

Study of the formation of lignin hydrogels with metal cations

Edward I. Evstigneyev, Elena V. Grinenko, Anton S. Mazur & Aleksander V. Vasilyev

To cite this article: Edward I. Evstigneyev, Elena V. Grinenko, Anton S. Mazur & Aleksander V. Vasilyev (2021) Study of the formation of lignin hydrogels with metal cations, Journal of Wood Chemistry and Technology, 41:2-3, 73-82, DOI: [10.1080/02773813.2021.1873389](https://doi.org/10.1080/02773813.2021.1873389)

To link to this article: <https://doi.org/10.1080/02773813.2021.1873389>



[View supplementary material](#)



Published online: 08 Feb 2021.



[Submit your article to this journal](#)



Article views: 89



[View related articles](#)



[View Crossmark data](#)



Study of the formation of lignin hydrogels with metal cations

Edward I. Evstigneyev^a, Elena V. Grinenko^a, Anton S. Mazur^b, and Aleksander V. Vasilyev^{a,b} 

^aDepartment of Chemistry, Institutsky per, Saint Petersburg State Forest Technical University, Saint Petersburg, Russia; ^bCenter for Magnetic Resonance, Research Park, Saint Petersburg State University, Saint Petersburg, Russia

ABSTRACT

Potentiometric titration, FTIR spectroscopy, ¹³C solid-state NMR spectroscopy and chemical analysis were used to study the gelation of technical lignins (oxidized hydrolysis, kraft, soda and lignosulfonates) and Pepper lignin in interaction with metal salts (CaCl₂, Mg(NO₃)₂, FeSO₄, Co(NO₃)₂, Pb(NO₃)₂, Fe(NO₃)₃, CuSO₄, AgNO₃). It has been found that compounds that are salts of weak base and strong acid possess an ability to gelation; the metal cation has a standard potential above a certain value, has moderate hydrolysis ability and the cation hydroxide formed in the hydrolysis reaction has a relatively low solubility. At the gel formation, a compounds of the composition R–COO–Me^z + –OOC–R, z = 2, 3 were formed. A scheme of intermolecular bonds at the point of lignin hydrogel formation was proposed, according to which, adjacent lignin molecules bound to each other by three types of bonds: ionic between carboxyl groups of lignin and metal cation, coordination between metal cation and water molecules included in the coordination sphere, and hydrogen bonds, binding all components of the system into a single whole. Lignin hydrogels have a high sorption ability with respect to heavy metals such as lead, iron and copper, that, depending on the content of acid groups in lignin and the molar mass of the sorbate, is approximately 25–50% by weight of lignin. This opens up the possibility of using a new type of lignin hydrogels for wastewater treatment of chemical plants.

KEYWORDS

Acid–base titration; carboxyl groups; lignin hydrogel; metal salts; oxidized hydrolysis lignin

Introduction

When choosing a lignin valorization strategy, two approaches are possible: processing lignin as a whole or isolating and using products of its destruction, for example, monomeric compounds with high added value. In recent years, lignin valorization through monomeric compounds has been most actively developed.^[1–7]

The traditional approach involves a use of technical lignins such as kraft lignin and lignosulfonates, mainly, to obtain dispersing or binding agents.^[8] The potential of hydrolysis lignin, a large-tonnage by-product of the hydrolysis industry, has not yet been realized in this direction.^[9]



Preparation and use of lignin hydrogels opens up new possibilities in this direction.^[10,11] Hydrogels are polymer crosslinked three-dimensional structures with high ability to swell in water, sensitive to changes in pH, temperature and other factors.

Hydrogels are classified according to various parameters, such as production method, ionic charge,

physical properties, biodegradability and some others.^[12] Depending on the nature of interactions, due to which a three-dimensional network is formed, hydrogels have been divided into chemical (formed due to covalent bonds) and physical ones (formed due to hydrogen bonds, hydrophobic interactions and van der Waals forces).^[11]

Hydrogels, including lignin hydrogels, have selective sorption ability in relation to various classes of compounds. Therefore, they are used in both in medicine, as a matrix for drug delivery,^[13–15] and in water purification systems.^[16–18]

The synthesis of lignin hydrogels is carried out mainly by polymerization methods. Exemplarily, alkali lignin is first subjected to acid-catalysed phenolation. Then, phenolated lignin is dissolved in dimethyl sulfoxide (DMSO) containing calcium chloride. Hydrogen peroxide, isopropylacrylamide and methylenebisacrylamide (crosslinking agent) were added to the resulting solution and heated in a water bath for 12 h at 70 °C. Then the gel was mixed with DMSO, left for 5 days, before DMSO was

CONTACT Edward I. Evstigneyev  edward_evst@mail.ru  Department of Chemistry, Institutsky per., Saint Petersburg State Forest Technical University, Saint Petersburg, Russia.

 Supplemental data for this article is available online at <https://doi.org/10.1080/02773813.2021.1873389>

© 2021 Taylor & Francis Group, LLC

replaced by water. After 12 h of residence time the gel was dried either under vacuum at 40 °C for 12 h or using freeze drying at -50 °C for 24 h.^[19]

Also methods for producing hydrogels in polymerization reactions of lignin with polyacrylic acid,^[17] in the interaction of lignosulfonate with graphene oxide,^[16] lignosulfonate with bentonite, acrylamide and maleic anhydride,^[20] lignin with ionic liquid^[21] were described. Unfortunately, these methods had the same drawbacks: multistage, duration and use of toxic reagents.

In this article, we propose a new method for producing lignin hydrogels, characterized in that the hydrogel is formed *in situ* upon the interaction of lignin with sorbate. The goal of our work was to study the physicochemical transformations that occur during the formation of lignin hydrogels of a new type and to elucidate their possible structure.

Experimental

Lignin samples

Oxidized hydrolysis lignin (OHL) is a technical hydrolysis lignin oxidized by hydrogen peroxide in an aqueous solution of sulfuric acid. The oxidation procedure was described in detail in our previous work.^[22]

Kraft and soda lignins were isolated from black liquors of laboratory cooking of spruce wood chips in accordance with the method of work.^[23] All cooks of spruce chips (37 g of o.d. wood) were carried out in a series of rotating autoclaves. The temperature was increased from 80 °C to 170 °C for 120 min, and temperature was held at 170 °C for 60 min. The active alkali charge for the soda cook was 18% (as Na₂O), for kraft cook, it was 15% (25% sulfidity). Lignin was isolated by a process of acidification of the black liquors with diluted sulfuric acid to pH 2.0, followed by the sample being centrifuged, washed repeatedly with water and dried by P₂O₅ in vacuum. The number-average molecular weight of kraft lignin (M_n), measured by vapor pressure osmometry, was 1587 and for soda lignin it was 1593. The content of phenolic hydroxyl groups in kraft lignin was 3.81 mmol/g and carboxyl ones 0.81 mmol/g. The total content of acidic groups in soda lignin was 2.84 mmol/g.

Lignosulfonic acids (LSAs) were obtained from Syassky PPM. Pepper lignin spruce was isolated according to the method of work.^[24] The method provides for the treatment of the extracted sawdust with a 9: 1 dioxane: water mixture containing 0.2 M HCl, refluxing, evaporation of the solution and precipitation of lignin by water. The content of carboxyl groups was determined by the modified ion-exchange

method using NaHCO₃,^[25] the content of phenolic hydroxyl groups was determined by the aminolysis method.^[26]

The method of preparation of hydrogels

A 40 mL solution containing 1 g of lignin and a stoichiometric amount of NaOH, calculated from acidic groups, was titrated with a 0.1 M titrant solution, for example Pb(NO₃)₂, with stirring in a thermostatic cell equipped with a magnetic stirrer at 20 °C. The point of gel formation was considered the titrant volume corresponding to a sharp increase in the viscosity of the solution with gel formation. The liquid phase was separated by centrifugation at a speed of 5000 rpm for 30 min, the resulting gel was dried at 101 °C to constant weight (Infrared Moisture Analyzer MA35, Germany) and ground in a porcelain mortar. There were no lead ions in the supernatant (test with KCl and KJ).

Substances

0.1 M solutions of the following salts were studied: CaCl₂, Mg(NO₃)₂, FeSO₄, Co(NO₃)₂, Pb(NO₃)₂, Fe(NO₃)₃, CuSO₄, AgNO₃, as titrants. All salts were of analytical grade and used without further purification. Lead benzoate was obtained by mixing stoichiometric amounts of sodium salt of benzoic acid and Pb(NO₃)₂. The precipitate was washed three times with ice water on a porous glass filter and dried at 101 °C to constant weight. Pb(OH)₂ was synthesized by the same procedure by mixing solutions of Pb(NO₃)₂ and NaOH.

Titration curves were obtained by potentiometric titration using a glass electrode and a saturated silver chloride reference electrode. Device: IPL Multitest (Russia).

FTIR-spectroscopy

Spectra of samples were recorded in a form of tablets (press-fit with KBr). Lignin hydrogel spectra were recorded using a thin film before drying. Device: FSM-1201 (Russia).

Solid-State ¹³C CP/MAS NMR

Solid-state ¹³C NMR spectra of 200 mg of samples were recorded at 25 °C using a Bruker Avance III 400 WB spectrometer, equipped with a Bruker H-F/X 4 mm CP/MAS probe head, at 100.64 MHz for ¹³C nuclei with TMS as an external reference. Crosspolarization technique (CP MAS) was applied, at

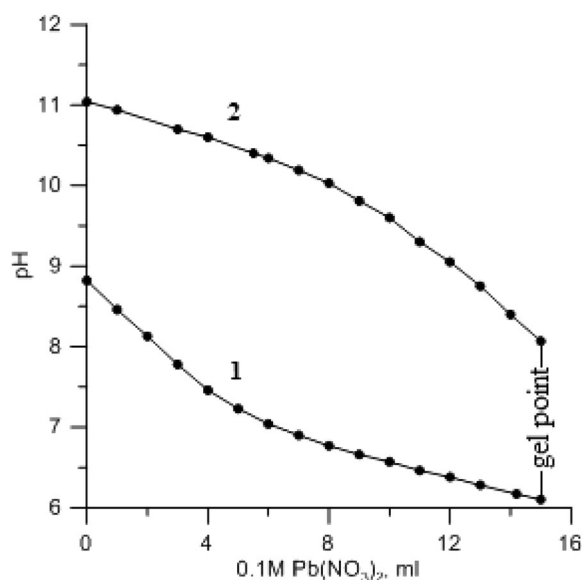


Figure 1. Titration curves of sodium salts of OHL (1) and kraft lignin (2) with a 0.1M solution of Pb(NO₃)₂. The concentration of lignin preparations was 25 g/L.

contact pulse duration of 2 ms, relaxation time 3 s, with scans number of 12,000 at the MAS rate of 12.5 kHz.

Results and discussion

Titration curves

Studying the sorption properties of lignin, it was found that upon titration of an alkaline OHL solution with Pb(NO₃)₂ solution, after an addition of a certain volume of titrant, a sharp increase in the viscosity of the system occurred and a gel was formed (Figure 1, curve 1).

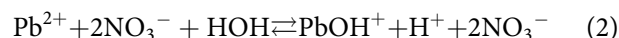
In accordance with the classical ideas of Flory,^[27] gelation occurs in the polymerization of polyfunctional monomers, resulting in the formation of branched polymers or in the crosslinking of linear polymer molecules containing active functional groups. The formation of a gel (gel point) indicates the formation of a three-dimensional infinite mesh structure. Obviously, water molecules also participate in the formation of hydrogels.

The formation of lignin hydrogel, apparently, occurred as a result of reaction between acidic groups of OHL and lead ions. The total content of acid groups in OHL is 4.5 mmol/g (Table 1), with carboxyl groups (2.5 mmol/g) prevailing among them, and the rest is phenolic hydroxyl groups. OHL was dissolved in aqueous alkali with a stoichiometric ratio of the amount of NaOH to the sum of acid groups (1: 1). In other words, lignin was in solution in the form of sodium salt.

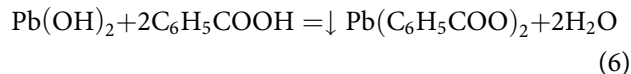
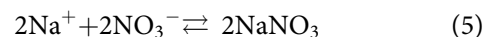
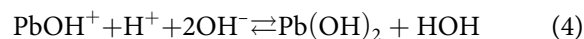
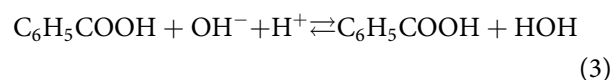
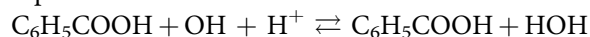
Unsubstituted organic acids are weak acids. For example, pK_a of aliphatic acids lies in the range of 3.7–5.1, and for aromatic (benzoic) acids it is 4.17.^[28] Therefore, salts of such acids with strong bases are hydrolyzed at the anion. Using benzoic acid as an example, this reaction can be represented as an equation:



Therefore, the pH of the OHL solution before titration was 8.82 (Table 1). The titrant, Pb(NO₃)₂, was a salt of a weak base and a strong acid. Such salts have been characterized by cation hydrolysis:



The pH of the titrant solution before titration was 4.65 (Table 1). In the titration process, two acid–base systems interacted with the formation of reaction products:



It should be noted that, in equilibrium systems, reactions proceed predominantly toward the formation of a sparsely soluble compound. As a result of all these reactions, the pH of the solution decreased and at the point of gel formation for OHL was 6.1 (Figure 1, curve 1, Table 1).

Another feature of weak acids is their ability to form buffer mixtures with salts of the strong bases of these acids, which is reflected in the titration curves. The maximum buffer capacity of the buffer mixtures is achieved at pH = pK_a acid.^[29] As already noted, OHL contained carboxyl and phenolic hydroxyl groups. In order to identify more clearly the behavior of these groups under titration conditions, at the first stage, titration curves of model compounds containing the following groups, benzoic acid and phenol, were investigated. The results are presented in Figure 2.

It can be noted that the titration curves of these compounds were significantly different from titration curve of a strong base with a strong acid. These differences reflect the formation of buffer solutions of benzoic acid and its sodium salt (Figure 2, curve 2)

Table 1. Preparation conditions and properties of lignin hydrogels.

Entry	Lignin sample	Content acidic groups, mmol/g	Lignin concentration, g/L; (hydromodule)	Titrant (concentration, mol/L); solution pH	pH of lignin stock solution	pH at the gel point	α^* at the gel point, %	β^{**} at the gel point, %
1	OHL, Na-salt	4.50	25 (40:1)	Pb(NO ₃) ₂ ; 0.1; 4.65	8.82	6.10	33.33	49.68
2	Kraft, Na-salt	4.61	25 (40:1)	Pb(NO ₃) ₂ ; 0.1; 4.65	11.04	8.06	32.54	49.68
3	Soda, Na-salt	2.84	25 (40:1)	Pb(NO ₃) ₂ ; 0.1; 4.65	11.35	7.86	45.77	44.57
4	Pepper lignin, Na-salt	2.66	25 (40:1)	Pb(NO ₃) ₂ ; 0.1; 4.65	11.5	9.56	41.35	34.32
5	LSA	2.48	25 (40:1)	Pb(NO ₃) ₂ ; 0.1; 4.65	3.7	No gelation		
6	LSA, Na-salt	2.48	25 (40:1)	Pb(NO ₃) ₂ ; 0.1; 4.65	10.5	No gelation		
7	OHL, Na-salt	4.5	25 (40:1)	Fe(NO ₃) ₃ ; 0.1; 1.67	8.2	4.4	31.11	33.32
8	OHL, Na-salt	4.5	25 (40:1)	CuSO ₄ ; 0.1; 3.91	8.6	5.5	33.33	23.94
9	OHL, Na-salt	4.5	25 (40:1)	CaCl ₂ ; 0.1; 9.33	8.7	No gelation		
10	OHL, Na-salt	4.5	25 (40:1)	Mg(NO ₃) ₂ ; 0.1; 5.94	8.6	No gelation		
11	OHL, Na-salt	4.5	25 (40:1)	FeSO ₄ ; 0.1; 3.50	8.5	No gelation		
12	OHL, Na-salt	4.5	25 (40:1)	Co(NO ₃) ₂ ; 0.1; 5.34	8.4	No gelation		
13	OHL, Na-salt	4.5	25 (40:1)	AgNO ₃ ; 0.1; 5.69	8.75	No gelation		

α^* – The number of acid groups bound at the point of gel formation, % of the content of acid groups in lignin.

β^{**} – The amount of titrant bound at the point of gel formation, % of lignin.

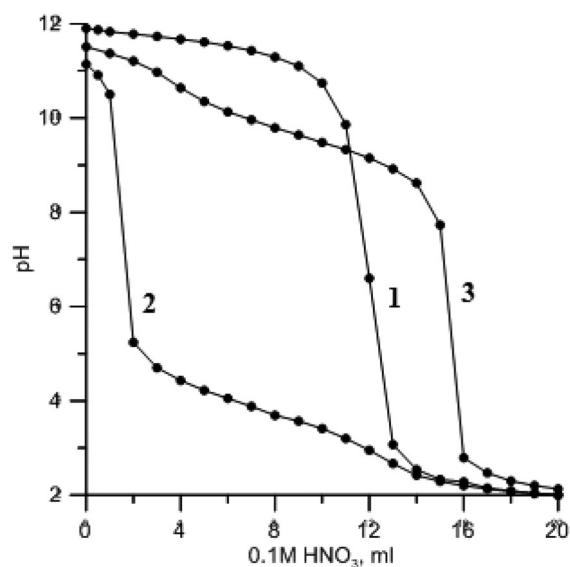


Figure 2. Titration curves of 0.028 M solutions of NaOH (1) and sodium salts of benzoic acid (2) and phenol (3) with 0.1 M HNO₃ solution.

and phenol and its sodium salt (Figure 2, curve 3) during the titration. Note that pK_a of benzoic acid is 4.17, and that of phenol is 9.98.^[28]

In light of these results, it became clear why the kraft lignin titration curve was so different from the OHL titration curve (Figure 1). Both of these lignin preparations contain approximately the same amount

of acid groups (Table 1), however, phenol hydroxyls (3.81 mmol/g) were predominating in kraft lignin, and the rest was carboxyl groups.

When titrating the OHL solution with strong acid (Figure 3, curve 1), the effect of the resulting buffer mixtures on the titration curve also manifested itself, as in Figure 2, but it was less pronounced due to polymer structure of lignin. This effect was almost imperceptible when titrating OHL solution with Pb(NO₃)₂ solution (Figure 3, curve 2), since Pb(NO₃)₂ hydrolyzed during titration, and therefore, the titration curve reflects pH changes during the interaction of several acid–base systems.

In addition to OHL and kraft lignin, gelation of soda lignin and Pepper lignin was studied (Table 1). The titration curves of these samples are given in the Supporting Information (Figures S1 and S2). Comparison of the results of study of various samples (Table 1) showed that not all acidic groups of lignin were involved in gelation, but only a part of them ($\alpha = 33\text{--}46\%$). The lower the content of acidic groups in the sample, the more they were necessary for gel formation. In other words, to reach the point of gel formation, a certain ratio of the amount of titrant to the number of acidic groups was necessary.

During the titration of lignosulfonic acid (LSA) and its sodium salt with a solution of Pb(NO₃)₂, gelation did not occur (Table 1, Supporting Information

Figures S3 and S4). LSA is a strong acid, therefore, it inhibits the hydrolysis of $\text{Pb}(\text{NO}_3)_2$ according to Equation (2) and pH of the solution changed slightly. The sodium salt of LSA, being a salt of a strong acid and a strong base, is completely dissociated in solution. The resulting hydroxide ions caused complete

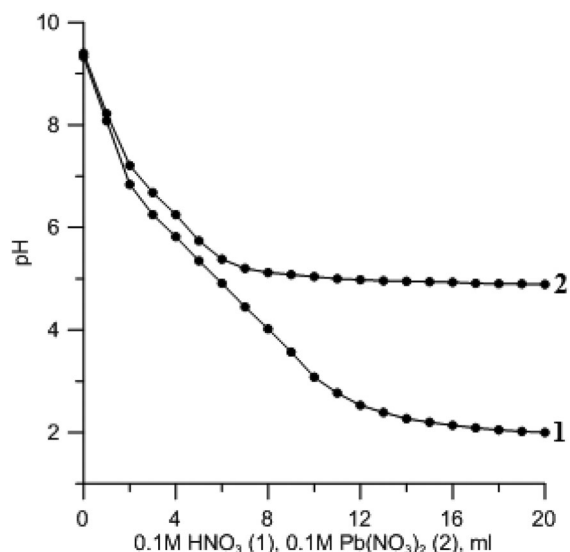


Figure 3. Curves of titration of a solution of the sodium salt of OHL with a 0.1 M solution of HNO_3 (1) and a 0.1 M solution of $\text{Pb}(\text{NO}_3)_2$ (2). Lignin concentration was 6.25 g/L.

hydrolysis of the titrant. Therefore, the curve in Supporting Information Figure S4 was a typical acid--base titration curve, in contrast to the OHL and kraft lignin titration curves in Figure 1.

In order to determine the conditions necessary for formation of lignin hydrogels, in addition to $\text{Pb}(\text{NO}_3)_2$, salts of other metals were studied (Table 1). Among them, only $\text{Fe}(\text{NO}_3)_3$ and CuSO_4 were found to be capable of gelation (Supporting Information Figures S5 and S6), while the rest did not have this ability (Supporting Information Figures S7–S11). In Table 2, all investigated compounds are given in accordance with their position in the electrochemical series of metal activity.

Based on the data shown in Table 2, a set of physicochemical properties of metal salts ... necessary to participation in the formation of lignin hydrogels was compiled. In detail, these compounds need to be salts of a weak base and strong acid, the metal cation is required to have a standard potential, $\varphi^0 = -0.126$ V and higher. It should have moderate hydrolysis ability, $K_h = 2.2\text{--}7.7$, and the cation hydroxide formed in the hydrolysis reaction (Equation (4)) has relatively low solubility, $S = 1 \cdot 10^{-4}$ g/100 g in water and below. The metals capable of hydrogel formation are highlighted in different color (cf. Table 2). Columns containing

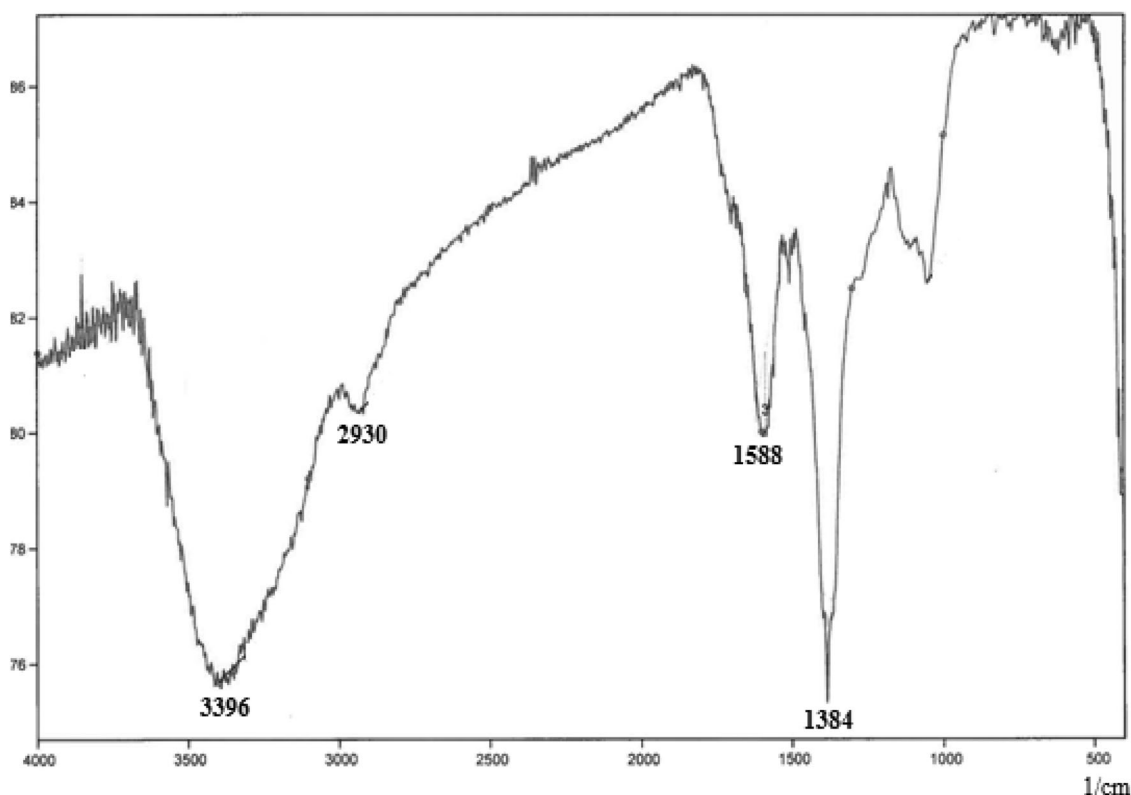


Figure 4. FTIR spectrum of the OHL hydrogel and $\text{Pb}(\text{NO}_3)_2$ before drying.

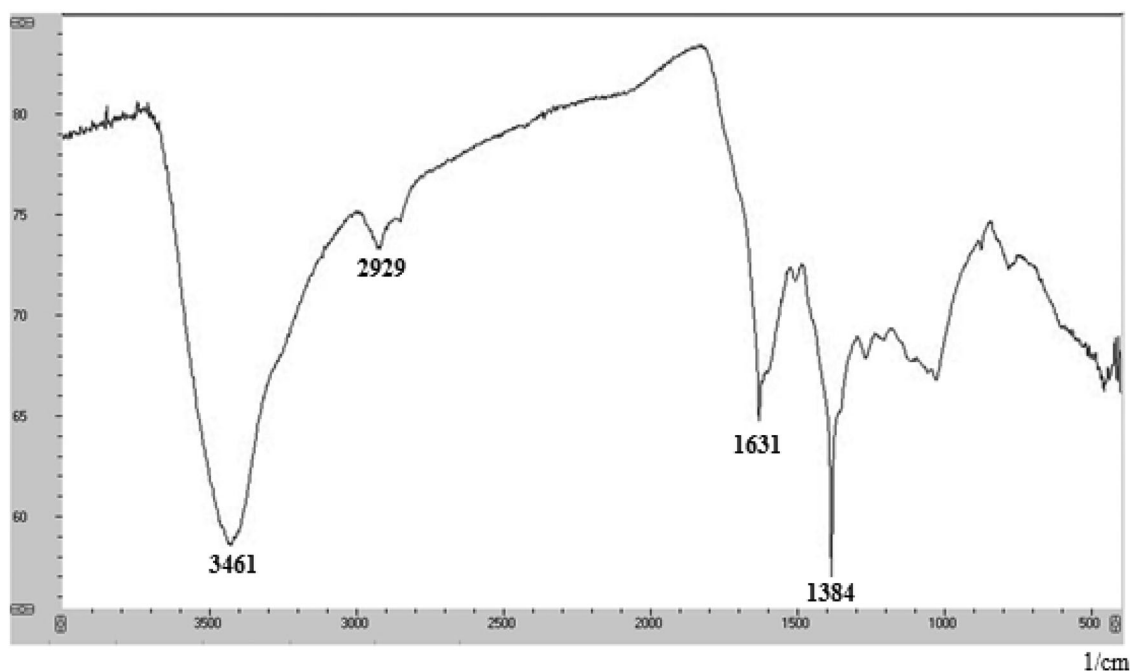


Figure 5. FTIR spectrum of the OHL hydrogel and $\text{Pb}(\text{NO}_3)_2$ after drying.

$\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and CuSO_4 should be highlighted in a different color

FTIR-spectroscopy

Considering the above-described reactions of the sodium salt of OHL with $\text{Pb}(\text{NO}_3)_2$ (Equations (1)–(6)), one may expect the presence of carboxyl groups bound to Pb^{2+} and the $\text{Pb}(\text{OH})_2$ band in the resulting hydrogel. The FTIR spectrum of the OHL gel and $\text{Pb}(\text{NO}_3)_2$ is shown in Figure 4.

The band at 3396 cm^{-1} corresponded to stretching vibrations of carboxyl groups involved in the formation of hydrogen bonds, and the band at 2930 cm^{-1} corresponds to stretching vibrations of CH groups.^[33] The band at 1588 cm^{-1} is located in the range of stretching vibrations of the ionized carboxyl group, $1630\text{--}1575\text{ cm}^{-1}$.^[34] For additional verification, we recorded the spectra of benzoic acid and lead benzoate formed according to Equation (6). The spectra are shown in Supporting Information Figures S12 and S13.

It can be noted that upon the transition from benzoic acid to lead benzoate, the vibrations of the carboxylate groups band (1689 cm^{-1}) characteristic to aromatic acids^[33] disappeared and a new band appeared at 1590 cm^{-1} , i.e., it corresponded to vibrations of ionized COOH. A new band also appeared at 1384 cm^{-1} .

To identify the band at 1384 cm^{-1} in the FTIR spectrum in Figure 4, $\text{Pb}(\text{OH})_2$ was synthesized and its spectrum was recorded (Supporting Information Figure S14). The most intense band in this spectrum

was located at 1385 cm^{-1} , which was in good agreement with the previously published spectrum of this compound.^[35]

It should be noted that after gel drying, a noticeable decrease in the band width and a slight shift of the vibration band of the ionized carboxyl group were observed in the spectrum (Figure 5). That, in our opinion, reflected partial destruction of hydrogen bonds due to removal of most of the water.

No noticeable changes in the chemical structure of OHL upon receipt of the lignin hydrogel were observed, as evidenced by a comparison of the solid state spectrum of hydrogel of the sodium salt of OHL and $\text{Pb}(\text{NO}_3)_2$ (Figure 6) with the spectrum of the sodium salt of OHL (Supporting Information Figure S15). The assignment of bands in the solid-phase spectra was based on the published data.^[36]

The mechanism of formation of lignin hydrogels

Metal cations in aqueous solutions are hydrated: $[\text{Me}(\text{H}_2\text{O})_n]^{z+}$, where n is a number of coordinated water molecules.^[37] The coordination number of lead (II) can take values of 1–12, depending on the nature of ligands included in complex compound.^[38] The coordination number of lead cation in aquacation has not yet been determined exactly, but it is known for bismuth, which occupies an adjacent position in the Periodic Table of Elements, for which $n=9$, for Cu^{2+} and Fe^{3+} $n=5$.^[37] Therefore, the formula of lead benzoate formed by

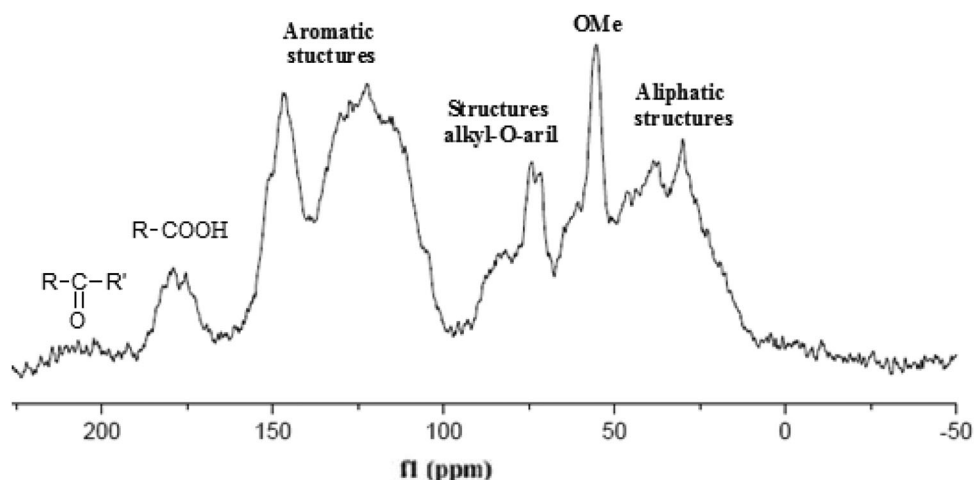


Figure 6. Solid state ^{13}C CP/MAS NMR spectrum of OHL hydrogel and $\text{Pb}(\text{NO}_3)_2$.

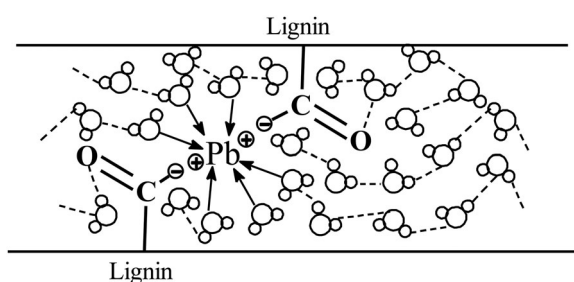
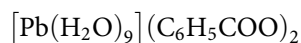


Figure 7. The proposed scheme of intermolecular bonds in lignin hydrogels.

Equation (6) can be written as:



Lignin is not an individual compound; therefore, it is not possible to write the exact hydrogel formula of lead cations and OHL. However, the obtained experimental data allow describing the transformations of OHL upon interaction with $\text{Pb}(\text{NO}_3)_2$ upon titration. The fact in itself of the formation of a lignin hydrogel indicated the formation of an infinite three-dimensional network formed by OHL, Pb^{2+} and H_2O .

At the point of gel formation, 1 g of lignin accounts for 55 g of water (3 mol). During titration of the sodium salt of benzoic acid with a solution of $\text{Pb}(\text{NO}_3)_2$, gelation did not occur. This indicated that only high molecular weight compounds possess gelling ability. The number average molecular weight of OHL is 2000.^[22]

The possible nature of the intermolecular bonds at the point of formation of the lignin hydrogel is illustrated in Figure 7. Adjacent lignin molecules bind to each other by three types of bonds: ionic between the carboxyl groups of lignin and lead cations, coordination between lead cations and water molecules in the coordination sphere, and hydrogen bonds that bind all components of the system into a single whole.

It can be estimated to what extent a number of carboxyl groups per lead cation is consistent with the titration results. As already noted, OHL contains 2.5 mmol/g of such groups. At the point of gel formation, 15 mL of a 0.1 M solution of $\text{Pb}(\text{NO}_3)_2$ (Figure 1) or 1.5 mmol is consumed. Based on one carboxyl group, this is 1.5 mmol: 2.5 mmol = 0.6. In other words, ≈ 2 carboxyl groups per 1 lead cation, which is generally consistent with the scheme in Figure 7. The total content of acidic groups in kraft lignin is 4.61 mmol/g. Among them, amount of carboxyl groups is only 0.8 mmol/g, and the rest are phenolic hydroxyl groups. This number of carboxyl groups is not enough to form a hydrogel. In addition, the titration curve of kraft lignin in Figure 1 was fundamentally different from the OHL titration curve. This suggested that some part of the phenolic hydroxyl groups was involved in the formation of hydrogel.

Phenylpropane units (PPU) of lignin differ in the acidity of OH_{phen} . Figure 8 shows the pK_a values of some model compounds.^[39] The bulk of the phenolic hydroxyl kraft lignin has a pK_a of about 10.3 which corresponds to the pK_a of creosol. If the side chain of the PPU contains conjugated electron-withdrawing substituents, then pK_a decreases significantly, approaching the level of weak organic acids.

Pyrocatechol units (cf. chemical structure 1 below) are another contender for the role of a gelling agent in interaction of lignin with $\text{Pb}(\text{NO}_3)_2$. Their content in kraft lignin was estimated at 6-9/100 PPU.^[40] Like many phenols, they are able to form colored compounds with metal ions. For example, 4-alkyl pyrocatechol structures have formed intensely colored complexes with iron ions **1** having an absorption maximum in the region of 550 nm.^[41] Pyrocatechol has been also known to form a compound with lead **2**.^[42]

Table 2. Physicochemical properties of the studied salts.

Salt	CaCl ₂	Mg(NO ₃) ₂	FeSO ₄	Co(NO ₃) ₂	Pb(NO ₃) ₂	Fe(NO ₃) ₃	CuSO ₄	AgNO ₃	References
Cation	Ca ²⁺	Mg ²⁺	Fe ²⁺	Co ²⁺	Pb ²⁺	Fe ³⁺	Cu ²⁺	Ag ⁺	–
φ^0 , V	-2.866	-2.363	-0.440	-0.277	-0.126	-0.037	0.337	0.779	[30]
pK _h	12.8	11.4	9.5	9.6	7.7	2.2	6.8	12.0	[31]
Cation hydroxide	Ca(OH) ₂	Mg(OH) ₂	Fe(OH) ₂	Co(OH) ₂	Pb(OH) ₂	Fe(OH) ₃	Cu(OH) ₂	AgOH	–
S, g/100 g water	8.21·10 ⁻²	8.4·10 ⁻⁴	1.44·10 ⁻⁴	6.8·10 ⁻⁶	1.2·10 ⁻⁴	1.1·10 ^{-36a}	1.47·10 ⁻⁶	1.54·10 ⁻³	[32]

^aSolubility equilibrium.

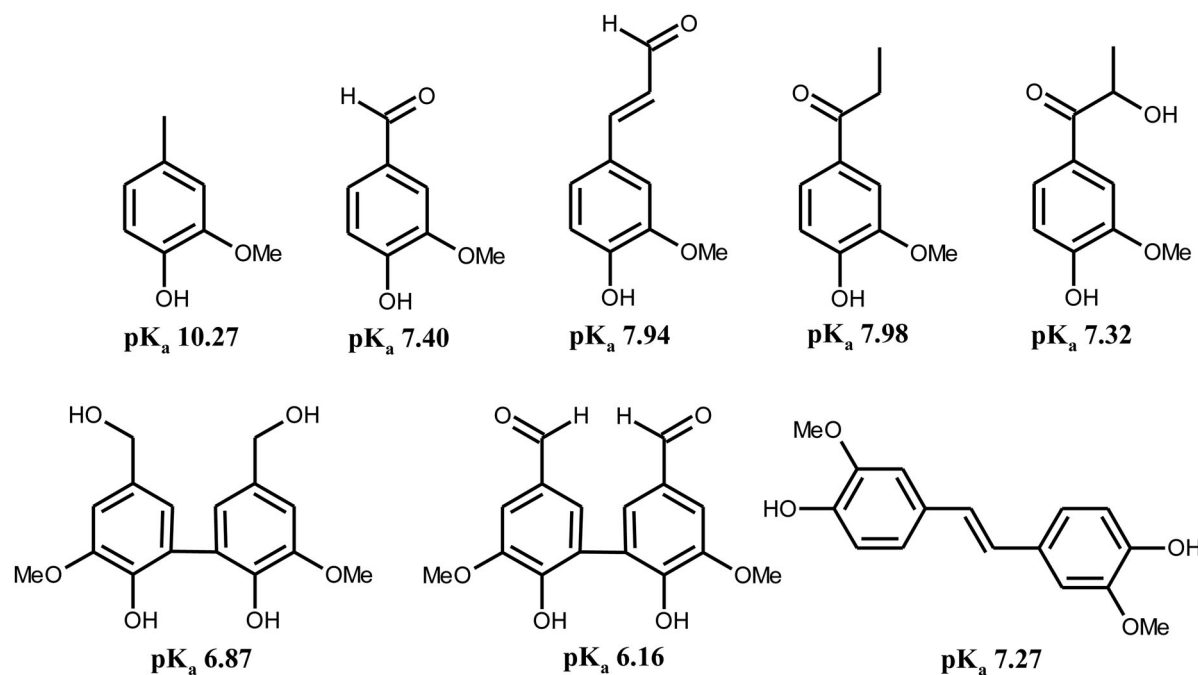


Figure 8. pK_a values of model lignin compounds.

It can be assumed that PPU of lignin with a relatively higher acidity of OH_{phen} and pyrocatechol structural units make a certain contribution to the formation of the hydrogel, but this issue requires further study. Formulas of compounds 1 and 2 are absent in the text.

Conclusion

The problem of biorefining plant materials, including valorization of lignin, has stimulated research in the field of new directions for modification and use of technical lignins. Among them, a special place is occupied by hydrolytic lignin, formed as a result of acid hydrolysis of wood, in order to obtain bioethanol. The widespread development of this technology is hindered by the formation of large quantities of hydrolysis lignin as waste.

One ton of coniferous wood yields 160–175 kg (45–49 gallons) of ethanol and 350–400 kg of lignin by-product to be a natural suggestion. In Russia, the stock of hydrolysis lignin is estimated to be around 95 million tons.^[43]

The ability of hydrolysis lignin and other technical lignins (except LSA), as well as Pepper lignin to form

hydrogels *in situ*, which was discovered when interacting with a sorbate, has both scientific and applied value. The spontaneous formation of an infinite three-dimensional network structure due to ionic, coordination and hydrogen bonds with a metal cation, which has well-defined physicochemical properties, is, in our opinion, of interest for colloid chemistry and lignin chemistry.

Funding

This publication has been produced with the financial assistance of Estonia-Russia Cross-Border Cooperation Program 2014-2020, Project ER 30.

ORCID

Aleksander V. Vasilyev  <http://orcid.org/0000-0003-3628-1492>

References

- [1] Ragauskas, A. J.; Beckham, G. T.; Bidy, M. J.; Chandra, R.; Chen, F.; Davis, M.; Davison, B. H.;

- Dixon, R. A.; Gilna, P.; Keller, M.; et al. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* **2014**, *344*, 1246843. DOI: [10.1126/science.1246843](https://doi.org/10.1126/science.1246843).
- [2] Li, C.; Zhao, X.; Wang, A.; Huber, G. W.; Zhang, T. Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem. Rev.* **2015**, *115*, 11559–11624. DOI: [10.1021/acs.chemrev.5b00155](https://doi.org/10.1021/acs.chemrev.5b00155).
- [3] Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijninx, P. C. A.; Weckhuysen, B. M. Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 8164–8215. DOI: [10.1002/anie.201510351](https://doi.org/10.1002/anie.201510351).
- [4] Galkin, M. V.; Samec, J. S. M. Lignin Valorization through Catalytic Lignocellulose Fractionation: A Fundamental Platform for the Future Biorefinery. *ChemSusChem* **2016**, *9*, 1544–1558. DOI: [10.1002/cssc.201600237](https://doi.org/10.1002/cssc.201600237).
- [5] Kärkäs, M. D.; Matsuura, B. S.; Monos, T. M.; Magallanes, G.; Stephenson, C. R. J. Transition-Metal Catalyzed Valorization of Lignin: The Key to a Sustainable Carbon-Neutral Future. *Org. Biomol. Chem.* **2016**, *14*, 1853–1914. DOI: [10.1039/C5OB02212F](https://doi.org/10.1039/C5OB02212F).
- [6] Sun, Z.; Fridrich, B.; de Santi, A.; Elangovan, S.; Barta, K. Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. *Chem. Rev.* **2018**, *118*, 614–678. DOI: [10.1021/acs.chemrev.7b00588](https://doi.org/10.1021/acs.chemrev.7b00588).
- [7] Schutyser, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S.-F.; Beckham, G. T.; Sels, B. F. Chemicals from Lignin: An Interplay of Lignocellulose Fractionation, Depolymerisation, and Upgrading. *Chem. Soc. Rev.* **2018**, *47*, 852–908. DOI: [10.1039/C7CS00566K](https://doi.org/10.1039/C7CS00566K).
- [8] Berlin, M.; Balakshin, M. Industrial Lignins, Analysis, Properties and Applications. In *Bioenergy Research: Advances and Applications*; Elsevier: London, **2014**; Chapter 18, pp 315–336. DOI: [10.1016/B978-0-444-59561-4.00018-8](https://doi.org/10.1016/B978-0-444-59561-4.00018-8).
- [9] Evstigneyev, E. I.; Shevchenko, S. M. Lignin Valorization and Cleavage of Arylether Bonds in Chemical Processing of Wood: A Mini-Review. *Wood Sci. Technol.* **2020**, *54*, 787–820. DOI: [10.1007/s00226-020-01183-4](https://doi.org/10.1007/s00226-020-01183-4).
- [10] Thakur, S.; Govender, P. P.; Mamo, M. A.; Tamulevicius, S.; Mishra, Y. K.; Thakur, V. K. Progress in Lignin Hydrogels and Nanocomposites for Water Purification: Future Perspectives. *Vacuum* **2017**, *146*, 342–355. DOI: [10.1016/j.vacuum.2017.08.011](https://doi.org/10.1016/j.vacuum.2017.08.011).
- [11] Rico-García, D.; Ruiz-Rubio, L.; Pérez-Alvarez, L.; Hernández-Olmos, S. L.; Guerrero-Ramírez, G. L.; Vilas-Vilela, J. L. Lignin-Based Hydrogels: Synthesis and Applications. *Polymers* **2020**, *12*, 81–104. DOI: [10.3390/polym12010081](https://doi.org/10.3390/polym12010081).
- [12] Khan, S.; Ullah, A.; Ullah, K.; Rehman, N. Insight into Hydrogels. *Des. Monomers Polym.* **2016**, *19*, 456–478. DOI: [10.1080/15685551.2016.1169380](https://doi.org/10.1080/15685551.2016.1169380).
- [13] Larrañeta, E.; Imízcoz, M.; Toh, J. X.; Irwin, N. J.; Ripolin, A.; Perminova, A.; Domínguez-Robles, J.; Rodríguez, A.; Donnelly, R. F. Synthesis and Characterization of Lignin Hydrogels for Potential Applications as Drug Eluting Antimicrobial Coatings for Medical Materials. *ACS Sustain. Chem. Eng.* **2018**, *6*, 9037–9046. DOI: [10.1021/acssuschemeng.8b01371](https://doi.org/10.1021/acssuschemeng.8b01371).
- [14] Musilová, L.; Mráček, A.; Kovalčík, A.; Smolka, P.; Minařík, A.; Humpolíček, P.; Vícha, R.; Ponížil, P. Hyaluronan Hydrogels Modified by Glycinated Kraft Lignin: Morphology, Swelling, Viscoelastic Properties and Biocompatibility. *Carbohydr. Polym.* **2018**, *181*, 394–403. DOI: [10.1016/j.carbpol.2017.10.048](https://doi.org/10.1016/j.carbpol.2017.10.048).
- [15] Ravishankar, K.; Venkatesan, M.; Preeth Desingh, R.; Mahalingam, A.; Sadhasivam, B.; Subramaniyam, R.; Dhamodharan, R. Biocompatible Hydrogels of Chitosan-Alkali Lignin for Potential Wound Healing Applications. *Mater. Sci. Eng. C Mater. Biol. Appl.* **2019**, *102*, 447–457. DOI: [10.1016/j.msec.2019.04.038](https://doi.org/10.1016/j.msec.2019.04.038).
- [16] Li, F.; Wang, X.; Yuan, T.; Sun, R. A Lignosulfonate-Modified Graphene Hydrogel with Ultrahigh Adsorption Capacity for Pb (ii) Removal. *J. Mater. Chem. A* **2016**, *4*, 11888–11896. DOI: [10.1039/C6TA03779H](https://doi.org/10.1039/C6TA03779H).
- [17] Sun, Y.; Ma, Y.; Fang, G.; Li, S.; Fu, Y. Synthesis of Acid Hydrolysis Lignin-g-Poly-(Acrylic Acid) Hydrogel Superabsorbent Composites and Adsorption of Lead Ions. *BioResources* **2016**, *11*, 5731–5742. DOI: [10.15376/biores.11.3.5731-5742](https://doi.org/10.15376/biores.11.3.5731-5742).
- [18] Wang, Y.; Xiong, Y.; Sun, F.-L.; Yang, Y.-Q.; Zhang, X.-D. Ultrasonic-Assisted Synthesis of a Superabsorbent Composite Hydrogel for the Responsive and Removal Properties of Pb (II). *Acta Phys. Chim. Sin.* **2016**, *32*, 2563–2573. DOI: [10.3866/PKU.WHXB201607122](https://doi.org/10.3866/PKU.WHXB201607122).
- [19] Jiang, P.; Sheng, X.; Yu, S.; Li, H.; Lu, J.; Zhou, J.; Wang, H. Preparation and Characterization of Thermo-Sensitive Gel with Phenolated Alkali Lignin. *Sci. Rep.* **2018**, *8*, 14450. DOI: [10.1038/s41598-018-32672-z](https://doi.org/10.1038/s41598-018-32672-z).
- [20] Yao, Q.; Xie, J.; Liu, J.; Kang, H.; Liu, Y. Adsorption of Lead Ions Using a Modified Lignin Hydrogel. *J. Polym. Res.* **2014**, *21*, 465–481.
- [21] Ji, X.; Zhang, Z.; Chen, J.; Yang, G.; Chen, H.; Lucia, L. A. Synthesis and Characterization of Alkali Lignin-Based Hydrogels from Ionic Liquids. *BioResources* **2017**, *12*, 5395–5406. DOI: [10.15376/biores.12.3.5395-5406](https://doi.org/10.15376/biores.12.3.5395-5406).
- [22] Evstigneyev, E. I.; Yuzikhin, O. S.; Gurinov, A. A.; Ivanov, A. Y.; Artamonova, T. O.; Khodorkovskiy, M. A.; Bessonova, E. A.; Vasilyev, A. V. Study of Structure of Industrial Acid Hydrolysis Lignin, Oxidized in the H₂O₂-H₂SO₄ System. *J. Wood Chem. Technol.* **2016**, *36*, 259–269. DOI: [10.1080/02773813.2015.1137945](https://doi.org/10.1080/02773813.2015.1137945).
- [23] Evstigneyev, E.; Maiyoroova, H.; Platonov, A. Lignin Functionalization and the Alkaline Delignification Rate. *Tappi J.* **1992**, *75*, 177–182.
- [24] Pepper, J. M.; Baylis, P. E. T.; Adler, E. The Isolation and Properties of Lignins Obtained by the Acidolysis of Spruce and Aspen Woods in Dioxane-Water Medium. *Can. J. Chem.* **1959**, *37*, 1241–1248. DOI: [10.1139/v59-183](https://doi.org/10.1139/v59-183).
- [25] Evstigneyev, E. I. Oxidation of Hydrolysis Lignin with Hydrogen Peroxide in Acid Solutions. *Russ. J. Appl. Chem.* **2013**, *86*, 258–265.

- [26] Mansson, P. Quantitative Determination of Phenolic and Total Hydroxyl Groups in Lignins. *Holzforschung* **1983**, 37, 143–146.
- [27] Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, **1953**.
- [28] Albert, A.; Sergent, E. *Ionization Constants of Acids and Bases*; Wiley: New York, **1962**.
- [29] Hulanicky, A.; Masson, M. R. *Reactions of Acids and Bases in Analytical Chemistry*; E. Horwood: Chichester, West Sussex, England; Halsted Press: New York, **1987**.
- [30] Glinka, N. L. *General Chemistry*; Chemistry: Leningrad, **1980**.
- [31] Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, **1976**.
- [32] Nikolsky, B. P., Ed. *Handbook of a Chemist*; Chemistry: Leningrad, **1965**; Vol. III.
- [33] Pretsch, E.; Bühlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds. Tables of Spectral Data*; Springer: New York, US, **2009**.
- [34] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley-Interscience: New York, London, **1970**.
- [35] Hepzi Pramila Devamani, R.; Alagar, M. Synthesis and Characterization of Lead (II) Hydroxide Nanoparticles. *IJASER*. **2012**, 1, 483–487. DOI: [10.6088/ijasr.0020101049](https://doi.org/10.6088/ijasr.0020101049).
- [36] Evstigneyev, E. I.; Mazur, A. S.; Kalugina, A. V.; Pranovich, A. V.; Vasilyev, A. V. Solid-State ^{13}C CP/MAS NMR for Alkyl-O-Aryl Bonds Determination in Lignin Preparations. *J. Wood Chem. Technol.* **2018**, 38, 137–148. DOI: [10.1080/02773813.2017.1393436](https://doi.org/10.1080/02773813.2017.1393436).
- [37] Richens, D. T. *The Chemistry of Aqua Ions: Synthesis, Structure and Reactivity: A Tour through the Periodic Table of the Elements*; Wiley: Hoboken, NJ, US, **1997**.
- [38] Swadźba-Kwaśny, M. Lead: Inorganic Chemistry. In *Encyclopedia of Inorganic and Bioinorganic Chemistry*; Bharara, M. S., Atwood, D. A., Eds.; Wiley: Hoboken, NJ, US, **2015**. DOI: [10.1002/9781119951438.eibc0111.pub2](https://doi.org/10.1002/9781119951438.eibc0111.pub2).
- [39] Ragnar, M.; Lindgren, C. T.; Nilvebrant, N.-O. Nilvebrant, N.-O. pK_a of Guaiacyl and Syringyl Phenols Related to Lignin. *J. Wood Chem. Technol.* **2000**, 20, 277–305. DOI: [10.1080/02773810009349637](https://doi.org/10.1080/02773810009349637).
- [40] Zakis, G. F. *Functional Analysis of Lignins and Their Derivatives*; TAPPI Press: Atlanta, GA, **1994**.
- [41] Gellerstedt, G. Chemistry of Pulp Bleaching. In *Lignin and Lignans. Advances in Chemistry*; Heitner, C., Dimmel, D.R., Schmidt, J.A., Eds.; CRC Press: Boca Raton, **2010**; pp 393–438.
- [42] Barkan, I. G. *Organic Chemistry*; High school: Moscow, **1973**.
- [43] Rabinovich, M. L. Wood Hydrolysis Industry in the Soviet Union and Russia: What Can Be Learned from History? In *Oral Presentations, Proceedings of NWBC*, Rautakivi, A., Ed.; Helsinki, Finland, **2009**, pp 111–120.