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ADVANCED BIOCOMPOSITES BASED ON SILICA AND LIGNIN PRECURSORS

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Abstract: A new method is proposed for obtaining biocomposites based on a combination of silica and lignin precursors. Amorphous silica was produced by two methods: one based on hydrolysis and condensation of tetraethoxysilane (sol–gel method) and the other involving precipitation in a polar medium. Additionally, the commercial silica known under the name of Syloid$^{®}$244 was used. The silica surface was modified to ensure better affinity of the support to activated lignin. The biocomposites obtained were carefully characterised by determination of their physicochemical and dispersive–morphological properties. Electrokinetic stability of the biocomposites was evaluated on the basis of zeta potential dependence on pH. Thermal stability of the biocomposites and their porous structure parameters (surface area, pore diameter and pore volume) were established. The results indicate that silica/lignin biocomposites are much promising for application in many areas of science and industry.

Keywords: *biocomposites, silica, lignin, physicochemical and structural properties*

Introduction

Increasing cost of energy and the necessity of the natural environment protection have shifted the interest from production of synthetic materials to their natural biodegradable correspondents. Much attention is paid to materials combining characteristic properties of a few substrates in the form of multifunctional composites. One of such materials undoubtedly is the inorganic–organic system of silica and lignin, showing biocompatibility with the natural environment, relatively low cost of production because of easy availability of the precursors and many other features valuable from the viewpoint of technological use. Lignin, which is a component of wood besides cellulose and hemicellulose, has become an interesting subject of intense research work. Its unique properties have attracted the attention of chemists,

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biologists, dieticians and technologists (Kovacs 2011). In wood, lignin plays the role of a scaffold, it stiffens the cell wall, protects wood against pathogens and abiotic factors, such as low or high temperature or the presence of heavy metals. Lignin is also important for the transport of metabolites and water (Novaes 2010).

Lignin makes a three–dimensional inhomogeneous polymer network of unique structure. It is composed of a mixture of organic aliphatic and aromatic compounds, with the greatest contribution of derivatives of *p*-coumaryl, coniferyl and sinapyl alcohols (Ralph 1999, Ek 2009, Collinson 2010). As a natural material being a waste product and hence cheap, it has recently become a subject of great interest. Because of the ease of modification and the possibility of isolation of many compounds from it, lignin has proved to be an excellent raw product for many branches of industry. As shown by Harmita (2009), Sciban (2011) and Brdar (2012), because of low cost and limited solubility in water, lignin can be used for water purification as adsorbent of heavy metals such as zinc, lead, cadmium, copper or nickel. It is also effective for removal of other substances such as dyes, surfactants and organic pollutants. After activation with amine groups (Cotoruelo 2012) lignin can be successfully applied for adsorption of phenols. Lignin being a natural polymer has been also used as an addition to synthetic polymers endowing them with characteristic features (Kunanopparat 2012, Morandim–Giannetti 2012). It is also important in electrochemistry. When used as an admixture in production of electrodes it shows valuable electrochemical properties following from the presence of electrocatalytic quinone in its structure. Because of low cost and ease of preparation, the electrodes can be used in electrochemical sensors, biosensors, converters and for connecting enzymes acting as bioplatforms (Milczarek 2007, 2009, 2010). The recent work on lignin in electrochemistry (Milczarek 2012) has been directed at production of environmentally friendly devices for electric energy storage.

The other component is silica which is one of the most common mineral on Earth. The most important methods of its production include the hydrolysis of alkoxysilanes based on the Stöber method (Stöber 1968, Ibrahim 2010), precipitation from water solution of sodium silicate in polar systems (Jesionowski 2001) or in nonpolar systems (Jesionowski 2002) and high-temperature combustion of silicon halogens in a gas phase (Wypych 2010). Because of a number of valuable physicochemical properties such as well–developed specific surface area, porosity and hardness, it has been widely used in many branches of industry. Owing to the content of siloxane and silanol groups, silica is an active filler and adsorbent supporting chemically bonded organic substances.

These highly valuable properties and many areas of prospective use have prompted us to make an attempt at combining lignin with inorganic silica support. The intention was to produce a multifunctional biocomposite combining the properties of lignin and silica. Results of this attempt and characterisation of the silica/lignin biocomposites obtained are reported in this paper where we also consider the potential applications of the biocomposites.

Experimental

Synthesis of silica/lignin biocomposites

The silica-lignin biocomposite was obtained in a two-stage process. In the first process a reactor containing dioxane and water (9:1, v/v) was charged with a specific amount of Kraft lignin from Sigma–Aldrich (3, 5, 10, 20, 30, 40, 50 wt./wt. relative to 100 weight parts of silica). Upon continuous stirring with a fast-speed stirrer Eurostar digital IKA-Werke GmbH (1200 rot/min) a water solution of sodium iodate(VII) (Sigma–Aldrich) was introduced in order to activate lignin. The process was performed in the dark for about 30 minutes. In the second stage the lignin solution obtained was introduced at the rate of 5 cm^3/min into a reactor with the earlier prepared silica modified with aminosilane, dispersed in 50 cm^3 of water. Three types of silicas were used: the silica synthesised by the sol–gel method, another one precipitated in a polar system and the third one was a commercial silica Syloid®244.

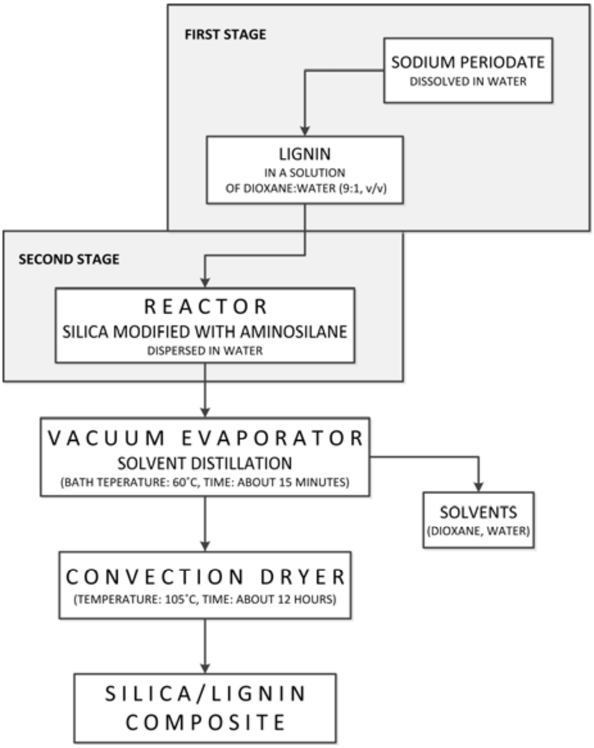


Fig. 1. Preparation of silica/lignin biocomposites – a schematic representation

The silica sample obtained by the modified Stöber method (sol–gel method) was synthesised with the use of tetraethoxysilane – TEOS (Sigma–Aldrich), ethyl alcohol and ammonia (Chempur). The appropriate amount of reagents was placed in a reactor and carefully dispersed for about 1 h. The second sample was obtained by precipitation in a polar system as a result of reaction between sodium silicate (Vitrosilicon SA) and sulphuric acid (Chempur). A detail description of the process conditions and substrates used is given in (Jesionowski 2002). The sample of commercial product Syloid®244 made by W.R. Grace and Company was used for comparative purposes. To activate silica, its surface was functionalised by introducing a modifying mixture of 5 weight parts by mass of *N*-2-(aminoethyl)-3-aminoprophyltrime-thoxysilane in a methanol–water solution of 4:1, v/v). This mixture was dosed into a reactor with a proper silica sample dispersed in water by a peristaltic pump at the rate of 3 cm^3/min. After introduction of the whole portion of the mixture, the contents of the reactor were stirred for about 30 minutes. After modification the silica was introduced into the above described lignin solution and the combined contents were stirred vigorously for about 1 h. After completion of the process the solvent was evaporated at 60 ºC in a vacuum evaporator and the precipitate was dried in a dryer (Memmert) at 105 ºC for about 12 h. A scheme of the process is given in Fig. 1.

Physicochemical evaluation

The silica/lignin biocomposites obtained were subjected to physicochemical and dispersive–morphological characterisation. The particle size distribution was determined by two instruments: Zetasizer Nano ZS (0.6–6000 nm) and Mastersizer 2000 (0.2–2000 μm) employing two measuring methods NIBS and laser diffraction, respectively. Both instruments were made by Malvern Instruments Ltd. The electrokinetic stability of the biocomposites was determined on the basis of zeta potential dependence on pH, using also Zetasizer Nano ZS (Malvern Instruments Ltd.) with an autotitrator attached. Measurements were made in a 0.001M NaCl solution. The thermal stability of biocomposites was evaluated on the basis of thermogravimetric measurements on a TG Jupiter STA449F3, made by Netzsch. Colorimetric analysis was made on a colorimeter Specbos 4000 (YETI Technische Instrumente GmbH) to confirm the effectivness of the proposed method of biocomposite synthesis. The samples obtained were also subjected to determination of their specific surface area BET and pore volume and diameter by the method of Barrett, Joyner, Halenda (BJH). The measurements were performed on ASAP 2020, made by Micromeritics Instrument Co.

Results and discussion

Dispersive and morphological characteristics

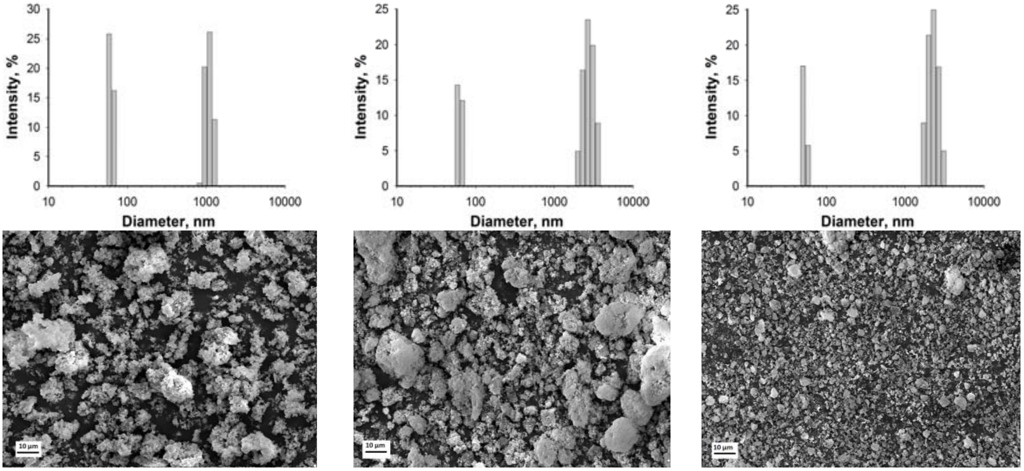
Table 1 presents results characterising dispersive properties of the biocomposites obtained. The particle size distribution was determined in two ranges of values by two instruments Zetasizer Nano ZS and Mastersizer 2000.

Table 1. Dispersive characteristic of silica/lignin biocomposites

Sample no.	Type of SiO_2	Content of Kraft lignin in relation to the silica matrix (wt./wt.)	Dispersive properties				
			Range of particle size from Zetasizer Nano ZS (nm)	Particle diameter from Mastersizer 2000 (µm)			
				d(0.1)	d(0.5)	d(0.9)	D[4.3]
1	Stöber silica	3	164–255 1280–2300	5.4	18.0	38.4	20.3
2		10	190–220 1480–3090	5.4	17.6	41.7	20.3
3		20	59–68 825–1280	4.3	15.8	37.1	18.6
4		50	122–164 3580–5560	4.2	17.4	38.9	19.8
5	Hydrated silica	3	68–79 2670–4800	4.2	17.4	38.9	19.8
6		10	106–122 1720–2300	4.9	18.9	42.0	21.5
7		20	59–68 1990–3580	5.4	18.0	38.4	20.3
8		50	142–164 2670–5560	5.6	21.5	47.6	24.4
9	Syloid® 244	3	712–955	2.5	6.7	28.7	11.8
10		10	33–39 2300–3580	2.6	8.2	29.2	12.6
11		20	51–59 1720–3090	2.7	8.8	30.5	13.3
12		50	68–91 1480–3580	2.7	8.3	31.5	13.3

Each product was found to show a tendency towards formation of particle clusters, which is in agreement with the results already reported by Klapiszewski (2012). The plots illustrating particle size distributions (additionally verified by microscopic observations) are given in Fig. 2. The most homogeneous is the sample obtained on the basis of commercial silica Syloid®244 (Fig. 2c). Less homogeneous are the biocomposites based on silica synthesised by the sol–gel method (Fig. 2a) and that precipitated in a polar medium (Fig. 2b).

Figure 3 presents the particle size distribution of biocomposites obtained from 20 weight parts of lignin relative to 100 weight parts of SiO_2 to permit a comparison of the products obtained from different silica precursors. The results presented by Klapiszewski (2012) suggested that the presence of small amount of lignin in a biocomposite was beneficial from the viewpoint of dispersive–morphological properties.



(a) (b) (c)

Fig. 2. Particle size distributions (Zetasizer Nano ZS) and SEM microphotographs of silica/lignin biocomposites containing 20 weight parts by mass of lignin in hybrid matrix prepared on the basis of silica precursors (a) Stöber silica, (b) hydrated silica, and (c) Syloid®244

For a detail analysis we have chosen the products containing 20 weight parts by mass of lignin relative to 100 weight parts by mass of SiO_2. As follows from Fig. 3, the greatest amount of particles in the range of the smallest diameters is in the biocomposite based on Syloid®244. The plots obtained for the other two biocomposites (samples 3 and 7) on the basis of Mastersizer 2000 measurements are similar. This result has confirmed the conclusions drawn from the analysis of Table 1 and Fig. 2.

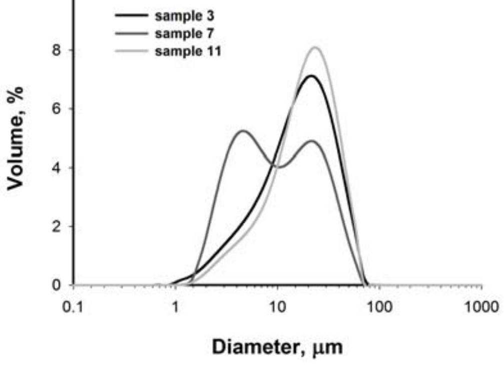
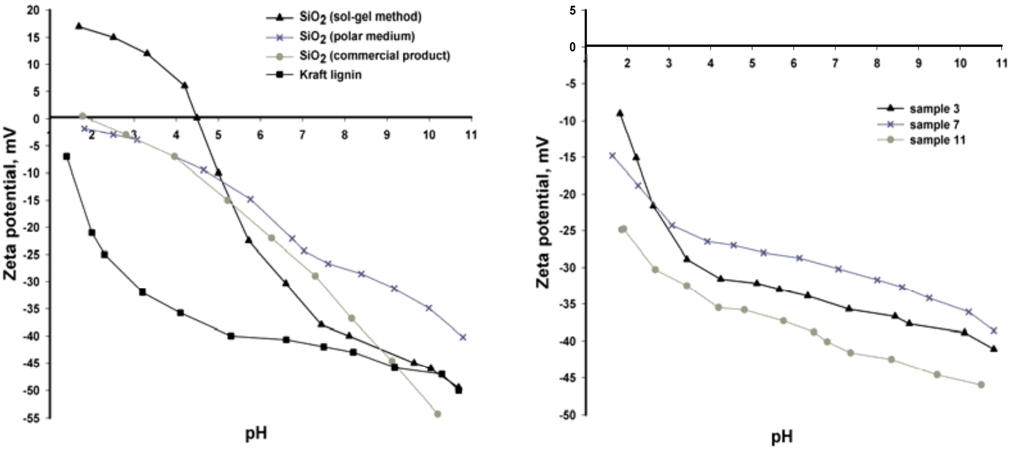


Fig. 3. Particle size distributions (Mastersizer 2000) of selected biocomposites

Electrokinetic characteristic

The electrokinetic potential (zeta) describes the degree of repulsion between the neighbouring particles of similar charges. The value of ζ potential is influenced by many factors of which the most important is pH. The sign and magnitude of zeta potential depends also to a significant degree on the medium in which the particles are dispersed (Weiner 1993, Elimelech 1994, Otterstedt 1998).



(a) (b)

Fig. 4. Zeta potential vs. pH of silicas used and Kraft lignin (a), and (b) selected biocomposites containing 20 weight parts by mass of lignin in silica matrix

Figure 4 presents the zeta potential as a function of pH for the three types of SiO_2 and Kraft lignin. The measurements were made in a 0.001M NaCl solution in the pH range from 1.7 to 11. The character of the electrokinetic curves presented differs depending on the type of silica used, which has also been reported by Xu (2003) and Jesionowski (2005). For the biocomposites based on Syloid®244 and on silica precipitated in a polar medium the zeta potential values in the acidic pH range were similar. The isoelectric point (i.e.p.) for the biocomposite based on Syloid®244 is noted at pH close to 2, while for the biocomposite based on SiO_2 precipitated in a polar medium no i.e.p. value was reached, but the curve suggests that it would be achieved at pH of about 1.7. Such i.e.p. values are consistent with literature data suggesting that i.e.p. of SiO_2 is reached for pH from 1.7 to 3.5. This implies that in acidic solutions there is a risk of coagulation. The zeta potential in this pH range reaches very low values. In the alkaline pH the commercial silica shows somewhat higher zeta potential so also a better electrokinetic stability. For the biocomposite based on SiO_2 obtained by the sol–gel method, the electrokinetic curve reached i.e.p. at pH close to 4.5. A positive value of surface charge below $pH_{i.e.p.}$~4.5 is not typical of silica but follows from the presence of a small number of $–NH_3^+$ groups incorporated in the spatial lattice of silica and is related to the method of synthesis applied (Kosmulski 2009).

Kraft lignin shows negative values of zeta potential in the whole pH range studied and the shape of the electrokinetic curve suggests a tendency towards reaching i.e.p. at pH close to 1. Kraft lignin shows negative surface charge in a wide range of pH. The charge is a consequence of ionisation of the surface hydroxyl and acidic groups as a result of lignin dispersion in water solutions (Dong 1996). Kraft lignin has a high electrokinetic stability in pH range from 3 to 11.

Figure 4b presents the zeta potential dependences on pH for the SiO_2/lignin biocomposites. All biocomposites show negative zeta potential in the whole pH range studied and good electrokinetic stability in the pH range from 4 to 11. The character of electrokinetic curves is an indirect confirmation of the effectiveness of the proposed method of SiO_2/lignin biocomposites synthesis.

Colorimetric analysis

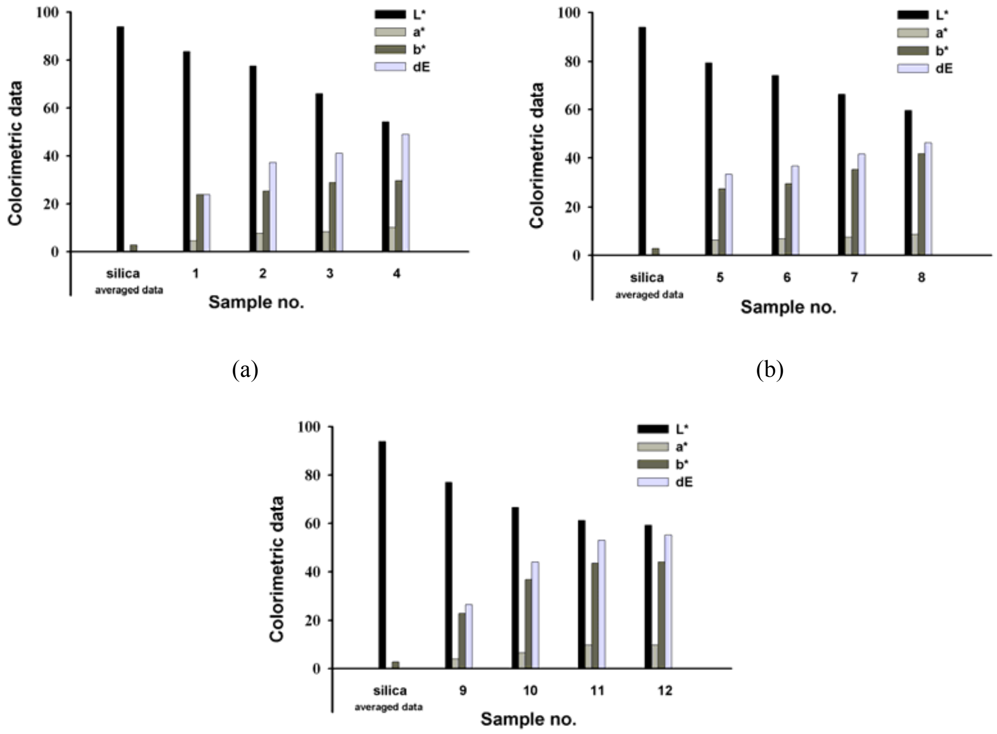
Analysis of the colorimetric data has brought another evidence indirectly confirming the effectiveness of the proposed method of silica functionalisation. The colorimetric parameters were determined in the colour space CIE $L^*a^*b^*$.

No significant difference in the colour was detected for the silicas obtained by different methods. Thus, for all silica samples an average value of L^* equal to 93.7 was assumed. With increasing content of lignin in the final biocomposite, the value of L^* decreases, confirming that the surface functionalisation took place to a satisfactory degree (Fig. 5). Moreover, the values of a^* and b^* increase, which indicates an increase in the contribution of red and yellow.

An additional parameter that can be of importance in colorimetric analysis is the value of dE factor component describing the total change in colour of particular samples. As expected, this value increases with increasing content of lignin in the biocomposite, which confirms a distinct differences in the colour between the samples containing different amounts of lignin

Thermal analysis

Thermal analysis is the main method for characterisation of thermal properties of chemical substances. Results of thermal analysis provide information on the elementary phenomena taking place and the thermal stability of a substance at elevated temperatures is one of the most important parameters defining the range of prospective application of materials. Such measurements were performed for the silica/lignin biocomposites.

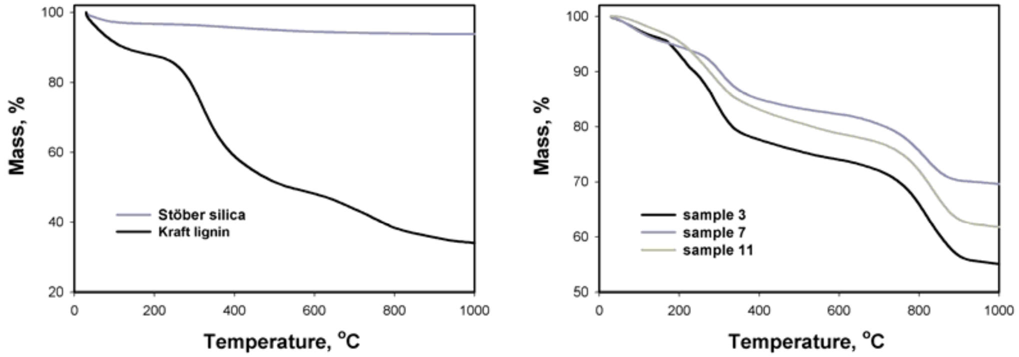


(a) (b)

(c)

Fig. 5. Colorimetric data of silica and silica/lignin biocomposites obtained on the basis of (a) Stöber silica, (b) hydrated silica and (c) Syloid®244

Figure 6a presents the thermogravimetric curves for the silica and lignin precursors used in the studies. Silica shows high thermal stability and within the temperature range considered its mass loss reaches only 5% (because for all types of silica the course of TG curves was similar, only one curve is presented in the figure). For lignin the mass loss over the temperature range studied was significant and reached 65%. This result confirms the data published in other works, also for the other types of lignin (Rodriguez-Mirasol 1993, Kijima 2011). The most distinct second stage of large mass loss of about 35% takes place in the range 200–600 °C. It corresponds to a complex process of thermal decomposition involving formation of new bonds as a result of crosslinking reactions. The final biocomposites show rather high thermal stability (Fig. 6b) especially samples 7 and 11, which – together with the fact of using a natural precursor – lignin – means that they offer a wide range of prospective applications.



(a) (b)

Fig. 6. Thermal analysis of (a) precursors and (b) silica/lignin biocomposites containing 20 wt./wt. of lignin in hybrid matrix

The attractive TG results obtained at this stage of the study suggest that the silica/lignin biocomposites can be used as polymer fillers of new generation. This possibility will be studied in the near future.

Porous structure properties

The structural properties of the biocomposites obtained were characterised on the basis of such parameters as: mean pore diameter, total pore volume and specific surface area BET. Values of these parameters determined for the initial silica samples and selected biocomposites are given in Table 2.

Table 2. Adsorption properties of silicas and silica/lignin biocomposites containing 20 weight parts by mass of lignin per 100 weight parts by mass of silica matrix

Sample Name	BET surface area (m^2/g)	Total volume of pores (cm^3/g)	Mean size of pores (nm)
Stöber silica	7	0.01	6.2
3	4	0.01	7.9
Hydrated silica	129	0,01	3,6
7	115	0.05	3.6
Syloid®244	262	1,2	18,0
11	223	0,9	14,3

The above presented results indicate that the newly proposed silica/lignin biocomposite can be applied as a natural adsorbent. Only the biocomposite based on silica synthesised by the modified Stöber method has a low BET surface area (Table 2). Biocomposites 7 and 11, based on hydrated silica and Syloid®244, had promising values of surface areas of 115 and 223 m^2/g, respectively. The highest values of the total pore volume and pore diameter were found for Syloid®244 and the biocomposite obtained on its basis (sample 11). The earlier reported results characterising adsorption properties of hydrated silica (Klapiszewski 2012) have been confirmed by the results presented in this work. The adsorption data obtained for the biocomposites studies have shown that their specific surface area BET is large enough to justify the tests of SiO_2/lignin biocomposites adsorption properties towards organic compounds and selected heavy metal ions.

Conclusions

The proposed method for the synthesis of new composites based on silica and lignin has brought promising results from the viewpoint of testing their use as advanced functional materials. The biocomposites obtained show attractive dispersive–morphological properties, especially those containing 10 and 20 weight parts by mass of lignin in silica matrix. With increasing content of lignin in the biocomposite the volume contribution of larger particles increases, leading to formation of aggregates and agglomerates. Results of the studies performed to characterise the obtained materials have proved that the silica/lignin biocomposites have good electrokinetic stability and are promising as polymer fillers or adsorbents of harmful chemical compounds, including heavy metals, thanks to their good thermal and porous structure properties.

Acknowledgements

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