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

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A B S T R A C T

A new-layered inorganic–organic magnesium organosilicate was synthesized through a single step template sol–gel route under mild conditions, using a new alkoxysilane, containing a 2-aminophenyldisulfide 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.

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 pollutants 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 $Si_8R_8Mg_6O_{16}(OH)_4$, based on the original parent talc structure, represented by $Si_8Mg_6O_{20}(OH)_4$ [20].

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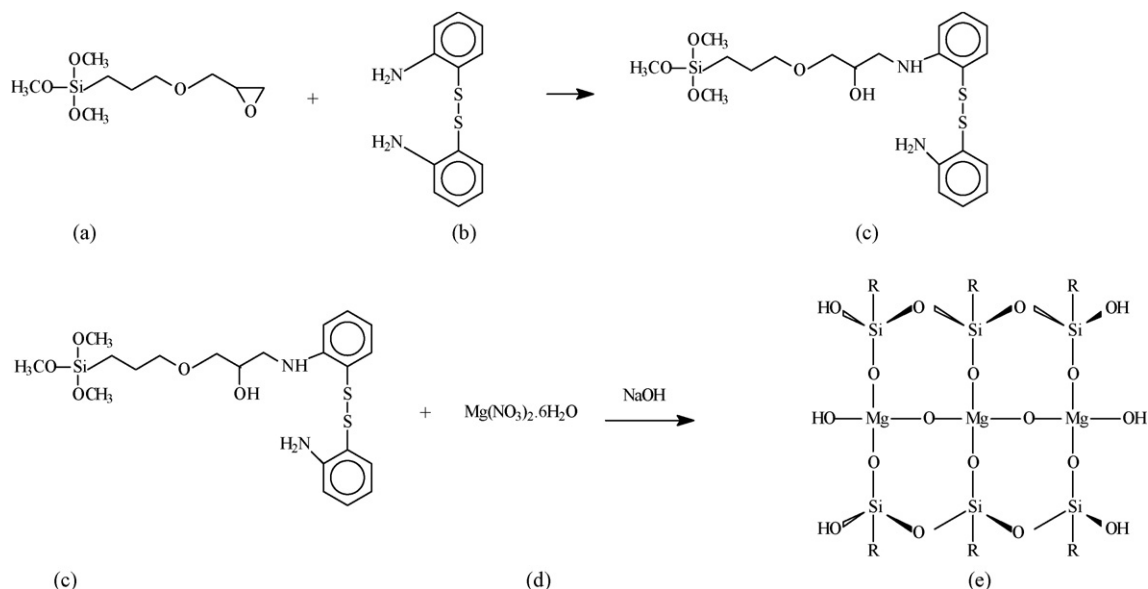
Fig. 1. Reaction of 3-glycidoxypropyltrimethoxysilane (a) with 2-aminophenyldisulfide (b) to yield the new silylating agent (c), and its reaction with magnesium nitrate (d) to yield the new magnesium organosilicate (e), R being the silylating agent attached to the inorganic backbone in interlayer space.

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 alkoxysilane, 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-expandable 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 tetrahedrically 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 cm^3 of dry ethanol, then 4.4 cm^3 (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 cm^3 of ethanol [22]. Approximately, 60 cm^3 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(radiation at 40 kV and 30 mA.

^{29}Si 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 cm^3 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

carefully pipetted and the amounts of metallic cation remaining in solution were determined by ICP-OES, by the wavenumbers 327.4; 220.4 and 228.80 nm for copper, lead and cadmium, respectively. A great importance and advantage of this analytical method is the acquisition of data without any reagent addition and minimum sample handing. The obtained data for these systems were fitted using Langmuir and Freundlich models.

3. Results and discussion

3.1. Synthetic features

The new silylating agent was synthesized by reacting 3-glycidoxypropyltrimethoxysilane (a) with aminophenyldisulfide (b), whose basic nitrogen atom has the ability to open the epoxide group, as previously observed for other amine molecules [10]. This freshly prepared agent reacted with magnesium nitrate (d), in basic conditions, to yield the new, well-structured magnesium organosilicate (e), as shown in Fig. 1.

3.2. Magnesium organosilicate characterization

Elemental analysis results for the synthesized magnesium organosilicate containing 2-aminophenyldisulfide gave 44.9, 5.0 and 5.7% for carbon, hydrogen and nitrogen, respectively. The degree of organofunctionalization 1.97 mmol g^{-1} in this nanocompound was calculated based on the nitrogen content.

The X-ray powder diffraction patterns illustrated in Fig. 2, for the new magnesium organosilicate, showed that the nanocompound has lower crystallinity compared with other phyllosilicates containing mercapto or amine groups [18,23]. This fact can be attributed by the organic chain inside interlayer space leading to a disordered inorganic framework or a turbostratic arrangement of stacked crystalline plates, or both [24]. The diffractogram exhibited a low intensity basal peak at 2θ equal to 9.4°, associated with interlayer spacing of 1044 pm.

Infrared spectroscopy is a simple and useful technique to confirm the integrity of organic functional groups and retention of the Si—C bond under synthetic conditions [24]. Characteristic absorptions from the organic functional groups and the inorganic framework are observed in the FTIR spectrum shown in Fig. 3, on which the attributed bands are indicated. The presence of the silylating agent covalently bonded in the interlayer space is clearly confirmed by the vibrations associated with the organic moieties, as illustrated by the appearance of new bands assigned to C—H
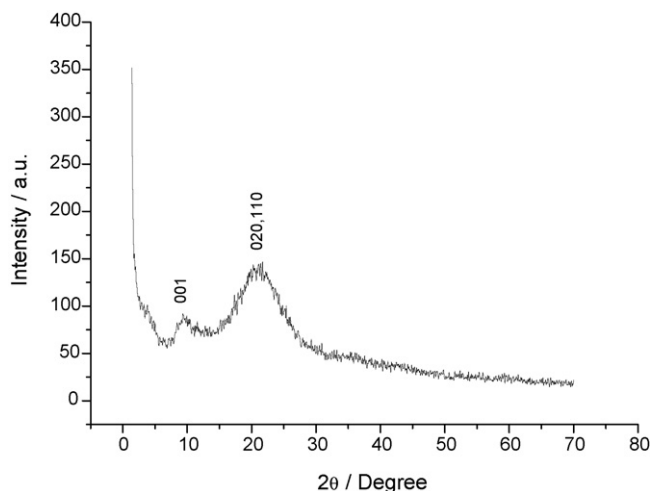

Fig. 3. Infrared spectrum of the new organosilicate.

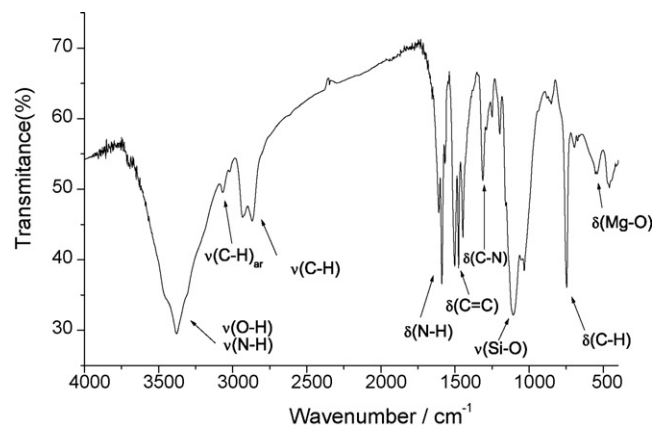stretching at 3050 cm^{-1} (ν-CH$_{ar}$), 2920 cm^{-1} (ν_s-CH$_2$), 2850 cm^{-1} (ν_a-CH$_2$) and also bending at 757 cm^{-1} that is characteristic to 1,2-disubstituted aromatic ring system [25]. In addition, the bending vibration for aromatic carbon–carbon double bond is located in the 1570–1440 cm^{-1} range. Other important vibrations are related to N—H bond, which stretching is part of the strong band with the maximum at 3370 cm^{-1} includes also the O—H bond from free silanol or water bonded to the inorganic structure, however, the bending appeared as sharp defined bands at 1608 and 1589 cm^{-1}. C—N and Si—C vibration bending [26] are sited at 1311 and 1200 cm^{-1}, respectively. The inorganic framework showed also the characteristic bands [27] attributed to the stretching ν(Si—O—Si) at 1024 cm^{-1} and the bending δ(Mg—O) at 550 cm^{-1}.

^{29}Si CP/MAS NMR spectroscopy in the solid state provides significant information about the different silicon species that constitute the structure formed, as well as the degree of condensation between the silicate sheets in the structure of the hybrid. The signals in −48, −56 and −67 ppm, shown in Fig. 4, are attributed to the organic silicon species T^1, T^2 and T^3, respectively [T^n=RSi(OM)(OSi)$_{n-1}$(OH)$_{3-n}$], derived from the trifunctional alkoxysilane used for the synthesis of the magnesium organosilicate. The superscript numbers are related to the number of siloxane bonds (≡Si—O), while R represents the organic moiety bonded to the silicon atom by the Si—C bond and M is related to the Mg^{2+} ion octahedrally coordinated in the structure of the organoclay. Com-
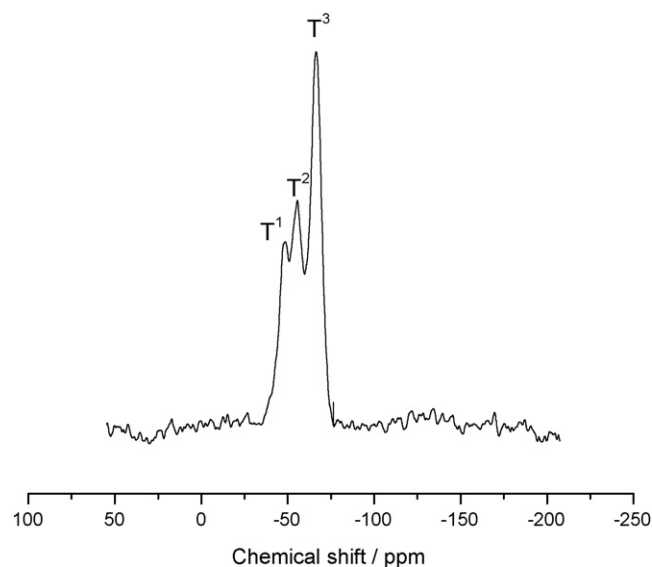

Fig. 2. X-ray diffraction pattern of the new organosilicate.

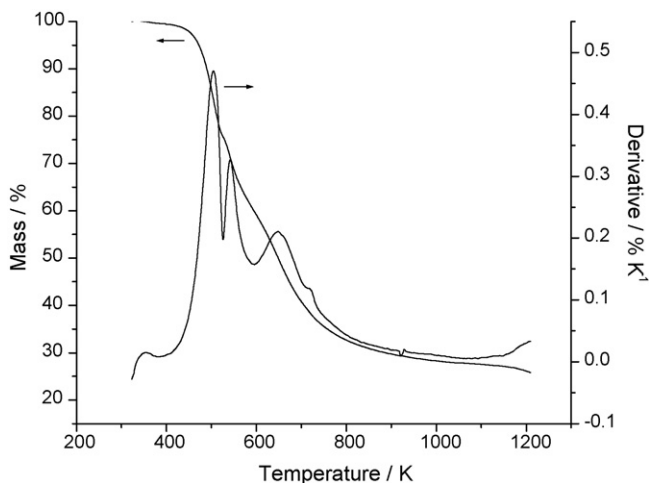**Fig. 4.** ^{29}Si CP/MAS NMR spectra of new magnesium organosilicate.

Fig. 5. Thermogravimetric curve for the new organosilicate.

paring the intensity of the peaks it is possible to conclude that the relative intensity for the T^3 species is higher than for the T^1 and T^2 species, suggesting a good degree of condensation and consequently, a lower number of defects in the hybrid structure [24].

The thermal stability of this new nanomaterial was evaluated by the thermogravimetric curve, whose decomposition process is represented in Fig. 5. The outlined curve apparently shows that the decomposition takes place in only one step with small shoulders. However, the actual stages are more clearly demonstrated through the derivative curve in the 323–1200 K interval. Thus, a small peak at low temperature could be related to the displacement of water bonded to the inorganic layer on heating. The three major peaks observed can be associated with the loss of organic moieties present inside the interlayer space. As the decomposition reached 469 K, before any significant mass loss occurred, which behavior indicates that this compound is stable up to this temperature.

3.3. Adsorption isotherms

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution at the solid/liquid interface determines the adsorption isotherm [28]. The Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the adsorption of components at the solid/liquid interface. The Langmuir model assumes a monolayer adsorption, while the Freundlich model is empirical in nature [29,30]. So, in order to investigate the sorption capacity of the new magnesium organosilicate, these equilibrium models were fitted to the experimental data, using the correlation coefficients, R^2, to compare the applicability of the isotherm equations.

3.3.1. Langmuir model

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface [31]. The corresponding isotherm model suggests that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between the sorbed molecules. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [32], by transposing into a linearized form [10], before adjusting the experimental data in the original equation:

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{(N_s b)}$$

N_f is equilibrium adsorption capacity (mmol g^{-1}), C_s the concentration of the divalent cations in the solution at equilibrium (mmol dm^{-3}), N_s the adsorption capacity at saturation (mmol g^{-1}) and b is the adsorption coefficient (dm^3 mmol^{-1}) related to the energy of adsorption. A linear plot of (C_s/N_f) against C_s was employed to give the values of N_s and b from the slope and intercept of the plot.

3.3.2. Freundlich model

The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation:

$$N_f = K_F C_s^{1/n}$$

N_f and C_s were defined previously, K_F is Freundlich constant (dm^3 g^{-1}), and $1/n$ is the heterogeneity factor. The constant K_F and the n affinity constants are empirical in nature and depend on several environmental factors [33]. The Freundlich equation can be linearized by taking logarithms to find the parameters K_F and n, as represented by:

$$\log N_f = \log K_F + \left(\frac{1}{n}\right) \log C_s$$

The isotherms of adsorption of divalent cations on synthesized magnesium organosilicate presented as a function of the equilibrium concentration of metal ions in the aqueous medium, as shown in Fig. 6, outlined similar shapes for copper and lead. These isotherms can be classified to the proposed theoretical adsorption, as previously established [34], indicating a fit to S2 and H4 models, respectively. On the contrary, the shape of cadmium isotherm was not adjusted to any proposed model. From these isotherms the maximum adsorption capacities obtained were 2.72, 1.27 and 0.38 mmol g^{-1}, for copper, lead and cadmium, respectively.

The distinguishable intensities in adsorption can be interpreted by considering the hardness and softness of the acidic and basicity of the atoms involved in the complexation process. Thus, the pendant chains contain both the borderline aromatic amine and soft disulfide atoms available to interact with the borderline copper and lead, and the soft cadmium cations [35]. As expected, the equivalence in behavior gives to the nitrogen basic center better adsorption for the borderline couple, while cadmium should be bonded to sulfur basic centers. Nevertheless, the low cadmium
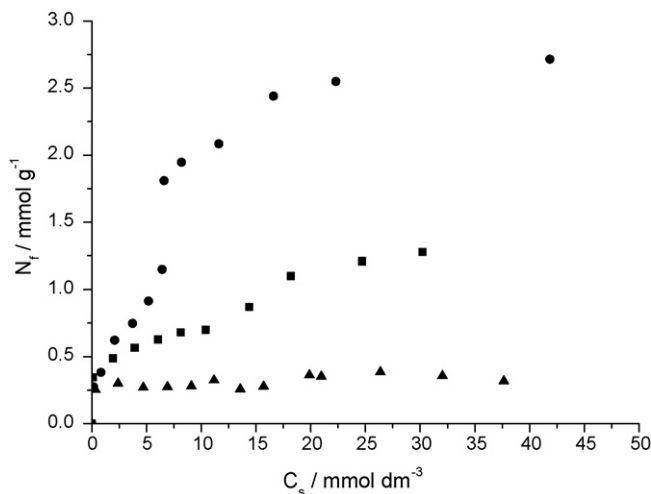

Fig. 6. Adsorption isotherms of divalent metals Cu^{2+}(●), Pb^{2+}(■) and Cd^{2+} (▲).

Table 1

Adsorption of divalent cations (M^{2+}) on magnesium organosilicate fitted by Langmuir and Freundlich models, related to equilibrium adsorption capacity (N_f), adsorption capacity at saturation (N_s), the constants b, n, K_F and the correlation coefficient (R^2)

M^{2+}	Langmuir				Freundlich		
	N_f (mmol g^{-1})	N_s (mmol g^{-1})	b (dm^3 mmol^{-1})	R^2	K_F (dm^3 g^{-1})	n	R^2
Cu	2.72	3.28	0.128	0.960	0.522	2.0	0.955
Pb	1.27	1.42	0.168	0.953	0.484	4.4	0.917
Cd	0.38	0.35	0.697	0.983	0.259	14.0	0.644

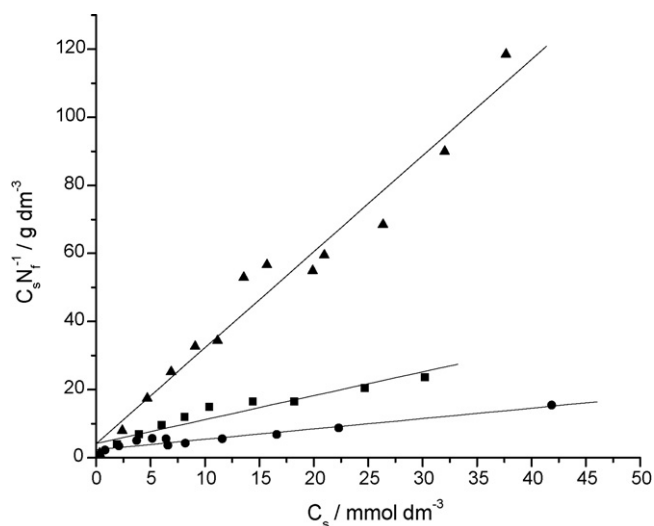Fig. 7. Langmuir isotherms of divalent metals Cu^{2+}(●), Pb^{2+}(■) and Cd^{2+} (▲).
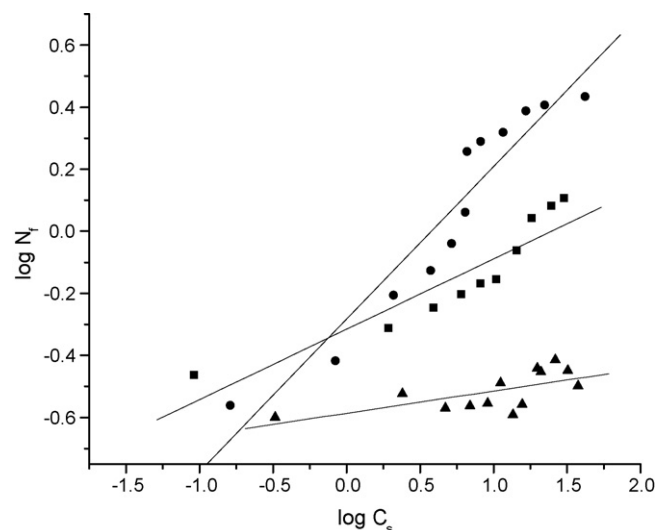

Fig. 8. Freundlich isotherms of divalent metals Cu^{2+}(●), Pb^{2+}(■) and Cd^{2+} (▲).

adsorption suggested that the disulfide group in this molecular arrangement is not so available for bonding this cation.

Langmuir and Freundlich models were applied to fit the experimental data. The results are shown in Figs. 7 and 8, respectively. The Langmuir and Freundlich parameters were calculated from the slope and intercept of the graphical representation, and the results are listed in Table 1. The fit to the linear form of the models was examined by calculating the coefficient of linearity (R^2). For copper and lead both models describe adsorption successfully according to linearity coefficients ($R^2 = 0.917$–0.960), while the R^2 values for

the Langmuir model was slightly better than that obtained for Freundlich model. For cadmium only the Langmuir model fit the data, according to the R^2 value. Considering that the new organosilicate contains different basic sulfur and nitrogen centers, the sorption of metal ions by the material occurs on a heterogeneous surface, so in this case it was expected that the Freundlich model would better fit the data than Langmuir. However, the results demonstrated the opposite. One possible explanation for this behavior is the presence of different basic centers that allows the metal ion to coordinate at various basic centers on the adsorbent, as proposed in Fig. 9.
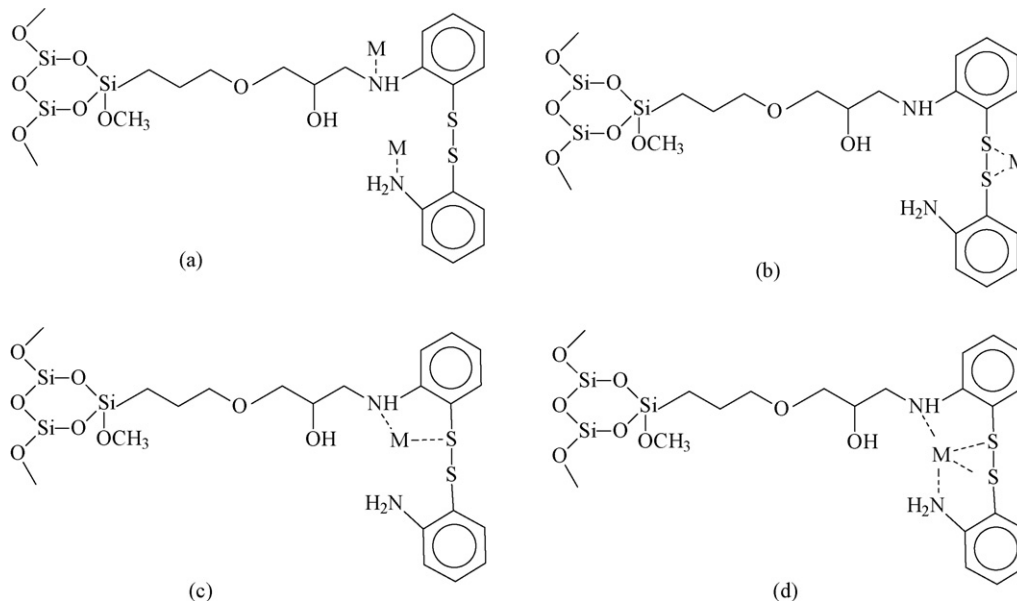

Fig. 9. The proposed divalent metal (M) interactions with different basic centers in the new magnesium organosilicate.

Table 2
Comparison of the maximum adsorption capacity (N_s) for divalent cations (M^{2+}) for new magnesium organosilicate and other adsorbents

M^{2+}	Adsorbent	N_s (mmol g^{-1})	References
Cu^{2+}	Aniline grafted silica gel	0.15	[36]
	Banana peel	0.09	[37]
	Ponkan peel	1.31	[38]
	Mesoporous silica modified with ethylenediamine	1.4	[39]
	Silica modified with 2-aminomethylpyridine	0.84	[40]
	Magnesium phyllosilicate modified with 3-Mercaptopropyltrimethoxysilane	4.31	[5]
	Talc modified with 3-aminopropyltrimetoxisilane	2.2	[41]
	Chitosan	0.38	[42]
	Magnesium phyllosilicate modified with 2-aminophenyldisufide	3.28	This work
Pb^{2+}	*Rhizopus nigricans*	0.80	[43]
	Activated phosphate	0.75	[44]
	Natural phosphate	0.56	[44]
	Zeolite	0.34	[45]
	Modified rice husk	0.52	[46]
	Chitosan membranes	0.33	[47]
	Magnesium phyllosilicate modified with 2-aminophenyldisufide	1.42	This work
Cd^{2+}	Activated carbon	0.075	[48]
	Chitosan functionalized with 2[-bis(pyridylme-thyl)aminomethyl]-4-methyl-6-formylphenol	0.34	[49]
	Leonardite	0.45	[50]
	Magnesium phyllosilicate modified with 2-aminophenyldisufide	0.35	This work

From this scheme, any of those metals can coordinate by using only nitrogen (a) or sulfur (b), or both (c and d). However, as mentioned before, the adsorption is governed by the hardness and softness properties, and also the availability of the amine groups favors the reaction in comparison to disulfide group, suggesting that structure (a) is the most probable in the present case.

The adsorption capacities of some adsorbents and magnesium organosilicate synthesized for divalent cation removal are given in Table 2, comparing the available results, and the present data for this new nanomaterial, whose maximum adsorption capacity reached 3.28, 1.42 and 0.35 mmol g^{-1} for copper, lead and cadmium, respectively. With the exception of other phyllosilicates containing meracapto groups attached to the inorganic backbone [5], for copper and lead, the present results are higher in comparison to other adsorbents, including some natural and modified polymeric materials, however, for cadmium the results obtained are of the same order of magnitude as those found for other polymeric organic and inorganic adsorbents. Thus, the new magnesium organosilicate synthesized by the sol–gel process under mild condition is revealed as a favorable inorganic–organic hybrid, with high potential for use as an adsorbent for cation removal from aqueous solutions using the solid/liquid interface.

4. Conclusion

A layered inorganic–organic magnesium organosilicate containing 2-aminophenyldisulfide was successfully synthesized from a single step sol–gel template route under mild conditions, by firstly synthesizing a specific silylating agent. The new nanomaterial showed a high degree of functionalization, 1.97 mmol g^{-1}, by attaching simultaneously different nitrogen and sulfur basic centers, a property that enabled the exploitation of the adsorption capacity of this hybrid material for cation removal from a simulated polluted aqueous effluent system.

The available basic centers attached to the pendant chains covalently bonded to the organosilicate structure adsorb copper, lead and cadmium cations, in the order Cu^{2+} > Pb^{2+} > Cd^{2+}, which experimental data were fitted to Langmuir and Freundlich models, with success for copper and lead, but cadmium only the first model was appropriated. Taking into account that all data are best fit to Langmuir procedure, this behavior suggested an existence of a surface containing only one kind of basic center, in agreement with the low accessibility of disulfide group in binding cations, resulting in a low adsorption for soft cadmium.

This new self-assembled nanomaterial has the ability to adsorb cations at a level comparable with those considerable to have high effectiveness at the solid/liquid interface. Thus, the adsorption capacity confers to this hybrid a property be applied as a promising nanomaterial for cation removal from a polluted ecosystem.

Acknowledgements

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