

**ADSORPTION PROPERTIES OF WASTE LIGNOCELLULOSIC MATERIALS
PRODUCED IN REPROCESSING OF WHEAT STRAW AND MAIZE STALKS BIOMASS**

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Abstract

The increase of the interest to bio-ethanol production from vegetal raw materials places the question for utilization of the waste hydrolyzed lignin containing some quantity of cellulose. One possibility to solve this problem is clarification of the potential to use such materials as adsorbents of metal ions, other elements and organic compounds from water solutions with the purpose of purifying waste and natural waters. The large internal surface of the lignocellulosic material and availability of different functional groups that could play the role of adsorption centers suggests such possibility.

There is investigated the adsorption of Cu^{2+} -ions from samples of hydrolyzed lignin (HL) and alkaline treated hydrolyzed lignin (AAHL), obtained from wheat straw and maize stalks. The adsorption mechanism, adsorption centers, specific surface and the potential for practical application of these materials are examined by BET analysis, IR-spectroscopy, EPR and TG-DSC analyses. It is found out that the adsorption isotherm of Cu^{2+} -ions on the examined samples is of Langmuir type, the parameters in Langmuir equation depending on the initial material and the respective treatment. The EPR spectra show that Cu^{2+} -ions orient to the oxygen ions and form tetrahedral complex.

Key words: adsorption, Cu^{2+} , mechanism, waste hydrolyzed lignocellulosic materials, alkaline treatment

INTRODUCTION

The sorption properties of hydrolyzed lignins are discussed in many publications. There is a high interest to utilization of waste lignin in relation with water purification from heavy metals (Hristov et al. 1999 and Harman et al. 2007). Waste lignin alone or in combination with other materials has been used for purification of Pb, Cu, Zn and Cd water solutions (Hristov et al. 1999 and Nenkova et al. 2003) as well as of Ni(II) ions (Penaranda et al. 2010). Materials that retain cellular structures and that have high lignin contents were highly effective (Harman et al. 2007). Publication (Tazrouti et al. 2009) shows that Langmuir equation is valid in the Cr(VI) adsorption on lignin. Publication (Abdel-Ghani et al. 2007), about the Pb adsorption, on rice husks, maize cobs sawdust follows Temkin's equation. Technical hydrolysis lignin (THL) is used as adsorbent for purification of waste waters from 2- nitrophenol (Allen et al. 2005) as well as for purification from petroleum contaminants (Nenkova 2007) by lignin containing composite.

The main question in the adsorption of metals such as Pb, Cu, Zn, Cr, Cd, etc., is which groups of THL play the role of adsorption centers and how these groups change if treated with various chemicals. Publication (*Dalimova 2006*) presents study of the changes of the different groups on the THL surface during treatment by H₂SO₄ and NaOH and how the THL adsorption ability changes in respect of water vapors. It is found that the alkaline treatment leads to adsorption ability increase.

In publication (*Flogeac et al. 2003*) through examination of the adsorption isotherms, EPR and EXAFS the conclusion is made that Cr(III) ions are in octahedral position. The same conclusion is reached in respect of the adsorption of the same ion in (*Wu et al. 2008*) the mechanism being ion exchange by formation of intra-spherical complexes. Langmuir equation is followed in the adsorption. In publication (*Guo et al. 2008*) it is said in relation to the adsorption ability that lignin isolated from black liquor has affinity with metal ions in the following order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). According to the authors the adsorption centers are phenol and carboxyl OH-groups, the phenol ones having higher affinity towards metal ions.

With a view to clarify the role of the functional groups of the components of the lignocellulosic materials as adsorption centers during the adsorption of metal ions from water solutions, the purpose of the present paper is investigation of Cu²⁺ ions adsorption from water solutions on hydrolyzed lignin (HL) from acid and subsequent enzyme hydrolysis of wheat straw and maize stalks and the alkaline activated hydrolyzed lignin (AAHL) produced of them.

EXPERIMENTAL

1. Materials

The acid hydrolysis of the agriculture lignocellulosic raw materials (wheat straw and maize stalks) was performed in 1L stainless steel laboratory autoclaves rotated at constant rate in a polyglycol bath under the following conditions: sulphuric acid charge 1%; hydromodul ratio 1:10; initial temperature 100°C; max. temperatures 140°C; heating time 60min. and time at maximum temperature from 60 min.; Enzymatic treatment conditions are: temperature 50°C, reaction time 24 hours, lignocellulosic consistency 10%, pH initial 5.5 - 6.0, pH final 4.2 - 4.6 and 5% charge of the cellulase enzyme complex NS50013 in combination with 0.5% β-glucosidase NS 50010 (*Tsekova et al. 2011*). The solid lignocellulosic mass (HL) which is in fact a waste product in this process is a suitable source of monomer phenolic compounds by alkaline treatment (*Radoykova et al. in press*). Samples are marked with HL(s), produced from wheat straw and HL(m), produced from maize stalks.

The alkaline treatment of waste hydrolyzed lignocellulosic materials was performed at temperature of 180°C for 4 hours. An aqueous solution 5% NaOH was used at lignin: NaOH ratio (hydromodul) 1:8. The destructed lignin suspension obtained by alkaline treatments has been filtered and the quantity of undissolved residue has been determined. The dissolved part has been precipitated by acidification with HCl (2 mol/L) to pH ~ 1 – 2 and alkaline activated lignin was separated (*Radoykova et al. in press*). Samples are marked with AAHL(s) for wheat straw and AAHL(m) for maize stalks.

2 SAMPLE CHARACTERIZATIONS

The samples were subjected to Thermal analysis (TG-DSC), EPR and FTIR spectroscopy.

2.1. IR spectroscopy

Infrared spectra were measured on a Varian 660 IR spectrometer. Spectra were collected in the mid-infrared region (4000-400 cm⁻¹). Samples were prepared by the standard KBr pellets method.

2.2 Specific surface area

The determination of the specific surface area of the samples was carried out by nitrogen adsorption at 77.4 K. Nitrogen adsorption isotherms were used to calculate the specific surface area (ABET) using the BET equation.

2.3 TG-DSC

Differential scanning calorimetric measurements were performed with STA PT1600 Simultaneous Thermal analyzer, using DSC measuring system, Type S (Pt 10%/ Pt-Rh), temperature range 20 - 1000°C, 10°C/min heating rate in oxidizing atmosphere.

2.4 EPR

EPR measurements were performed at room temperature on JEOL JES-FA 100 spectrometer operated in X-band. Standard cylindrical cavity TE₀₁₁ were used. The powder samples were placed in quartz tubes and directly measured without previous sample preparation.

3 ADSORPTION STUDIES

Adsorption evaluation of Cu(II) cations by the samples was conducted through an adsorption test under static conditions at different Cu(II) concentration, constant pH 5.0 and temperature 20 °C. The Cu(II) concentration was changed from 10 to 75 mg/L. The following methods was used: series of samples of 0.3g of each material and 100 ml of CuSO₄ solution were mixed in 250 ml flask and placed for 24 hours in a thermostat at periodically stirring to establish equilibrium. Then samples were filtered and values of the pH of the filtrate and Cu(II) concentration were measured. The concentration of Cu(II) was determined photometrically at $\lambda = 560$ nm using DR 2800 Spectrophotometer (Hach Lange).

The adsorption capacity was calculated as:

$$A = \frac{(C_0 - C) \times V}{m}, \quad (1)$$

Where: A – adsorption capacity (mg/g); C₀ – original Cu(II) concentration in solution (mg/L); C – Cu(II) concentration in solution after 24 h. (mg/L); V – Cu(II) solution volume (L); m – mass of the samples (g).

The data obtained from the adsorption were checked to what extent they satisfy Langmuir and Freundlich equation.

The constants in the isotherms were determined by linearized forms as follows:

Langmuir isotherm:

$$\frac{C_e}{A_e} = \frac{1}{A_m \times b} + \frac{1}{A_m} \times C_e \quad (2)$$

Where: C_e – equilibrium concentration (mg/L), A_e – equilibrium adsorption capacity (mg/g), A_m – maximum adsorption capacity (mg/L), b – constant in Langmuir equation related to the adsorption heat (L/mg).

The change of adsorption energy was calculated by the formula:

$$\Delta G = -RT \ln(1000 \times b) \quad (3)$$

Where : R – gas constant (8.314 J/mol), T – temperature (K), b – constant in Langmuir equation (L/mmol).

Freundlich isotherm:

$$\lg A_e = \lg K_f + \frac{1}{n} \lg C_e \quad (4)$$

Where: K_f and n –Freundlich constants

RESULTS AND DISCUSSIONS

The determination of Klason lignin was carried out according to TAPPI standard test method T 222 om-1. The results are respectively 40.20 % for HL(s) and 45.93 % mass for HL(m) .

Fig.1 and Fig.2 present TG-DSC curves of analyzed samples.

As seen from the dependences in the figures, significant changes occur at temperatures above 200°C. In the temperature range 310 - 402°C exothermal peaks related to destruction of the polysaccharide part in the initial hydrolyzed lignocellulosic materials HL(s) and HL(m) are observed. The destruction processes in these samples finish to 450°C. The separated after alkaline treatment AAHL(s) and AAHL(e) are based on destruction stages after 450°C and above 700°C.

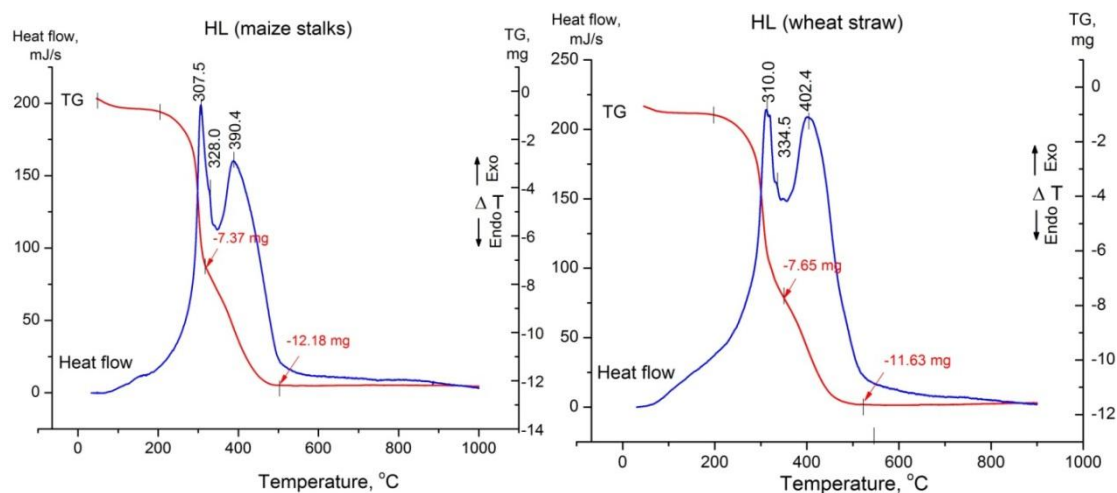


Figure 1. TG-DSC curves of HL(s) (1 a) and HL(m) (1 b)

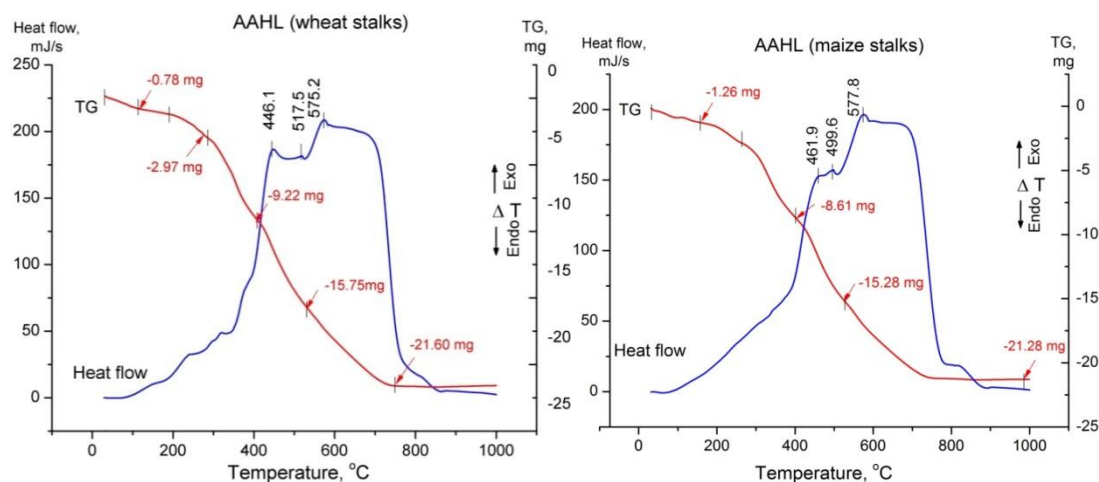


Figure 2. TG-DSC curves of AAHL(s) (2 a) and AAHL(m) (2 b)

Figure 3 shows Cu (II) adsorption for the four samples as concentration function. It is seen that the adsorbed quantity for 1g of sample is greater for the samples HL(s) and HL(m) compared to that retained by AAHL(s) and AAHL(m). The Cu (II) adsorption increases with the increase of the concentration; for samples HL(s) and HL(m) it has clearly expressed trend to saturation while for alkaline treated samples the adsorption capacity grows in the whole examined concentration range. Under the conditions of the experiment, sample HL(m) displays the best adsorption ability that is probably due to structural features of the lignocellulosic material. The alkaline activation does not lead to increase of the adsorption capacity of 1 g of sample.

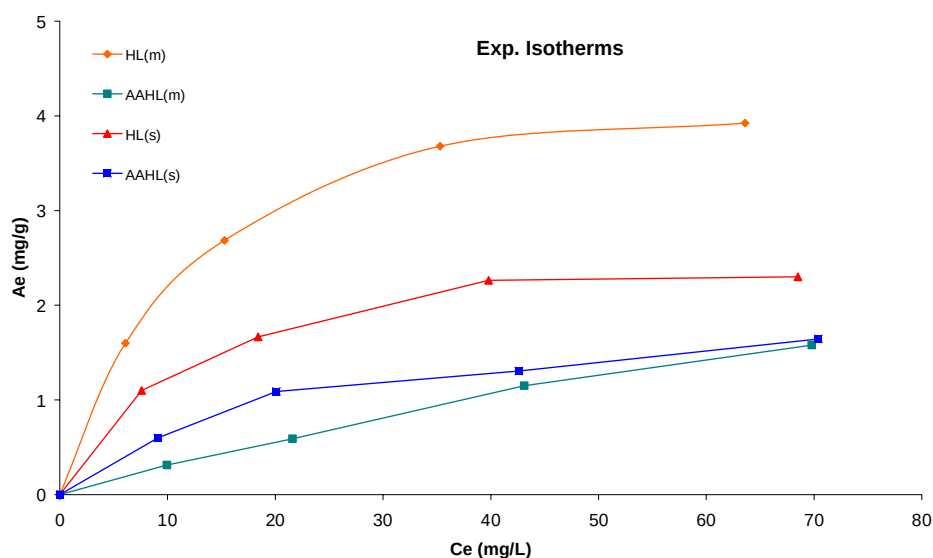


Figure 3. Adsorption isotherms of the studied samples

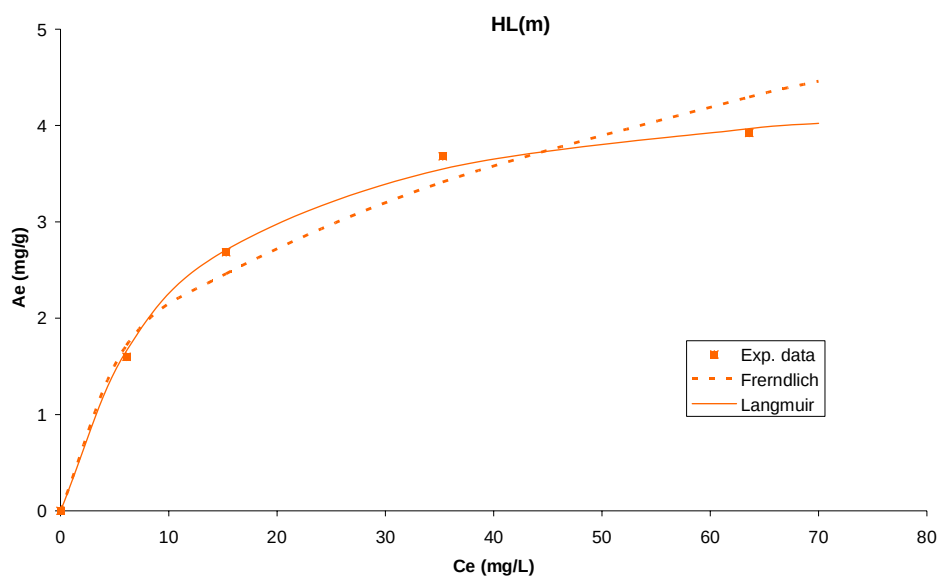


Figure 4. Theoretical adsorption isotherms according to Langmuir and Freundlich for sample HL(m)

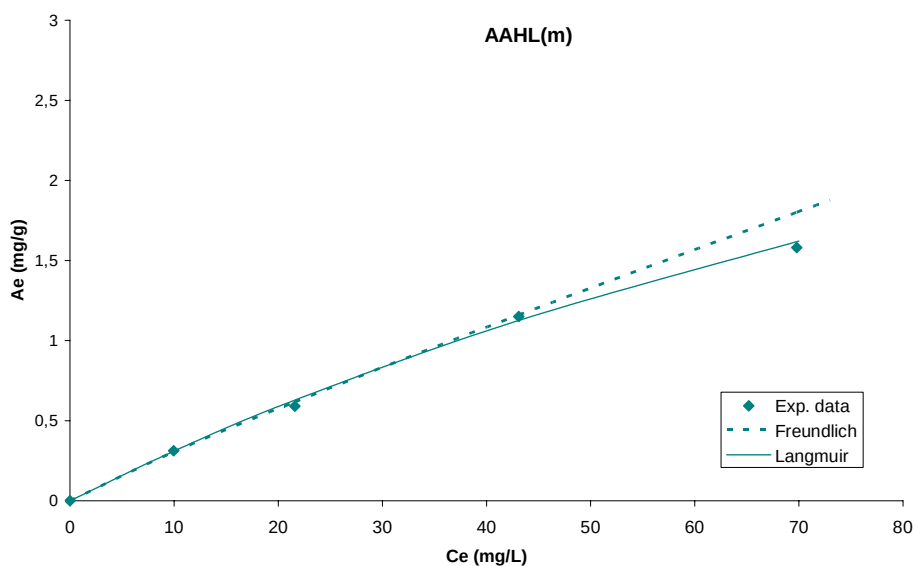


Figure 5. Theoretical adsorption isotherms according to Langmuir and Freundlich for sample AAHL(m)

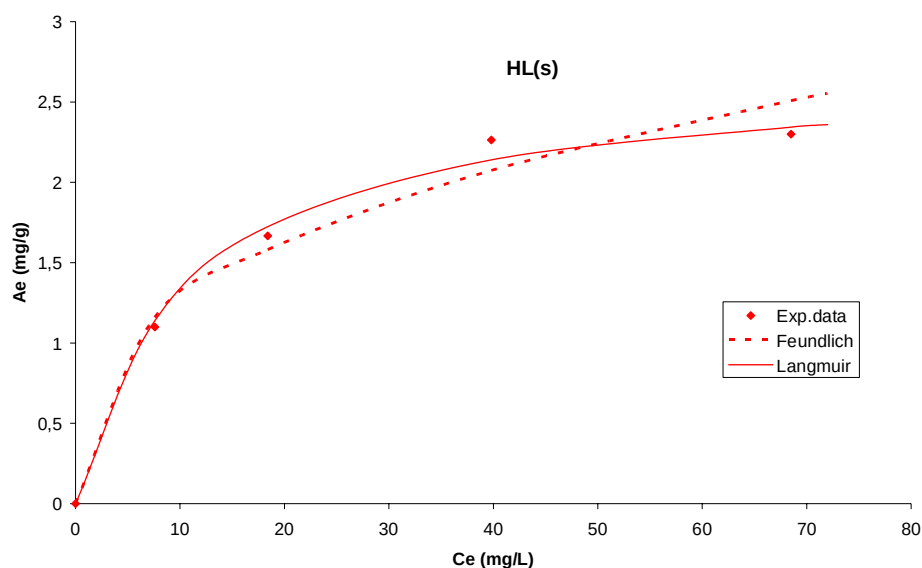


Figure 6. Theoretical adsorption isotherms according to Langmuir and Freundlich for sample HL(s)

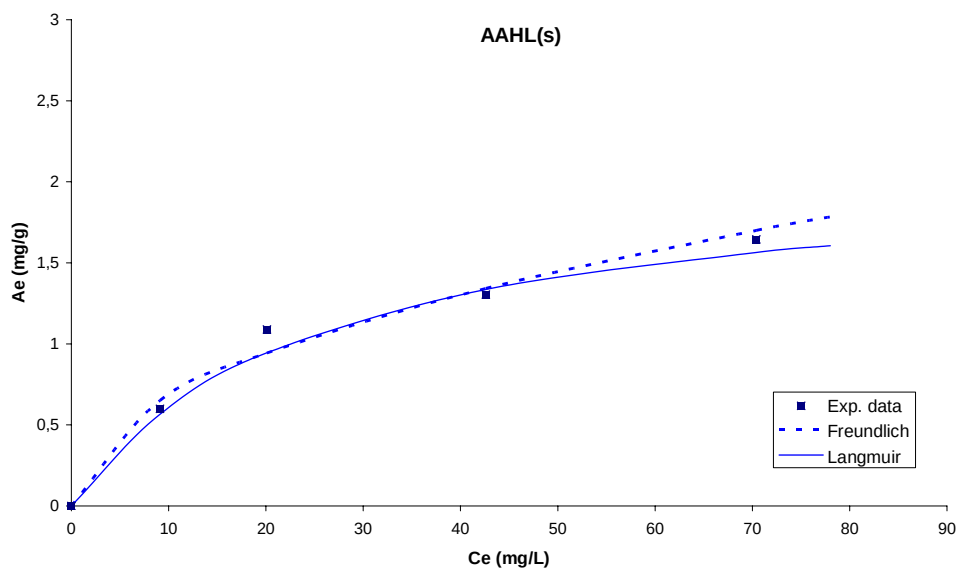


Figure 7. Theoretical adsorption isotherms according to Langmuir and Freundlich for sample AAHL(s)

The experimental adsorption data for every sample were assessed by Freundlich and Langmuir isotherms presented in Figures 4-6. The calculated constants in the isotherms and the corresponding

correlation coefficients are presented in Table 1. For assessment of the adsorption ability of every sample, their specific surface and the adsorption energy variation are taken into account. These data are also presented in Table 1.

However, the maximum adsorption coefficient for unit surface for the samples activated by alkaline treatment is higher than that for samples without such treatment. Particularly clearly that is seen in a comparison of the samples HL(m) and AAHL(m). The alkaline treatment leads to increase of the maximum adsorption capacity for unit surface by approximately 56% for AAHL(m).

The adherence to Langmuir equation shows that the adsorption centers do not interact (directly) as the adsorption does not depend on surface filling. In respect of the type of the adsorption centers it should be assumed that as a result of acid and enzyme treatment they form (samples HL) different adsorption centers from those after alkaline treatment (samples AAHL). This is confirmed by the values of the constant b , which for the samples HL is of the order of $9.1 \cdot 10^{-2} - 9.6 \cdot 10^{-2}$ while for the samples AAHL it is of the order $0.6 \cdot 10^{-2} - 4.4 \cdot 10^{-2}$. This significant difference is determined mainly by the different heat of Cu (II) adsorption on the surface of the adsorbents.

Table 1. Adsorption parameters

Adsorption isotherms	HL(m)	AAHL(m)	HL(s)	AAHL(s)
Langmuir:				
A_m	4.65	5.48	2.70	2.12
b	0.091	0.006	0.096	0.044
R^2	0.9980	0.9273	0.9949	0.9848
Freundlich:				
K_f	0.85	0.04	0.57	0.23
N	2.56	1.10	2.85	2.12
R^2	0.9474	0.9982	0.9421	0.9481
S_o (m ² /g)	65.4	49.5	87.2	48.3
A_m/S_o (mg/m ²).10 ²	7.11	11.07	3.10	4.39
ΔG (kJ/mol)	-21.10	-14.49	-21.23	19.36

The oxidizing state of copper is Cu^{2+} and there is no change during the adsorption. That is confirmed by the EPR spectra of the samples after adsorption of the copper ions, presented in Fig. 9. Fig. 8. shows EPR Spectra of samples before Cu^{2+} adsorption.

Spectra with the following parameters: $g_{||} = 2.287 \pm 0.004$ and $g_{\perp} = 2.065 \pm 0.004$; $A_{||} = 15.0 \text{ mT} \pm 0.3 \text{ mT}$, which are characteristic for copper (II) complexes, were detected by EPR spectroscopy. In addition for all samples a singlet line with $g = 2.004 \pm 0.001$ due to a stable free radicals were detected. Copper ions are coordinated to oxygen atoms and form a tetrahedron complex.

Observing Langmuir equation, established by the adsorption studies, shows that Cu^{2+} -ions adsorption for each sample runs on the same type of adsorption centers, of similar adsorption heat, which does not depend on the quantity of the adsorbed ions. The adsorption centers for the samples HL(s) and

HL(m) are close in adsorption heat but they differ from those obtained after autoclave treatment. It is known that Cu(II)-ions have higher stabilization energy in tetrahedral coordination. The emergence of 4 lines in the EPR spectrum shows that the Cu^{2+} -ions are separated and cannot realize exchange interaction between them. Therefore, they are located in comparatively afar places on the lignin surface.

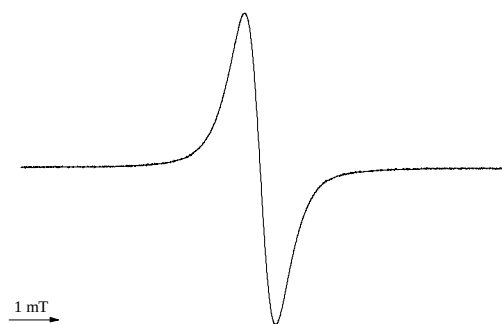


Figure 8. EPR Spectra of samples before Cu^{2+} adsorption
1-HL(s); AAHL(s); HL(m); AAHL(m)

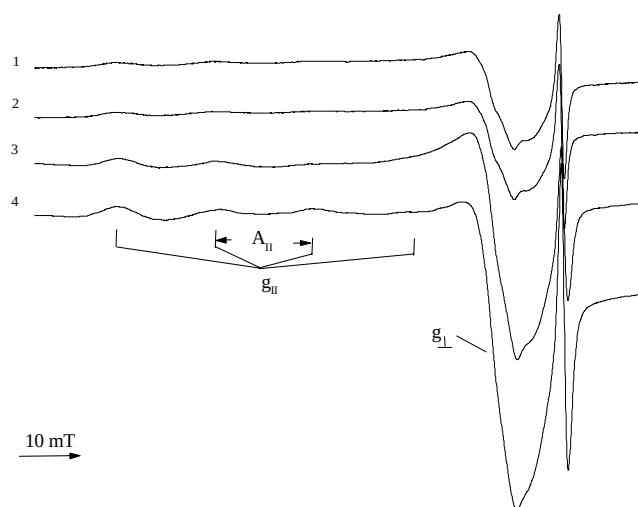


Figure 9. EPR Spectra of samples after Cu^{2+} adsorption
(1-HL(s) ; 2- AAHL(s) ; 3 – HL(m) ; 4 – AAHL(m))

Fig.10 and Fig.11 present IR spectra of analyzed samples.

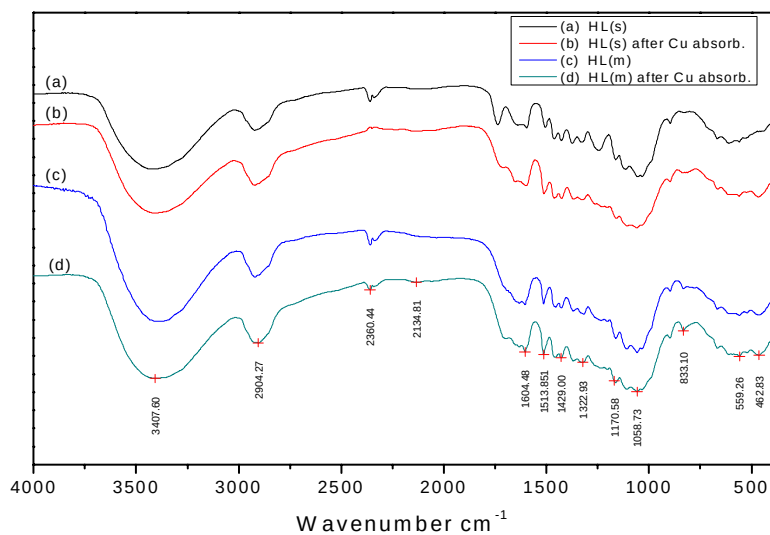


Figure 10. IR spectra of HL(s) and HL(m) samples, before and after Cu²⁺ adsorption

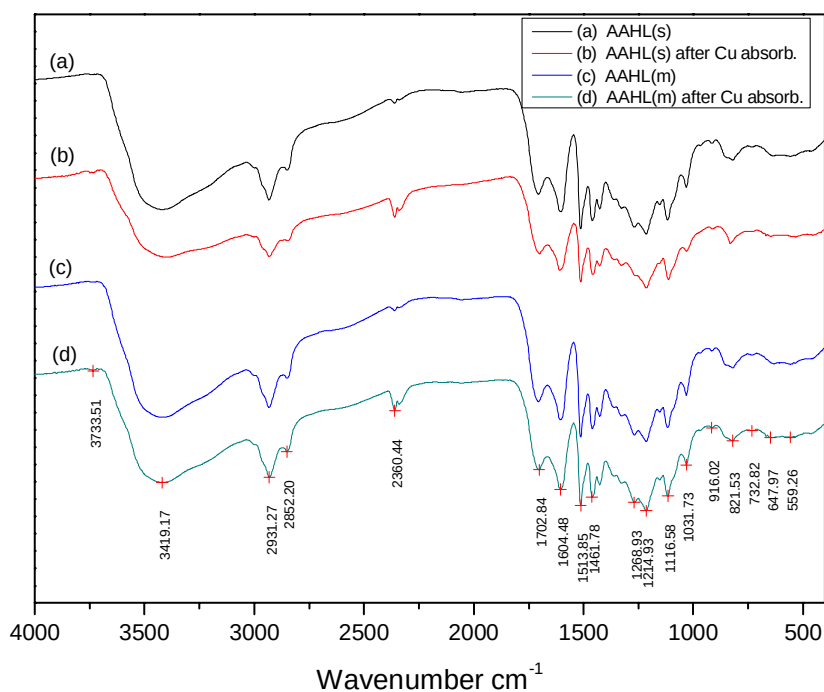


Figure 11. IR spectra of AAHL(s) and AAHL(m) samples, before and after Cu²⁺ adsorption

The participation of OH-groups in complex formation is difficult to be registered by IR-spectra because they take part in the formation of hydrogen bonds in the initial sample, too. This is seen in the broad band in the zone $3500\text{--}3100\text{ cm}^{-1}$, which is due to stretching vibrations of the alcohol and phenol hydroxyl groups included in hydrogen bonds. The free OH-groups show absorption at 3600 cm^{-1} . Eventual participation of the OH-groups may reflect on change of the band profile in this zone which could be due to change in the strength of the hydrogen bonds as a result of their participation in complex formation that occurs in samples (b) and (d) in Fig. 10.

The zone $1600\text{--}1760\text{ cm}^{-1}$ is characteristic for the carbonyl absorption. In this zone the reflection of the participation of the OH-groups from COOH in the complex formation on the stretching vibrations of the carbonyl groups is more visible (Nakamoto 1970). This is particularly observable in the IR-spectrum of HL(s) before and after Cu^{2+} adsorption (Fig. 10). Visible change is seen in the bands at 1700 cm^{-1} and $1000\text{--}1200\text{ cm}^{-1}$, which shows that the carbonyl group is engaged (Fig. 10, a and b). This difference in the spectra of samples c and d (Fig.10) is not so great. In the amorphous compounds the small differences in the spectra due to the participation of part of the groups in complex formation is not clearly expressed. In the spectra of samples a and b (Fig. 11) there is difference in the relation between the bands at 1702 cm^{-1} and 1604 cm^{-1} .

In all spectra there is a comparatively intensive band in the range $3000\text{--}2850\text{ cm}^{-1}$. These bands refer to different types of stretching vibrations of the C-H bonds in methyl and methylene groups.

The next bands that appear in the spectra of almost all lignins are at 1600 and 1510 cm^{-1} , the second being usually stronger. These bands are connected with skeleton vibrations of the aromatic rings. It is thought that the bands at 1460 cm^{-1} , as well as at 1412 cm^{-1} are related to CH deformation vibrations in the methoxyl groups.

The band at 832 cm^{-1} is ascribed to deformation vibrations of the C-H bonds in siringyl groups in position 2 and 6.

CONCLUSION

It is found out that the adsorption isotherm of Cu^{2+} -ions on the examined samples is of Langmuir type, the parameters in Langmuir equation depending on the initial material and the respective treatment. The EPR spectra show that Cu^{2+} -ions orient to the oxygen ions and form tetrahedral complex.

Under the conditions of the experiment, sample HL(m) displays the best adsorption ability for 1g of sample. However, the maximum adsorption coefficient for unit surface for the samples activated by alkaline treatment is higher than that for samples without such treatment.

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