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Lignocellulosics in an ionic liquid, 1-ethylpyridinium chloride: reaction behavior and ion adsorption properties of corresponding humins

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Abstract

Herein, we studied the reaction behavior of cellulose, Japanese beech (*Fagus crenata*), and Japanese cedar (*Cryptomeria japonica*) in an ionic liquid, 1-ethylpyridinium chloride ([EtPy][Cl]), at 120 °C. Depolymerization occurred initially in all of the samples in a manner that formed low molecular weight compounds, followed by polymerization. The obtained polymers were black in color and ultraviolet-absorbing, and morphologically as well as chemically different from the raw materials, indicating that they were humins. These humins adsorbed cations in the order $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Cs}^+ > \text{K}^+ > \text{Na}^+, \text{Li}^+$. There was selectivity for adsorption of cations; cellulose-derived humins adsorbed Ca^{2+} particularly easily. The adsorptivity of humins was superior in the order cellulose-derived > beech-derived $\geq$ cedar-derived. The cation exchange capacity of cellulose-derived humins was higher than that of soil and comparable with that of natural zeolite, suggesting that humins obtained by [EtPy][Cl] treatment can be used as cation adsorbents.

Keywords Ionic liquid, 1-Ethylpyridinium chloride, Lignocellulosic, Humin, Ion adsorption

Introduction

To help minimize use of fossil resources, there is increasing focus on renewable resources and energy as alternatives. Biomass, a biological resource, is an alternative to fossil resources. Among various types of biomass, lignocellulosics are a nonedible resource and thus an active area of research. Therefore, research and development on using lignocellulosics have increased.

Lignocellulosics mainly consists of cellulose, hemicellulose, and lignin. Various compounds obtained by decomposing these chemical components are thought to be capable of replacing many petrochemical products. Much research has been conducted on both thermochemical

and biochemical technologies for efficiently obtaining useful low molecular weight compounds from lignocellulosics. Various studies have been reported on fast pyrolysis [1, 2], pyrolysis [3, 4], acid hydrolysis [5, 6], enzymatic saccharification [7–9], hot compressed water treatment [10–12], and supercritical fluid treatment [13–15]. However, these methods have many issues, such as low conversion efficiency, the need for severe processing conditions such as high temperature and high pressure, the difficulty of maintaining facilities, as well as high cost. Hence, there is a demand for simpler, efficient, and environmentally friendly processing techniques. Ion liquid treatment is one such novel technology.

Ionic liquids [16–18] are organic salts that are liquid near ambient temperature and pressure. They are synthesized by combining cations and anions, enabling a wide range of molecular design. By changing the combination of cations and anions as well as altering the

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molecular structure, ionic liquids with various properties can be readily synthesized. Ionic liquids are environmentally friendly solvents because of their chemical stability, recyclability, nonvolatility, flame resistance, and low viscosity [19]. Certain ionic liquids dissolve not only cellulose, hemicellulose, and lignin—the major components of wood—but also wood itself [20–24]. These properties have led to research efforts using ionic liquids for component separation of woody biomass [25–27] and pretreatment for various biorefinery processes [28–31].

Swatloski et al. subjected fibrous cellulose to ionic liquid treatment at 70 °C and exposed it to microwave irradiation for 3–5 s, resulting in dissolution of 5–7 wt% in [C4mim][Br] (1-butyl-3-methylimidazolium bromide) and [C4mim][SCN] (1-butyl-3-methylimidazolium thiocyanate) [20]. Furthermore, when wood is treated with 1-butyl-3-methylimidazolium chloride ([C4mim][Cl]) at 130 °C for 15 h, partial dissolution of the wood occurs [32]. Additionally, using 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) for treatment results in complete dissolution of the wood [33].

Not only dissolution but also decomposition reactions occur. Hang et al. reported that when cellulose is treated with 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) or 1-ethylpyridinium chloride ([EtPy][Cl]) at 120 °C in a system containing water, cellulose was decomposed, resulting in formation of low molecular weight compounds. The composition of the decomposition products obtained varies depending on the ionic liquid used. The yield of decomposition products is different: in the former case, monosaccharides accounted for 24% and 5-hydroxymethylfurfural (5-HMF) accounted for 19%; whereas in the latter case, monosaccharides accounted for 32% and 5-HMF accounted for 3%. This suggests that [EtPy][Cl] exhibits high selectivity toward monosaccharide formation [34].

Ohno et al. reported that cellulose, when treated with [C2mim][Cl] at temperatures ranging from 100 °C to 140 °C, not only dissolved but also decomposed into low molecular weight compounds. Subsequently, further processing led to polymerization [35]. Furthermore, when cellulose was treated with [EtPy][Cl]—a type of pyridinium-based ionic liquid—at 120 °C, decomposition and subsequent polymerization of cellulose occurred, similarly to the treatment with [C2mim][Cl]. The reaction with [EtPy][Cl] proceeded more rapidly compared with [C2mim][Cl] [36]. The polymers obtained in this process were amorphous and exhibited ultraviolet (UV) absorption, characteristics that distinguish them from cellulose. Consequently, the generated polymers were humins. Humin is obtained from polymerization of monosaccharides generated by hydrolysis that occurs when lignocellulose is treated with acid; various low molecular weight

compounds such as furfural, 5-HMF, and levulinic acid are generated by further degradation of the monosaccharides. Hoang et al. characterized humins obtained from treating glucose with sulfuric acid; these humins exhibited a structure in which various furan compounds were polymerized through various types of chemical bonding [37]. Furthermore, formation of humins during ionic liquid treatment has also been reported [38–41]. When adding CrCl₃ as a catalyst to Brønsted acid ionic liquids, such as 1-methylimidazolium hydrogen sulfate or 1-butyl-3-methylimidazolium hydrogen sulfate, and subjecting glucose to heat treatment, not only 5-HMF but also humins formed [38]. Furthermore, Sievers et al. reported that when glucose, fructose, xylose, and other sugars (as well as furan compounds such as 5-HMF and furfural) were treated at 120 °C in a reaction system consisting of 1-butyl-3-methylimidazolium chloride and sulfuric acid, humins were formed as solid residues [39].

Despite these results, the properties and functions of humins obtained through ionic liquid treatment of various biomass sources remain unclear. Moreover, when cellulose is used as the starting material, the yield of humins is relatively high: 35% of the initial cellulose mass [36]. Therefore, elucidating the function of humins could facilitate new prospects for using lignocellulosics. In this study, [EtPy][Cl] treatment on cellulose, Japanese beech, and Japanese cedar were conducted and their reaction behavior was evaluated. Additionally, their cation adsorption properties were examined.

Materials and methods

Samples and chemicals

Wood flours (90–180 µm) from Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*) were extracted with ethanol/benzene (1/2, v/v) for 24 h in a Soxhlet apparatus. The extracted wood flour was oven-dried at 105 °C for 24 h prior to use. Cellulose (Whatman CF1) was also oven-dried at 105 °C for 24 h before use.

Next, 1-ethylpyridinium chloride ([EtPy][Cl], Tokyo Kasei Kogyo) was used as the ionic liquid. Dehydrated dimethyl sulfoxide (DMSO, Wako Pure Chemical Industries) and potassium bromide (Wako Pure Chemical Industries) were used without further purification. Metal chlorides (lithium chloride, sodium chloride, potassium chloride, cesium chloride, strontium chloride, and calcium chloride) as well as formic acid, acetic acid, sodium hydroxide, and potassium hydroxide were purchased from Wako Pure Chemical Industries. The metal chlorides were dried at 105 °C for 24 h prior to use. A 10 mM aqueous solution of sodium ethylenediaminetetraacetate (hereinafter termed the titrant) and 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (hereinafter termed the NN indicator) were obtained from

Dojin Chemical Research Institute. Ammonium acetate, sodium 2-biphenylol tetrahydrate, sodium nitroprusside dihydrate [sodium pentacyanonitrosylferrate(III) dihydrate], trisodium citrate dihydrate, and sodium hypochlorite solution (antiformin) were all purchased from Wako Pure Chemical Industries and used without further purification. Ammonium chloride, purchased from Wako Pure Chemical Industries, was dried at 105 °C for 24 h before use.

Amberlite IR124Na (Organo) was used as the ion-exchange resin (IER). Prior to use, the IER was regenerated by treating it with 1 M hydrochloric acid. For regeneration, a sufficient quantity of hydrochloric acid was placed in a beaker. The IER was added to the beaker and stirred with a glass rod. It was allowed to stand for 1 h and then decanted, followed by washing with ultrapure water 10× to remove the hydrochloric acid and convert it into the IER R–H type. The resulting wet IER was used in various adsorption experiments without drying. The mass of IER contained per unit volume of wet IER was 0.5 mg/μL.

Treatment with [EtPy][Cl]

[EtPy][Cl] (3.0 g) was placed into a 100-mL round-bottom flask and heated to 120 °C with an oil bath. A 0.09-g sample was introduced, and the ionic liquid treatment was conducted by stirring for 0–24 h.

Analysis of the [EtPy][Cl] water-insoluble portion

After treating the sample with [EtPy][Cl], the flask was removed from the oil bath. Then, 100 mL of distilled water was added to the flask to precipitate the [EtPy][Cl] water-insoluble portion. The resulting mixture was stirred for 24 h at room temperature to wash the [EtPy][Cl] water-insoluble portion. Subsequently, the [EtPy][Cl] water-soluble portion was removed through filtration, and the obtained [EtPy][Cl] water-insoluble portion was thoroughly washed with distilled water. Afterward, the [EtPy][Cl] water-insoluble portion was collected by filtration and dried at 105 °C for 24 h. For the obtained [EtPy][Cl] water-insoluble portion, a mass measurement was performed; the yield was calculated with the following equation:

$$\text{Yield (\%)} = \frac{\text{Mass of obtained [EtPy][Cl] water-insoluble portion (g)}}{\text{Initial mass of sample (g)}} \times 100.$$

The obtained [EtPy][Cl] water-insoluble portion was Au-coated and then studied with a scanning electron microscope (SEM; JEOL JSM-5510LV) at an accelerating voltage of 15 kV. The obtained [EtPy][Cl] water-insoluble portion was subjected to Fourier-transform infrared

spectroscopy (FTIR; Shimadzu, model 8200PC) analysis by the KBr method. The measurement conditions were as follows: wavenumber range, 400–4000 cm^{−1}; number of scans, 20; measurement mode, absorbance.

Crystal structure analysis of the [EtPy][Cl] water-insoluble portion was performed by X-ray diffraction (XRD; Rigaku, Ultima IV). The measurement conditions were as follows: anode, Cu; voltage, 40 kV; current, 30 mA; scanning range (2θ), 5° to 45°.

Gel permeation chromatography analysis of compounds dissolved in [EtPy][Cl]

The molecular weight distribution of the compounds solubilized in [EtPy][Cl] was evaluated. After starting treatment of the samples with [EtPy][Cl] as previously described, 90 μL of the reaction medium was added to 90 μL of DMSO and mixed until homogeneity. DMSO dissolved completely in [EtPy][Cl] without any precipitate.

The mixture was passed through a 0.45-μm filter, and gel permeation chromatography (GPC) was carried out on the filtrate. The GPC conditions were as follows: column, Shodex SB-803 HQ; flow rate, 0.3 mL min^{−1}; eluent, DMSO/LiCl (0.1 M); detectors, refractive index detector (RID) and UV–visible detector set at 280 nm; column temperature, 60 °C. Pullulan (Shodex standard P-82) was used as the standard for measuring the molecular weight distribution.

Preparation of humin for adsorption tests

[EtPy][Cl] (3.0 g) was placed in a 100-mL round-bottom flask and heated to 120 °C with an oil bath. A 0.3-g sample was introduced and the ionic liquid treatment was conducted by stirring for 24 h. Subsequently, the flask was removed from the oil bath and 100 mL of distilled water was added to the flask. This caused precipitation of humin as the [EtPy][Cl] water-insoluble portion. The mixture was stirred at room temperature for 24 h. Subsequently, the humin was subjected to washing and then collected by filtration. The collected humin was thoroughly washed with distilled water and then recovered again by filtration. The recovered humin material was dried at 105 °C for 24 h.

Measurement of ion exchange capacity of humin

Humin (0.1 g) or 0.2 mL of IER was placed into a 15-mL centrifuge tube, followed by adding 5 mL of 1 M aqueous ammonium acetate. After shaking for 30 min, centrifugation was undertaken at 6312 g for 15 min. The product

was passed through a 0.45- μm membrane filter and the supernatant liquid was discarded. Subsequently, 5 mL of 1 M aqueous ammonium acetate was added once again, and the same procedure was repeated 4 $\times$.

Furthermore, after discarding the supernatant, 5 mL of ultrapure water was added to the tube and stirred for 2 min. Subsequently, centrifugation was carried out at 9500 rpm for 15 min, followed by discarding the supernatant by passing through a 0.45- μm membrane filter. This procedure was repeated 3 $\times$ by adding ultrapure water again and performing the same steps.

After this process, which washes away excess NH_4^+ , 3 mL of aqueous 10 w/v% NaCl was added. The mixture was stirred and then shaken for 1 h, followed by centrifugation at 9500 rpm for 15 min. Subsequently, the supernatant was passed through a 0.45- μm filter and the filtrate was collected. Again, 3 mL of aqueous NaCl was added, and the same process was repeated 3 $\times$. Finally, the volume was adjusted to 10 mL with aqueous NaCl. For the colorimetric test, this solution was further diluted 100 $\times$ with ultrapure water.

Adsorption test

To evaluate the adsorption properties of humins for various metal cations, adsorption tests were conducted as follows. One milliliter of various metal chloride solutions (LiCl , NaCl , KCl , CsCl , and SrCl_2) adjusted to concentrations of 0.1, 1.0, and 10 mM was added to microtubes. Then, 40 mg of humin or IER were added to each tube, followed by 3 min of stirring and a 1-h period of settling. Because the mass of IER per unit volume of wet IER was 0.5 mg/ μL , 80 μL of wet IER was added in this experiment. Subsequently, filtration was performed with a 0.45- μm filter; the resulting filtrate was considered the solution after adsorption treatment.

Quantitative analysis of metal cations in this solution after adsorption treatment was performed by ion chromatography. The analysis conditions were as follows: column, Shodex YS-50; eluent, 4 mM methanesulfonic acid; flow rate, 1.0 mL/min; column oven temperature, 40 $^\circ\text{C}$; injection volume, 10 μL ; detector, conductivity detector.

The residual cation (percentage) was calculated with the following formula:

$$\text{Residual cation (\%)} = \frac{\text{Molar concentration of metal cations in the solution after adsorption treatment (mM)}}{\text{Molar concentration of metal cations in the solution before adsorption treatment (mM)}} \times 100.$$

Aqueous indophenol A was prepared by dissolving 3 g of sodium 2-biphenylol tetrahydrate and 0.012 g of sodium nitroprusside dihydrate in ultrapure water, and adjusting the volume to 100 mL. Aqueous indophenol B was prepared by dissolving 8 g of trisodium citrate dihydrate, 0.8 g of sodium hydroxide, and 1.6 mL of sodium hypochlorite solution (antiformin) in ultrapure water; and adjusting the volume to 200 mL.

After adding 2.5 mL of aqueous indophenol A to 2.5 mL of 100 $\times$ -diluted sample solution, the mixture was shaken for 15 min. Subsequently, 5.0 mL of aqueous indophenol B was added, followed by another 15-min shaking period. The mixture was then allowed to stand for 1 h to develop coloration.

For preparing a calibration curve, aqueous NH_4Cl was adjusted to predetermined concentrations (0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 mM). These solutions were subjected to the same indophenol colorimetric test as the sample solution.

Subsequently, the absorbance (wavelength: 625 nm) of this solution was measured with a UV-visible spectrophotometer (Shimadzu, UVmini-1240) and the ion exchange capacity was calculated:

Thirty milliliters of aqueous calcium chloride (CaCl_2) at various concentrations (0.1, 1.0, and 10 mM) was prepared and placed in a centrifuge tube. Then, 1200 mg of humin or IER were added, followed by stirring for 3 min and allowing it to stand for 1 h. Because the mass of IER per unit volume of wet IER was 0.5 mg/ μL , 2400 μL of wet IER was added in this experiment. Subsequently, filtration was performed with a 0.45- μm filter; the obtained filtrate was designated as the solution after adsorption treatment.

The resulting 20 mL of solution was transferred to a 100-mL beaker. To this beaker, 2 mL of 8 M aqueous potassium hydroxide was added, and the mixture was stirred for approximately 3 min. Then, 40 mg of NN indicator was added, and the solution was stirred until it uniformly turned a reddish-purple color. At this point, the titrant was slowly added dropwise; the titration was stopped upon reaching a blue titrate color. The quantity of calcium ions was calculated from the volume of titrant with the following formula:

$$\text{Ca weight (mg)} = \text{Volume of titrant added (mL)} \times 0.4008^*$$

$$\text{Ion exchange capacity (cmol/kg)} = \frac{\text{Quantity of adsorbed ammonium ions } \text{NH}_4^+ \text{ (cmol)}}{\text{Sample mass (kg)}}$$

[* = Mass of Ca reacting with the titrant per unit volume (mg/mL)].

The residual Ca^{2+} was determined with the following equation:

$$\text{Residual Ca}^{2+}(\%) = \frac{\text{Concentration of Ca}^{2+} \text{ in the solution after adsorption treatment (mg/mL)}}{\text{Concentration of Ca}^{2+} \text{ in the solution before adsorption treatment (mg/mL)}} \times 100.$$

Experiments were also conducted with mixed solutions as aqueous solutions. The mixed solutions were prepared by adjusting the concentration of each metal chloride (LiCl , NaCl , KCl , CsCl , and SrCl_2) to the desired concentrations (0.1, 1.0, and 10 mM). One milliliter of this mixed solution was added to a microcentrifuge tube, and a pre-determined quantity of humin (0, 10, 20, and 40 mg) was added. After stirring for 3 min, the mixture was allowed to stand for 1 h. Subsequently, filtration was performed with a 0.45- μm filter; the obtained filtrate was considered the solution after adsorption treatment. Quantification

of various metal cations in this solution was carried out by ion chromatography. The analysis conditions and the

calculation method for the residual metal cations were the same as previously described.

Results and discussion

GPC analysis of compounds solubilized in ionic liquids

Figure 1 shows GPC chromatograms of the solubilized compounds in $[\text{EtPy}][\text{Cl}]$. Figure 1a shows the results for cellulose, Fig. 1b for Japanese beech, and Fig. 1c for Japanese cedar. In the case of cellulose treatment Fig. 1a, the results from the RID detector exhibited a broad peak at a retention time of ca. 20 min at

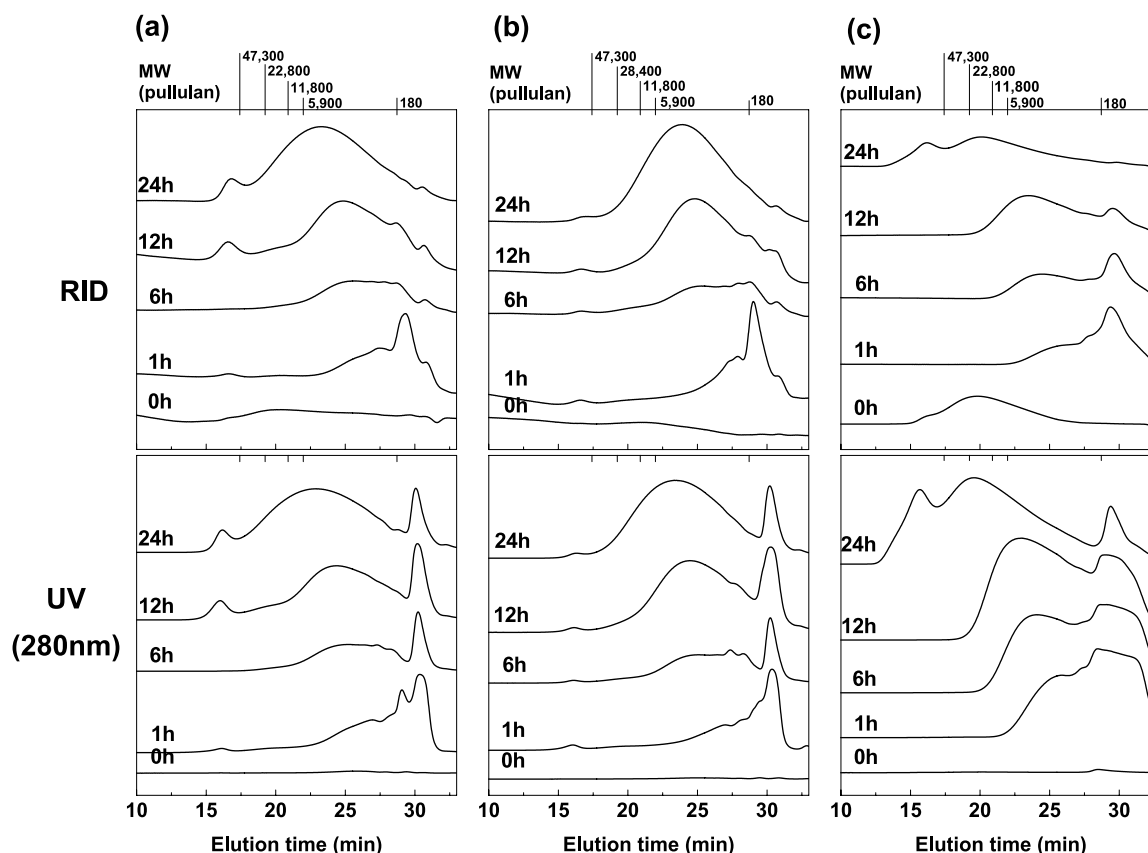


Fig. 1 GPC chromatograms of compounds solubilized in $[\text{EtPy}][\text{Cl}]$ from **a** cellulose, **b** Japanese beech, and **c** Japanese cedar at 120 °C for various treatment times. Top, refractive index detector (RID); bottom, UV detector ($\lambda = 280 \text{ nm}$)

a reaction time of 0 h. This peak corresponds to a molecular weight of ca. 22,800 and is because of dissolved cellulose. However, at a reaction time of 1 h, a distinct peak was observed at a molecular weight of ca. 180. Cellulose was depolymerized during [EtPy][Cl] treatment. As the reaction time progressed, this peak broadened and peaks in the high molecular weight region became evident; and at a reaction time of 24 h, a substantial peak was observed at ca. 5900. This suggests that once cellulose was depolymerized in a manner that formed low molecular weight compounds, these compounds subsequently reacted and polymerized, resulting in higher molecular weight products. Furthermore, compounds with UV absorbance were present in both the low molecular weight compounds formed initially and the higher molecular weight compounds formed subsequently at reaction times ranging from 1 to 24 h. In other words, when cellulose was treated with [EtPy][Cl], a reaction occurred in which cellulose was depolymerized in a manner that formed low molecular weight compounds and these compounds polymerized in a manner that formed high molecular weight compounds with UV absorption, which differs from cellulose. This result is consistent with a previous study [36].

In the case of Japanese beech, there were essentially no peaks observed in the RID at 0 h of treatment (Fig. 1b, top). However, after 1 h of treatment, a substantial peak was evident at a molecular weight of ca. 180. Because this peak was not evident at 0 h, it can be inferred that [EtPy][Cl] treatment resulted in partial decomposition and depolymerization of Japanese beech. Furthermore, as the treatment continued, the peak gradually shifted toward the higher molecular weight region. After 24 h of treatment, a peak was observed at a molecular weight of approximately 5,900. Furthermore, the peak intensity in the low molecular weight region at ca. 180 decreased. The peaks corresponding to RID were also observed in the UV (Fig. 1b, bottom), indicating that both these low and high molecular weight compounds exhibited UV absorption.

Similar results were obtained when Japanese cedar was treated (Fig. 1c). After 1 h of treatment, a peak was observed at a molecular weight of approximately 180. As the treatment time increased, the peak gradually shifted toward the higher molecular weight region, and the peak at a molecular weight of ca. 180 decreased in intensity. Peaks corresponding to those evident in RID were also observed in the UV, indicating that both these low and high molecular weight compounds, as well as Japanese beech, exhibited UV absorption.

Accordingly, Japanese beech and Japanese cedar were depolymerized followed by formation of high molecular weight compounds, which is similar to when cellulose

was treated. Lignocellulose depolymerizes when heated in acidic solvent, resulting in formation of low molecular weight compounds such as various monosaccharides, 5-HMF, and furfural. Further heating causes polymerization of these compounds and various low molecular weight compounds derived from 5-HMF, in a manner that forms humins. The [EtPy][Cl] used in this reaction is also an acidic ionic liquid. Previous studies on the treatment of cellulose with acidic ionic liquids have shown that furan compounds such as 5-HMF and furfural are produced after treatment [35, 36], and the peak around 30 min in elution time in Fig. 1, i.e., at molecular weight below 180, are due to these compounds. Therefore the high molecular weight compounds observed in the GPC analysis are hypothesized to be humins. However, because Japanese beech and Japanese cedar contain hemicellulose and lignin, it is unclear whether the properties of humins obtained from Japanese beech and Japanese cedar are the same as those obtained from cellulose.

Yield of [EtPy][Cl] water-insoluble portion

Figure 2 shows the changes in yield of the [EtPy][Cl] water-insoluble portion during ionic liquid treatment of cellulose, Japanese beech, and Japanese cedar. In the case of cellulose, the yield decreased to 4% after 1 h of treatment and then gradually increased with continued processing, reaching 35% after 24 h [36]. In contrast, the yields during the treatments of Japanese beech and Japanese cedar decreased to 33% after 1 h and then increased; reaching 51% and 55%, respectively, after 24 h. From the results of GPC analysis (Fig. 1), it is evident that during [EtPy][Cl] treatment, cellulose, Japanese beech, and Japanese cedar are initially depolymerized; followed by formation of high molecular

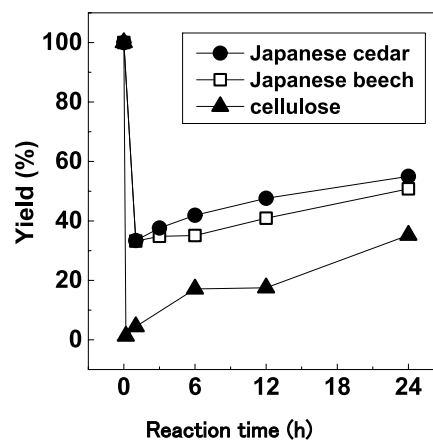


Fig. 2 Changes of yields of [EtPy][Cl] water-insoluble portions obtained from cellulose, Japanese beech, and Japanese cedar treated with [EtPy][Cl] at 120 °C

weight compounds. Hence, the decrease in yield of the [EtPy][Cl] water-insoluble portion in the initial stage of the reaction is considered to be because of depolymerization of the sample into water-soluble low molecular weight compounds and leached out during the washing. The subsequent increase in the yield is considered to be because of the increase in humins, which is a high molecular compound and water-insoluble. The higher yields of [EtPy][Cl] water-insoluble portions with Japanese beech and Japanese cedar compared with cellulose might be because lignin in Japanese beech and Japanese cedar was less susceptible to dissolution as well as decomposition than cellulose, and remained unreacted.

Appearance of [EtPy][Cl] water-insoluble portions

Figure 3 shows photos of [EtPy][Cl] water-insoluble portions from cellulose (Fig. 3a2), Japanese beech (Fig. 3b2), and Japanese cedar (Fig. 3c2) obtained after [EtPy][Cl] treatment for 24 h, compared with each untreated sample (Fig. 3a1–c3, respectively). SEM images of [EtPy][Cl] water-insoluble portions each untreated sample (Fig. 3a4–c4, respectively) are also shown, compared with each untreated sample (Fig. 3a3–c3, respectively).

Comparing Fig. 3a1–c1 with Fig. 3a2–c2 indicates that all [EtPy][Cl] water-insoluble portions became black powder after 24 h of treatment with any sample. The SEM images indicate that the structure of the samples before treatment was completely lost after 24 h of treatment. These SEM images also indicate no clear differences in shape between the samples. Humins are generally black compounds. Therefore, on the basis of the results in Fig. 3, humins were formed after 24 h of treatment.

Characterization of [EtPy][Cl] water-insoluble portions

Figure 4 shows the results of FTIR analysis on [EtPy][Cl] water-insoluble portions from cellulose, Japanese beech, and Japanese cedar after 24 h of treatment; compared with each untreated sample.

In the untreated cellulose, characteristic absorptions were observed at 1430 cm^{-1} (CH_2 bending vibrations), 1110 cm^{-1} (in-plane stretching vibrations of the pyranose ring), and 1375 cm^{-1} (CH bending vibrations); which are distinctive features of cellulose with a Type I crystalline structure [42]. However, after 24 h of treatment, these peaks were either no longer evident or became substantially smaller, and a new peak at 1705 cm^{-1} , not observed in the untreated sample, was detected. This peak is derived from the C=O bond [43], indicating the presence of structures in the [EtPy][Cl] water-insoluble portions from cellulose that are not present in cellulose. This suggests that cellulose treated with [EtPy][Cl] for 24 h resulted in compounds that differ from cellulose [36].

Similarly, the results are consistent with Japanese beech and Japanese cedar samples. In the untreated samples, characteristic peaks of cellulose such as 1110 , 1375 , and 1430 cm^{-1} were observed [42]. However, after 24 h of treatment, both in Japanese beech and Japanese cedar, the peak at 1110 cm^{-1} was no longer evident, and the intensity of the peak at 1375 cm^{-1} decreased. However, a peak at 1705 cm^{-1} , which was not present in the untreated samples, was observed. This suggests that similarly to cellulose, Japanese beech and Japanese cedar were converted into compounds that differ from the original samples after treatment with [EtPy][Cl] for 24 h. Furthermore, in the untreated samples, a peak derived from hemicellulose was observed at 1735 cm^{-1} [44]. However, after 24 h of treatment, this peak was no longer evident. This indicates that when Japanese beech and Japanese cedar were treated with [EtPy][Cl], not only cellulose but also hemicellulose was converted.

On the other hand, the peak at 1510 cm^{-1} and 1270 cm^{-1} indicates the aromatic skeletal vibration and guaiacyl ring of lignin, respectively [43]. These peaks observed in Japanese cedar and Japanese beech did not change significantly before and after treatment, suggesting that the lignin in these wood samples remained mostly in [EtPy][Cl] water-insoluble portion. This is consistent with the results in Fig. 2.

Figure 5 shows XRD patterns of the [EtPy][Cl] water-insoluble portion from cellulose, Japanese beech, and Japanese cedar obtained after 24 h of treatment with [EtPy][Cl]. For comparison, XRD patterns of each untreated sample are also shown. The peaks at $2\theta = 14.8^\circ$, 16.8° , and 22.6° correspond to cellulose I. In the XRD patterns of untreated samples, the peak at 22.6° was observed in all samples. Regarding the peaks at 14.8° and 16.8° , whereas they were somewhat less distinct in the untreated samples of Japanese beech and Japanese cedar, peaks were observed in this vicinity. Accordingly, the cellulose, Japanese beech, and Japanese cedar samples all exhibited a crystalline structure characteristic of cellulose I. However, after 24 h of treatment, these peaks were not evident in any of the samples. This indicates that treatment with [EtPy][Cl] for 24 h results in cellulose, Japanese beech, and Japanese cedar all becoming noncrystalline, amorphous substances. Figures 1, 2, 3, 4, 5 reveal that cellulose and wood can be converted into macromolecules with different chemical and crystalline structures compared with the raw materials after [EtPy][Cl] treatment for approximately 24 h. Moreover, the yield of the macromolecules reaches up to ca. 50%. The macromolecule recovered was considered to be humins. Thus, [EtPy][Cl] can be considered as a reaction medium capable of converting cellulose and wood into humins. To elucidate the performance of the obtained humins, adsorption tests

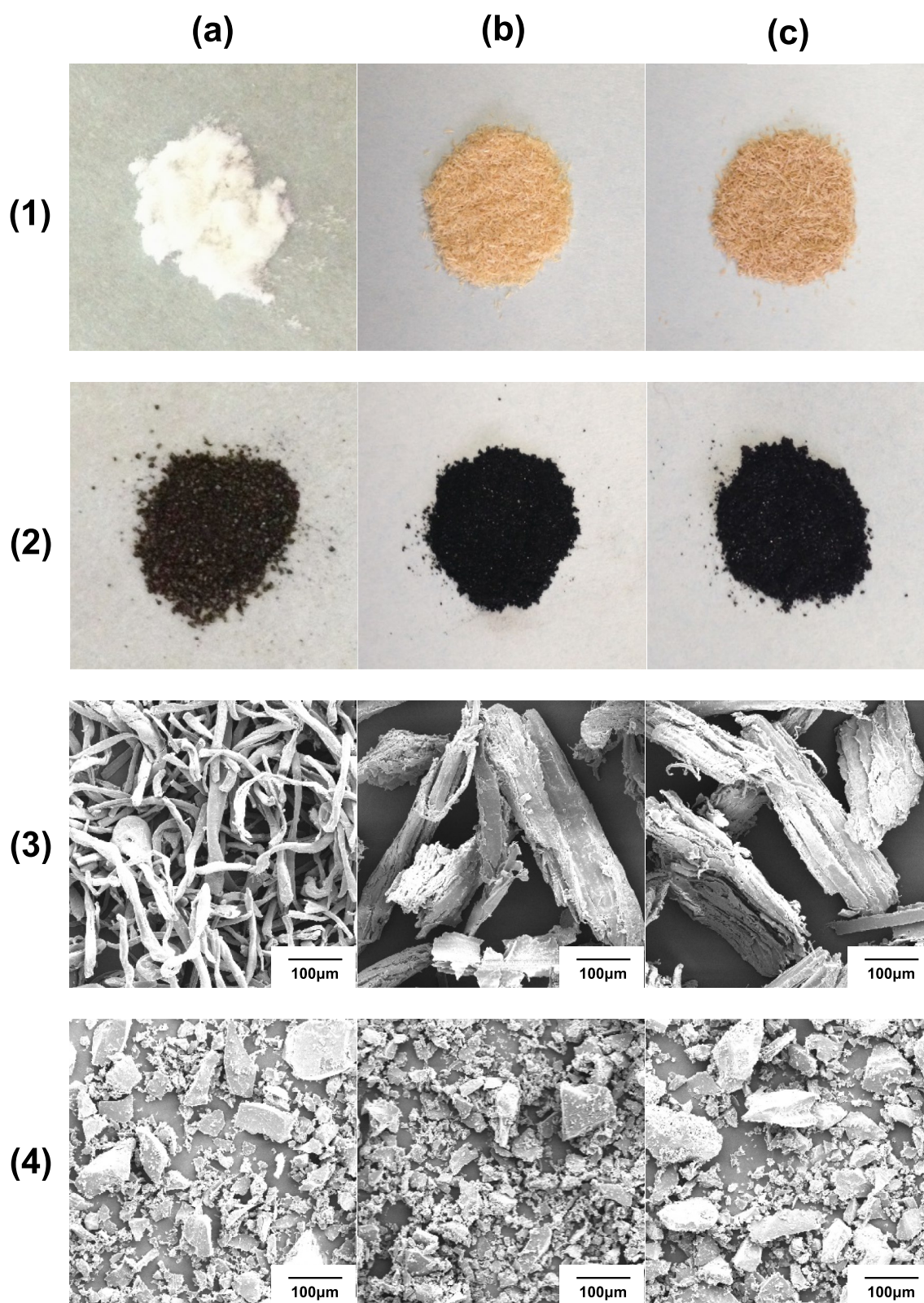


Fig. 3 Photographs [(1) untreated, (2) treated for 24 h] and SEM images [(3) untreated, (4) treated for 24 h] of [EtPy][Cl] water-insoluble portions obtained after treatment of **a** cellulose, **b** Japanese beech, and **c** Japanese cedar

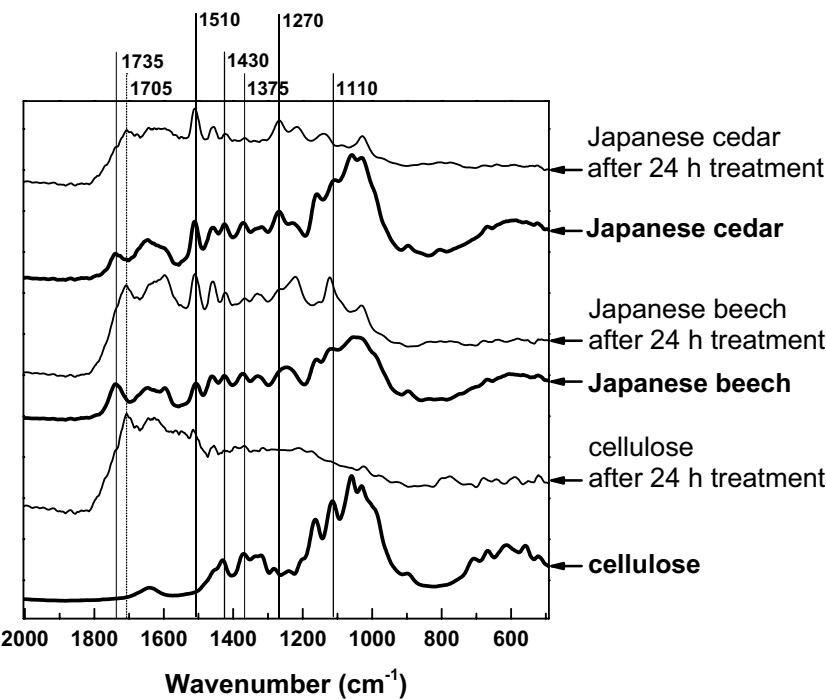


Fig. 4 FTIR spectra of [EtPy][Cl] water-insoluble portion obtained from cellulose, Japanese beech, and Japanese cedar compared to each untreated sample

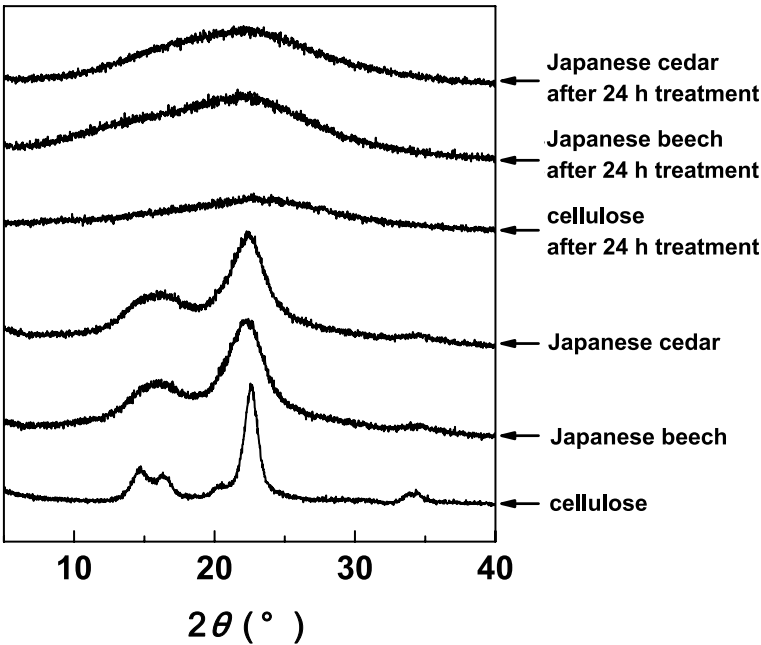


Fig. 5 X-ray diffraction patterns of [EtPy][Cl] water-insoluble portions obtained from cellulose, Japanese beech, and Japanese cedar compared to each untreated sample

Table 1 Rate of residual cations after adsorption tests by various humins and IER

Concentration of each ion in sample solutions (mM)	Humins from	Residual cations (%)					
		Li ⁺	Na ⁺	K ⁺	Cs ⁺	Ca ²⁺	Sr ²⁺
10	Cellulose	94.1	90.5	83.5	85.2	85.5	95.7
	Japanese beech	97.8	97.7	95.7	93.8	88.1	96.9
	Japanese cedar	98.7	98.0	97.1	94.2	96.9	96.9
	IER	2.4	10.8	1.1	12.7	13.4	0.1
1.0	Cellulose	93.5	82.2	65.5	49.3	42.0	68.7
	Japanese beech	98.5	96.0	90.4	85.6	80.0	85.5
	Japanese cedar	98.2	97.5	93.0	88.2	75.0	83.5
	IER	0.5	8.3	0.0	12.3	13.0	2.0
0.1	Cellulose	88.5	86.7	66.8	32.8	0.0	0.0
	Japanese beech	100.0	100.0	86.2	67.2	40.0	48.9
	Japanese cedar	100.0	99.0	97.7	80.4	45.0	51.7
	IER	9.4	0.0	0.0	0.0	12.0	0.0

were conducted on their metal ion adsorption properties. Metal ion adsorbent materials are considered crucial materials from the perspective of water purification and recovering metal resources.

Adsorption of various metal ions solubilized in water

Table 1 shows that the residual cations after adsorption tests were conducted on sample solutions containing metal cations using the humins obtained after treating cellulose, Japanese beech, and Japanese cedar with [EtPy][Cl] for 24 h. Three sample solutions with metal ion concentrations of 10, 1.0, and 0.1 mM were used. For comparison, the results when using an IER commonly used for ion adsorption are also shown.

The residual rate of Li⁺ decreased slightly in the case of cellulose-derived humins for all ion concentrations in the sample solutions. In contrast, when using humins derived from Japanese beech or Japanese cedar, the residual rate of Li⁺ remained almost unchanged at a high level, indicating that Li⁺ was not adsorbed. Compared with humins derived from cellulose and wood, IER exhibited a substantial decrease in the Li⁺ residual rate. In the Li⁺ adsorption tests, there was no clear correlation between the ion concentration in the sample solution and the residual rate.

For Na⁺ as well, similarly to Li⁺, using cellulose-derived humins led to a slight reduction in the Na⁺ residual rate at all ion concentrations in the sample solutions. However, when using humins derived from Japanese beech or Japanese cedar, the residual rate for Na⁺ remained high, with the lowest value being 96%; indicating that Na⁺ was negligibly adsorbed. However, IER exhibited a substantial reduction in the residual rate. For Na⁺ as well, similarly to Li⁺, there was no clear

correlation between the ion concentration and residual rate.

The residual K⁺ when cellulose-derived, Japanese beech-derived, Japanese cedar-derived humins, and IER were added to the sample solutions with ion concentrations of 10 mM were 83.5%, 95.7%, 97.1%, and 1.1%, respectively. For ion concentrations of 1.0 mM, the rates were 65.5%, 90.4%, 93.0%, and 0.0%, respectively; and for 0.1 mM, they were 66.8%, 86.2%, 97.7%, and 0.0%, respectively. When cellulose-derived humins were used, the residual rate of K⁺ decreased substantially compared with Li⁺ and Na⁺. Furthermore, with Japanese cedar-derived humins, there was no substantial change in the residual rate regardless of the ion concentration of the sample solution. However, in the case of Japanese beech-derived humins, a decrease in ion concentration of the sample solution corresponded to a decrease in the K⁺ residual rate. Thus, K⁺ was more readily adsorbed in the following order: IER > cellulose-derived humins > Japanese beech-derived humins > Japanese cedar-derived humins. Cellulose-derived and Japanese beech-derived humins exhibited a trend of decreasing residual rate as the ion concentration decreased.

For Cs⁺, regardless of whether cellulose-derived humins, Japanese beech-derived humins, Japanese cedar-derived humins, or IER was used, the residual rate of Cs⁺ decreased as the ion concentration in the sample solution decreased. In the case of cellulose-derived humins, the residual rate was substantially reduced to 32.8%, particularly in the low concentration solution of 0.1 mM, indicating that approximately 67% of Cs⁺ was adsorbed. In contrast to Li⁺, Na⁺, and K⁺, both Japanese cedar-derived and Japanese beech-derived humins exhibited a lower decrease in residual rate. Comparing various humins,

cellulose-derived humins exhibited substantially reduced Cs^+ residual rates compared with Japanese beech-derived and Japanese cedar-derived humins. Furthermore, when comparing Japanese beech-derived humins and Japanese cedar-derived humins, there was little difference observed in solutions with ion concentrations of 10 and 1.0 mM. However, in the low concentration solution of 0.1 mM, Japanese beech-derived humins adsorbed Cs^+ more strongly than Japanese cedar-derived humins. Thus, Cs^+ (similarly to K^+) exhibited an affinity for adsorption in the following order: IER > cellulose-derived humins > Japanese beech-derived humins > Japanese cedar-derived humins.

For Ca^{2+} , regardless of whether cellulose-derived humins, Japanese beech-derived humins, Japanese cedar-derived humins, or IER was used, the residual rate of Ca^{2+} decreased with decreasing ion concentration in the sample solution. In the case of 1.0 mM and 0.1 mM, the residual rate of Ca^{2+} for all types of humins tested was either similar to or lower than the residual rate for Cs^+ . At 0.1 mM concentration, the residual rates for both Japanese cedar-derived and Japanese beech-derived humins were substantially lower compared with Li^+ , Na^+ , K^+ , and Cs^+ . In particular, cellulose-derived humins exhibited a residual rate of 0.0% for Ca^{2+} , indicating that cellulose-derived humins are excellent Ca^{2+} adsorbents.

For Sr^{2+} , regardless of whether cellulose-derived humins, Japanese beech-derived humins, Japanese cedar-derived humins, or IER was used, as the ion concentration in the sample solution decreased, the residual rate of Sr^{2+} decreased. At 0.1 mM concentration, both Japanese beech-derived and Japanese cedar-derived humins adsorbed approximately half of Sr^{2+} , whereas cellulose-derived humins completely adsorbed Sr^{2+} . Additionally, for Sr^{2+} , the order of adsorptivity was IER > cellulose-derived humins > Japanese beech-derived humins = Japanese cedar-derived humins.

IER thus adsorbed Li^+ , Na^+ , K^+ , Cs^+ , and Sr^{2+} regardless of the ion concentration in the sample solution, whereas humins exhibited higher adsorption ability in the order $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. Thus, humins exhibited adsorptivity for various cations and selectivity in cation adsorption. In the case of cellulose-derived humins, the fact that the Ca^{2+} residual rate was 0.0% suggests a high affinity for Ca^{2+} compared with other metal cations such as Li^+ , Na^+ , K^+ , Cs^+ , and Sr^{2+} . Differences in adsorption properties were also observed depending on the raw material from which the humins are produced, exhibiting superior adsorption performance in the order of cellulose-derived > Japanese beech-derived $\geq$ Japanese cedar-derived.

Thus, the adsorptivity of these metal cations are hypothesized to be because of the structure formed,

especially when cellulose is treated with $[\text{EtPy}][\text{Cl}]$. Furthermore, humins adsorbed these metal cations more readily with decreasing ion concentration in the sample solution.

Yamaguchi et al. [45] conducted adsorption experiments of cesium ions in a cesium chloride aqueous solution using oak-derived wood charcoal and activated carbon. When using 32 mg/mL adsorbent and conducting adsorption treatment at room temperature (around 20 °C) for 24 h, over 60% of Cs^+ was adsorbed with wood charcoal, and over 35% with activated carbon in a 0.025 mM Cs^+ solution. As the ion concentration in the solution increased, the adsorption rate of Cs^+ decreased. At 0.25 mM Cs^+ concentration, there was a further decrease of a few percentage points compared with 0.025 mM, with approximately 55% being adsorbed. Furthermore, when the quantity of adsorbents to the solution studied was reduced, the adsorption rate also decreased. Cellulose-derived humins prepared in this study, when used as an adsorbent at 40 mg/mL in 0.1 mM Cs^+ , adsorbed approximately 67% of Cs^+ . Thus, cellulose-derived humins exhibited cesium adsorption capacities at least as effective as oak-derived charcoal. Watanabe et al. [46] conducted adsorption experiments using 10 mg/mL of mordenite-based and clinoptilolite-based zeolites as adsorbents in 7.5 mM aqueous Cs^+ , and reported almost 100% Cs^+ adsorption. Compared with these adsorbents, the Cs^+ adsorption capacity of the humins obtained in this study was relatively low.

Yamaguchi et al. [45] also conducted Cs^+ adsorption experiments in the presence of metal chlorides (LiCl , NaCl , KCl , MgCl_2 , CaCl_2 , and SrCl_2) and reported that these coexisting metal cations inhibit adsorption of Cs^+ . Moreover, they reported that this inhibitory effect is more pronounced with Group 1 cations compared with Group 2 cations. Therefore, to investigate the adsorption behavior of various humins obtained in this study in mixed solutions of various metal chlorides, adsorption tests were conducted with mixed solutions of metal chlorides as sample solutions and by varying the concentration of cellulose-derived, Japanese beech-derived, and Japanese cedar-derived humins in the sample solutions. Figures 6, 7, 8 show changes of various residual cations after adsorption tests. In Figs. 6, 7, 8, parts a–c refer to ion concentrations of 10, 1.0, and 0.1 mM, respectively. For Ca^{2+} , whereas concentration analysis was possible in single sample solutions as in Table 1, this was not possible in mixed sample solutions because of overlapping peaks with other metal ions during ion chromatography analysis, and therefore Ca^{2+} was not included in the sample solutions.

Figure 6 shows the results when cellulose-derived humins were used as the adsorbent. When

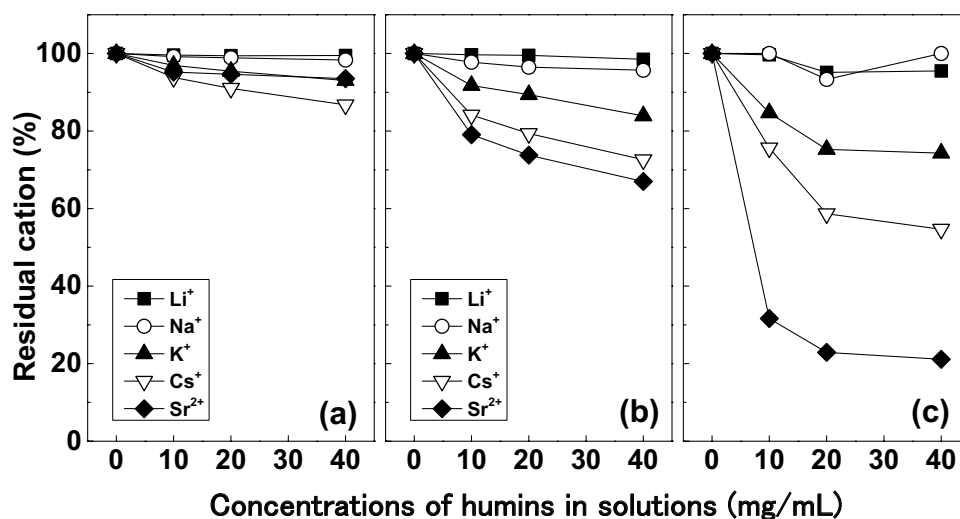


Fig. 6 Residual cations after adsorption tests by cellulose-derived humins at **a** 10 mM, **b** 1.0 mM, and **c** 0.1 mM of each cation

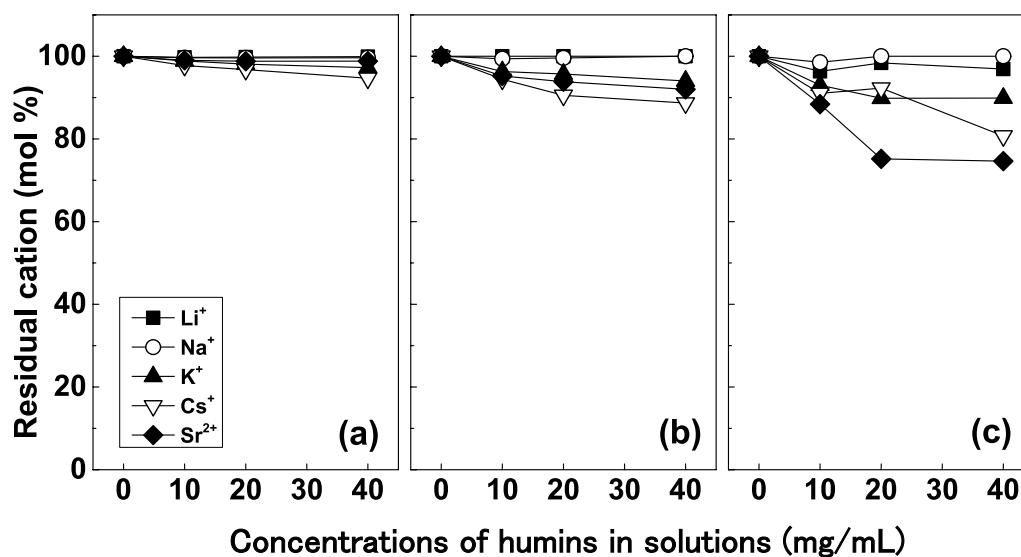


Fig. 7 Residual cations after adsorption tests by Japanese beech-derived humins at **a** 10 mM, **b** 1.0 mM, and **c** 0.1 mM of each cation

cellulose-derived humins were added at a concentration of 40 mg/mL, at 10 mM (Fig. 6a), the residual rate decreased in the following order: Li^+ (99%) > Na^+ (98%) > Sr^{2+} (94%) > K^+ (93%) > Cs^+ (88%). Similarly, at 1.0 mM (Fig. 6b), the residual rates decreased in the following order: Li^+ (98%) > Na^+ (96%) > K^+ (84%) > Cs^+ (73%) > Sr^{2+} (67%). At 0.1 mM (Fig. 6c), the residual rates decreased in the following order: Na^+ (100%) > Li^+ (96%) > K^+ (74%) > Cs^+ (55%) > Sr^{2+} (21%). The residual rates of Li^+ and Na^+ remained almost unchanged irrespective of the added concentration, consistent with the

results of the adsorption tests in the individual solutions (Table 1). For K^+ , Cs^+ , and Sr^{2+} , whereas there were no substantial differences in the residual rates at the high concentration of 10 mM, at lower concentrations of 1.0 and 0.1 mM, the order of adsorption was observed as K^+ > Cs^+ > Sr^{2+} ; in agreement with the results of the adsorption tests in the individual solutions (Table 1).

Figure 7 shows the results when Japanese beech-derived humins were used as the adsorbent. When Japanese beech-derived humins were added at a concentration of 40 mg/mL, at 10 mM (Fig. 7a), the residual rates

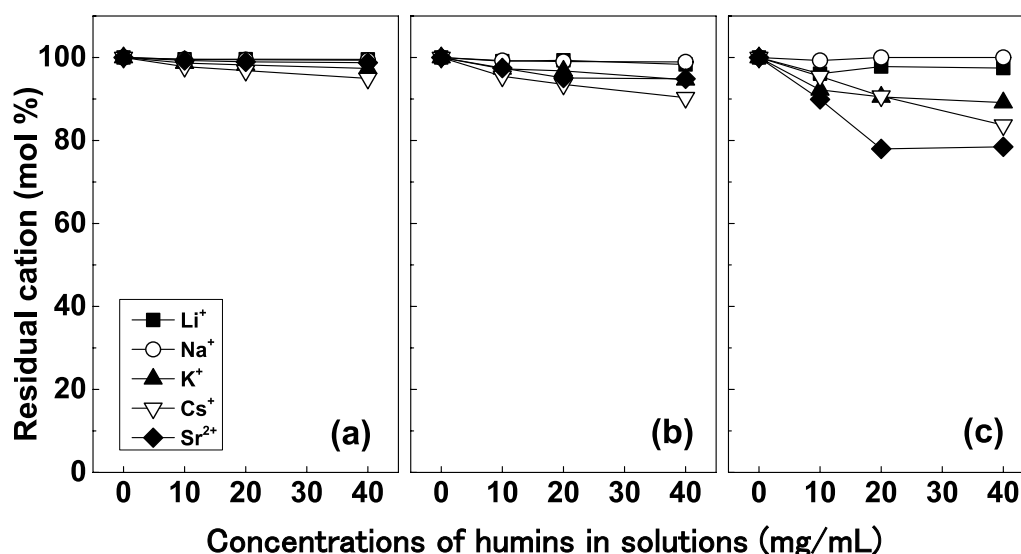


Fig. 8 Residual cations after adsorption tests by Japanese cedar-derived humins at **a** 10 mM, **b** 1.0 mM, and **c** 0.1 mM of each cation

were as follows: Li^+ (100%) > Na^+ (99%) > Sr^{2+} (99%) > K^+ (97%) > Cs^+ (95%); no substantial differences were observed. However, at 1.0 mM (Fig. 7b), the residual rates were as follows: Na^+ (100%) > Li^+ (100%) > K^+ (94%) > Sr^{2+} (92%) > Cs^+ (89%); and at 0.1 mM (Fig. 7c), they became: Na^+ (100%) > Li^+ (97%) > K^+ (90%) > Cs^+ (81%) > Sr^{2+} (75%), in decreasing order. In the case of Japanese beech-derived humins, similarly to the results for cellulose-derived humins, there was little change in the residual rates for Li^+ and Na^+ . The differences in residual rates for K^+ , Cs^+ , and Sr^{2+} are relatively small compared with those observed for cellulose-derived humins.

Figure 8 shows the results when Japanese cedar-derived humins were used as the adsorbent. Japanese cedar-derived humins exhibited similar results to those obtained when Japanese beech-derived humins were used. When Japanese cedar-derived humins were added at a concentration of 40 mg/mL, at 10 mM (Fig. 8a), the residual rate was as follows: Na^+ (100%) > Li^+ (99%) > Sr^{2+} (99%) > K^+ (97%) > Cs^+ (95%); the differences are negligible. In contrast, at 1.0 mM (Fig. 8b), the residual rate was as follows: Na^+ (99%) > Li^+ (98%) > Sr^{2+} (95%) > K^+ (95%) > Cs^+ (90%); and at 0.1 mM (Fig. 8c), it became Na^+ (100%) > Li^+ (97%) > K^+ (90%) > Cs^+ (83%) > Sr^{2+} (78%), in decreasing order.

The selectivity of the humins obtained in this study for cation adsorption was thus maintained even in mixed sample solutions. This selectivity was particularly pronounced in the case of low concentration solutions, such as 0.1 mM. When compared with the results from individual sample solutions, however, the residual rates of each metal cation after adsorption tests in mixed

Table 2 Cation exchange capacity (CEC) for various humins and IER

Humins	CEC (cmol/kg)
Humins from cellulose	171
Humins from Japanese beech	67
Humins from Japanese cedar	66
IER	422

sample solutions were higher. For instance, when cellulose-derived humins were added at a concentration of 40 mg/mL to a 0.1 mM sample solution, in individual solutions, Sr^{2+} was completely removed, resulting in a 0% residual rate. However, in the mixed solution, 21% of Sr^{2+} remained.

The quantity of metal cations adsorbed by humins thus varied with the sample solution concentration, composition, and quantity of humins added. Moreover, whereas selectivity in adsorption was evident, the presence of competing ions in the solution was hypothesized to inhibit their adsorption.

Cation exchange capacity measurement

Table 2 shows the cation exchange capacity (CEC) for various humins and IER. The CEC values for cellulose-derived, Japanese beech-derived, Japanese cedar-derived humins, and IER were 171, 67, 66, and 422 cmol/kg, respectively.

These results are consistent with the trends observed in the adsorption performance of metal cations that

have been previously discussed. For example, it has been observed that in solutions containing ions such as Sr^{2+} , Cs^+ , and K^+ that have been demonstrated to be selectively adsorbed, cellulose-derived humins exhibited higher adsorption compared with Japanese beech and Japanese cedar-derived humins. These results are because of the larger ion exchange capacity of cellulose-derived humins (Table 2). It is hypothesized that the adsorption of metal cations by the humins obtained in this study might be influenced by their electrical properties.

In addition to ion-exchange resins and ion-exchange membranes, zeolites and soils containing clay minerals are materials with ion-exchange properties. These CEC values typically range from 1 to 100 cmol/kg for soils [47] and ca. 175 cmol/kg for natural zeolites [48]. Cellulose-derived humins exhibit a higher CEC than that of soils and comparable to that of natural zeolites.

In order to clarify the adsorption capacity and selectivity of cations of humin obtained in this study, it is necessary to study various properties of humin as a future work that are thought to be related to adsorption properties, such as lignin content and elemental composition in humin, in addition to anionic functional groups, surface charge, specific surface area and so on.

Conclusions

Cellulose, Japanese beech, and Japanese cedar can be converted (by using [EtPy][Cl]) into humins with yields of 30%–50%. These humins exhibited cation adsorption and exhibited selectivity toward cation adsorption. Particularly, they exhibited high selectivity toward Ca^{2+} , Sr^{2+} , Cs^+ , and K^+ . This selectivity was maintained even in mixed solutions containing various ions. However, it was also hypothesized that the presence of competing ions can inhibit their adsorption. Additionally, when a large quantity of ions that can inhibit adsorption were present, it was difficult to adsorb ions with high selectivity, even if the selectivity for these ions was low.

Humins exhibited higher adsorption efficiency when the ion concentration in the sample solution was lower. Increasing the quantity of humins added to the solutions resulted in an increase in the quantity of adsorbed ions. However, this increase in quantity did not necessarily proportionally correspond to the quantity added.

Humins obtained through [EtPy][Cl] treatment can thus be used as adsorbents for cation adsorption. Well-known adsorbents such as artificial zeolites and charcoal require high-temperature treatment during preparation. However, the preparation conditions for the humins obtained in this study involve a low temperature range of ca. 120 °C, rendering preparation convenient and straightforward. Ion adsorbents are useful functional materials with potential applications in, e.g.,

water purification and resource recovery, contributing to the solution of environmental issues. The findings of this study, which have demonstrated production of functional materials from renewable resources such as cellulose and wood, might contribute to sustainable development.

Abbreviations

[EtPy][Cl]	1-Ethylpyridinium chloride
[C4mim][Br]	1-Butyl-3-methylimidazolium bromide
[C4mim][SCN]	1-Butyl-3-methylimidazolium thiocyanate
[C4mim][Cl]	1-Butyl-3-methylimidazolium chloride
[C2mim][OAc]	1-Ethyl-3-methylimidazolium acetate
[C2mim][Cl]	1-Ethyl-3-methylimidazolium chloride
[EtPy][Cl]	1-Ethylpyridinium chloride
5-HMF	5-Hydroxymethylfurfural
UV	Ultraviolet
[EtPy][Cl]	1-Ethylpyridinium chloride
IER	Ion exchange resin
SEM	Scanning electron microscope
FTIR	Fourier-transform infrared spectroscopy
XRD	X-ray diffraction
GPC	Gel permeation chromatography
RID	Refractive index detector
CEC	Cation exchange capacity

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Author contributions

AM and HM conceived and designed research. AM conducted experiments. AM and HM analyzed data. AM and HM wrote the manuscript. All authors read and approved the manuscript.

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Availability of data and materials

The datasets used and analyzed in the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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