How to reduce environmental burden caused by lignocellulosic waste: a solution from the pharmaceutical industry with green solvents

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Abstract: In order to reduce environmental burden caused by lignocellulosic waste, lignin from *Eucommia ulmoides* residue was extracted via alkali treatment and acid precipitation, yielding 61.58% purity. Degradation using [N_{4222}]Im and [Ch]Im under atmospheric and microwave conditions was analyzed by elemental, UV, and FT-IR methods. Microwave treatment gave higher hydroxyl (340.54 mg KOH/g) and phenolic hydroxyl (0.32 mmol/g) contents than atmospheric degradation. Gas chromatography analysis showed aromatic compounds accounted for 75.64% of products, dominated by guaiacol and derivatives. This work supports high-value utilization of herbal residues, which is expected to protect our environment.

1 Introduction

With the rapid development of the great health industry, China produces about 70 million tons of herbal residues every year. After extracting the active ingredients, most of the solid residue is naturally degraded by long-term accumulation or directly burned [1]. It has caused significant environmental pollution and waste of resources [2]. Therefore, how to effectively and reasonably utilize them is an unavoidable and important issue in achieving modern production of natural medicines [3]. The energy and harmless utilization of medicinal residues is a necessary way to achieve sustainable development of China's pharmaceutical industry.

The main applications of herbal residues today are composting, edible mushroom cultivation, and feed production [4]. Most composting processes use natural simple composting, but due to the long fermentation cycle and poor hygiene conditions, it is now rarely used; The use of herbal residue for edible mushroom cultivation may inhibit mycelial growth due to the complex composition of the residue, and the separation of the residue is also very difficult. When processing medicinal residues into feed additives, further in-depth and detailed research is needed due to the potential impact of their medicinal functions on animal growth and development. Due to immature technology and limitations, the above utilization methods cannot yet achieve large-scale promotion and application [5].

Similar to some plant resource waste generated in the food industry, herbal residue contains a large amount of components such as crude fiber, crude protein, crude fat, and trace elements [6], which require effective means to achieve their reuse. *Eucommia*

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ulmoides is a precious Chinese medicinal herb commonly cultivated in western, northwestern, and eastern China, belonging to the *Eucommia ulmoides* family. It has the effects of nourishing the liver and kidneys, strengthening muscles and bones, anti hypertension, antioxidant, and anti gastric ulcer [7]. Considering the more and more applications of ionic liquids (ILs) used in the field of biomass in recent years, this study mainly focuses on the degradation of lignin in discarded *Eucommia ulmoides* residue with such green solvents. Firstly, lignin was extracted by traditional acid precipitation and alkali precipitation, and then lignin was degraded by two ILs. The changes in surface hydroxyl groups of lignin before and after degradation and the components degraded into small molecules are measured. At the same time, the difference between extracted lignin and commercialized lignin was also determined. It is expected to provide useful references for reducing waste pollution and resource utilization.

2 Experimental

2.1 Pretreatment

The *Eucommia ulmoides* residue used in this study was obtained after crude extraction of bioactive components from raw material with 95% (v/v) ethanol. The raw residue was soaked in distilled water at a liquid-solid ratio of 20:1 at room temperature to remove residual dust and water-soluble impurities. The suspension was filtered, and the washing procedure was repeated twice. The resulting filter residue was dried in an oven at 50 ℃, ground with a laboratory grinder, and sieved through a 40-100 mesh screen. The sieved residue was then mixed with distilled water at a liquid-solid ratio of 50:1, stirred at 60 ℃ for 1 h, followed by 2 h of standing at room temperature. After filtration, the material was dried in an oven at 50 ℃ to a constant weight and stored in a desiccator.

2.2 Extraction of Lignin

A 20 g (dry weight) portion of pretreated *Eucommia ulmoides* medicinal residue was mixed with 7% (w/w) sodium hydroxide solution at a liquid-solid ratio of 40:1. The suspension was stirred vigorously at 60 ℃ for 6 h. Upon completion of the reaction, the mixture was cooled to room temperature and vacuum filtered to remove the cellulose-rich residue. The filtrate was adjusted to pH=2 with 20% (w/w) sulfuric acid and maintained at 50 ℃ for 1 h to allow lignin precipitation. The suspension was centrifuged at 4000 rpm for 15 min, and the resulting precipitate was collected by filtration, washed repeatedly with distilled water until neutral, and dried at 100 ℃ to constant weight, yielding a brown solid lignin fraction.

2.3 Purification of Lignin

0.2 g powdered lignin was weighed and placed into a centrifuge tube, followed by the addition of 20 mL of hydrochloric acid solution (pH=3). The suspension was shaken thoroughly to disperse the lignin evenly in the acid solution and soaked for 5 min. The mixture was centrifuged at 4000 rpm, and the supernatant was discarded. This washing procedure was repeated three times with fresh hydrochloric acid solution (pH=3), followed by repeated washing with distilled water until the filtrate reached neutral pH. The residue was dried at 100 ℃ to constant weight. An accurately weighed portion of the dried product was used for lignin content determination. This treatment effectively removed residual acid-soluble carbohydrates, including cellulose hydrolysis fragments and hemicelluloses trapped or adsorbed in the lignin during precipitation, thereby yielding purified lignin.

2.4 Preparation of ionic liquids (ILs)

According to the screening in pilot experiments, two ILs were successfully synthesized as shown in **Fig. 1**. One was used for the degradation under normal pressure and the other was treated with microwave for comparison.

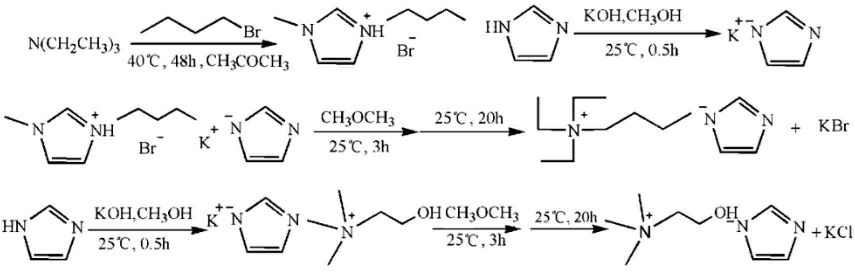

Fig. 1. The synthesis route of ionic liquids [N4222]Im and [Ch]Im.

2.5 Degradation of lignin with [N4222]Im

2.0 g lignin was added to a flask containing 60 mL of distilled water, followed by the addition of 0.1 mol/L ionic liquid and 0.5 mol/L hydrogen peroxide solution. The mixture was reacted at 80 °C for 4 h under normal pressure, after which the reaction was quenched to terminate the reaction. The pH of the solution was adjusted with 1 mol/L hydrochloric acid, and the suspension was centrifuged at 14000 rpm to separate the solid fraction. The recovered solids were vacuum dried at 50 °C to constant weight. The hydroxyl content of the lignin degradation products was subsequently determined.

2.6 Degradation of lignin with [Ch]Im

2.0g lignin was added to a flask containing 60 mL of distilled water, followed by the addition of 0.1 mol/L ionic liquid and 0.5 mol/L hydrogen peroxide solution. The mixture was subjected to 300 W microwave irradiation for 2 h, then rapidly cooled to terminate the reaction. The pH of the resulting solution was adjusted with 1 mol/L hydrochloric acid, and the suspension was centrifuged at 14000 rpm to separate the solid fraction. The recovered solids were vacuum dried at 50 °C to constant weight, and the hydroxyl content of the lignin degradation products was subsequently determined.

2.7 Sample preparation for gas chromatography analysis

Under the optimized conditions, the supernatant obtained by centrifugation at 4000 rpm was extracted three times with 25 mL portions of ethyl acetate. The combined organic layers were dried over anhydrous magnesium sulfate, filtered to remove the drying agent, and concentrated by rotary evaporation at 30 °C. The resulting residue was subsequently analyzed by gas chromatography.

3 Results and discussion

3.1 Analysis of *Eucommia ulmoides* residue

The quantitative method reported in a previous study [8] was employed to determine the contents of cellulose, hemicellulose, and lignin in the pretreated *Eucommia ulmoides* medicinal residue. During cellulose determination using the 72% concentrated sulfuric acid hydrolysis method, a portion of cellulose may undergo hydrolysis and loss, leading to measured values that are approximately 2%–3% lower than the actual content. In lignin measurement, acid hydrolysis of the residue with 72% sulfuric acid effectively removes cellulose and hemicellulose; however, a small fraction of lignin may also be lost, resulting in values that are about 1%–2% lower than the true content. The analytical results are presented in **Fig. 2(a)**.

3.2 Purified lignin content and elemental analysis

The contents of the three components in the purified lignin were also determined using the previously described method, and the results are presented in **Fig. 2(b)**. Following extraction and purification, the lignin content increased significantly from 14.06% to 61.58%. Because both hemicellulose and lignin are alkali-soluble and difficult to separate completely, the relative proportion of hemicellulose remained high, whereas cellulose, being insoluble in both acid and alkali, exhibited the lowest content.

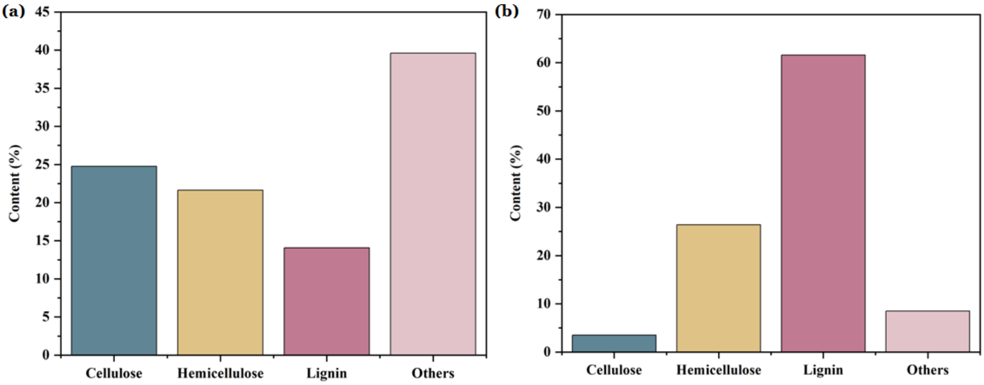

Fig. 2. (a) Composition of *Eucommia ulmoides* medicinal residue after pretreatment; (b) basic composition of purified lignin.

Since elemental analysis cannot directly determine the oxygen content, all elements other than C, H, and N were collectively attributed to oxygen. As shown in **Fig. 3**, the proportions of C, H, and O were relatively consistent. Lignin is primarily composed of C, H, and O, while the nitrogen content is comparatively low, suggesting minimal impurities. The extracted lignin contained 2.15% nitrogen, indicating the presence of a small amount of impurities.

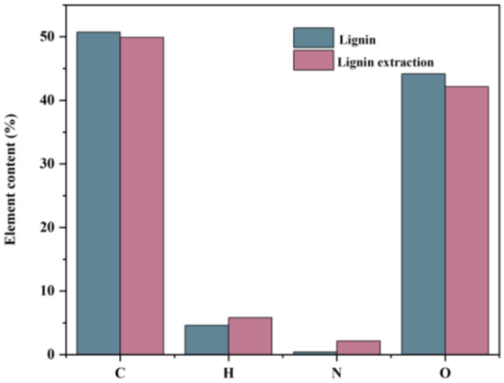

Fig. 3. Elemental composition of purified lignin.

3.3 Spectral analysis of lignin

As shown in **Fig. 4**, the extracted and purified lignin exhibit characteristic absorption peaks at approximately 205 nm and 280 nm. The peak at 280 nm corresponds mainly to the benzene ring and is consistent with the typical spectral features of lignin. However, at the same concentration, the extracted lignin shows a less pronounced peak at 280 nm with lower absorbance. In addition, the absorption band near 205 nm for the extracted lignin exhibits a slight deviation compared with purified lignin, which can be attributed to the relatively high hemicellulose content and incomplete purity of the extracted sample.

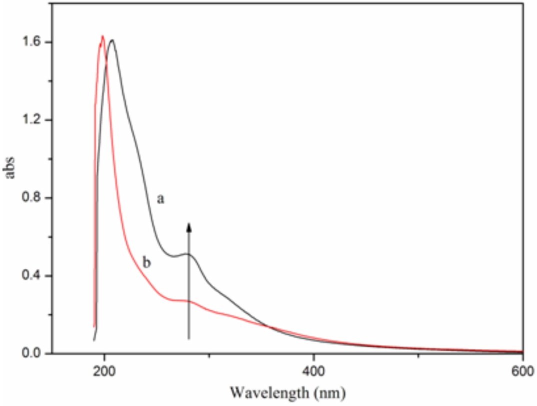

Fig. 4. Ultraviolet (UV) spectra of lignin: (a) native lignin; (b) purified lignin.

As shown in **Fig. 5**, the structural features of lignin are largely consistent with those of the extracted and purified lignin. The O-H stretching vibration of hydroxyl groups appears around 3448 cm⁻¹, while the C-H stretching of aliphatic chains is observed at 3000–2850 cm⁻¹. The C-H stretching of methyl or methylene groups occurs near 2931 cm⁻¹, and the carbonyl (C=O) stretching absorption peak is located at approximately 1718 cm⁻¹. Characteristic absorption bands of the benzene ring are found in the range of 1467–1639 cm⁻¹. In addition, the stretching vibrations of C-C or C-O appear near 1120 cm⁻¹, the C-O stretching of $O\text{-}CH_3$ or C-OH groups is observed around 1047 cm⁻¹, and the aromatic C-H bending vibration occurs at approximately 900 cm⁻¹. Compared with lignin, the purified lignin exhibits weaker benzene ring absorption within 1467–1639 cm⁻¹, indicating a lower aromatic ring content [9]. The ether bond content is also relatively reduced.

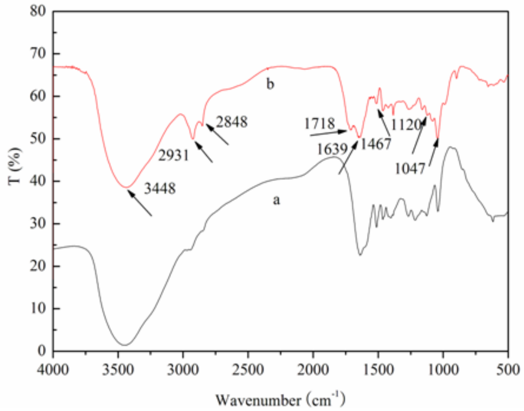

Fig. 5. Fourier-Transform Infrared Spectroscopy (FTIR) spectra of lignin: (a) native lignin; (b) purified lignin.

3.4 Characterizations on lignin degradation products

Based on the ionic liquid degradation method described earlier, elemental analysis was performed to examine the changes in C, H, O, and N before and after degradation, thereby further verifying the structural transformations of lignin. As shown in **Fig. 6**, the C and N contents of lignin increased after degradation, while the O content decreased. The increase in C content may be attributed to the stability of aromatic rings, as the C–C bonds are less susceptible to cleavage compared with ether bonds. Meanwhile, other functional groups or side chains may be degraded into smaller molecules, leading to a higher degree of C–C condensation and consequently elevated C content. The decrease in O content can be explained by the cleavage of methoxy groups during the reaction. The higher N content likely results from the presence of non-degradable N-containing impurities, which increase the relative proportion of N after the reaction. Furthermore, elemental analysis of atmospheric-pressure and microwave degradation products revealed a significant increase in H content, indicating that ether bond cleavage generated additional hydroxyl groups. This also explains the higher hydroxyl content observed in lignin degraded by microwave compared with atmospheric-pressure degradation. The reduction in O content further suggests that microwave-assisted degradation proceeds to a greater extent.

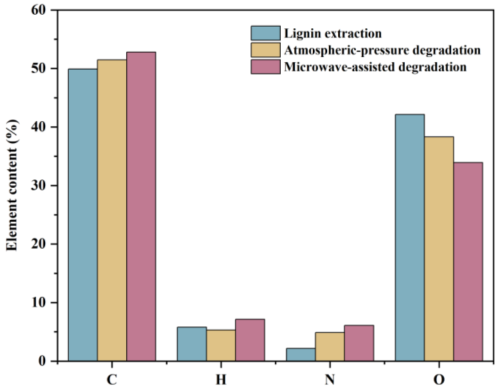

Fig. 6. Elemental composition of degradation of purified lignin and raw lignin.

As shown in **Fig. 7**, after lignin degradation, the absorption peak at 205 nm remains largely unchanged, whereas the peak at 280 nm is no longer pronounced, and the overall absorbance in the higher-wavelength region decreases significantly. These changes indicate that the conjugated structure of lignin has been substantially disrupted.

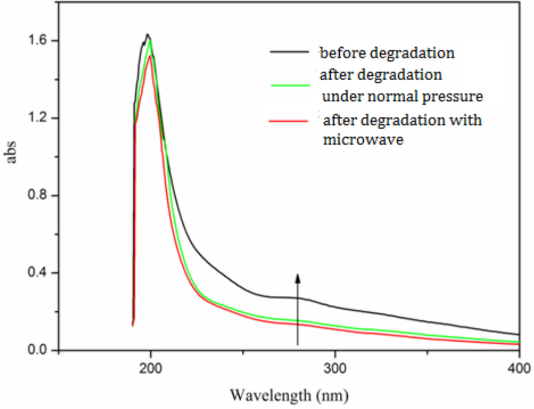

Fig. 7. UV spectra of degraded lignin.

As shown in **Fig. 8**, the FTIR spectra of degraded lignin are generally consistent with those of lignin prior to degradation. The O-H stretching vibration of hydroxyl groups appears around 3437 cm^{-1}, C-H stretching of methyl or methylene groups near 2925 cm^{-1}, C-H stretching of methoxy groups around 2850 cm^{-1}, and the carbonyl (C=O) stretching vibration at approximately 1709 cm^{-1}. Characteristic absorption bands of the benzene ring are observed between 1467–1639 cm^{-1}, C-C or C-O stretching near 1126 cm^{-1}, C-O stretching in O-CH_3 or C-OH groups around 1045 cm^{-1}, and aromatic C-H bending at approximately 900 cm^{-1}. Notably, the microwave-degraded lignin exhibits the highest intensity at 1126 cm^{-1}, corresponding to the in-plane C-O vibration of guaiacol. This increased intensity indicates the formation of a substantial guaiacol structure during degradation, which also explains the higher surface hydroxyl content observed after microwave-assisted treatment.

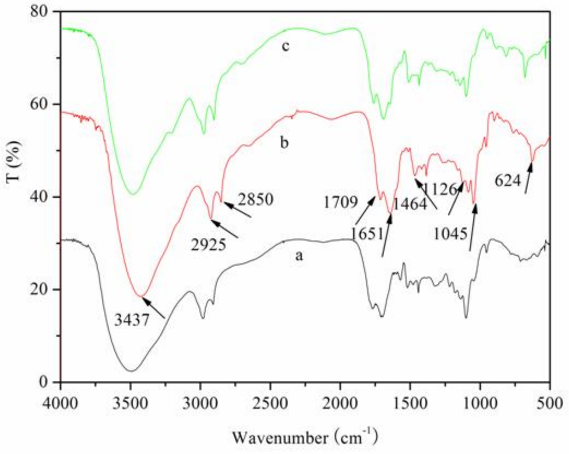

Fig. 8. FTIR spectra of lignin: (a) before degradation, (b) after degradation under atmospheric pressure, (c) after microwave-assisted degradation (KBr pellet).

GC analysis revealed that the lignin degradation products primarily consist of acids, alcohols, aldehydes, esters, and other small molecules. Aromatic compounds account for approximately 75.64% of the total products, with guaiacol representing about 30.89% of the aromatics and 2-methoxy-4-vinylphenol reaching 38.38%, indicating that guaiacol-based monomers are the predominant species in *Eucommia ulmoides* residue. Structural analysis further confirms that the degradation mainly targets the cleavage of β-O-4 ether bonds [10].

4 Conclusions

Lignin was extracted and purified from *Eucommia ulmoides* medicinal residue under optimized conditions, and the hydroxyl content of the resulting oligomeric lignin, as well as the composition of derived small-molecule products, was analyzed. The residue contained 24.77% cellulose, 21.62% hemicellulose, and 14.06% lignin, while the purified lignin reached 61.58% content.

Characterization by elemental analysis, UV spectroscopy, FTIR, and other techniques showed that the structural features and elemental composition of the extracted lignin were largely consistent with commercial lignin. Degradation under atmospheric-pressure and microwave-assisted conditions indicated that microwave treatment was more effective, producing higher aliphatic (340.54 mg KOH/g) and phenolic (0.32 mmol/g) hydroxyl contents. GC–MS analysis revealed that aromatic compounds, particularly guaiacol-based monomers, predominated among the degradation products, confirming efficient cleavage of lignin structures.

From an industrial perspective, the abundant and low-cost *Eucommia ulmoides* residue represents a sustainable feedstock for lignin valorization. The combination of established extraction and purification processes with microwave-assisted degradation enables scalable production of small-molecule aromatic compounds, which can serve as precursors for bio-based chemicals, resins, and functional polymers. This strategy provides a green, efficient, and practical approach for high-value industrial applications of lignin.

Special thanks to the support from National Natural Science Foundation of China (82273814) and Fundamental Research Funds for the Central Universities/Sichuan University-Luzhou Science and Technology Innovation Platform Construction Project (2022CDLZ-20). We would like to thank Xiang Lin from Center of Engineering Experimental Teaching, School of Chemical Engineering, Sichuan University for FTIR.

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