10. Effect of variation of concentration of metal ions upon adsorption process.

A number of layered inorganic–organic hybrid materials, containing nitrogen and sulfur basic centers attached to pendant groups, were previously synthesized and explored for their metal adsorption properties [1,6,17,18]. For example, Sales et al. [6] evaluated the adsorption of divalent mercury for which the free energy value was calculated to be $-10.1\,kJ\,mol^{-1}$ approximately, presuming mercury to be coordinate only by basic centers of the pendant groups such as sulfur and nitrogen. Adsorption of a number of other cations like cobalt, nickel, copper, and zinc were reported for magnesium phyllosilicate modified with mercapto-propyl group [14]. Interestingly, with the exception of copper, all other systems presented exothermic entropic values consistent with occurrence of favoured reactions. The free energy change indicates spontaneous processes in the order $Cu^{2+} < Zn^{2+} < Ni^{2+} < Co^{2+}$ attributed to an ordering in structure by decreasing the e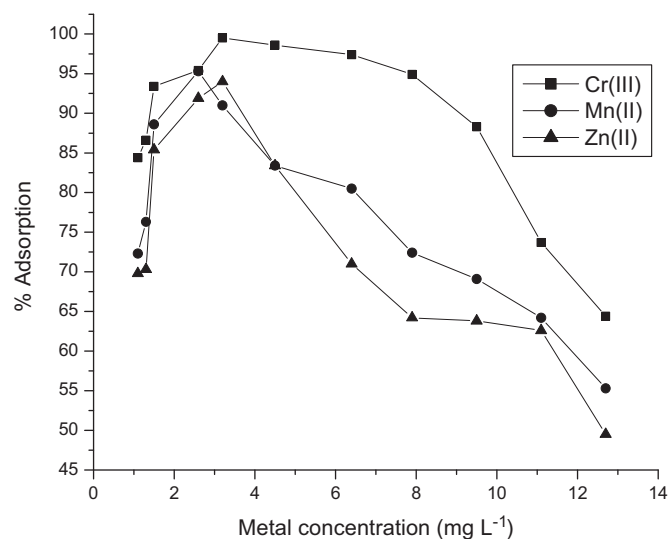ntropic values. Adsorption of copper by phyllosilicate could also lead to formation of new inorganic structure with copper partially inserted into the octahedral position to considerably increase the adsorption of metal ions [18]. In this aspect, the presence of multiple coordination sites such as nitrogen and sulfur in the hybrid material, (Mg-GTPS-TU), and its related metal adsorption properties suggested the favorable metal coordination processes for a number of toxic and heavy metal ions like mercury, lead, cadmium, etc., from dilute aqueous solutions which shall be explored in future investigations.

4. Conclusions

A new hybrid material containing magnesium as the basic center resembling talc like structure was synthesized via the condensation reaction involving magnesium cation and new
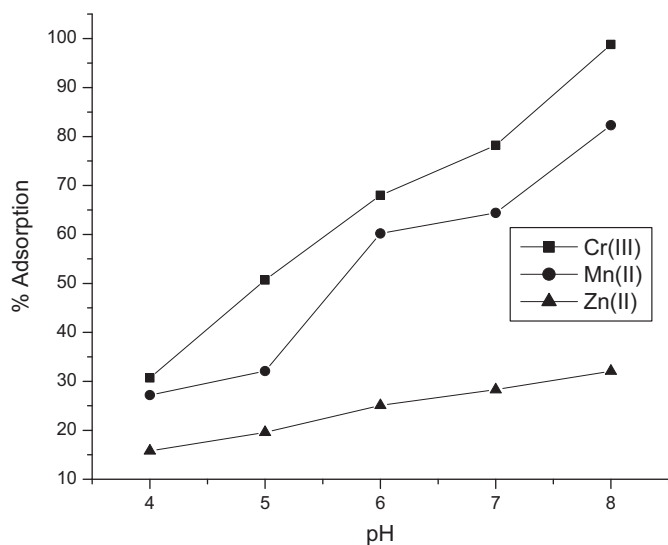
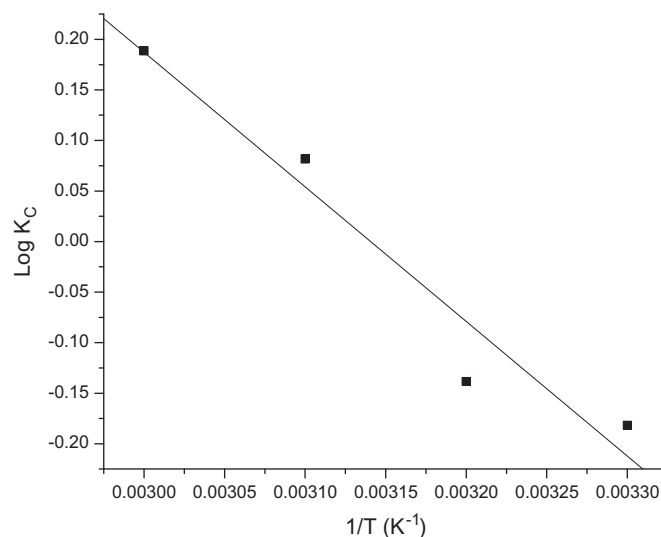**Fig. 11.** Effect of variation of solution pH upon adsorption process.

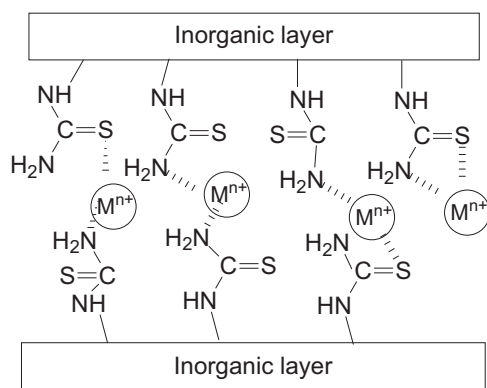**Fig. 14.** Plot of $\log K_C$ vs. $1/T$ (van't Hoff's plot).

Fig. 12. Proposed structure of complex formed on hybrid material–metal ion interaction.
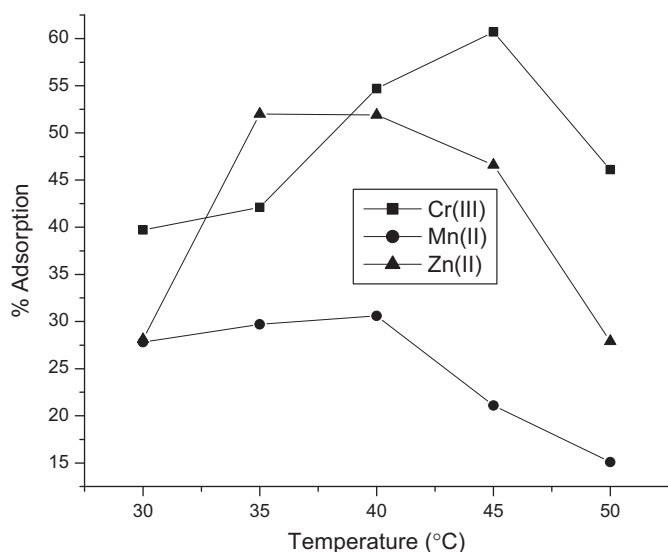

Fig. 13. Effect of variation of temperature upon adsorption process.

silylating agent (GTPS-TU), containing both nitrogen and sulfur as metal coordination sites, in a single-step route. The adopted synthetic method under mild conditions based on sol–gel process

result a self-assembled material in which the organic chains are present inside the interlayer cavity, thus facilitating the construction of layered structure with organic chains linked covalently to the inorganic silicon tetrahedral layer framework. Determination of related metal adsorption properties showed higher chromium adsorption in comparison to manganese and zinc. Evaluation of thermodynamic parameters for Cr(III) adsorption showed the spontaneity of adsorption process at relatively higher temperature. The new hybrid material is expected to find a number of applications in metal coordination chemistry because of presence of multiple ligating sites in the layered structure.

Acknowledgments

References

[1] M.G. Fonseca, E.C. Silva Filho, R.S.A. Machado Jr., L.N.H. Arakaki, J.G.P. Espínola, J. Solid State Chem. 177 (2004) 2316.
[2] I.L. Lagadic, M.K. Mitchell, B.D. Payne, Environ. Sci. Technol. 35 (2001) 984.
[3] Y.S. Al-Degs, M.I. El-Barghouthi, A.A. Issa, M.A. Khraisheh, G.M. Walker, Water Res. 40 (2006) 2645.
[4] Y. Özdemir, M. Doğan, M. Alkan, Micropor. Mesopor. Mater. 96 (2006) 419.
[5] G. Crini, Bioresource Technol. 97 (2006) 1061.
[6] J.A.A. Sales, G.C. Petrucelli, F.J.V.E. Oliveira, C. Airoldi, J. Colloid Inter. Sci. 297 (2006) 95.
[7] A.J. Patil, E. Muthusamy, S. Mann, J. Mater. Chem. 15 (2005) 3838.
[8] K. Tamura, H. Nakazawa, Clays Clay Miner. 44 (1996) 501.
[9] L.M. Nunes, C. Airoldi, Mater. Res. Bull. 34 (1999) 2121.
[10] K. Fujii, S. Hayashi, H. Kodama, Chem. Mater. 15 (2003) 1189.
[11] E. Lindner, M. Kemmler, H.A. Mayer, P. Wegner, J. Am. Chem. Soc. 116 (1994) 348.
[12] Y. Fukushima, M. Tani, J. Chem. Soc. Chem. Commun. (1995) 241.
[13] S.L. Burkett, A. Press, S. Mann, Chem. Mater. 9 (1997) 1071.
[14] M.G. Fonseca, C. Airoldi, Thermochim. Acta 359 (2000) 1.
[15] C.R. Silva, M.G. Fonseca, S. Barone, C. Airoldi, Chem. Mater. 14 (2002) 175.
[16] N.T. Whilton, S.L. Burkett, S. Mann, J. Mater. Chem. 8 (1998) 1927.
[17] M.G. Fonseca, C.R. Silva, J.S. Barone, C. Airoldi, J. Mater. Chem. 10 (2000) 789.
[18] M.G. Fonseca, C. Airoldi, J. Mater. Chem. 10 (2000) 1457.
[19] M.G. Fonseca, C. Airoldi, J. Chem. Soc. Dalton Trans. (1999) 3687.
[20] P. Burattin, M. Che, C. Louis, J. Phys. Chem. B 103 (1999) 6171.
[21] L. Ukrainczyk, R.A. Bellman, A.B. Anderson, J. Phys. Chem. B 101 (1997) 531.
[22] M. Jaber, J. Miehe-Brendle, L. Delmotte, R. Le Dred, Micropor. Mesopor. Mater. 65 (2003) 155.

[23] J. Minet, S. Abramson, B. Bresson, C. Sanchez, V. Montouillout, N. Lequex, Chem. Mater. 16 (2004) 3955.
[24] R. Sasai, H. Itoh, I. Shindachi, T. Shichi, K. Takagi, Chem. Mater. 13 (2001) 2012.
[25] M. Richard-Plouet, S. Vilminot, Solid State Sci. 1 (1999) 381.
[26] W. Whilton, S.L. Brukett, S. Mann, J. Mater. Chem. 8 (1998) 1927.
[27] M.G. Fonseca, C.R. Silva, C. Airoldi, Langmuir 15 (1999) 5048.
[28] P.A. Wight, M.E. Davis, Chem. Rev. 102 (2002) 3589.
[29] M.E. Mahmoud, M.M. El-Essawi, S.A. Kholeif, E.M.I. Fathalla, Anal. Chim. Acta 525 (2004) 123.
[30] P.K. Roy, A.S. Rawat, P.K. Rai, Talanta 59 (2003) 239.
[31] K. Fujii, S. Hayashi, Appl. Clay Sci. 29 (2005) 235.
[32] C. Sanchez, G.D.A. Soler-Illia, F. Ribot, D. Grosso, C. R. Chimie 6 (2003) 1131.
[33] J.A.A. Sales, C. Airoldi, J. Non-Crystal. Solids 330 (2003) 142.
[34] L. Mercier, C. Detellier, Environ. Sci. Technol. 29 (1995) 1318.
[35] M. Richard-Plouet, S. Vilminot, M. Guillot, M. Kurmoo, Chem. Mater. 14 (2002) 3829.
[36] I.L. Lagadic, Micropor. Mesopor. Mater. 95 (2006) 227.
[37] A.G.S. Prado, J.A.A. Sales, R.M. Carvalho, J.C. Rubim, C. Airoldi, J. Non-Cryst. Solids 333 (2004) 61.
[38] B. Perdikatsis, H. Burzlaff, Z. Kristallogr. 156 (1981) 177.
[39] K.A. Carrado, L. Xu, R. Csencsits, J.V. Muntean, Chem. Mater. 13 (2001) 3766.
[40] M. Jaber, J. Miéhé-Brendlé, L. Delmotte, R. Le Dred, Micropor. Mesopor. Mater. 65 (2003) 155.
[41] E.M. Soliman, M.E. Mahmoud, S.A. Ahmed, Talanta 54 (2001) 243.