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## Magnesium silicate conjugated with calcium lignosulfonate: In situ synthesis and comprehensive physicochemical evaluations

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**Abstract:** The aim of this study was to effectively combine synthetic magnesium silicate with the lignin-derived biopolymer calcium lignosulfonate, using the *in situ* sol-gel route. Magnesium ethoxide and tetraethoxysilane were used as precursors of MgO and SiO<sub>2</sub>. The synthesis was carried out in alcoholic solution with the addition of ammonia solution as a promoter of hydrolysis. Calcium lignosulfonate was introduced to the reaction medium prior to the synthesis of magnesium silicate. The resulting hybrid powder material was thoroughly characterized, including morphology and particle sizes (SEM microscopy and the DLS technique), porous structure parameters (the BET method and BJH model), thermal stability (TG analysis) and electrokinetic stability (LDV measurements). FTIR spectral analysis was carried out to confirm the effectiveness of the proposed synthesis methodology. Based on the results, a mechanism is proposed for the MgSiO<sub>3</sub>/lignosulfonate interactions. The resulting novel type of hybrid material combines the multifunctional nature of the biopolymer (diversity of functional groups) with the well-developed porous structure of synthetic magnesium silicate. Its physicochemical parameters were found to depend significantly on the quantity of lignosulfonate used in the synthesis.

**Keywords:** synthetic magnesium silicate, biopolymers, calcium lignosulfonate, in situ sol-gel route, hybrid materials

### 1. Introduction

Materials of biological origin have recently been attracting increasing interest at many leading scientific centers worldwide. Reasons for this include their availability and costs of acquisition, but most importantly the unique physicochemical properties that they offer. These properties result from the chemical structure of the materials, including the diversity of functional groups that can easily react with numerous organic as well as inorganic compounds. There are many reports concerning the combination of biopolymers with substances such as inorganic oxides, which leads to the formation of multifunctional hybrid materials with wide-ranging applications (Ciesielczyk et al., 2014; Ciesielczyk et al., 2017; Klapiszewski et al., 2015a; Kolodynska et al., 2016; Pandey and Shahi, 2013; Patel et al., 2013; Rangelova et al., 2014). Commonly known biopolymers used for this purpose include lignin and cellulose, as well as chitin and its derivative, chitosan. The idea of the conjugation of biopolymers with mineral substances is to obtain hybrid materials that will exhibit novel and unique properties as a result of the combination of the physicochemical parameters of each separate component. Due to the numerous different functional groups in their structure, most of the materials of natural origin exhibit relatively high activity, but have limited porous structure in most cases – for example, the surface area of the aforementioned biopolymers is around 1–2 m<sup>2</sup>/g (Ciesielczyk et al., 2014; Klapiszewski et al., 2015b). On the other hand, there are many mineral substances that can be easily synthesized via various chemical methods (precipitation, the sol-gel route, hydro- or solvothermal methods, microwave-

assisted sol-gel method, etc.) to obtain synthetic materials, mostly with defined porous structure parameters (Cui and Sun, 2015; Qu and Tian, 2010; Zhang and Zhao, 2013). Thus, the multifunctionality of a biopolymer may be complemented with the porosity of synthetic inorganic materials. A similar situation exists with regard to the thermal stability of synthetic oxides (high stability) and biopolymers (low stability) (Bula et al., 2015; Klapiszewski et al., 2016). Such hybrid materials can be synthesized both by chemical methods (*in situ* or direct) (Klapiszewski et al., 2015a; Klapiszewski et al., 2015b) and by mechanical methods (Bula et al., 2015; Klapiszewski et al., 2016). The selection of a method of synthesis is mostly determined by the type of the biopolymer and the synthetic mineral, and their form. The preparation of a specific synthetic mineral is also a very important step, because the selection of a methodology for its synthesis affects its porosity and reactivity, which are responsible for its combination with other compounds such as biopolymers (Ciesielczyk et al., 2014; Jesionowski and Krysztafkiewicz, 2000; Portugal et al., 2010; Singh et al., 2010; Siwinska-Stefanska et al., 2012).

Such multifunctional combinations may find applications as, for example, selective biosorbents of selected organic/inorganic impurities present in water systems, relatively cheap polymer fillers, or electrode materials. There are reports (Ciesielczyk et al., 2014; Ciesielczyk et al., 2017) concerning the combination of lignin with synthetic magnesium silicate, synthesized via a typical precipitation method or the sol-gel route (giving a surface area of 700 m<sup>2</sup>/g), which resulted in hybrid materials with unique properties, mostly determined by the quantity of biopolymer used in the synthesis. The physicochemical properties of such hybrid materials have been verified in the process of removal of ions such as copper(II) and cadmium(II) from model and real waste waters (Ciesielczyk et al., 2014; Ciesielczyk et al., 2017). The adsorption process was very effective, providing direct justification for the idea of producing such hybrid biosorbents.

Moreover, the great availability of biopolymers and their biological nature, in combination with silica, for instance, enable the production of excellent polymer fillers (Bula et al., 2015; Klapiszewski et al., 2016), electrode materials or biosensors (Jesionowski et al., 2014), designed with unique physicochemical properties (increased thermal stability, porosity and functionality) and – more importantly – produced at low cost. The specific applications of biopolymer-based materials result from their physicochemical properties, which in most cases are determined by the quantity of biopolymer used for their synthesis (Klapiszewski et al., 2013; Witoon et al., 2009; Xiong and Yang, 2015; Yu and He, 2016).

The goal of the present study was to synthesize and comprehensively analyze a hybrid material of MgSiO<sub>3</sub>/lignosulfonate type, a topic that is not addressed in existing publications. The novelty of the research concerns not only the material itself, but also the methodology used for its preparation – the *in situ* sol-gel route. The experimental results show that the proposed synthesis route leads to a hybrid material with enhanced multifunctional properties as compared with each component separately (magnesium silicate and calcium lignosulfonate).

## 2. Experimental

### 2.1 Synthesis of MgSiO<sub>3</sub>/calcium lignosulfonate hybrid material

Synthesis of a hybrid material of MgSiO<sub>3</sub>/lignosulfonate type was performed via an *in situ* sol-gel route, using organic precursors of magnesium silicate, methyl alcohol as a solvent, and ammonia as a promoter of hydrolysis (see Fig. 1). Firstly 7.5 g of magnesium ethoxide was dissolved in 250 cm<sup>3</sup> of solvent, in a 500 cm<sup>3</sup> conical flask. The mixture was stirred for 30 min at room temperature. After this time a controlled quantity (10 or 20 wt./wt.) of biopolymer was slowly added, followed by another 30 min of stirring. The key stage was the parallel introduction of 8.5 cm<sup>3</sup> of 25% ammonia solution and 34 cm<sup>3</sup> of tetraethoxysilane solution, which enabled the formation of a gel. The whole reaction medium was continuously stirred for 1 h. Finally, the mixture was placed in a special flask for ageing, which lasted for 24 h. The gel was then dried at 105 °C for 24 h. After this stage the product was washed several times with hot distilled water to remove residual reagents, and once again dried in the same conditions. The prepared raw magnesium silicate (sample MS) and hybrid materials containing 10 wt./wt. (sample MS\_10CLS) and 20 wt./wt. (sample MS\_20CLS) of biopolymer were classified in a mortar and then using a sieve (80 μm), and underwent comprehensive analysis. A sample of calcium lignosulfonate (sample CLS) was used as a reference. Fig. 2 shows the structure of the biopolymer.

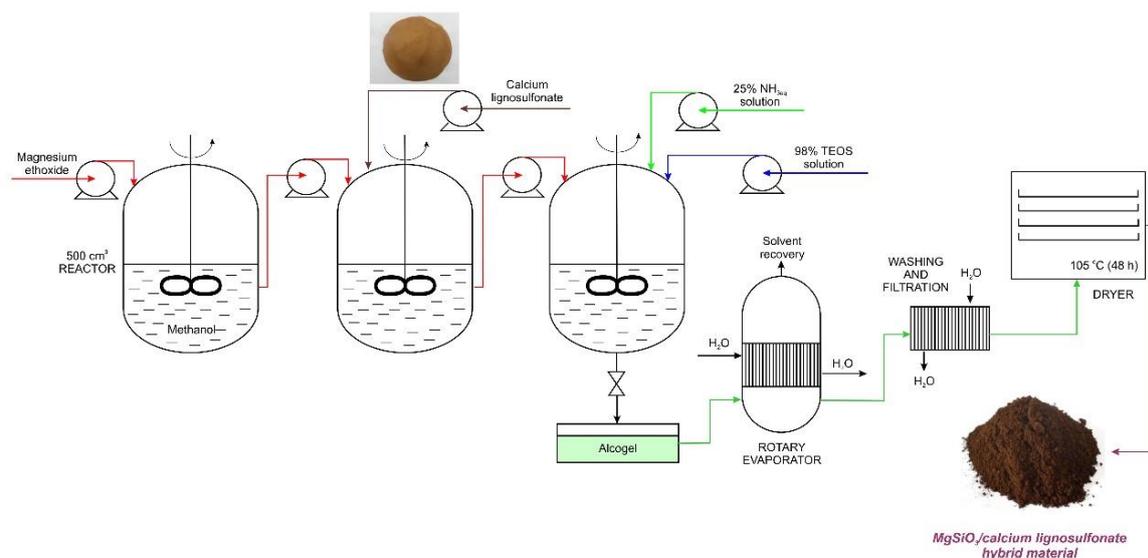


Fig. 1. *In situ* sol-gel synthesis of  $\text{MgSiO}_3$ /lignosulfonate hybrid material

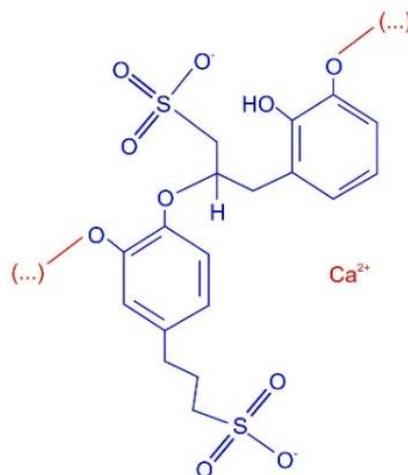


Fig. 2. Structure of calcium lignosulfonate

## 2.2 Physicochemical analysis

The comprehensive physicochemical analysis of the prepared hybrid materials included evaluation of morphology and particle sizes (SEM microscopy and the DLS technique), porous structure parameters (the BET method and BJH model), thermal stability (TG analysis) and electrokinetic stability (LDV measurements). FTIR spectral analysis was performed to confirm the effectiveness of the proposed methodology of synthesis.

First, the morphology (SEM) and dispersive characteristics (DLS) of the synthesized  $\text{MgSiO}_3$ /lignosulfonate hybrids were evaluated. The observations enabled evaluation of the degree of dispersion, the structure of particles and their tendency towards aggregation or agglomeration. SEM images were recorded from an EVO40 scanning electron microscope (Zeiss). Before testing, the samples were coated with Au for a time of 20 seconds using a Balzers PV205P coater. Particle size distributions were determined using a Mastersizer 2000 (Malvern Instruments Ltd.), which enables measurements of particle diameters in the range 0.02–2000  $\mu\text{m}$ . The measurements were performed using a wet unit (Hydro 2000G) in which an appropriate quantity of powder material was dispersed in a water medium. After establishing the instrument background, appropriate measurements were performed. The  $A_{\text{BET}}$  surface area (BET method) as well as pore size distribution (BJH method) were obtained based on measurement data from low-temperature ( $-196^\circ\text{C}$ ) adsorption of nitrogen. The nitrogen

adsorption/desorption isotherms were recorded using an ASAP 2020 apparatus (Micromeritics Instrument Co.). Before the measurements, samples were degassed under low pressure for 4 h at 120°C. In addition, a thermogravimetric analyzer (Jupiter STA 449F3, Netzsch) was used to investigate the thermal stability of the analyzed samples. Measurements were carried out under nitrogen flow ( $10 \text{ cm}^3 \cdot \text{min}^{-1}$ ) at a heating rate of  $10^\circ\text{C} \cdot \text{min}^{-1}$  over a temperature range of 30–1000°C, with an initial sample weight of approximately 5 mg. Additionally, to evaluate the surface charge of the synthetic hybrid materials, the zeta potential was determined as a function of pH. Electrokinetic tests were performed in 0.001 M NaCl electrolyte using a Zetasizer Nano ZS instrument (Malvern Instruments Ltd.) equipped with an MPT-2 automatic titration system. FTIR spectra were obtained using a Vertex 70 spectrometer (Bruker). The samples were analyzed in the form of tablets, made by pressing a mixture of anhydrous KBr (ca. 0.25 g) and 1 mg of the tested substance in a special steel ring, under a pressure of 10 MPa. Analysis was performed over a wavenumber range of 4000–400  $\text{cm}^{-1}$  (resolution 0.5  $\text{cm}^{-1}$ ; number of scans: 64).

### 3. Result and discussion

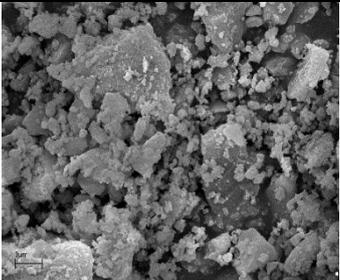
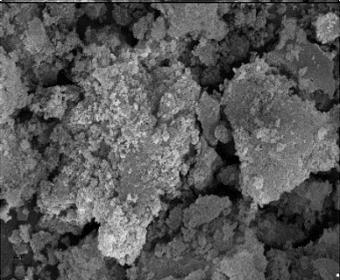
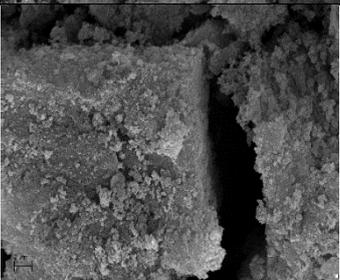
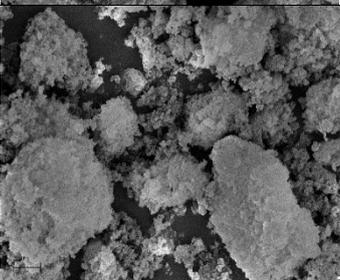
#### 3.1 Morphology and particle sizes

The first stage of physicochemical analysis included evaluations of the morphology and dispersive parameters of the obtained hybrid materials (Table 1). Sol-gel synthesis of  $\text{MgSiO}_3$  powder led to a material characterized by micrometric-sized and irregularly shaped particles. The mean particle diameter of the MS sample was 12.6  $\mu\text{m}$ . Slightly larger particles were observed in the CLS (calcium lignosulfonate) sample, for which the particle diameter range was 5.4–46.7  $\mu\text{m}$  with a mean of 18.7  $\mu\text{m}$ . Combination of the synthetic magnesium silicate with calcium lignosulfonate led to hybrids with significantly changed morphology. The particle sizes increased with an increase in the quantity of biopolymer used in the synthesis. The addition of 10 wt./wt. (sample MS\_10CLS) or 20 wt./wt. (sample MS\_20CLS) of lignosulfonate results in higher values of the mean particle diameter as compared with raw magnesium silicate (15.9  $\mu\text{m}$  and 17.8  $\mu\text{m}$  respectively). Moreover, a greater tendency to form agglomerates was observed in the case of the hybrid materials. All samples were found to have similarly shaped particles and fairly similar morphology (see SEM images, Table 1), which confirms the suitability of the proposed synthesis route. The results are in agreement with previous reports referring to the influence of the quantity of biopolymer used for the synthesis of similar materials on particle sizes and the tendency to form larger aggregates (Klapiszewski et al., 2013).

#### 3.2 Parameters of the porous structure

Fig. 3 shows adsorption/desorption isotherms for the obtained materials. There were significant differences in the quantity of adsorbed nitrogen, and thus in the surface areas of the analyzed samples. The largest surface area was found in the case of raw magnesium silicate powder ( $A_{\text{BET}}=682 \text{ m}^2/\text{g}$ ). This sample also had a pore volume of  $1.12 \text{ cm}^3/\text{g}$  and a pore size of 6.2 nm (Fig. 3a). On the other hand, limited porosity ( $A_{\text{BET}}=0.92 \text{ m}^2/\text{g}$ ,  $V_p=0.0008 \text{ cm}^3/\text{g}$  and  $S_p=29.6 \text{ nm}$ ), indicated by the smallest quantity of adsorbed nitrogen, was observed in the case of the calcium lignosulfonate sample (Fig. 3a). It is notable that the CLS sample had pores with relatively large diameter, but very low volume. For this reason, its combination with synthetic magnesium silicate can be expected in particular to result in increased surface area. The isotherms obtained for the  $\text{MgSiO}_3$ /lignosulfonate hybrids are of similar type (Fig. 3b), indicating that all of the analyzed materials can be classified as mesoporous (type IV isotherms with no visible hysteresis loop). The samples MS\_10CLS and MS\_20CLS differed in terms of the quantity of adsorbed nitrogen. When a larger quantity of biopolymer was used to prepare the hybrid material, less nitrogen was adsorbed, indicating a smaller surface area. The same applies to the pore volume and pore diameter. The synthesis of a hybrid material using 10 wt./wt. of lignosulfonate results in a surface area of  $281 \text{ m}^2/\text{g}$ , while the use of 20 wt./wt. of lignosulfonate gives  $A_{\text{BET}}=115 \text{ m}^2/\text{g}$ . These values are intermediate between those recorded for raw magnesium silicate and lignosulfonate. This fact provides indirect confirmation of the assumptions underlying the synthesis method and demonstrates the significant influence of the quantity of biopolymer on the physicochemical properties of the resulting materials.

Table 1. Particle sizes and morphology of synthesized MgSiO<sub>3</sub>/lignosulfonate hybrids

| Sample symbol | Particles size range (μm) | Mean particle diameter (μm) | SEM image (scale 3 μm)   |
|---------------|---------------------------|-----------------------------|--|
| MS            | 3.2-31.6                  | 12.6                        |    |
| CLS           | 5.4-46.7                  | 18.7                        |    |
| MS_10CLS      | 4.1-38.9                  | 15.9                        |   |
| MS_20CLS      | 4.7-44.3                  | 17.8                        |  |

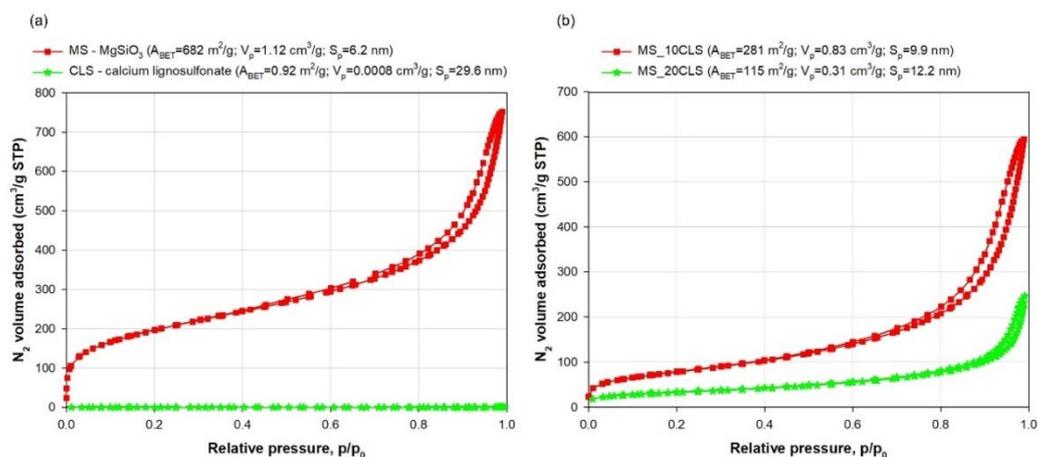


Fig. 3. Adsorption/desorption isotherms of initial reagents (a) and synthesized hybrid materials (b)

### 3.3 Thermal and electrokinetic stability evaluations

The next stage of physicochemical analysis concerned the thermal stability of the initial reagents and the synthesized hybrid materials. Calcium lignosulfonate has low thermal stability, as confirmed by a total 64% weight loss when it is heated up to 1000°C (Fig. 4a). The first weight loss (of 10%) was recorded in the temperature range 25–200 °C, resulting from the elimination of water physically bound in the biopolymer structure. The second weight loss (49%) relates to the degradation of bonds in the lignosulfonate structure due to thermal treatment, as well as further elimination of water constitutionally bound to the biopolymer, in the range 200–400 °C. The entire second degradation stage covered a temperature range of 200–600 °C. Heat treatment above 600 °C results in the partial elimination of fragments of lignosulfonate containing carbon (a weight loss of 5%). The fragmentation process of the lignosulfonate molecule takes place via unknown reactions; however, it is assumed that the later weight loss is related to a partial degradation of the biopolymer structure. Significant better thermal stability was exhibited by the synthetic magnesium silicate sample (Fig. 4a). This is a direct result of the method of synthesis, using the sol-gel route. The total weight loss for this sample was measured as 22% (in the temperature range 25–1000 °C) and mostly resulted from the elimination of water molecules physically and constitutionally bound to the  $\text{MgSiO}_3$  structure. Compared with the initial biopolymer sample, the hybrid materials displayed improved thermal stability (Fig. 4b). Very similar thermograms were obtained for both samples of  $\text{MgSiO}_3$ /lignosulfonate hybrids. Three degradation steps are observed – the first and second, in temperature ranges of 25–200 °C and 200–500 °C respectively, result from the elimination of water molecules present in the structure, while the third, in the temperature range 600–1000 °C, is related to a partial degradation of the biopolymer structure. Importantly, the thermal stability of the obtained materials is strongly dependent on the quantity of biopolymer used in their synthesis. The higher the content of lignosulfonate in the hybrid structure, the lower the thermal stability. This is confirmed by the total percentage weight loss, which was 29% and 37% for samples MS\_10CLS and MS\_20CLS respectively. These values are smaller than the total weight loss recorded for the initial biopolymer, which indirectly confirms the higher thermal stability of the hybrids. This is a very important property, considering the potential application of the synthesized materials as relatively cheap polymer fillers. Once again, the results obtained are in agreement with previous reports concerning the synthesis of different types of combinations of biopolymers and synthetic mineral supports (Bula et al., 2015; Ciesielczyk et al., 2014; Klapiszewski et al., 2016).

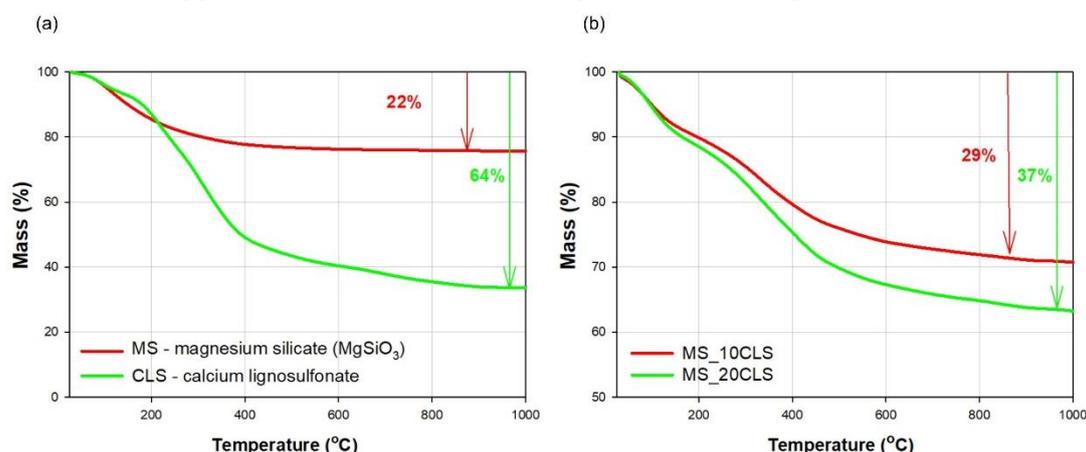


Fig. 4. Thermograms of initial reagents (a) and synthesized hybrid materials (b)

Analysis of the electrokinetic stability of the obtained hybrid materials makes it possible to calculate the pH values at which magnesium silicate/calcium lignosulfonate systems form a stable dispersion. This is very important for the potential application of the materials as (for instance) selective sorbents of inorganic or organic impurities present in wastewaters. The zeta potential values calculated for the initial materials (sol-gel-derived magnesium silicate and calcium lignosulfonate) differ from each other. Magnesium silicate has a negative zeta potential over the whole of the analyzed pH range, with the highest values of (-14) – (-19) mV in the pH range 5.5–10.3. The lowest values of zeta potential were

recorded at acidic pH, as a result of protonation of the surface hydroxyls of  $\text{MgSiO}_3$  with  $\text{H}^+$  and a change in the nature of the surface charge (Ciesielczyk et al., 2014). The pH values at which the zeta potential takes the highest negative or positive values are the region in which the analyzed material exhibits good stability in water systems—for the magnesium silicate sample this was observed at  $\text{pH}=9.5$ – $10.5$ . Relatively better electrokinetic stability was observed in the case of the lignosulfonate sample, which had zeta potential values of  $(-17)$ – $(-34)$  mV in the whole analyzed pH range. The nature of the electrokinetic curve is quite similar to that obtained for magnesium silicate, but the zeta potential takes larger negative values. The largest negative values of  $(-30)$ – $(-34)$  mV, and thus the best stability of dispersion, were recorded in the pH range 4–9, while the highest zeta potential ( $-14$  mV) occurred at  $\text{pH}=1.7$ . For both the magnesium silicate and the calcium lignosulfonate samples, the isoelectric point (the pH at which the zeta potential is zero) was not reached. Intermediate values of the zeta potential were recorded for the  $\text{MgSiO}_3$ /calcium lignosulfonate hybrid materials. The two hybrids have similar electrokinetic curves and exhibit relatively good stability, which results from combining the initial substrates. Slightly larger negative values of zeta potential were recorded for the hybrid material obtained with the use of 20 wt./wt. of biopolymer, as was to be expected based on the electrokinetic behavior of that polymer. Samples MS\_10CLS and MS\_20CLS took zeta potential values of  $(-9)$ – $(-16)$  mV and  $(-11)$ – $(-25)$  mV respectively. More importantly, both samples exhibited greater stability of zeta potential values in the analyzed pH range. These results are in agreement with previous reports (Ciesielczyk et al., 2013; Jesionowski et al., 2014; Klapiszewski et al., 2013) and provide indirect confirmation of the effective combination of magnesium silicate with lignosulfonate.

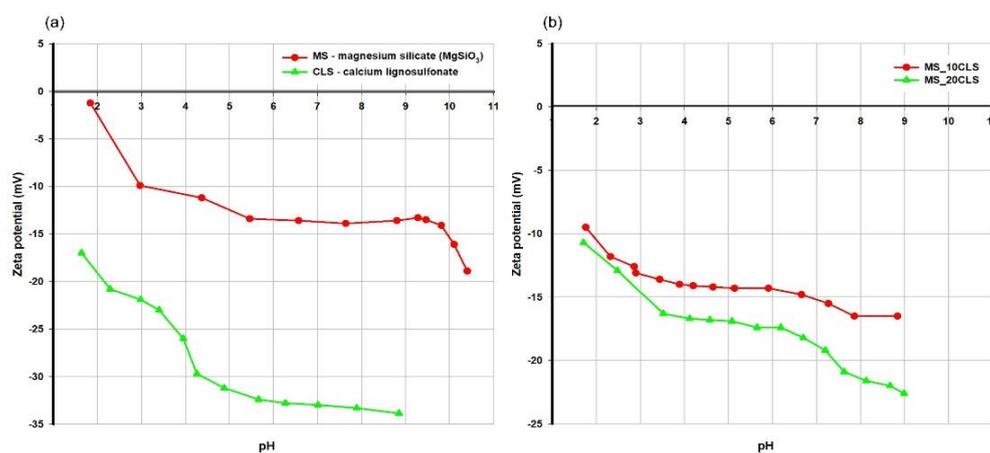


Fig. 5. Electrokinetic curves of initial reagents (a) and synthesized hybrid materials (b)

### 3.4 FTIR analysis and mechanism of interaction

FTIR analysis was carried out to confirm the effective bonding between magnesium silicate and calcium lignosulfonate. Fig. 6 presents the FTIR spectra of the initial reagents and the synthesized hybrid materials. The spectrum of the  $\text{MgSiO}_3$  sample (Fig. 6a) contains a wide band of high intensity generated by stretching vibrations of  $-\text{OH}$  groups ( $3600$ – $3200$   $\text{cm}^{-1}$ ) and a narrow, less intense band at  $1633$   $\text{cm}^{-1}$ , corresponding to water physically bound to the silicate. There are also two characteristic signals corresponding to stretching vibrations of  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  groups, with maxima at  $1090$   $\text{cm}^{-1}$  and  $950$   $\text{cm}^{-1}$ . An additional signal was observed at approximately  $700$   $\text{cm}^{-1}$ , generated by deformation vibrations of  $\text{O}-\text{Mg}-\text{O}$  bonds. The most important bands confirming the effective synthesis of magnesium silicate are those produced by deformation vibrations of  $\text{Si}-\text{O}-\text{Mg}$  bonds, observed at  $650$   $\text{cm}^{-1}$ . There is also a signal corresponding to stretching vibrations of  $\text{O}-\text{Si}-\text{O}$  bonds at  $530$   $\text{cm}^{-1}$ . The spectrum of calcium lignosulfonate (Fig. 6b) contains many bands produced by various functional groups, which is a result of the extremely complex chemical structure of the biopolymer. It includes signals generated by stretching vibrations of such groups as  $-\text{OH}$  ( $3500$ – $3400$   $\text{cm}^{-1}$ ),  $-\text{CH}_2$ ,  $-\text{CH}_3$  ( $2960$ – $2835$   $\text{cm}^{-1}$ ) and  $=\text{C}=\text{O}$  ( $1650$   $\text{cm}^{-1}$ ). There are also characteristic bands confirming the presence of aromatic rings, produced by stretching vibrations of  $\text{C}-\text{C}$  bonds, which appear at  $1600$   $\text{cm}^{-1}$ ,  $1510$   $\text{cm}^{-1}$ ,  $1420$   $\text{cm}^{-1}$  and  $650$   $\text{cm}^{-1}$ . The presence of aromatic structures is also confirmed by bands in the range  $960$ – $600$   $\text{cm}^{-1}$  generated by out-

of-plane vibrations of  $-C-H_{Ar}$  groups. Signals at  $1265\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  correspond to stretching vibrations of  $\equiv C-O-C\equiv$  and  $\equiv C-O-$  groups. The results are in agreement with those previously published (Klapiszewski et al., 2013; Klapiszewski et al., 2015a; Klapiszewski et al., 2015b).

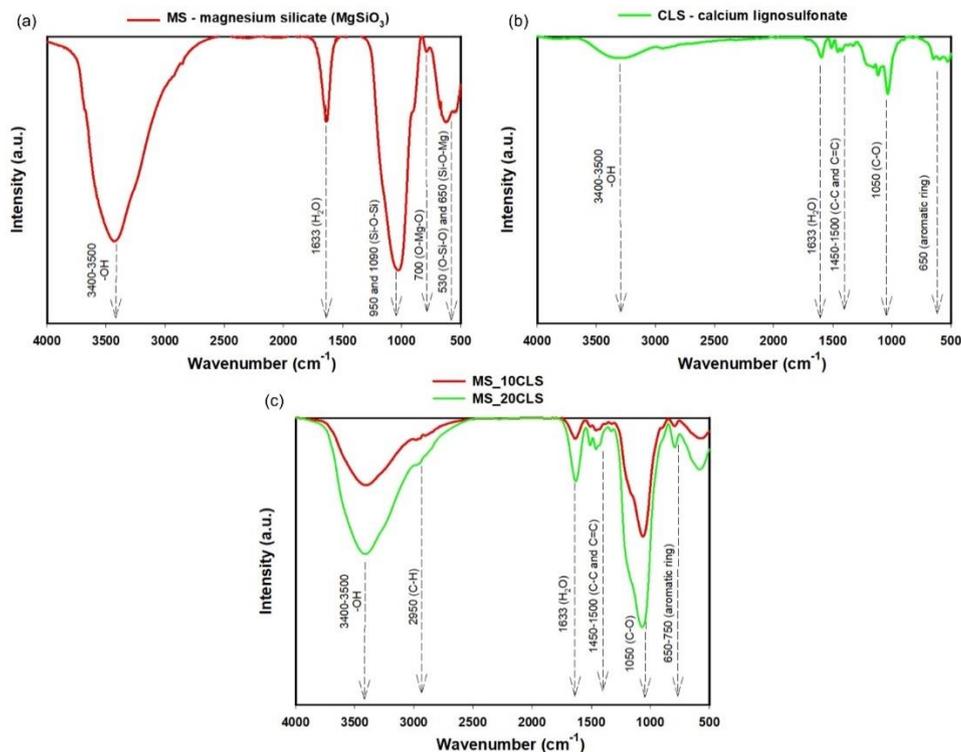


Fig. 6. FTIR spectra of initial reagents (a, b) and synthesized hybrid materials (c)

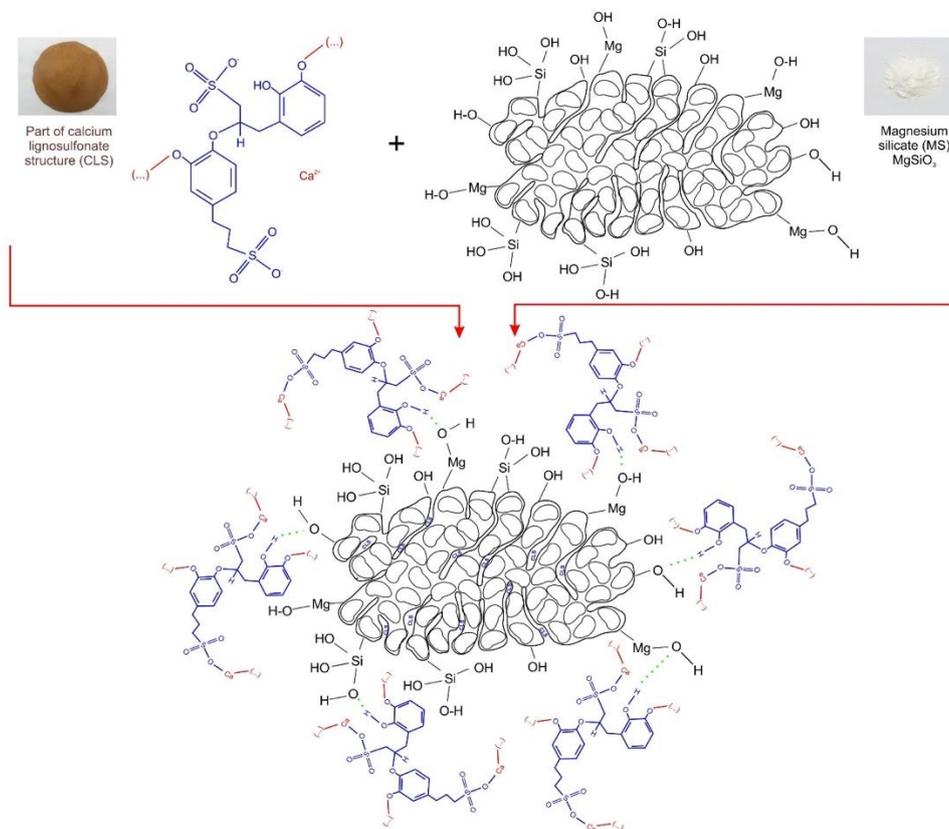


Fig. 7. Proposed mechanism of interaction between synthetic magnesium silicate and calcium lignosulfonate

Fig. 6c shows the spectra obtained for MgSiO<sub>3</sub>/calcium lignosulfonate materials. Both spectra are quite similar to that of the initial magnesium silicate sample, but they also contain signals characteristic for the biopolymer. The effective bonding between the reagents is confirmed by the characteristic signals for aromatic rings observed at 750–650 cm<sup>-1</sup> and 1500–1450 cm<sup>-1</sup>. Besides these, the spectra also contain other characteristic bands that were previously observed especially on the spectrum of the MgSiO<sub>3</sub> sample. More intense signals appeared on the spectrum of sample MS\_20CLS, obtained with the use of 20 wt./wt. of biopolymer. This finding is in agreement with previously noted patterns for other physicochemical parameters. The results directly confirm the effective combination of calcium lignosulfonate with sol-gel-derived magnesium silicate, and together with previously reported findings make it possible to propose a mechanism for the interaction between the reagents (Ciesielczyk et al., 2017; Klapiszewski et al., 2013). This mechanism is based mainly on the interaction of surface hydroxyls (magnesium silicate) with selected functional groups present in the biopolymer structure.

#### 4. Conclusions

In this study, hybrid materials have been prepared from synthetic magnesium silicate (MgSiO<sub>3</sub>) and calcium lignosulfonate. The effectiveness of the *in situ* sol-gel synthesis method was confirmed by physicochemical evaluation of the resulting materials. It was shown that such parameters as particle size, surface area, and thermal and electrokinetic stability are mainly determined by the quantity of biopolymer used in the synthesis of the hybrids. Superior morphology and electrokinetic stability were observed for the sample obtained with the addition of 20 wt./wt. of lignosulfonate, while the hybrid synthesized with the addition of 10 wt./wt. of biopolymer had greater thermal stability and surface area. These properties result from the greater contribution of magnesium silicate or biopolymer to the hybrid structure. FTIR spectra confirmed the effective combination of the inorganic matrix and the natural-origin material and made it possible to propose a mechanism for their interaction, which is based mainly on the interaction of surface hydroxyls (magnesium silicate) with selected functional groups present in the biopolymer structure.

It has been proved that the synthesized materials exhibit novel and unique physicochemical properties as compared with the initial reagents. These properties can be easily controlled by changing the quantity of biopolymer in the hybrid structure. This is a crucial factor when analyzing potential applications of such materials in various branches of industry.

#### Acknowledgements

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