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PREPARATION AND CHARACTERISATION OF HYDRATED SILICA/LIGNIN BIOCOMPOSITES

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Abstract. Silica/lignin biocomposites were obtained by a new method proposed and fully characterised. Silica was precipitated from aqueous solution of sodium silicate (as an SiO₂ precursor) and sulphuric acid (as a precipitating agent). The support obtained was subjected to surface functionalisation with aminosilane and then modified with Kraft lignin preliminary activated with sodium periodate solution. The products were characterised by elemental (N, C, H, S) and colorimetric analyses. Adsorption properties of the products were evaluated on the basis of determination of specific surface area, pore volume and pore diameter. The influence of the amount of lignin incorporated into the silica matrix on the physicochemical properties of the biocomposites was proved to be significant. The materials obtained can be used as selective adsorbents of heavy metals or pro-ecological polymer fillers.

keywords: silica/lignin biocomposites, silica, Kraft lignin, modification, physicochemical properties

1. Introduction

Dynamic development of production technologies of new materials has been focused on getting products of specific target properties. A large group of such new materials is based on silica and show a large variety of morphological features. Particularly interesting is production of composites with an addition of organic origin polymer such as for instance lignin. The use of biodegradable materials such as lignin in an inorganic matrix offers a possibility of obtaining a new generation of highly functional biocomposites of prospective economic importance.

Silica belongs to the most abundant natural materials. The most often used methods of its production include: hydrolysis and condensation of tetraalkoxysilanes according to the Stöber method (Stöber, 1968; Ibrahim, 2010), precipitation from sodium metasilicate aqueous solution in polar and nonpolar systems (Jesionowski, 2001, 2002) and high-temperature combustion of silicon halogens in the gas phase (Wypych, 2010). Because of a number of valuable physicochemical properties such as large surface area, high hardness, chemical resistance and high mechanical resistance, silica has been widely used in many branches of industry and in everyday use products.

Lignin is the second most abundant natural renewable material from the group of polymers and has been for a long time viewed as an attractive material for versatile use (Lora, 2002). Complex chemical structure of lignin, its valuable physicochemical properties and a variety of chemical compositions, have made it a subject of interest of many research groups. Recently, large amounts of lignin has been produced as a side product in the so-called Kraft process (Chakar, 2004; Wallberg, 2006). Lignin, obtained in this process or isolated by some extraction methods, has been used for instance to produce energy (Sannigrahi, 2010), in electrotechnology, electrochemistry (Milczarek, 2009), pharmacy (Tolba, 2011) and in production of modern functional biocomposites of specific properties (Gosselink, 2004).

Increasing cost of energy and the need to protect the natural environment have directed much attention to biodegradable materials based on renewable resources, being environmentally friendly and cheaper. Such interesting new materials are for example silica/lignin biocomposites of a wide range of potential applications. According to the so far published scarce literature on such materials, they can be used as adsorbents of harmful organic compounds or heavy metal ions (Hayashi, 1997; Qu, 2010) or as polymer fillers (Ignat, 2011).

The aim of this study was to obtain a silica/lignin composite in the process of silica (silica was precipitated in a polar system) surface modification with an appropriate lignin solution and a thorough characterisation of the product.

2. Experimental

2.1. Hydrated silica/lignin biocomposite synthesis

Silica used for the study was precipitated in a polar system as a result of reaction between aqueous solution of sodium silicate (Vitrosilicon SA) and 5% sulphuric acid (Chempur[®]). The reaction mixture was subjected to intense stirring (1800 rev/min) in a high-speed stirrer Eurostar digital made by IKA–Werke GmbH. The reaction was carried out at 85°C. The silica suspension obtained was filtered off under reduced pressure and washed a few times with water. The final white precipitate was dried by the convection method at 105°C for about 24 h. Part of the product was subjected to preliminary surface functionalisation *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane to activate the silica surface.

The initial silica and the silica preliminarily modified with silane were subjected to proper functionalisation with Kraft lignin. Two solutions were made. One was labelled as S1. It was lignin dissolved in a dioxane:water (9:1, v/v) mixture. The other was labelled as S2 and it was an aqueous solution of sodium iodate. The S1 solution was placed in a reactor to which S2 was introduced in doses at a constant rate. After introduction of the whole S2 solution, the reaction solution was stirred for 30 minutes. The process of lignin compounds activation was performed with no access of light. To the mixture of solutions, a certain amount of silica (unmodified or modified with the above-mentioned silane) was added and the stirring was continued for 1 hour. The

final product, silica/lignin biocomposite, was moved to a vacuum evaporator to distil off the solvent. The composite was dried for about 24 h at 105°C. The process of SiO₂/lignin biocomposite synthesis is schematically illustrated in Fig. 1.

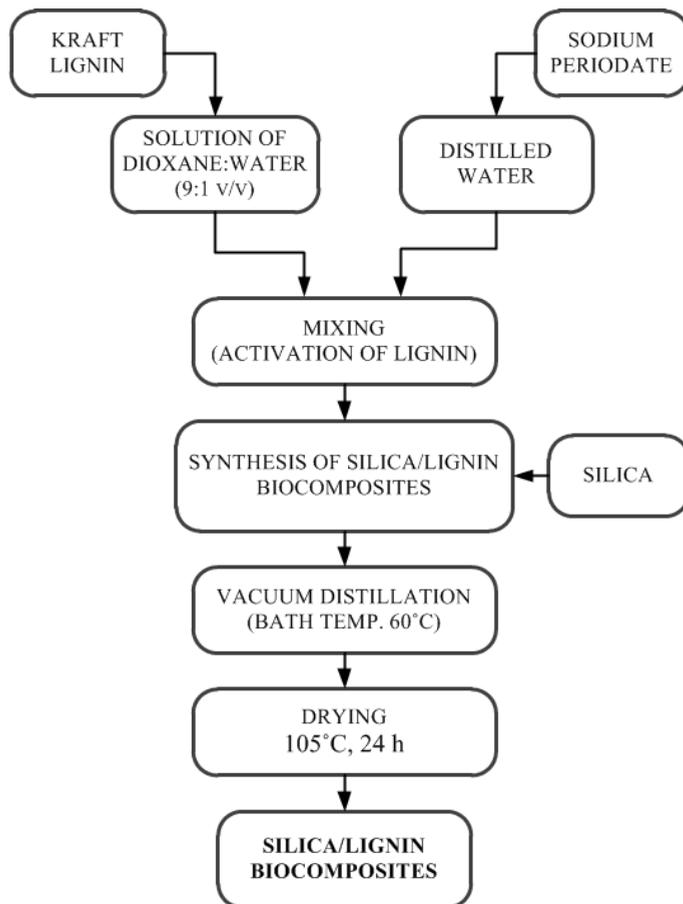


Fig. 1. The simplified scheme for obtaining of silica/lignin biocomposites

2.2. Physicochemical evaluation

The silica/lignin biocomposites were subjected to a thorough physicochemical and dispersive–morphological analysis. The particle size distribution was determined by two different methods and in different ranges using a Zetasizer Nano ZS employing the NIBS technique in the range of 0.6–6000 nm and Mastersizer 2000 employing the laser diffraction technique in the range of 0.2–2000 μm. Both instruments were made by Malvern Instruments Ltd. Elemental composition of the samples (N, C, H, S) was made using a Vario EL Cube made by Elementar, while their colorimetric analyses

were made with a Specbos 4000 colorimeter (YETI Technische Instrumente GmbH). Adsorption properties of some samples were characterised by determination of the specific surface area BET, total pore volume and pore size calculated by the BJH method. Relevant measurements were made on an ASAP 2020 instrument made by Micromeritics Instrument Co.

3. Results and discussion

Table 1 presents the data characterising physicochemical properties of the initial unmodified silica (sample 1) and SiO₂/lignin biocomposites obtained on the basis of this silica (samples 2–8). The particle size distributions were determined by a Zetasizer Nano ZS (in the range of 0.6–6000 nm) and Mastersizer 2000 (in the range of 0.2–2000 μm).

Table 1. Dispersive properties of unmodified silica and silica/lignin biocomposites

| Sample No. | Content of lignin in relation to the unmodified silica matrix (wt./wt.) | Dispersive properties | | | | |
|------------|---|--|--|--------|--------|--------|
| | | Particle size distribution from Zetasizer Nano ZS (nm) | Particle diameter from Mastersizer 2000 (μm) | | | |
| | | | d(0.1) | d(0.5) | d(0.9) | D[4.3] |
| 1 | 0 (unmodified silica) | 44–59 | 4.63 | 19.40 | 43.31 | 25.12 |
| | | 1110–5560 | | | | |
| 2 | 3 | 91–122 | 4.60 | 16.85 | 37.33 | 19.20 |
| | | 220–295 1480–5560 | | | | |
| 3 | 5 | 106–190 | 4.60 | 17.71 | 38.01 | 19.80 |
| | | 712–4150 | | | | |
| 4 | 10 | 79–106 | 4.74 | 18.82 | 40.44 | 21.03 |
| | | 1990–5560 | | | | |
| 5 | 20 | 79–122 | 4.50 | 19.41 | 42.16 | 22.72 |
| | | 1720–4150 | | | | |
| 6 | 30 | 79–106 | 4.33 | 19.51 | 42.29 | 22.92 |
| | | 1990–5560 | | | | |
| 7 | 40 | 79–142 | 5.38 | 21.63 | 44.57 | 23.75 |
| | | 1280–4800 | | | | |
| 8 | 50 | 79–142 | 5.24 | 23.14 | 48.35 | 25.43 |
| | | 1280–4150 | | | | |

The primary particles in sample 1 of precipitated and unmodified silica had diameters in the range of 44–59 nm. These particles showed a tendency to form agglomerates of the size 1110–5560 nm in size. As follows from the Mastersizer 2000 results, 10% of the sample particles have diameters smaller than 4.63 μm, while 90% of the sample particles have diameters smaller than 43.31 μm. The particle size distributions obtained for the silica/lignin biocomposites studied are nanometric. The

particles show a tendency to formation of agglomerates and this tendency is the stronger the greater is the content of lignin. The particle size distribution recorded on Mastersizer 2000 indicates that 90% of particles in sample 2 have diameters below 37.33 μm , while 90% of particles in sample 8 (containing 50 weight parts of lignin per 100 weight parts of silica) have diameters below 48.35 μm .

The best dispersive–morphological properties show the biocomposites containing the lowest amount of lignin. The samples containing 30 weight parts by mass or more of lignin (samples 6, 7, 8) show greater inhomogeneity, which is most probably a consequence of the lack of lignin oxidation and its partial degradation. Figure 2 presents dispersive–morphological results for sample 5, containing 20 weight parts by mass of lignin. The particle size distribution obtained on Zetasizer Nano ZS revealed two bands, the first covering the range of 79–122 nm and the second corresponding to agglomerates, covering the range 1720–4150 nm range. The maximum intensity of 19.5% corresponds to particles of the 91 nm in size. The results are confirmed by the SEM image showing the presence of small particles of diameters below 100 nm and greater agglomerate structures.

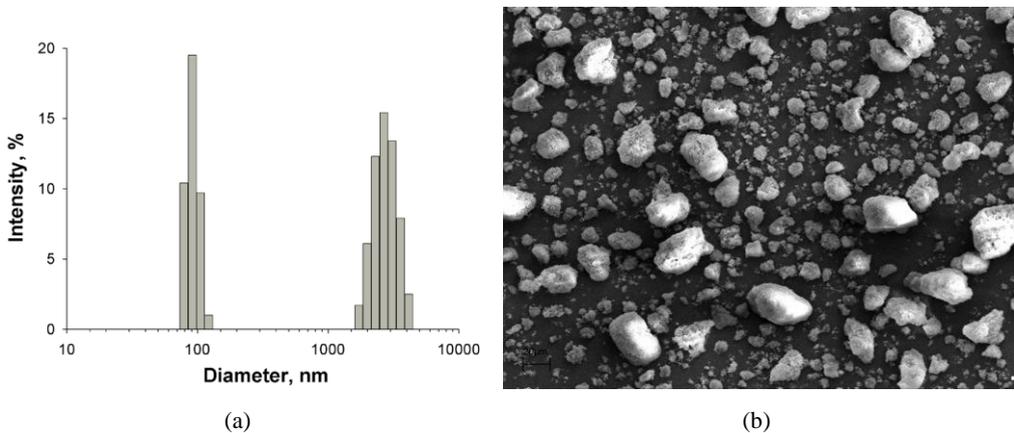


Fig. 2. (a) Particle size distribution (Zetasier Nano ZS) and (b) SEM microphotograph of silica/lignin biocomposite (sample 5) prepared on the basis of unmodified silica

An additional confirmation of the tendency to agglomerate formation with increasing content of lignin in the silica matrix is the particle size distribution recorded with Mastersizer 2000 (Fig. 3). With increasing content of lignin the particle size distribution peaks are shifted towards greater particle diameters. The greatest contribution of large diameter particles and the lowest contribution of the smallest size ones was observed for sample 8.

Figure 4 presents results of colorimetric analysis of the biocomposite samples, confirming the correctness of the process of modification. The surface functionalisation of the unmodified silica with a lignin solution caused a significant

decrease in the lightness parameter L^* . For the unmodified silica (sample 1) $L^*=93.78$, as a result of modification with a lignin solution the value of this parameter decreases: $L^*=85.68$ for sample 2 and $L^*=46.17$ for sample 8. The value of dE^* describing a total change in colour, increases with increasing content of lignin in the biocomposite.

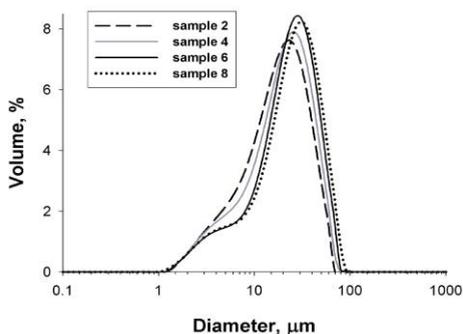


Fig. 3. Particle size distribution (Mastersizer 2000) of silica/lignin biocomposites

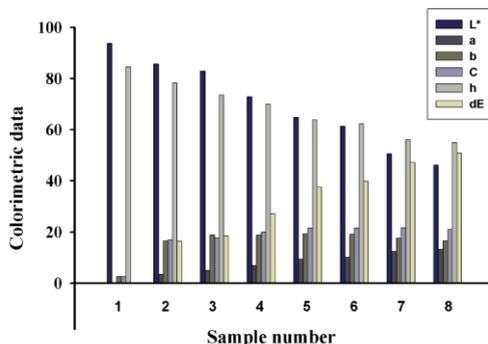


Fig. 4. Colorimetric data of unmodified silica (sample 1) and silica/lignin biocomposites (samples 2–8)

Table 2. Chemical content of unmodified silica (sample 1) and silica/lignin biocomposites (samples 2–8) on the basis of unmodified silica

| Sample No. | Elemental content (%) | | |
|------------|-----------------------|------|------|
| | C | H | S |
| 1 | 0.31 | 1.28 | - |
| 2 | 1.56 | 1.37 | 0.14 |
| 3 | 2.33 | 1.43 | 0.20 |
| 4 | 3.42 | 1.48 | 0.33 |
| 5 | 5.01 | 1.53 | 0.50 |
| 6 | 6.80 | 1.67 | 0.66 |
| 7 | 8.94 | 1.70 | 0.80 |
| 8 | 10.56 | 1.86 | 1.03 |

Results of elementary analysis (N, C, H, S) of the biocomposite samples based on unmodified silica are given in Table 2. As shown, with increasing content of lignin the contents of carbon, hydrogen and sulphur increase. For example, sample 2 with the lowest content of lignin per unmodified silica (3 wt./wt.) contains 1.56% of carbon and 1.37% of hydrogen. Sample 8, containing 50 weight parts by mass of lignin, has 10.56% of carbon and 1.86% of hydrogen. A small increase in the content of sulphur in the samples with increasing content of lignin is related to the presence of sulphur in the commercial Kraft lignin used in the study.

The above results were compared with those obtained for silica/lignin biocomposites based on silica preliminary modified with N-2-(aminoethyl)-3-aminopropyltrimethoxysilane. The data characterising dispersive properties of samples based on silane modified silica are presented in Table 3.

Table 3. Dispersive properties of silica modified with aminosilane and of silica/lignin biocomposites

| Sample No. | Content of lignin in relation to the silica matrix modified with aminosilane (wt./wt.) | Dispersive properties | | | | |
|------------|--|--|---|--------|--------|--------|
| | | Particle size distribution from Zetasizer Nano ZS (nm) | Particle diameter from Mastersizer 2000 (μm) | | | |
| | | | d(0.1) | d(0.5) | d(0.9) | D[4.3] |
| 9 | 0 (silica modified with aminosilane) | 59–106 1480–5560 | 5.75 | 22.66 | 47.84 | 22.11 |
| 10 | 3 | 44–79 1280–4800 | 4.41 | 16.12 | 34.15 | 18.01 |
| 11 | 5 | 68–122 2300–5560 | 4.69 | 16.20 | 34.29 | 18.15 |
| 12 | 10 | 59–122 1110–5560 | 4.80 | 20.31 | 42.74 | 23.41 |
| 13 | 20 | 68–122 712–1480 2670–5560 | 4.90 | 21.43 | 44.22 | 24.43 |
| 14 | 30 | 68–91 342–396 1480–4150 | 4.80 | 21.45 | 44.16 | 23.39 |
| 15 | 40 | 68–122 531–2670 | 5.56 | 23.53 | 47.19 | 25.42 |
| 16 | 50 | 68–106 459–4150 | 5.01 | 22.82 | 48.15 | 26.08 |

According to the data presented in Table 3, modified silica (sample 9) shows increased particle size and a greater tendency to agglomeration when compared with the unmodified one (sample 1). In sample 9, 10% of particles have diameter smaller than 5.75 μm , while 90% of particles have diameters smaller than 47.84 μm . In unmodified silica (sample 1) 10% of particles have diameters up to 4.63 μm , while 90% of particles have diameters smaller than 43.31 μm . Modification of silica was responsible for a small shift of the particle size distribution towards larger particle diameters. The above data are corroborated by the results recorded on Zetasizer Nano ZS. The dispersive-morphological features of samples 10–16 based on silane modified silica are similar to those of samples 2–8 based on unmodified silica. With increasing content of lignin, the biocomposite samples show increasing tendency to agglomeration, similarly as it was observed for the samples based on unmodified silica (Table 1).

Figure 5 presents the particle size distribution recorded in the Zetasizer Nano ZS and SEM image of sample 13 (20 weight parts by mass of lignin in relation to silane-grafted silica). Three peaks are obtained: the first corresponds to primary particles and covers the range of 68–122 nm, the second corresponds to aggregations and covers the range of 712–1480 nm and the third in the range of 2670–5560 nm corresponds to agglomerates. The results are confirmed by the SEM image (Fig. 5b) showing the presence of small particles and larger agglomerate clusters. No significant differences in dispersive and morphological properties were found between the samples based on unmodified and silane modified silica. This conclusion is confirmed by the results obtained with Mastersizer 2000 (Fig. 6) showing that with increasing content of lignin the contribution of greater size particles increases.

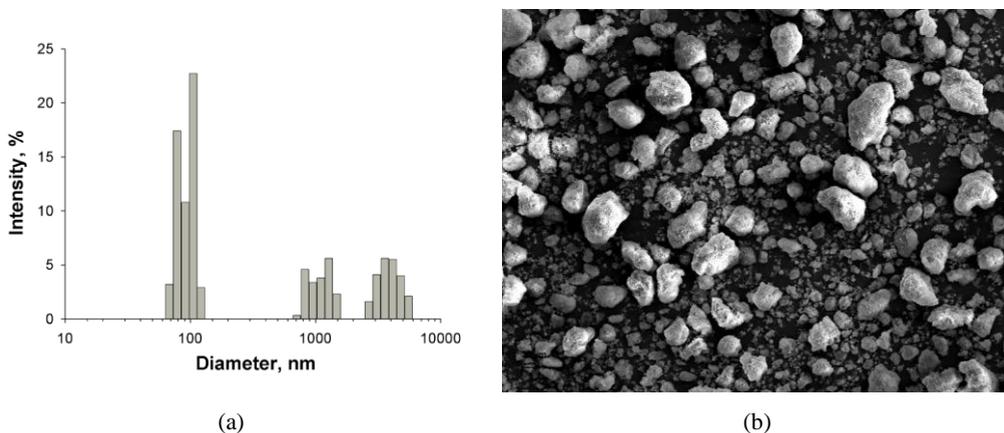


Fig. 5. (a) Particle size distribution (Zetasizer Nano ZS) and (b) SEM microphotograph of silica/lignin biocomposite (sample 13) prepared on the basis of silica modified with aminosilane

As follows from the colorimetric analysis (Fig. 7) with increasing content of lignin in the samples based on modified silica, the lightness L^* decreases while the total colour change dE^* increases. A comparison of colorimetric results obtained for unmodified and silane modified silica has shown that the silane modification leads first of all to reduction in the lightness L^* . For example the lightness of samples 6 (unmodified silica) and 13 (modified silica) containing 20 weight parts by mass of lignin was $L^*=64.75$ and $L^*=60.19$, respectively. This results indicates an increase in the silica affinity to lignin as a result of preliminary silane functionalisation of the former.

Data on the chemical composition of silane modified silica (sample 9) and biocomposites based on modified silica (samples 10–16) are given in Table 4.

As follows from the data, the effect of the preliminary silane modification was an increase in the nitrogen content to 0.61%. Analysis of the data for samples 10–16 has shown an increase in the content of carbon, hydrogen and sulphur with increasing content of lignin. The results are consistent with expectations. Moreover, greater

contents of N, C, H and S in the samples based on silane modified silica illustrates the significance of changes caused by the silane applied.

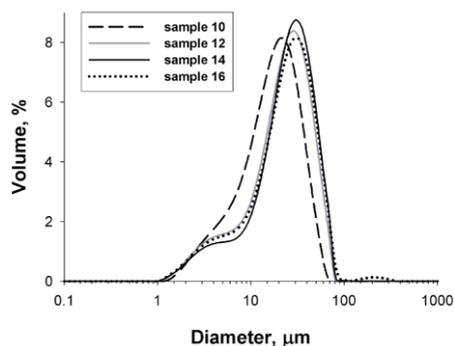


Fig. 6. Particle size distribution (Mastersizer 2000) of silica/lignin biocomposites

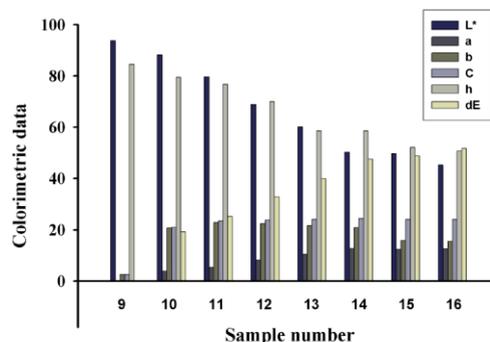


Fig. 7. Colorimetric data of silica modified with aminosilane (sample 9) and silica/lignin biocomposites (samples 10–16)

Table 4. Chemical content of silica modified with aminosilane (sample 9) and silica/lignin biocomposites (samples 10–16) on the basis of silica modified with aminosilane

| Sample No. | Elemental content (%) | | | |
|------------|-----------------------|-------|------|------|
| | N | C | H | S |
| 9 | 0.61 | 1.44 | 1.48 | - |
| 10 | 0.44 | 2.60 | 1.47 | 0.18 |
| 11 | 0.49 | 3.45 | 1.53 | 0.23 |
| 12 | 0.42 | 5.04 | 1.67 | 0.39 |
| 13 | 0.40 | 6.70 | 1.75 | 0.57 |
| 14 | 0.40 | 7.97 | 1.81 | 0.70 |
| 15 | 0.36 | 10.15 | 1.88 | 0.87 |
| 16 | 0.31 | 11.33 | 1.93 | 1.03 |

Table 5 presents the data characterising adsorption properties of unmodified silica (sample 1), preliminary silane modified silica (sample 9) and selected silica/lignin biocomposites (samples 4, 8, 12, 16). The specific surface area of these products varies from 108 to 131 m²/g. Preliminary modification with silane leads to a small increase in the surface area relative to the unmodified silane sample. The mean pore size for all samples are similar and vary from 3.55 to 3.61 nm, which confirms their mesoporous character. Surface functionalisation of silica, either unmodified or modified, with Kraft lignin solution did not affect significantly the adsorption properties of the materials studied

Table 5. Adsorptive properties of silica and silica/lignin biocomposites

| Sample No. | BET surface area (m ² /g) | Total volume of pores (cm ³ /g) | Mean size of pores (nm) |
|------------|--------------------------------------|--|-------------------------|
| 1 | 129 | 0.009 | 3.55 |
| 4 | 115 | 0.004 | 3.59 |
| 8 | 108 | 0.002 | 3.61 |
| 9 | 131 | 0.010 | 3.55 |
| 12 | 118 | 0.006 | 3.58 |
| 16 | 109 | 0.004 | 3.55 |

4. Conclusions

The proposed method of silica/lignin biocomposites synthesis permits obtaining products with well-defined dispersive, morphological and adsorption properties. These properties were found to be significantly influenced by the content of lignin introduced and the modification with the selected aminosilane. With increasing content of lignin in relation of silica matrix (either unmodified or modified) the contribution of greater size particles increases, so does the tendency to agglomeration. The biocomposites with the lowest content of lignin show the best dispersive and morphological properties. As follows from elemental and colorimetric analyses, preliminary silica modification with silane has brought an increase in the surface activity of the material permitting binding a greater amount of lignin at the same weight contributions. Determination of the adsorption properties of the products obtained has confirmed their mesoporous character.

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References

- CHAKAR F.S.R., RAGAUSKAS A.J., 2004, *Review of current and future softwood Kraft lignin process chemistry*, Ind. Crop. Prod., 20, 131–141.
- GOSELINK R.J.A., de JONG E., GURAN B., ABÄCHERLI A., 2004, *Coordination network for lignin – standardisation, production and applications adapted to market requirements (EUROLIGNIN)*, Ind. Crop. Prod., 20, 121–129.
- HAYASHI J., SHOJI T., WATADA Y., MUROYAMA K., 1997, *Preparation of silica–lignin xerogel*, Langmuir, 13, 4185–4186.
- IBRAHIM I.A.M., ZIKRY A.A.F., SHARAF M.A., 2010, *Preparation of spherical silica nanoparticles: Stöber silica*, J. Am. Sci., 6, 985–989.
- IGNAT L., IGNAT M., CIOBANU C., DOROFTEI F., POPA V.I., 2011, *Effects of flax lignin addition on enzymatic oxidation of poly(ethylene adipate) urethanes*, Ind. Crop. Prod., 34, 1017–1028.
- JESIONOWSKI T., 2001, *Preparation of colloidal silica from sodium metasilicate solution and sulphuric acid in emulsion medium*, Colloid Surf. A, 190, 153–165.
- JESIONOWSKI T., 2002, *Effect of surfactants on the size and morphology of the silica particles prepared by an emulsion technique*, J. Mater. Sci., 37, 5275–5281.

- LORA J.H., GLASSER W.G., 2002, *Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials*, J. Polym. Environ., 10, 39–48.
- MILCZAREK G., 2009, *Preparation, characterization and electrocatalytic properties of an iodine lignin-modified gold electrode*, Electrochim. Acta, 54, 3199–3205.
- QU Y., TIAN Y., ZOU B., ZHANG J., ZHENG Y., WANG L., LI Y., RONG C., WANG Z., 2010, *A novel mesoporous lignin/silica hybrid from rice husk produced by a sol–gel method*, Bioresource Technol., 101, 8402–8405.
- SANNIGRAHI P., PU Y., RAGAUSKAS A., 2010, *Cellulosic biorafineries – unleashing lignin opportunities*, Curr. Opin. Environ. Sustain., 2, 383–393.
- STÖBER W., FINK A., BOHN E., 1968, *Controlled growth of monodisperse silica spheres in the micron size range*, J. Colloid Interf. Sci., 26, 62–69.
- TOLBA R., WU G., CHEN A., 2011, *Adsorption of dietary oils onto lignin for promising pharmaceutical and nutritional applications*, BioResources, 6, 1322–1335.
- WALLBERG O., LINDE M., JÖNSSON A.S., 2006, *Extraction of lignin and hemicelluloses from Kraft black liquor*, Desalination, 199, 413–414.
- WYPYCH G., 2010, *Handbook of Fillers*, ChemTec Publishing, Toronto 2010.

