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Characterization of structural and physical properties of dichloromethane- and methanol-fractionated Kraft lignin and its adsorption capacity of Cu (II) and Ni (II) ions

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ABSTRACT

This work investigates the effect of the molecular weight and polydispersity of Kraft lignin (KL) on its capacity to remove copper and nickel ions from aqueous solutions. KL and its fractions were characterized by gel permeation chromatography, ^{1}H NMR, ^{31}P NMR and attenuated total reflectance—Fourier transform infrared spectroscopy, elemental and ash analyses. Moreover, the glass transition temperature of lignin samples was determined by dynamic mechanical analysis. The fractionated lignin exhibited lower molecular weight and narrower polydispersity than the original KL. Accordingly, the successive solvent extraction herein applied would appear to be a convenient way to extract low molecular fractions admixed with sulphur from KL. A pseudo-second-order rate model was utilized to describe the sorption kinetics of metal ions. The KL fractionated with dichloromethane and methanol possessed a greater capacity for copper and nickel sorption than the original KL. Maximum uptake was 5.94 mg of copper and 7.95 mg of nickel per gram of the fractionated KL. The results obtained demonstrate that molecular weight characteristics can influence the metal scavenging efficiency of the KL.

Keywords: Adsorption capacity; Lignin; Metal ions; Molecular weight distribution; Water treatment

1. Introduction

The contamination of water with heavy metals represents a health risk to an aquatic ecosystem, wildlife and humans. Protecting and cleaning water are big challenges, one requiring a complex strategy and/or methodology. Recent investigations have shown that lignin, as an aromatic biopolymer, exhibits a great potential for trapping metal ions.

Lignin is a variable, amorphous, three-dimensional polymer with p-hydroxyphenyl propane units, connected by non-regular C–C and/or C–O–C bonds. Lignin phenolic polymers occur in types of softwood (25–30%), hardwood (20–25%) and grasses (below 20%). However, isolating lignin directly from plants or wood is a long, complicated and expensive process, producing low yields. Nevertheless, technical lignins

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such as Kraft lignin(KL), Sulphite lignin and Organosolv lignin can be obtained as by-products of pulp and paper production. The Kraft pulping process is considered to be the globally dominant pulping procedure [1]. About 170 million metric tons of black liquor (although calculated as dry solid) are produced worldwide every year by pulp and paper industries [2]. The primary application of a concentrated and condensed form of this black liquor finds as an energy source for pulp mills. Indeed, KL can be isolated from industrial black liquors by ultrafiltration or acid precipitation [3–7]. KL may be described as a polydisperse compound containing phenyl propane units with carbonyl, hydroxyl, methoxyl, carboxyl and sulphur substitutions [8].

KL could be considered an aromatic, renewable material with a high content of carbon (~60%). Alongside common adsorbents of metal ions such as activated carbon, KL has been investigated as an agent for trapping metal ions in water solvents [9–17]. The most important functional groups that support the metal binding behaviour of lignin were identified as phenolic and carboxylic groups [15]. The mechanism for removing metal ions from water by lignin has been described as a parallel effect of surface adsorption, ion exchange and complexation action [8–13]. Primary factors influencing the metal sorption capacity of KL are suggested as being the pH of the environment, ionic strength, the surface properties of lignin and reaction time [15,16]. However, the use of KL as a bioadsorbent has not been applied in practise for several reasons. One of them is its relatively low adsorption capacity and adsorption rate in comparison with other sorbents, which are associated with a lack of sufficient adsorption groups. Variability in the physical and chemical properties of KLs can also be a factor limiting the wider application of this waste by-product in biosorption technologies. [18,19]. Enhancing the adsorption capacity of lignins by carrying out surface modifications to functional groups, for example via a Mannich reaction with amino acids and oxidation, has previously been reported [9,12]. Most recognized studies focus on the chemical modifications of lignin, with a view to introducing specific chemical moieties.

However, the modifying of the chain dimensions of the KL macromolecule—expressed as a molecular weight characteristic—may also influence its metal ion adsorption capacity. It is reported that low-molecular KLs contain a significantly higher concentration of phenolic structural units than high-molecular weight KLs [20]. In addition, the chain length of lignin and its uniformity have been described as crucial factors in its antioxidant activity in polymer composites systems [21–23].

Large macromolecules of KL can be partitioned by fractionation, receiving moieties with differing chemical and physical properties. Fractionation can be provided by ultrafiltration, by alternating pH values during precipitation from black liquor and by successive extraction with organic solvents possessing various solubility parameters [4,20,24–26].

The aim of this work was to investigate the effect of the molecular dimensions of KL on its capacity for heavy metal ion adsorption.

Herein, Cu (II) and Ni (II) ions were selected as common, representative, metallic contaminants in water. The molecular weight properties of KL were modified by extraction in dichloromethane and methanol. The combination of elemental analysis, nuclear magnetic resonance and ATR–FTR spectroscopy, molecular weight distribution and dynamic mechanical analysis was used to obtain information on the chemical and physical properties of KL and its derivate, after fractionation.

2. Materials and methods

2.1. Materials

Black liquor (pH 11.0, total solids 88.9%, Klasson lignin 25.1% and ash 63.8%) was received from Zellstoff Pöls AG, Austria. The black liquor was produced as a by-product during Kraft pulping 70% spruce, 25% pine and 5% larch. Hydrochloric acid (37%), dichloromethane (99.9%), methanol (99.9%), tetrahydrofuran (99.9%), pyridine (99.9%) and acetic anhydride (98%) were obtained from Sigma–Aldrich, Germany. Copper sulphate ($CuSO_4$) (99%) and $NiSO_4$ (99%) in p.a. quality were supplied by Roth, Austria.

KL was isolated from black liquor by precipitation with 37% hydrochloric acid until it had reached pH 2. The precipitate was filtered and washed twice with distilled water, thereby removing unreacted compounds. The filtered sample was dialysed for 7 days in fresh distilled water and subsequently freeze-dried.

The polydisperse KL was fractionated in accordance with the work of Mörck et al. [26].

2.2. Analytical methods

CHNS Elemental analysis of 2 mg, vacuum-dried, non-acetylated samples was performed on a Universal Elemental analyser, type Vario El III.

Proton nuclear magnetic resonance (^1H NMR) was performed using a Bruker Avance III spectrometer, operating at 300 MHz in deuterated DMSO-d6 solution containing 0.03% TMS standard. All spectra were obtained at the following settings: 25˚C, 90˚ pulse angle, 5s delay and 1,024 scans. For the improvement of solubility, all lignin samples were acetylated [27].

^{31}P NMR spectra of phosphitylated lignin samples were obtained on a Varian XL-500 spectrometer and evaluated using the method described by Argyropoulos [28]. Lignin was phosphitylated using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, in accordance with a procedure published by Gosselink [29].

Fourier transform infrared spectroscopy (FTIR) of the lignins was performed on an FTIR spectrometer Alpha (Bruker Optics, Ettlingen, Germany) equipped with an ATR unit. Scanning took place in the range 400–4,000 cm^{-1} with a resolution of 4 cm^{-1}. One hundred and twenty-eight scans of the samples were taken.

The molecular average weights of the lignin samples were determined on an SEC-3010 (WGE-DR. Bures) instrument equipped with an ultraviolet and refractive indexes. The pure GPC-ORG columns were calibrated using a series of polystyrene standards (Polymer Standard Service). The acetylated lignin samples [27] were dissolved in tetrahydrofurane, at a concentration of 4 mg mL^{-1} and analysed at room temperature. Tetrahydrofurane was used as an eluent, at the flow rate of 1.0 mL min^{-1} and the injection volume was 100 μL.

The viscoelastic properties of the lignin samples in powder form were determined using a Dynamic Mechanical Analyzer DMA Q800, TA Instruments, by applying a non-tensioning powder holder embedded in a dual cantilever clamp. The powder holder was developed by Hawkins [30]. The glass transition temperature (T_g) was determined as the peak of mechanical loss factor values (tan δ) (tan $\delta = E''/E'$, where E' is the storage modulus and E'' is the loss modulus), measured for all samples in the frequency strain mode at 1 Hz, at temperatures from 30˚C to 200˚C and at the heating rate of 3˚C min^{-1}. A sample of approximately 300 mg was distributed uniformly in the aluminium powder holder, the size of which was 35 mm × 11.5 mm × 1.8 mm.

The metal ion adsorption capacity of lignin was determined via a batch technique in a background electrolyte of 0.01-M $NaNO_3$ at 21˚C. Stock solutions of Cu (II) and Ni (II) were prepared in distilled water. Sorption tests of metal ions on unfractionated (KL) and dichloromethane–methanol KL (KL_2) were performed by mixing 2 g L^{-1} the lignin suspension with Cu (II) and Ni (II) ions, utilized in a concentration of 110 mg L^{-1}. The pH of the final suspension was maintained at 4.4 and mixed for 5 h at the constant speed of 150 rpm. The adsorption of metal ions by lignin was detected at hourly intervals by an atomic absorption spectrophotometer (240 FS AA, Agilent Technologies). All determinations were performed three times and the resulting average values are provided.

In order to describe Cu (II) or Ni (II) sorption kinetics on unfractionated and fractionated KL, a pseudo-second-order rate law expression was applied [31,32]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

where k is the rate constant of adsorption (g mg^{-1} min), q_e is the amount of divalent metal ions adsorbed at equilibrium (mg g^{-1}) and q_t is the amount of divalent metal ions on the surface of the adsorbent at time t (mg g^{-1}).

Integrating Eq. (1) gives the linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{2}$$

and providing that $kq_e^2 = h$, Eq. (3) can be rearranged thus:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{3}$$

where h is the initial adsorption rate (mg g^{-1} min).

3. Results and discussions

3.1. Chemical and physical properties of KL and its fractions

KL was fractionated in dichloromethane and methanol (see Fig. 1). The initial fractionation with dichloromethane was conducted so as to remove low molecular admixtures from heterogeneous starting KL and the methanol fraction [25,26].

Lignin is a network polymer exhibiting limited solubility [33]. Molecular weight properties and functionality stand out as the most important properties influencing its solubility [34]. Following the dissolution of lignin, the soluble fragments contain macromolecules of varying sizes [35]. In accordance with the principle of fractionation in solvents with differing values of Hildebrand solubility parameters, KL was initially extracted by dichloromethane with a yield of 14% (KL_1), while the undissolved fraction was further extracted by methanol with a yield of 46% (KL_2).

Molecular weight properties were determined by size exclusion chromatography and solubility in tetrahydrofurane of the original KL and its two

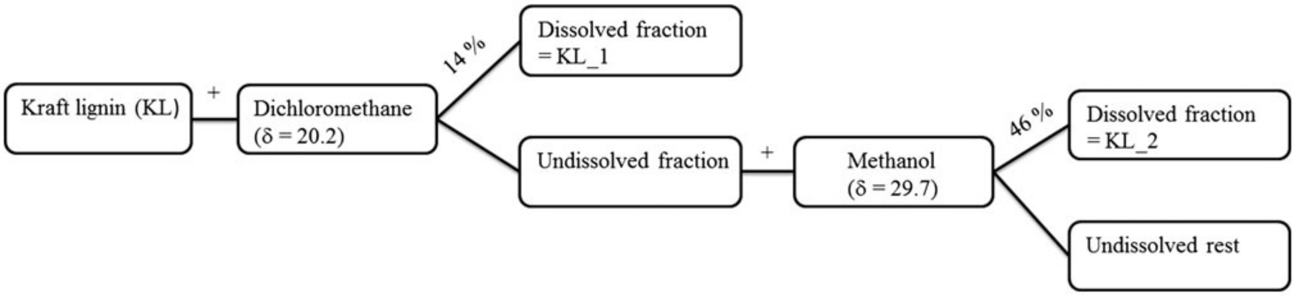

Fig. 1. Fractionation of KL with organic solvents (*δ*—Hildebrand solubility parameter).

fractions were enhanced by acetylation. The molecular weight distribution of the acetylated KL and its samples is shown in Fig. 2.

It was clear that solvent fractionation modified the molecular weight distribution of the lignin fractions. Table 1 displays the weight average ($\overline{M_w}$), number average ($\overline{M_n}$), molecular-weight and polydispersity ($\overline{M_w}/\overline{M_n}$) values for the lignin samples. The obtained data show that the original sample was high-molecular weight lignin with 5,000 g mol^{-1} possessing large molecular weight distribution. The first lignin fraction (KL_1), compared to the original KL, was a low-molecular weight sample with $\overline{M_w}$ of 800 g mol^{-1} and a narrow polydispersity index of 1.44. Based on the determined molecular weight of KL monomer, i.e. 180 g mol^{-1}, it was observed that dichloromethane only extracted low-molecular weight fragments from the starting material (KL) [36]. In contrast, methanol extracts a lignin fraction with a higher molecular weight ($\overline{M_w}$ = 2,790). The value given for the number-average molecular weight of KL_2 is comparable with original lignin, albeit with a narrower polydispersity index of 1.95. The molecular weight properties determined for the KL fractions show that the two-step fractionation with dichloromethane and methanol is capable of delivering KL with relatively low-molecular weight values and narrow molecular weight distribution.

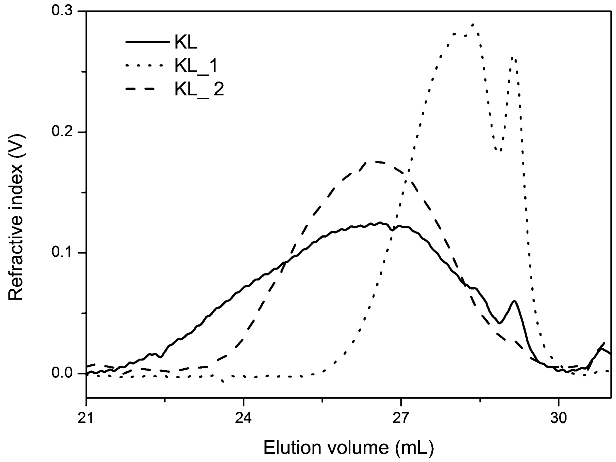

Fig. 2. SEC chromatograms of acetylated lignins KL (unfractionated KL), KL_1 (first fraction dissolved in dichloromethane) and KL_2 (second fraction dissolved in methanol).

Table 1
SEC analysis data of KL and its fractions

Sample	$\overline{M_n}$ (g mol^{-1})	$\overline{M_w}$ (g mol^{-1})	$\overline{M_w}/\overline{M_n}$
KL	1,380	5,000	3.62
KL_1	550	800	1.44
KL_2	1,430	2,790	1.95

Table 2 presents the elemental composition of KL and its fractions, which reveals approximately 2.6 times more sulphur and 0.7 times less oxygen in the first fraction (KL_1) than in the original KL. The elemental composition of the second fraction (KL_2) is comparable to the unfractionated lignin (KL), except that the presence of carbon was about 1.2% higher than for the original KL. The higher content of sulphur in low-molecular weight fractions of KL is connected with the pulping process. During this procedure, episulphide structures are generated as well as organically bound sulphur, the latter being combined predominantly with low molecular weight fragments of lignin [20].

Table 2
Elemental composition KL samples

Sample	C (%)	H (%)	N (%)	S (%)	O (%)
KL	60.7	5.9	0.1	3.4	28.0
KL_1	60.9	6.1	0.1	12.5	19.9
KL_2	61.9	6.0	0.1	3.5	27.8

The structures of the unfractionated lignin and its soluble fractions in dichloromethane and methanol were studied via ATR–FTIR spectroscopy. The spectrum of the unfractionated lignin (KL) appeared as follows: vibration typical for softwood KL (Fig. 3) at 3,404 cm^{-1} (OH); 2,933 and 2,852 cm^{-1} (stretching vibrations CH_2); 1,706 cm^{-1} (non-conjugated CO); 1,593 and 1,510 cm^{-1} (aromatic skeletal vibrations); 1,450, 1,425 and 1,363 cm^{-1} (ring-stretching CH vibrations in-plane deformation); and 1,363 cm^{-1} (vending vibration of phenolic OH). The bands at 1,264 and 1,208 cm^{-1} pertain to the ring breathing with CO stretching. The band at 1,143 cm^{-1} is assigned to the aromatic CH in-plane deformation for the guaiacyl nuclei; two bands at 1,122 and 1,028 cm^{-1} also belong to the guaiacyl unit (C–O). The out-of-plane C–H vibrations in positions 2, 5 and 6 for guaiacyl unit appear at 851 and 812 cm^{-1}. The remaining bands can be assigned to sulphur compounds: at 1,077 cm^{-1} (C = S), 624 cm^{-1} (Ar–S), 556 cm^{-1} (C–S stretching vibrations) and 450 cm^{-1} (S–S stretching). The spectrum for the first fraction (KL_1) shows the distinctive high intensity of aliphatic CH bands, as well as four peaks at 1,152, 1,120, 962 and 731 cm^{-1}, which were not apparent for the original KL. From the spectra it was determined that the KL_1 fraction contains 0.9 times more carbonyls than the original KL sample. The similarity in the structures of the original KL and fractionated KL_2 is in accordance with the elemental composition detected.

Furthermore, the effect of the two-step fractionation on the chemical structure of KL was evaluated using ^1H NMR spectroscopy. Fig. 4 shows the qualitative ^1H NMR characterization of the unfractionated and fractionated samples. Six functional regions were found in the original KL: (1) an aliphatic and aromatic side acetoxyl chain region ($\delta = 1.6$–2.5 ppm); (2) a methoxy region ($\delta = 3.5$–4.0 ppm); (3) a H_α and H_β aliphatic region ($\delta =$ 4.0–6.3 ppm); (4) an aromatic region (δ = 6.3–7.9 ppm); (5) a phenolic region (δ = 7.9–9.4 ppm); and (6) a carboxylic region ($\delta = 11.0$–14.0 ppm) [37,38]. Based on the structures obtained by proton nuclear magnetic resonance, it can be concluded that the first lignin fraction (KL_1)

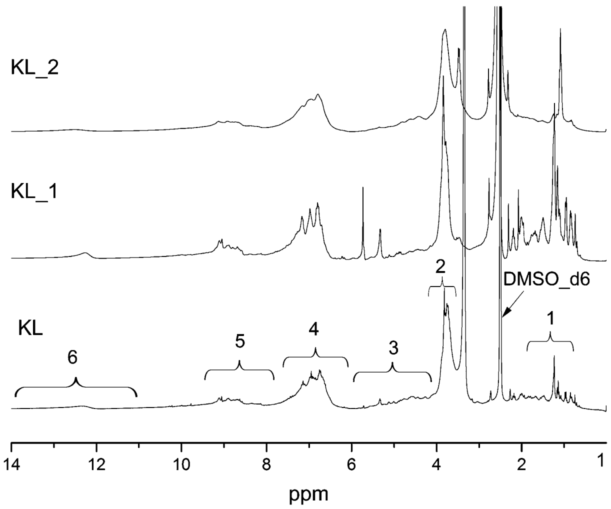

Fig. 4. ^1H NMR spectra for the unfractionated KL and fractionated samples (KL_1 and KL_2).

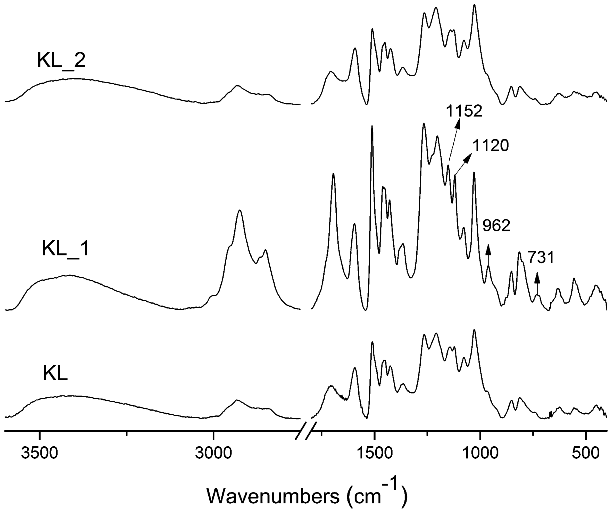

Fig. 3. ATR–FTIR spectra for the original KL, first lignin fraction in dichloromethane (KL_1) and second lignin fraction in methanol (KL_2).

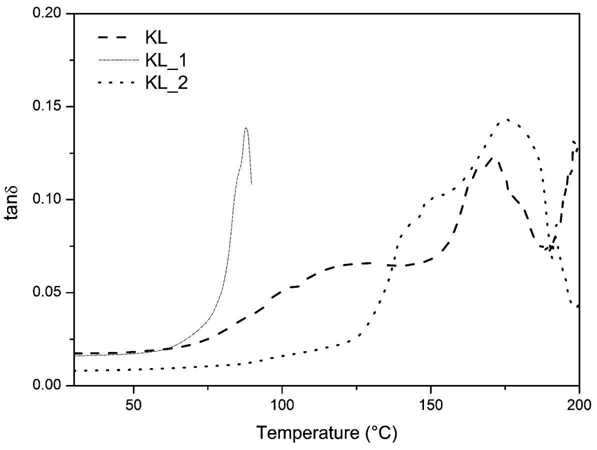

Fig. 5. Dependence on temperature of the mechanical loss factor of the unfractionated lignin (KL) and its fractions (KL_1 and KL_2).

contains numerous low-molecular contaminants compared to both the original KL and second lignin fraction (KL_2). The first fractionation with dichloromethane can be considered a purification step, removing low molecular fragments with organically bound sulphur, resulting in a lignin sample with a more consolidated structure.

Glass transition temperature ($\underline{T}_g$) is an important value for lignin, this reflecting the transition from a glassy to rubbery state, which depends on free volume for its molecular motion. However, it seems difficult to discern a value for T_g by carrying out differential scanning calorimetry (DSC) [39]. As recently reported, dynamic mechanical analysis is a more sensitive means for determining T_g as DSC [40]. Herein, the glass transition temperatures for the lignin samples were determined from the peak value of the mechanical loss factor, measured by the dynamic mechanical analysis using a powder holder. As shown in Fig. 5, the viscoelastic behaviour of KL reflects its large polydispersity.

The original lignin (KL) showed two distinct transition peaks that allocate two transition temperatures at 129°C and 172°C. The occurrence of more glass transition temperatures indicates the presence of different macromolecules in the structure of the polymer. Nevertheless, the fractionated low-molecular weight lignin with narrow polydispersity (KL_1) exhibited only one T_g at 88°C. Measuring the viscoelastic behaviour of KL_1 was detectable only till 98°C due to the liquefaction of the low-molecular weight sample. The high-molecular lignin fraction (KL_2) showed, similarly to the original KL, two glass transition temperatures. However, the shift in T_g to higher temperatures indicates the presence of fragments with greater molecular weight. Furthermore, the distance of two tan δ is shorter that indicates the increased homogeneity of the sample. Based

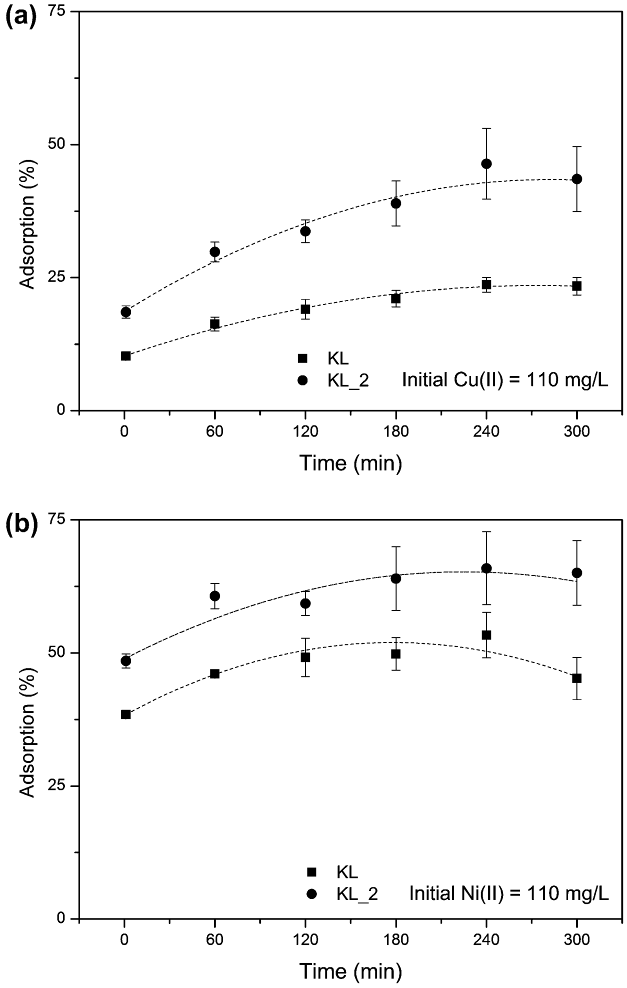

Fig. 6. Removal of (a) Cu (II) and (b) Ni (II) by KLs KL and KL_2.

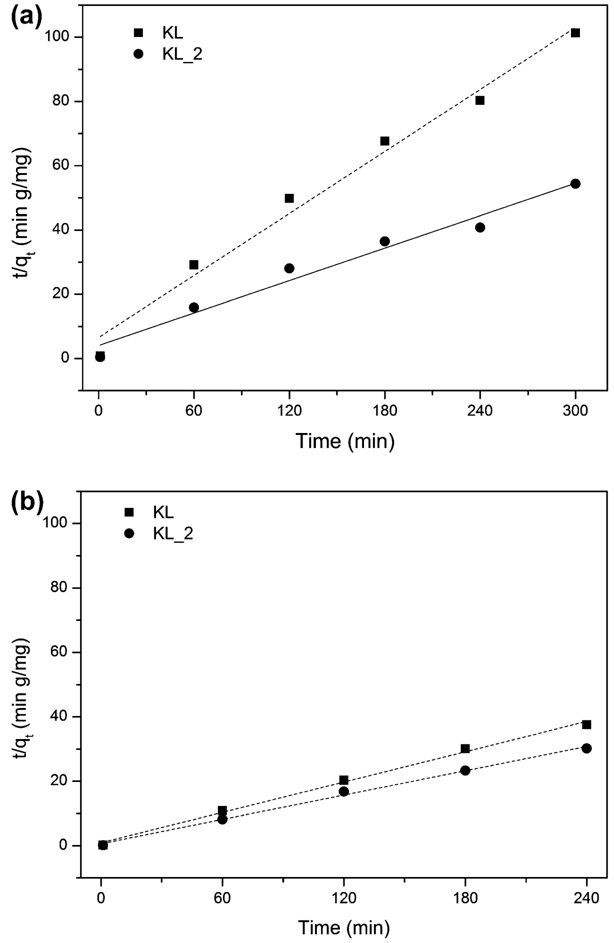

Fig. 7. Pseudo-second-order kinetic model fitting for (a) Cu (II) and (b) Ni (II) adsorption on lignins KL and KL_2.

Table 3
Pseudo-second-order kinetic constants for an adsorption of metal ions on lignin

Metal ions[a]	Lignin	q_e (mg g^{-1})	k (mg g^{-1})	h (mg g^{-1} min^{-1})	r^2
Cu (II)	KL	3.11	1.59×10^{-2}	0.15	0.99
Cu (II)	KL_2	5.94	0.70×10^{-2}	0.25	0.97
Ni (II)	KL	6.37	2.60×10^{-2}	1.06	0.99
Ni (II)	KL_2	7.95	2.52×10^{-2}	1.59	0.99

[a] Initial metal ion concentration was 110 mg L^{-1}.

Table 4
Composition of functional groups of the unfractionated KL and its second fraction (KL_2)

Sample	[a]Aliphatic OH (mmol g^{-1})	[a]Condensed phenolic OH (mmol g^{-1})	[a]Guajacyl phenolic OH (mmol g^{-1})	[a]Carboxyl OH (mmol g^{-1})	[b]Carbonyl (%)
KL	1.20	0.99	1.38	0.23	4.4
KL_2	1.19	0.66	0.86	0.19	4.8

[a] Determinated by ^{31}P NMR spectrometry [28].
[b] Determinated by ATR–IR spectrometry [43].

on the findings given, it can be suggested that the dynamic mechanical analysis of powdered lignin samples can serve as a quick method for analysing the effect of fractionation on the homogeneity of a lignin sample.

3.2. Kinetic adsorption of metal ions

In order to analyse the sorption capacity of lignin, pertaining to Cu (II) and Ni (II) ions, the original starting lignin (KL) and a second fraction of the same that was free of low molecular admixtures were selected (KL_2). Fig. 6(a) and (b) shows that the fractionated lignin (KL_2) without low-molecular weight fractions exhibits a greater removal efficiency for Cu (II) and Ni (II) than the original, highly polydisperse, KL.

The metal ion sorption kinetic on the lignin samples was evaluated by a pseudo-second-order model (Fig. 7(a) and (b)).

Table 3 displays the kinetic constants obtained relating to the removal of Cu (II) and Ni (II) ions by KL.

The carboxylic, phenolic and carbonyl groups present in lignin are regarded as functional sites responsible for its metal scavenging ability [15,16,41,42]. Analyses of the abundance of these functional groups showed that the two-step fractionation with dichloromethane followed by methanol decreased the amount of aliphatic and aromatic hydroxyl groups in KL and slightly increased the concentration of carbonyl groups (Table 4) [28,43]. Despite the decreased concentration of carboxylic and phenolic groups, the fractionated lignin showed a rise in the adsorption of Cu (II) and Ni (II) by about 91 and 25%, respectively. Such heightened capacity for metal scavenging potentially indicates easier accessibility of the functional sites present in KL_2 than in KL, which is attributed to the modified molecular structure.

The adsorption capacity of commercial ion-exchange compounds and non-commercial materials, based on ligno–cellulosic material, has been determined in the range of 1.8–146 mg g^{-1} for cuprum ions and from 7.5 to 138 mg g^{-1} for nickel ions [41]. The removal efficiency of cuprum and nickel ions by the original starting KL with low molecular admixtures can be compared to the modified oak sawdust. Sorption data show that the removal efficiency of KL can be slightly increased by fractionation, which separates both low and high molecular fragments from the lignin macromolecule.

4. Conclusions

High-molecular weight polydisperse KL was fractionated by the two-step successive extraction in dichloromethane and methanol. Elemental analysis, ^{1}H NMR, ATR–FTIR analyses, gel permeation chromatography and dynamic mechanical analysis proved that initial extraction with dichloromethane could eliminate, from KL, low-molecular weight admixtures containing organically bound sulphur. The second methanol fraction presents a sample free of low-molecular fractions with much higher homogeneity than the original KL. It was detected that the two-step fractionation in dichloromethane and methanol increased by about 25–91% the heavy metal scavenging capacity of the fractionated lignin with reduced polydispersity, compared to the original polydisperse KL.

Information about an effect of fractionation of KL is of great importance for its utilization as low-cost renewable material. However, the fractionated KL has still a lack of sufficient adsorption groups and further chemical modification is needed to improve its final adsorption capacity.

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References

[1] P. Bajpai, Environmental Friendly Production of Pulp and Paper, John Wiley & Sons, New York, NY, 2010, pp. 11–17.
[2] P. Bajpai, Black Liquor Gasification, Elsevier, London, 2014, pp. 7–12.
[3] A.G. Kirkman, J.S. Gratzl, L.L. Edwards, Kraft lignin recovery by ultrafiltration: Economic feasibility and impact on the kraft recovery system, Tappi J. 69(5) (1986) 110–114.
[4] S.Y. Lin, Commercial Spent Pulping Liquors, in: S.Y Lin, C.W Dence (Eds.), Methods in Lignin Chemistry, Springer-Verlag, Berlin, 1992, pp. 75–80.
[5] F. Öehman, H. Theliander, P. Tomani, P. Axegard, Method for separating lignin from black liquor, Patent Pub. No: WO/2006/031175, Int. Appl. No: PCT/SE2005/001301 (2006).
[6] P. Tomani, The lignoboost process, Cellul. Chem. Technol. 44(1–3) (2010) 53–58.
[7] O. Wallberg, A.S. Jönsson, R. Wimmerstedt, Ultrafiltration of kraft black liquor with a ceramic membrane, Desalination 156 (2003) 145–153.
[8] J. Marton, in: K.V. Sarkanen, C.H. Ludwig (Eds.), Lignins; Occurrence, Formation, Structure and Reactions, Wiley – Interscience, New York, NY, 1971, pp. 665–666.
[9] R. Brežný, L. Paszner, M.M. Micko, D. Uhrín, The ion-exchanging lignin derivatives prepared by mannich reaction with amino acids, Holzforschung 42 (1988) 369–373.
[10] D.R. Crist, R.H. Crist, J.R. Martin, A new process for toxic metal uptake by a kraft lignin, J. Chem. Technol. Biotechnol. 78 (2003) 199–202.
[11] D. Mohan, J.C.U. Pittman, P.H. Steele, Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin—A biosorbent, J. Colloid Interface Sci. 297 (2006) 489–504.
[12] G.C. Quintana, G.J.M. Rocha, A.R. Gonçalves, J.A. Velásquez, Lignins for heavy metal removal, Bioresource 3(4) (2008) 1092–1102.
[13] M. Betancur, P.R. Bonelli, J.A. Velásquez, A.L. Cukierman, Potentiality of lignin from the Kraft pulping process for removal of trace nickel from wastewater: Effect of demineralisation, Bioresour. Technol. 100(3) (2009) 1130–1137.
[14] M.B. Šćiban, M.T. Klašnja, M.G. Antov, Study of the biosorption of different heavy metal ions onto Kraft lignin, Ecol. Eng. 37(12) (2011) 2092–2095.
[15] X. Guo, S. Zhang, X. Shan, Adsorption of metal ions on lignin, J. Hazard. Mater. 151 (2008) 134–142.
[16] H. Harmita, K.G. Karthikeyan, X. Pan, Copper and cadmium sorption onto kraft and organosolv lignins, Bioresour. Technol. 100 (2009) 6183–6191.
[17] Y. Wu, S. Zhang, X. Guo, H. Huang, Adsorption of chromium (III) on lignin, Bioresour. Technol. 99 (2008) 7709–7715.
[18] M. Notely, M. Norgren, Lignin: Functional biomaterial with potential in surface chemistry and nanoscience, in: L.A. Lucia, O.J. Rojas (Eds.), The Nanoscience and Technology of Renewable Biomaterials, Blackwell Publishing Ltd, John Wiley & Sons, West Sussex, 2009, pp. 173–198.
[19] K. Nieminen, S. Kuitunen, M. Paananen, H. Sixta, Novel insight into lignin degradation during kraft cooking, Ind. Eng. Chem. Res. 53(7) (2014) 2614–2624.
[20] M. Helander, H. Theliander, M. Lawoko, G. Henriksson, L. Zhang, M.E. Lindström, Fractionation of technical lignin: Molecular mass and pH effects, Bioresource 8(2) (2013) 2270–2282.
[21] T. Dizhbite, G. Telysheva, V. Jurkjane, U. Viesturs, Characterization of the radical scavenging activity of lignins—Natural antioxidants, Bioresour. Technol. 95 (2004) 309–317.
[22] A. Gregorova, B. Kosikova, R. Moravcik, Stabilization effect of lignin in natural rubber, Polym. Degrad. Stab. 91 (2006) 229–233.
[23] A. Gregorova, Z. Cibulkova, B. Kosikova, P. Simon, Stabilization effect of lignin in polypropylene and recycled polypropylene, Polym. Degrad. Stab. 89 (2005) 553–558.
[24] J.T. Wells, M. Kosa, A.J. Ragauskas, Polymerization of Kraft lignin via ultrasonication for high-molecular-weight applications, Ultrason. Sonochem. 20 (2013) 1463–1469.
[25] H. Yoshida, R. Mörck, K.P. Kringstad, Fractionation of kraft lignin by successive extraction with organic solvents, Holzforschung 41(3) (1987) 171–176.

[26] R. Mörck, A. Reimann, K.P. Kringstad, Fractionation of kraft lignin by successive extraction with organic solvents. III. Fractionation of kraft lignin from birch, Holzforschung 42(2) (1988) 111–116.

[27] W.G. Glasser, V. Davé, C.E. Frazier, Molecular weight distribution of (Semi-) commercial lignin derivatives, J. Wood Chem. Technol. 13(4) (1993) 545–559.

[28] D.S. Argyropoulos, Quantitative phosporus-31 NMR analysis of lignins, a new tool for the lignin chemist, J. Wood Chem. Technol. 14(1) (1994) 45–63.

[29] R.J.A. Gosselink, Lignin as a Renewable Aromatic Resource for the Chemical Industry, PhD Thesis, Wageningen University, Wageningen, NL 2001, pp. 96–97.

[30] N. Hawkins, Novel Holder for Investigating Powers by Dynamic Mechanical Analysis, APN023, TA Instruments, Crawley, UK, 2001.

[31] Y.S. Ho, Pseudo-isotherms using a second order kinetic expression constant, Adsorption 10 (2004) 151–158.

[32] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater. B 136 (2006) 681–689.

[33] E. Adler, Structural elements of lignin and solonetzic and black chernozenic soils of Alberta, Ind. Eng. Chem. 49 (1957) 1377–1383.

[34] E.I. Evstigneev, Factors affecting lignin solubility, Russ. J. Appl. Chem. 84(6) (2011) 1040–1045.

[35] D.A.I. Goring, The physical chemistry of lignin, Pure Appl. Chem. 5 (1971) 233–254.

[36] S.E. Lebo Jr., J.D. Gargulak, T.J. McNally, Lignin, in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons Inc., New York, NY, 2001.

[37] K. Lundquist, Proton (1H) NMR Spectroscopy, in: S.Y Lin, C.W Dence (Eds.), Methods in Lignin Chemistry, Springer-Verlag, Berlin, 1992, pp. 242–249.

[38] A.R. Gonçalves, U. Schuchardt, M.L. Bianchi, A.A.S. Curvelo, Piassava fibers (*Attalea funifera*): NMR spectroscopy of their Lignin, J. Braz. Chem. Soc. 11(5) (2000) 491–494.

[39] H. Hatakeyama, Thermal analysis methods in lignin chemistry, in: S.Y Lin, C.W Dence (Eds.), Springer-Verlag, Berlin, 1992, pp. 200–214.

[40] K.P. Menard, Dynamic Mechanical Analysis, A Practical Introduction, CRC Press Taylor & Francis Group, NW, 2008, pp. 103–105.

[41] M.E. Argun, S. Dursun, C. Özdemir, M. Karatas, Heavy metal adsorption by modified sawdust: Thermodynamics and kinetics, J. Hazard. Mater. 141 (2007) 77–85.

[42] S. Schiewer, B. Volesky, Modeling of the Proton–Metal ion exchange in biosorption, Environ. Sci. Technol. 29 (12) (1995) 3049–3058.

[43] O. Faix, C. Grünwald, O. Beinhoff, Determinaiton of phenolic hydroxyl group content of milleed wood lignins (MWLs) from different botanic origins using selective aminolysis, FTIR, ^{1}H-NMR, and UV spectroscopy, Holzforschung 46 (1992) 425–432.