SYNTHESIS OF LIGNIN-BASED INORGANIC/ORGANIC HYBRID MATERIALS FAVORABLE FOR DETOXIFICATION OF ECOSYSTEM COMPONENTS

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Combination of lignin matrices (including those modified with silicon oligomers or quaternary ammonium compounds) and such inorganic building blocks as copper and manganese cations (Cu^{2+}, Mn^{2+}) made it possible to synthesize novel hybrid organic-inorganic materials. The synthesized hybrid materials were characterized with significantly increased (2-9 times) values of specific surface area in comparison with those for non-modified and Si-modified precursor matrices. The Cu^{2+}-containing hybrid materials differed by enhanced sorption capacity towards proteins and bacteria.

Keywords: Lignin; Sorption properties; Modification; Environmental decontamination

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INTRODUCTION

Recent research in the area of pollutants removal from water sources, wastewaters, sediments, and soil has focused on the development of materials with increasing affinity, capacity, and selectivity towards target pollutants. Natural materials or waste products from industrial or agricultural processes with large adsorptive capacities can be ideal sorbents, since they are abundant in nature, require little processing, and they can be disposed in a sustainable manner if necessary (Bailey et al. 1999; Crini 2006). The use of technical lignins for sequestration, precipitation of contaminants has been extensively studied (Basso et al. 2004; Ray et al. 2004).

Nowadays the interest in synthesis of hybrids based on the polymeric matrices of natural origin has increased. High efficiency of cellulose-inorganic hybrid sorbents for concentration and sequestration of heavy metals and radionuclides from aqueous media has been demonstrated (Bandong et al. 2001). Intercalation of bactericide cations (e.g. Cu^{2+}) has been shown to significantly enhance sorption capacity of organosilicon sorbents towards microorganisms (Shvets et al. 2003).

The present work continues our investigations (Telysheva et al. 2002, 2006), which have shown high potential of the water-insoluble lignins as raw materials for design of sorbents intended for decontamination of soil and water from organic/biological pollutants. Novel hybrid products containing silicon and transition elements (Cu and Mn) were obtained on the basis of the two commercial lignins (kraft lignin, hydrolysis lignin), and their sorption properties were characterized.

EXPERIMENTAL

Chemicals and Starting Materials

Commercially available hydrolysis lignin (Kedaynjay plant, Lithuania) was used as raw material for modification.

Si-modified hydrolysis lignin (Si-HL) (Telysheva and Lebedeva 1998) was manufactured on the pilot plant at the Latvian State Institute of Wood Chemistry, using hydrolysis lignin (HL) as raw material.

$CuSO_4$ and $MnSO_4$ were purchased from Merk.

Lignin-based Hybrid Materials

Surface modification of lignin matrices with Cu^{2+} and Mn^{2+} cations was carried out by adsorption from $CuSO_4$ and $MnSO_4$ solutions in acetate buffer (pH 5) followed by washing with the acetate buffer and deionized water and drying.

Methods

Parameters of porous structure of the samples in terms of BET specific surface area, pores volume, and pore size distribution were calculated from the nitrogen gas adsorption-desorption isotherm determined at 77K using a KELVIN 1042 sorptometer. The surface fractal dimensionality, d_{fs}, calculated in accordance with the Neimark approach (Neimark 1990), was applied for quantitative characterization of microsurface structural transformation caused by lignin modification.

Lignin's and Si-lignin's sorption properties towards Cu^{2+} and Mn^{2+} cations were studied in batch experiment on equilibrium adsorption from cations solutions in acetate buffer (pH 5.0) within a wide range of concentrations (0.01 – 50 g/L). Monitoring cation and proton levels in initial and final equilibrium supernatant solutions was carried out for characterization of ion exchange in sorption interaction between lignin and $CuSO_4$ (batch experiment, 10 mM $CuSO_4$ water solution, pH 5.0). The metals content was determined by Atomic Absorption Spectroscopy (AAS).

The sorption capacity towards alanine was estimated by sorption isotherms method using the batch equilibrium procedure. 2-days cell culture of gramnegative and grampositive pathogenic bacteria (*E. coli and B. subtilus*) was used to assess the sorption properties of samples towards biological contaminants. Each sample (0.1 g) was put in the tube, and 10 mL of bacteria cell suspension in sodium chloride isotonic solution ($(3.\pm0.2)*10^8$ cells per 1 mL) was added; then the tube was closed and shaken for 1 hour in order to avoid biodegradation of organic substances. Sorbents were filtered off, and the amount of cells in filtrate was accounted. The filtrates obtained under the same conditions from bacteria suspensions without sorbents addition were used as blank probe.

Spectra of Electronic Paramagnetic Resonance (EPR) were recorded as first derivatives with a Bruker EMX spectrometer working at X-band frequency (9.6 GHz) with 100 kHz modulation. The magnetic field was varied between 100 and 7000 Gauss. All spectra were recorded at room temperature and presented in the form of the 1st derivative of absorbance line. The WINEPR SimFonia program was used for g-value and hyperfine splitting (HFS) constant determination.

RESULTS AND DISCUSSION

Synthesis of Lignin-based Hybrid Materials

As a result of lignin modification with silicon compounds, the new adsorption sites, in particular silanol groups Si-OH, are formed on the matrix surface, and the porous structure of lignin changes significantly (Telysheva et al. 2006). Data obtained in the present work on Cu^{2+} and Mn^{2+} equilibrium adsorption showed that modification with Si-oligomers significantly increased lignin sorption capacity towards these cations (Table 1).

Table 1. Langmuir Isotherm Parameters for Cu^{2+} and Mn^{2+} Adsorption by Lignin-based Sorbents

Cation	Hydrolysis lignin		Si-modified hydrolysis lignin	
	Q_{max}, mM/kg	K, L/mM	Q_{max}, mM/kg	K, L/mM
Cu^{2+}	212±6	0.24±0.02	667±25	0.11±0.1
Mn^{2+}	133±4	0.24±0.01	182±5	0.27±0.2

Monitoring of cations, anions, and proton levels during adsorption made it possible to assess the impact of ion exchange and complexing mechanisms on the sorption interaction between lignin-based matrices and metal cations. It was found that modification with silicon oligomers enhanced both cation exchange and complexing properties of lignin surface. Thus, the amount of cation exchange sites increased after modification of HL from 0.50 up to 1.40 mequiv/g (Table 2). The total amount of Cu^{2+} sorbed by HL was equal to 7.88 mequiv/l, whereas the amount of Ca^{2+}, Mg^{2+} and H^+ released owing to Cu^{2+} cation exchange was 7.27 mequiv/l (Table 3). It could be suggested that the remained part of sorbed Cu^{2+} (about 0.60 mequiv/l or 8 %) is fixed on lignin together with anion SO_4^{2-} by the mechanism of so-called molecular complexing of copper on the substrate.

Table 2. Influence of Si-modification on the Total Cation Exchangeable Sites of Hydrolysis Lignin

Sample	Amount of proton echangeable metallic cations release under the treatment with 2M HCl, mg/g DM sample			
	Mg	Ca	Na	Cu
Lignin	1.29±0.21	7.52±0.60	0.09±0.01	0.08±0.01
Si-lignin	0.49±0.04	4.25±0.51	27.38±0.82	0.08±0.01

Upon the interaction of Si-lignin with 10 mM $CuSO_4$ solution, 12.43 mequiv/l Cu^{2+} were sorbed due to cation exchange and 5.46 mequiv/l by complexing. Therefore, in the case of Si-modified lignin, the share of Cu^{2+} ions involved in complexing with sorbent increased up to 31% from total Cu^{2+} adsorbed amount.

Table 3. Monitoring Cations and Proton Levels in Initial and Final Equilibrium Supernatant Solutions for Sorption Interaction between HL and $CuSO_4$

Concentration of ions, mM, in:	Mg^{2+}	Ca^{2+}	Na^{+}	Cu^{2+}	H^{+}	SO_4^{2-}
Initial solution	0.34±0.04	1.05±0.15	0.18±0.01	10.39±0.32	0.02±0.005	12.51±0.10
Equilibrium solution	0.69±0.04	4.29±0.31	0.15±0.01	6.45±0.25	0.14±0.007	12.19±0.11
ΔC (mM)	0.35	3.24	-0.03	-3.94	0.12	0.32

The increasing complexing ability of Si-modified lignin towards transition metals was demonstrated also by EPR spectroscopy. Figure 1 shows EPR spectra of Cu-containing HL and Si-KHL samples (Cu-HL and Cu-Si-HL, respectively).

Both spectra exhibit anisotropic features with partially resolved hyperfine structure (HFS) due to interaction of unpaired electron with nuclear magnetic moments of ^{63,65}Cu nuclei with spin $I = 3/2$ (Gonella et al. 1999). The analysis of the EPR data (Table 4) showed axial anisotropic nature with axial pattern, where $g_{||} > g_{\perp}$, which is characteristic of tetragonal copper complexes (Zhang and Kamden 2000). Besides the EPR spectrum of Cu^{2+}, a strong narrow signal with $g = 2.0040+0.0002$ attributed to free radical of lignin was observed in the spectra recorded (Fig. 1).

For an axial symmetry, the relation between $g_{\perp}$ and $g_{||}$ expressed as $G = (2-g_{||})/(2-g_{\perp})$ is used as a measure of the exchange interaction between copper centres in the solid matrix (Zhang and Kamden, 2000; Chandra and Gupta 2005; Masoud et al. 2005). If the G value is less than 4, it indicates a considerable exchange interaction between metal ions in the solid complexes, while the more than 4 value of G testifies to negligible interaction. For the Cu-HL hybrid, G was greater than 4, which is characteristic for the presence of mononuclear complexes of hydrated Cu^{2+} ions immobilized in certain chemically active sites of lignin. However, in the case of Cu-Si-HL, the G parameter was 3.5, indicating some alterations in type of symmetry of Cu^{2+} complexes in comparison with Cu-HL sample and the considerable exchange interaction between metal ions associated with Cu^{2+} complexes.

Characterization of Sorption Properties of Lignin Hybrids

The synthesized copper- and manganese-containing hybrid materials were found to have significantly modified porous structure (Table 5) in comparison with those for non-modified and Si-modified precursor matrices (HL and Si-HL, respectively).

Conditions chosen for introduction of Cu^{2+} and Mn^{2+} cations into the lignin matrix lead to increase of surface area and pore volume; the number of mesopores increased, and micropores had been formed. In particular, a high increase in these characteristics was observed when Si-modified lignin was used as a matrix for interaction with the cations.

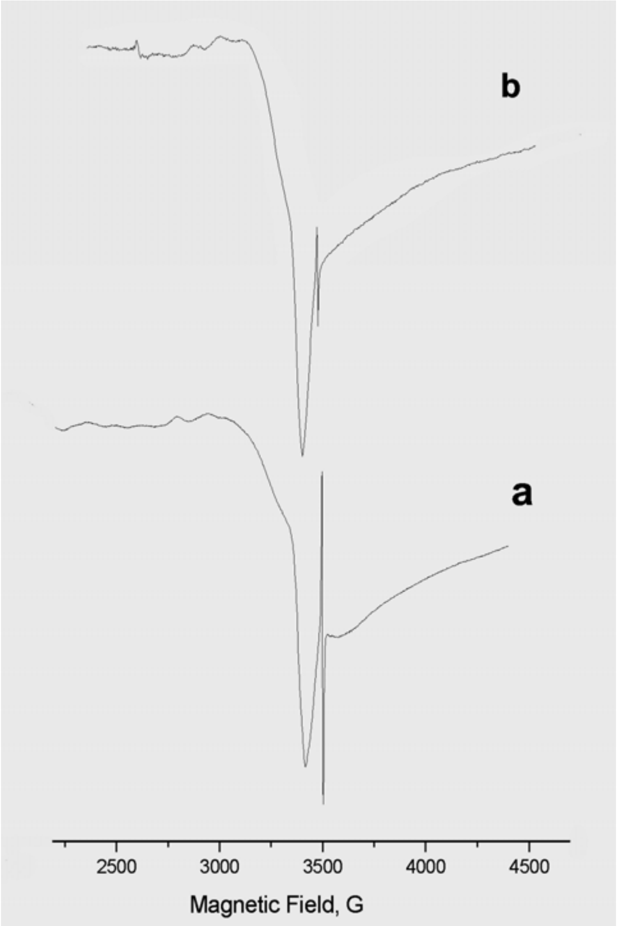

Fig. 1. EPR Spectra of lignin-based hybrid materials: (a) Cu-HL and (b) Cu-Si-HL

Table 4. Parameters of ESR spectra of Cu^{2+} in Lignin Products

Sample	$g_\perp$	$g_{||}$	$A_{||}$, gauss	$G = (2-g_{||})/(2-g_\perp)$
Cu-HL	2.06±0.01	2.37±0.01	131±1.3	5.1±0.8
Cu-Si-HL	2.09±0.01	2.27±0.01	130±1.3	3.5±0.3

$g_\perp$ and $g_{||}$ - diagonal components of Cu^{2+} g-tensor: $g_\perp$ - perpendicular to magnetic field, $g_{||}$ - parallel; $A_{||}$ - the HFS constant

The structural transformation of microsurface caused by lignin modification was quantitatively analyzed by applying the surface fractal dimensionality calculated from nitrogen gas adsorption isotherms using Equation 1 in accordance with the Neimark (1990) theory:

$$df_s = 3 + \frac{d\ln[N(\chi)]}{d\ln[-\ln(\chi)]} \qquad (1)$$

where d_{fs} is the surface fractal dimensionality, χ is the relative adsorbate pressure and $N(\chi)$ is the number of molecules adsorbed.

Table 5. The Characterization of Porous Structure of Lignin Hybrid Products in Terms of Low Temperature Nitrogen Gas Adsorption

Sample	Volume of pores, mm^3/g~~,~~				BET Specific surface, total, m^2/g~~;~~
	Total	Micropores	Mesopores	Macropores	
HL	10.38		6.53	3.85	5.68
Si-HL	39.14	0	30.8	9.06	19.36
Cu-HL	43.80	0	27.00	16.80	8.30
Mn-HL	59.0	0			15.1
Cu-Si-HL	83.57	0.30	67.99	15.48	44.64
Mn-Si-HL	96.7	0.32			50.4

The Neimark approach is based on thermodynamic theory of adsorption and consideration of fractal surface as a hierarchic system of self-similar pores of different sizes. The plotting of experimental isotherms of nitrogen adsorption in the coordinates of the Equation (1) (see Fig. 2) provided an opportunity to establish the values of surface fractal dimensionality of lignin products, as shown in Table 6.

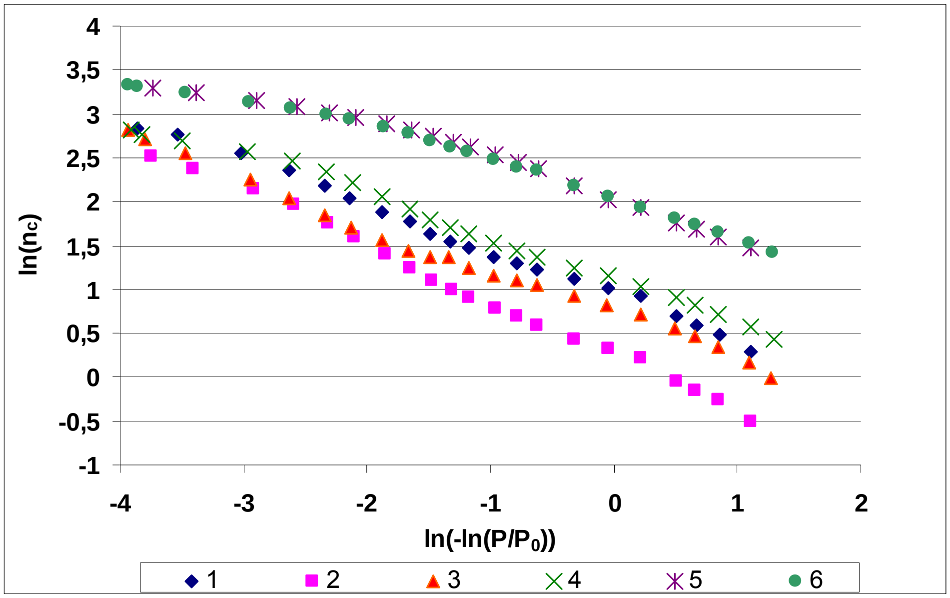

Fig. 2. The relationship between logarithmic nitrogen content, n_c, weight % (corresponds to $N(\chi)$) and double logarithmic relative pressure of nitrogen gas, P/P_o (corresponds to χ). 1 – HL, 2 – Cu-HL, 3 – Mn-HL, 4 – Si-HL, 5 – Cu-Si-lignin, 6 – Mn-Si-HL

Consideration of the surface fractal dimensionality values (Table 6) showed slightly increasing complexity of lignin matrix microsurface as a result of modification with Si-oligomers: d_{fs} changes from 2.46 (the value typical for isolated lignins) to 2.57. The following treatment of Si-lignin with Cu^{2+} or Mn^{2+} led to the further significant increase in this microsurface parameter (up to 2.79), revealing increasing complexity of the hybrid material surface and its inclining to a three-dimensional surface.

Table 6. Surface Fractal Dimensionality of Lignin Products

Sample	Surface fractal dimensionality, d_{fs}
HL	2.46
Cu-HL	2.35
Si-HL	2.57
Cu-Si-HL	2.79
Mn-Si-HL	2.82

Fixation of Cu^{2+} cation onto the surface of Si-modified lignins significantly increased their adsorption properties towards proteins; e.g., sorption capacity towards alanine increased by 1.5 times (Fig. 3). Obviously, this is owing to both increasing of the specific surface values and enhanced cation- π interaction between Cu^{2+} and protein aromatic moieties.

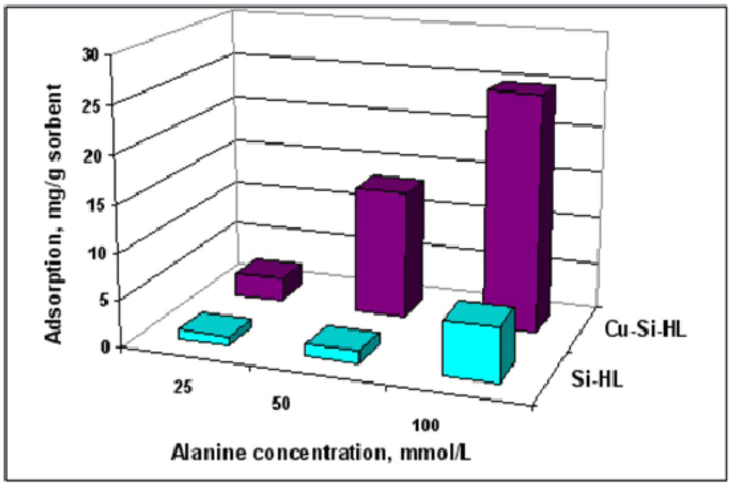

Fig. 3. Alanine sorption by lignin-based products

In order to decrease the influence of pathogenic microorganisms on the environment, the sorbents have to be able to decrease their functional activity. The results of tests of lignin products sorption activity towards pathogenic microorganisms show (Table 7) that Cu-HL and Cu-Si-HL were characterized by enhanced sorption capacity towards both gramnegative and grampositive bacteria, *Escherichia coli* and *Bacillus subtilis,* in comparison with HL and Si-HL. The Cu-containing Si-modified hydrolysis lignin (Cu-Si-HL) had the highest sorption activity towards the both bacteria and, besides that, totally suppressed the vital activity of bacteria sorbed.

Table 7. Pathogenic Bacteria Sorption by Lignin-Based Products

Sample	Numbers of sorbed cells per 1 g of sorbent		Sorption efficacy, % of initial cells numbers in bacteria suspension	
	Escherichia coli	*Bacillus subtilis*	*Escherichia coli*	*Bacillus subtilis*
HL	$(1.2 \pm 0.2)*10^{10}$	$(1.3 \pm 0.3)*10^{10}$	40	43
Si-HL	$(2.5 \pm 0.2)*10^{10}$	$(1.2 \pm 0.1)*10^{10}$	83	40
Cu-HL	$(2.3 \pm 0.2)*10^{10}$	$(2.1 \pm 0.2)*10^{10}$	77	70
Mn-HL	$(1.7 \pm 0.2)*10^{10}$	n.d.	57	n.d.
Cu-Si-HL	$(2.8 \pm 0.2)*10^{10}$	$(2.6 \pm 0.1)*10^{10}$	93	87
Mn-Si-HL	$(2.0 \pm 0.2)*10^{10}$	n.d.	67	n.d.

CONCLUSIONS

1. Novel lignin-based organic-inorganic hybrid materials with increased surface area, micro-, and meso-pore volume, enhanced sorption properties, and biocide activity were obtained using modified lignin matrices as organic precursors.
2. Interaction of Si-modified lignins with Cu^{2+} cations yielded materials with improved sorption ability and antipathogenic activity. When Si-modified lignin was used as a matrix for design of Cu-containing sorbents, the vital activity of pathogenic bacteria was totally suppressed.

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