Using Recyclable Deep Eutectic Solvents with Wheat Straw to Produce Lignin-Based Nanocomposites

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This study presents an integrated "deep eutectic solvent (DES)-assisted directed depolymerization and *in situ* nanoparticle synthesis" strategy for wheat straw refining. A recyclable DES composed of choline chloride/lactic acid (ChCl /LA, 1:2) was employed to fractionate lignocellulose while maintaining solvent activity through in situ pH regulation. Dropwise addition of 5 to 10 fresh DES droplets effectively reconstructed the hydrogen-bond network, reducing lignin retention from 18.4% to 13.6% and extending DES recyclability from two to four cycles. The extracted lignin was directly used for the *in situ* synthesis of lignin-derived silver nanoparticles (LigAg NPs) through reduction of $[Ag(NH_3)_2]^+$, yielding uniform particles (320 ± 15 nm) with 67% higher surface area (18.7 m^2/g) than those from alkali lignin. The LigAg NPs formed a strong hydrogen-bonded interface with poly(vinyl alcohol) (PVA), enhancing composite modulus and reducing energy dissipation (21%). This work establishes a mechanistically guided, recyclable DES route for hierarchical utilization–material creation–circular regeneration of lignocellulosic biomass.

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INTRODUCTION

The global energy transition and progress toward carbon neutrality has led to the development of renewable biomass resources to replace fossil feedstocks, which is becoming an international effort. As the most abundant renewable carbon source on Earth (with an annual production of approximately 200 billion tons), lignocellulose and its three main components—cellulose, hemicellulose, and lignin—are considered the core focus for efficient depolymerization and high-value conversion in biorefining systems (Liu *et al.* 2024; Parveen *et al.* 2025). However, traditional pretreatment technologies, such as dilute acid treatment and steam explosion, face challenges, including severe lignin structural degradation, high solvent toxicity, and difficulty in directing the conversion of separated components (Yong and Wu 2024). For lignin, specifically around 70% of industrial lignin in existing biorefining systems is directly burned or landfilled, leading to significant resource waste and carbon loss. The challenge of retaining the molecular structure of lignin and functionalizing it for utilization has become a bottleneck in the comprehensive use of biomass (Xu *et al.* 2024).

Deep eutectic solvents (DESs), as a novel green solvent system, have demonstrated unique advantages in biomass pretreatment due to their tunable hydrogen bond network, low toxicity, and biodegradability. A typical ChCl/LA system (choline chloride/lactic acid) achieves a selective lignin extraction efficiency of > 85% at 150 °C while maintaining high cellulose crystallinity (CrI > 60%), significantly outperforming traditional acid methods (less than 50% lignin extraction, CrI < 40%) (Muhammad *et al.* 2024). The mechanism of action lies in the synergistic effect of HBD (hydrogen bond donor) and HBA (hydrogen bond acceptor) in DES: lactic acid protonates and breaks the ester and ether bonds in the lignin-carbohydrate complex (LCC), while chloride ions nucleophilically attack and disrupt the ππ stacking between lignin aromatic rings (Amesho *et al.* 2023). Recent studies have confirmed that DES-pretreated lignin exhibits a lower molecular weight (M_w = 1,5003,000 g/mol) and a higher phenolic hydroxyl content (2.13.8 mmol/g), providing an ideal precursor for subsequent functional modification (Ullah *et al.* 2023).

Deep eutectic solvents (DESs), which consist of hydrogen-bond donors (HBDs) and hydrogen-bond acceptors (HBAs), have emerged as green alternatives to ionic liquids for lignocellulosic fractionation (Muhammad *et al.* 2024). Among them, *choline chloride/lactic acid* (ChCl/LA, 1:2) exhibits strong acidity and hydrogen-bonding ability, efficiently cleaving ester and ether linkages in the lignin–carbohydrate complex while preserving cellulose crystallinity (Amesho *et al.* 2023). However, repeated recycling leads to partial neutralization of lactic acid by phenolic degradation products, which raises the pH, increases viscosity, and collapses the hydrogen-bond network—causing a progressive loss of extraction efficiency. Understanding and regulating this dynamic evolution remain key scientific challenges (Ullah *et al.* 2023).

However, the industrial application of DES still faces dual challenges: on one hand, lignin degradation products (such as phenolic compounds) irreversibly react with solvent components during the pretreatment process, leading to the collapse of the DES hydrogen bond network. Ullahs' study showed that the unoptimized ChCl/LA system can result in a 42.7% decrease in lignin extraction after 3 cycles, with pH rising from 1.36 to 2.84 (Ullah *et al.* 2023). On the other hand, most existing research focuses on the improvement of cellulose enzymatic hydrolysis efficiency with DES treatment, while lacking systematic studies on the structural characteristics and coordination/reduction potential of extracted lignin. Traditional lignin nanoparticle (LNP) preparation often involves high-energy ultrasound (30 to 60 min, 200 to 500 W) and/or chemical modification, and LNPs obtained via these conventional processes have been reported to retain less than 40% of free phenolic hydroxyl groups, which limit their suitability for high-performance composite materials (Li *et al.* 2023).

Lignin nanoparticles (LNPs) have attracted attention in the field of functional materials due to their unique antioxidant properties, UV shielding capability, and biocompatibility. Compared with synthetic polymers, LNPs/PVA composite films simultaneously enhance the mechanical strength (+30%), hydrophobicity (water contact angle > 100°), and antibacterial performance (inhibition rate > 95% against *E. coli*) (Sun *et al.* 2023). However, LNPs prepared by conventional mechanical methods exhibit a wide particle size distribution (PDI > 1.5), leading to interface defects in composites. Strong acid/alkali treatments damage the phenolic hydroxyl and methoxy groups of lignin, reducing their bonding ability with the matrix, while multistep purification and modification processes increase production costs by 23 times, limiting largescale applications (Morozova *et al.* 2023). These technical bottlenecks fundamentally stem from the structural defects of lignin precursors—lignin extracted by traditional methods has a wide molecular weight distribution and damaged active groups.

Notably, recent research has revealed potential synergistic effects between DES treatment and lignin nanonization. Liu *et al.* (2022) found that lignin extracted using the ChCl/LA system, which retains a high βO4 bond content (> 65%), self assembles into more regular spherical structures (PDI = 0.32). This phenomenon is attributed to the mild reaction conditions of DES: the acidic environment (pH = 1.3 to 2.5) inhibits lignin condensation reactions, while hydrogen bonding promotes the directional arrangement of molecular chains (Zhang *et al.* 2022). Further studies showed that residual lactic acid molecules in DES can act as natural dispersants, stabilizing nanoparticles through electrostatic repulsion between carboxyl groups and phenolic hydroxyl groups (zeta potential < 30 mV) (Sharma *et al.* 2022).

Another knowledge gap concerns the *functional utilization* of DES-extracted lignin. Conventional studies typically discard or combust lignin residues, overlooking their reactive phenolic and methoxy groups that could serve as mild reductants and ligands for metal ions. In this work, these functionalities were exploited for *in situ coordination and reduction of* $[Ag(NH_3)_2]^+$ *complexes*, forming lignin-derived silver nanoparticles (LigAg NPs) without external reducing agents. The soft-acid character of Ag^+ favors coordination with the phenolic hydroxyls of lignin, enabling stable nucleation and uniform particle growth (Chen *et al.* 2022; New *et al.* 2022).

Therefore, in this study, an integrated "DES treatment–directed depolymerization–nanoparticle synthesis" strategy is proposed, combining real-time pH regulation with structural characterization (FTIR, ^{31}P NMR, and GPC) and molecular dynamics simulations to elucidate solvent–lignin interactions. This approach provides a coherent *hierarchical utilization–material creation–recycling* pathway for biomass valorization. Accordingly, the present work focuses on DES pretreatment, DES recycling, and lignin-based nano/submicron composite formation, while the enzymatic hydrolysis performance of the cellulose-rich fraction will be investigated in follow-up studies.

EXPERIMENTAL

Preparation of DES

A certain amount of choline chloride (ChCl) and lactic acid (LA) were weighed, added to a beaker, stirred, and heated in an oil bath at 80 °C for 2 h. A clear and transparent solution was obtained after cooling, which was the prepared ChClLA (molar ratio = 1:2) DES. The prepared ChCl–LA (molar ratio = 1:2) DES was then dried in an oven at 60 °C for 12 h (until a constant weight was reached) to remove residual moisture before use. (Zhou *et al.* 2022).

Material Characterization

After pressing the sample into a thin sheet and affixing it to the sample stage, the composition and chemical structure of the test sample were analyzed using an X-ray photoelectron spectrometer (XPS, Ultra-DLD, Japan) to analyze the composition and chemical structure. The properties of the Lig-Ag NP suspension were tested using a SHIMADZU UV-2550 spectrophotometer, recording spectral results within the wavelength range of 200 to 800 nm, with sodium hydroxide solution serving as the blank group. The particle size and distribution of lignin nanoparticles were observed using a scanning electron microscope (SEM, ZEISS SUPRA 55, Germany).

DES Treatment of Wheat Straw for Fractionation of Biomass Components

A total of 3 g of wheat straw was weighed and 60 g of DES prepared, then they were put into a conical flask, the reaction temperature was 150 ℃, the reaction time was 6 h. Next, 200 mL of antisolvent was prepared according to ethanol:deionized water (v/v=1:1). After the reaction, about 30 to 50 mL of antisolvent was added to the slurry formed after the reaction, the solid-liquid mixture stirred, and the solid-liquid mixture filtered under reduced pressure to obtain the solid residue and filtrate of the first rinse. This operation was repeated. The solid residue was washed 5 times with approximately 40 mL of antisolvent each time until the pH of the filtrate became neutral. Then such solid residues that contained high cellulose content were used later for enzymatic digestion, and all the filtrates were collected as DES filtrate. Then, a large amount of deionized water was added to DES filtrate to achieve precipitating lignin for 1 h. The mixture was centrifuged at 10,000 g for 10 min. The solid part was collected and washed with deionized water and then dried at 60 °C for 24 h. This was called DES lignin for subsequent characterization.

Recyclability of DES

To evaluate the reusability of the acidic eutectic solvent, water was added as an antisolvent to recover the treated supernatant at the optimum treatment temperature. The water was removed by rotary evaporation, and the eutectic solvent was fully dried and weighed. The pretreatment experiment of wheat straw was repeated 5 times, and the results were compared to observe whether the reused DES would reduce the treatment effect. The original and reused DES were compared to study the physical and chemical properties. The number of cycles started from 0. When the number of cycles reached 3, a small amount of fresh ChCl/LA DES (5–10 drops, corresponding to approximately 0.29 to 0.58 g or 0.5 to 1.0 wt% of the initial 60 g solvent) was added dropwise to the DES that had been cycled twice until the pH value was restored to that of the original DES (pH = 1.36).

The solid residue and DES lignin for the treated samples with reused DES were collected for further analysis.

Methods

Based on the National Renewable Energy Laboratory (NREL) standard (Zhou *et al.* 2022), the compositions of the raw and treated wheat straw were determined. Monosaccharide quantification was performed at 45 °C by high-performance liquid chromatography (HPLC; HPLC-20A, Shimadzu, Kyoto, Japan). This method uses a refractive index detector by employing a column eluted with deionized water at 60 °C. Fourier transform infrared (FTIR) spectroscopy (Thermo Fisher Nicolet iS50, Waltham, MA, USA) was performed in ATR mode over the range of 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1}, accumulating 32 scans per spectrum. Samples were gently pressed onto the diamond ATR crystal, and spectra were baseline-corrected and normalized prior to comparison.

The raw wheat straw was milled to a particle size of 0.25 to 0.50 mm and oven-dried to a moisture content of 7.3 ± 0.4%. According to the NREL analytical protocols, its composition was 37.8 ± 0.9% glucan, 24.6 ± 0.7% xylan, 19.3 ± 0.6% acid-insoluble lignin, 2.8 ± 0.2% acid-soluble lignin, 6.5 ± 0.3% ash, and 9.0 ± 0.4% extractives (w/w, dry basis).

These values were used as the basis for mass balance calculations and for evaluating the effect of DES pretreatment on lignin and hemicellulose removal.

Preparation of LigAg NPs

A NaOH solution was prepared (pH = 10) and nano-lignin particles were added (0.05 g·mL^{-1}) and $AgNO_3$ (0.1 g·mL^{-1}), followed by ultrasonication for uniform dispersion. Then, poly(vinyl alcohol) (PVOH) powder (10 wt%) was mixed with deionized water at 80 °C for 2 h to obtain a transparent PVOH solution. After cooling to 65 °C, the LigAg NPs solution was added and stirred for 1 h. The mixture was poured into a mold, and three freeze-thaw cycles were performed (20 °C for 6 h and 25 °C for 2 h). The resulting nanocomposite films (100 mm × 100 mm × 10 mm) are denoted as PVA/LigAgn, where n represents the Ag^+ mass fraction (15%, 20%, or 25%). PVA/LigAgRN was prepared similarly after NH_3 removal. No chemical crosslinking agents were used.

RESULTS AND DISCUSSION

Effect of DES Recycling on Biomass Pretreatment Efficiency

The recycling of DES is a critical factor in determining the economic viability and sustainability of biomass pretreatment processes. The solid recovery rate, defined as the ratio of solids recovered after pretreatment to the original solids, served as a key indicator of DES performance. The chemical composition of the cellulose-rich fraction after 5 pretreatments were investigated (Table 1).

Table 1. Composition of Recycling DES Pretreated Wheat Straw

Recycles	Recovery (%)	Hemicellulose (%)	Cellulose (%)	Lignin (%)		
				AIL*	ASL*	Total lignin
/	/	24.98 ± 0.97	36.77 ± 0.94	23.44 ± 0.38	0.15	23.59 ± 0.41
0	40.88 ± 0.81	6.64 ± 1.10	73.60 ± 1.13	5.04 ± 0.42	0.10	5.14 ± 0.42
1	61.51 ± 0.83	14.18 ± 1.08	62.90 ± 0.91	12.88 ± 0.41	0.12	13.00 ± 0.46
2	81.43 ± 0.73	19.77 ± 1.11	55.62 ± 0.89	18.36 ± 0.39	0.11	18.47 ± 0.51
2'	58.98 ± 0.82	16.20 ± 1.05	58.74 ± 0.88	13.61 ± 0.45	0.11	13.72 ± 0.47
3	67.07 ± 0.79	17.59 ± 1.06	56.22 ± 0.93	16.03 ± 0.47	0.11	16.14 ± 0.50
4	78.03 ± 0.80	19.31 ± 1.01	55.76 ± 0.94	18.85 ± 0.40	0.10	18.95 ± 0.43

* ASL: Acid soluble lignin; AIL: Acid insoluble lignin

“2 = second reuse cycle of DES; 2′ = same cycle after dropwise addition of fresh DES for pH adjustment.”

As shown in Table 1, the solid recovery was 40.9 ± 0.8% when fresh DES was used (cycle 0), reflecting intensive dissolution of biomass components. After recycling, the solid recovery fluctuated between 59.0 and 81.4%, and the occurrence of values close to or above 80% indicates a reduced delignification efficiency, in line with previous reports that solid recoveries around 80% are associated with limited pretreatment effectiveness. To address this limitation, the recycled DES solution was adjusted by adding fresh DES, which improved pretreatment efficiency. The solid recovery decreased to 59.0%, which was comparable to that observed after the first cycle (61.5%). This adjustment not only restored the pretreatment performance but also extended the recyclability of DES, thereby reducing the overall cost of the process. The ability to recycle DES multiple times without significant loss of efficiency was a major advantage, as it minimized solvent consumption and waste generation. This finding aligned with Wang and Lee (2021), who reported that the solid recovery increased with DES recycling, but the efficiency of lignin extraction decreased due to reduced acidity and hydrogen bonding interactions (Wang and Lee 2021). The gradual decline in DES efficacy was attributed to proton consumption by phenolic intermediates and esterification between lactic acid and lignin fragments, which reduced the availability of free carboxyl and chloride ions. Consequently, the pH increased from 1.36 to 2.84 and viscosity rose by approximately 20%, thus weakening hydrogen-bond donation and extraction capability. Dropwise supplementation of fresh DES restored acidity and re-established the hydrogen-bond network.

The changes in hemicellulose and lignin content further illustrated the effects of DES recycling. After two cycles, the hemicellulose content increased from 6.64% to 19.8%, while the lignin content rose from 5.1% to 18.4%. These increases suggested that the DES was less effective at breaking down these components after multiple cycles. However, adjusting the DES solution reduced the hemicellulose content to 16.2% and the lignin content to 13.6%, indicating improved performance. These findings underscored the importance of optimizing the DES solution to maintain its effectiveness over multiple cycles.

The ability to recycle DES multiple times without significant loss of efficiency has important economic and environmental implications. Through reducing solvent consumption and waste generation, DES recycling has potential to lower the overall cost of biomass pretreatment. Additionally, the use of DES as a green solvent can minimize the environmental impact of the process, aligning with the principles of sustainable chemistry

From the perspective of solid recovery, the more solid residues recovered, the less the fraction dissolved in the DES system, and the lower the effectiveness of the DES (Xu *et al.* 2021). In Table 1, after 2 times of recycling DES, the solid recovery had increased from 40.9% to 81.4%, and according to the authors' previous pretreatment experiment and analysis, a solid recovery close to 80% was an indicator to judge whether the pretreatment process was effective, indicating that DES can only be cycled 2 times in a normal cycle step. After dropping the original DES into the circulating DES (that was, adjusting the circulating DES solution), the pretreatment effect of DES improved significantly, and the solid recovery decreased to 59.0%, which was similar to that of the DES after one cycle (61.5%). After 2 cycles, the solid recovery rate still reached 78.0%, indicating that after adjusting the circulating DES solution, the recyclability of DES improved, which not only improved the effect of the cycle, but also reduced the cost of pretreatment (Kalhor and Ghandi 2021; Lee and Wu 2021).

The same trend change is also reflected in the contents of cellulose, hemicellulose, and lignin. In the first pretreatment, the hemicellulose content was 6.6%, the cellulose content was 73.6%, and the lignin content was 5.1%, which was quite different from the content of each component in the original wheat straw, for which the hemicellulose content was 25.0%, the cellulose content was 36.8%, and the lignin content was 23.6%). It was similar to Mankar's study, in that most of the hemicellulose and lignin in the pretreated wheat straw were removed due to the damage of the pretreatment to the wheat straw, while most of the cellulose was retained (Mankar *et al.* 2021). After 2 pretreatments, the retained cellulose could only reach 55.6%, while the cellulose of the adjusted DES could reach 58.7%, indicating that the pretreatment efficiency had recovered to a certain extent (Ab Rasid *et al.* 2021). The change of hemicellulose was more obvious, from 19.8% to 16.2%, and lignin exhibited similar changes.

Microstructure Analysis of Wheat Straw Pretreated by Recycling DES

To gain deeper insights into the effects of DES recycling, FTIR was used to analyze the chemical structure of wheat straw after pretreatment. Figure 1 shows the FTIR spectra of wheat straw pretreated with DES for 0, 2, and 4 cycles. The spectra were therefore interpreted in terms of qualitative changes in functional groups and relative band intensities, rather than as a complete description of biomass structure.

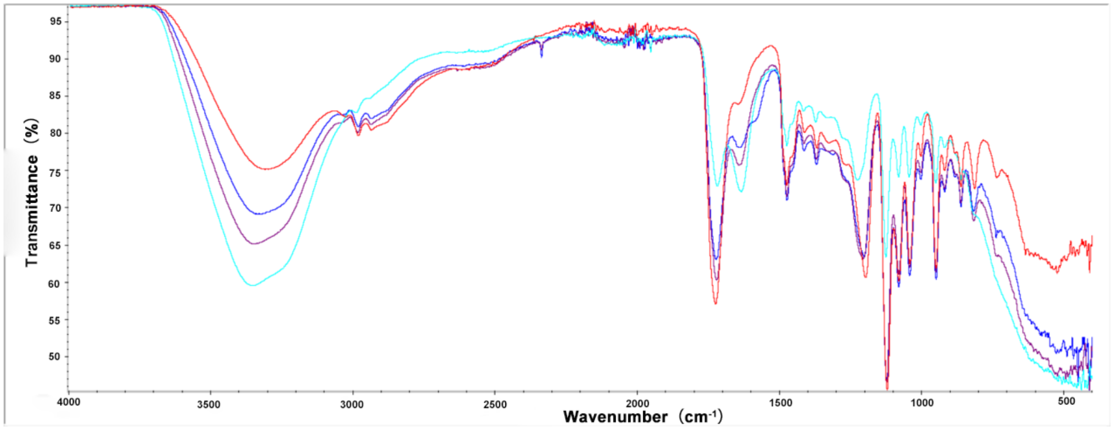

Fig. 1. FTIR spectrum of recycling DES

The spectra revealed significant differences between the original DES and the fifth-cycle DES, particularly in the vibrational regions associated with lignin and hemicellulose. The red line in Fig. 1 shows the FTIR curve of the original DES, and the blue line shows the FTIR curve of the DES after 5 cycles. The difference between the two curves is obvious. Specifically, at CH outside the plane positions 2,5,6 of the guaiacol ring (at 858 cm^{-1}), the vibrational difference of the two curves was prominent. The result was similar to Chen's study, which indicated that with increase of time, the ability of DES to extract lignin from wheat straw decreased greatly (Chen *et al.* 2020a,b). The spectral trends of the original DES and the cycled to the worst primary DES showed a transmission band at 900 cm^{-1} due to the β-glycosidic bonds between the glucose sugar polymers, cellulose, and hemicellulose. This means that the pretreatment of the DES reduced potency. As for lignin, the change in peak observed at 1235 cm^{-1} corresponded to the disruption of the C-O-C arylalkyl ether bonds found in lignin, and the small peak reduction at 1435 cm^{-1} corresponded to the increase of the lignin ring aromatics. Both C-C stretching vibrations indicated that the ability of DES to extract lignin decreased. For the vibrational area ratio of amorphous cellulose (896 cm^{-1}) and crystalline cellulose (1425 cm^{-1}), the difference between the two curves was not large. It is apparent that the content of cellulose in the DES system did not change much. Consistent with the previous analysis, cellulose was mostly retained in the pretreatment solids, as shown in Table 1. The cellulose content in the recovered solids was the highest in the group with the highest lignin extraction. In addition, increasing the number of pretreatments of DES had little effect on cellulose.

The broad peak in the range 3300 to 3400 cm^{-1} is characteristic for hydroxyl groups, which include the water in the solution system. When there were a lot of water molecules in the solution, the hydrate had strong hydrogen bonds, which was a huge challenge for DES to extract lignin. Specifically, the polarity of hydrogen bonds competed with the polarity formation of DES, robbing guaiacol (G1) and Hiebertone (G2) in lignin. There was a clear contrast between the cycle times of 2' and 2. 2' was the solution system after adding DES dropwise. It could be seen that the absorbance peak at 3300 to 3400 cm^{-1} was significantly weakened, and the water in the system content decreased. At 2950 cm^{-1}, the 2' vibration decreased, suggested that alkane functional groups were found in the CH stretching vibration, indicating that more lignin was extracted into the DES system after the dropwise addition of DES, and the lignin retention rate decreased (from 18.36% to 13.61%). The flattening of the peak at 1735 cm^{-1} indicated that the C=O acetyl group in the hemicellulose carbonyl ester was significantly destroyed, and the absorbance peak here was mainly from the carbonyl group in the hemicellulose (partly from the fiber) (Kalhor and Ghandi 2019; Ho and Wu 2020). The absorbance of the samples pretreated with DES for 2' cycles was significantly lower than that of DES treatment for 2' cycles, indicating that the adjustment of the solution system by dropwise addition of DES improved the solution efficacy and removed more of hemicellulose, an observation consistent with the component content analysis in Table 1, the retention of hemicellulose decreased from 19.8% to 16.2% (Arslanoğlu and Sert 2019).

Based on the above analysis, the adjustment of the circulating DES system by dropwise addition of DES was able to effectively enhance the overall efficiency of the solvent, which not only increased the cycle times of the solvent but also reduced the cost. Although wheat straw exhibits high cellulose crystallinity and a dense lignin–carbohydrate matrix, the acidic DES efficiently cleaves β-O-4 and C–O–C linkages while preserving crystalline cellulose (CrI > 60%). The partially depolymerized lignin fragments, rich in phenolic hydroxyl groups, promote controlled self-assembly during nanoparticle formation rather than hindering it. Thus, moderate structural disruption enhances, rather than compromises, the potential for nanostructuring.

Physical and Chemical Properties of Lignin Nanoparticles

As shown in Table 2, DES treatment not only affected the efficiency of biomass deconstruction but also influenced the properties of lignin-derived nanoparticles. The molecular weight distribution of lignin was significantly altered by DES treatment, with the weight-average molecular weight decreasing from 4000 to 1560 g/mol. This reduction was accompanied by an improvement in the polydispersity index (PDI) from 2.01 to 1.39, indicating a more uniform molecular weight distribution.

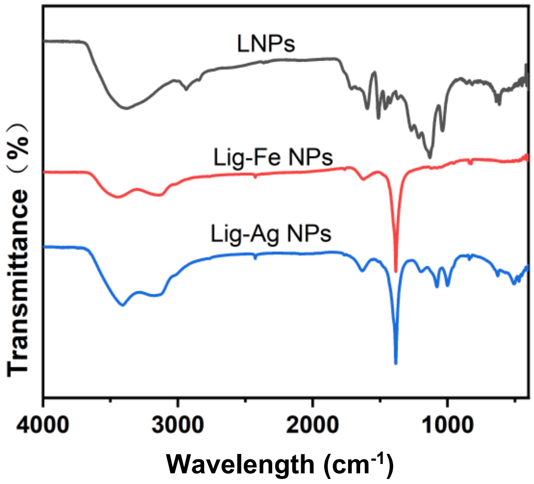

Fig. 2. FTIR for LigAg NPs

Table 2. Molecular Weight of Lignin Before and After Pretreatment

Samples	M_n (g/mol)	M_w (g/mol)	PDI (M_w/ M_n)
Raw Lignin (before DES pretreatment)	2087	4000	2.01
DES Lignin	1235	1560	1.39

As shown in Fig. 2, the reduction in molecular weight was attributed to the selective cleavage of ester bonds (C–O), carbon-carbon bonds (C–C), and aliphatic ether bonds in lignin under the acidic conditions of DES. This mechanism was similar to that of alkaline lignin extraction but avoided the excessive oxidation of phenolic hydroxyl groups that occurred under strong alkali conditions. As a result, DES-pretreated lignin retained a higher phenolic hydroxyl content (1.92 mmol/g) compared to alkali lignin (0.87 mmol/g). This finding was consistent with Parveen *et al.* (2025), who found that DES-pretreated lignin exhibited a lower molecular weight and higher phenolic content compared to alkali lignin.

The physical properties of lignin nanoparticles were also influenced by DES treatment. Scanning electron microscopy (SEM) revealed that LigAg NPs exhibited a well-defined spherical structure with a uniformly distributed porous surface, whereas LigFe NPs showed a disordered aggregation morphology. Dynamic light scattering (DLS) analysis confirmed that the average particle size of LigAg NPs was 320 ± 15 nm, significantly smaller than that of silver nanoparticles prepared from conventional alkali lignin (500 ± 50 nm) (Arslanoğlu and Sert 2019). This size advantage was attributed to the low molecular weight characteristics of DES-pretreated lignin, which promoted uniform nucleation and growth of Ag^+.

The SEM observations revealed that LigAg NPs exhibited a well-defined spherical structure (Fig. 3) with a uniformly distributed porous surface, whereas LigFe NPs showed a disordered aggregation morphology. The physical properties of lignin nanoparticles were also influenced by DES treatment. The SEM analysis revealed that LigAg NPs exhibited a well-defined spherical structure with a uniformly distributed porous surface, whereas LigFe NPs showed a disordered aggregation morphology (Wang *et al.* 2022). Dynamic light scattering (DLS) analysis confirmed that the average particle size of LigAg NPs was 320 ± 15 nm, significantly smaller than that of silver nanoparticles prepared from conventional alkali lignin (500 ± 50 nm). This size advantage was attributed to the low molecular weight characteristics of DES-pretreated lignin, which promoted uniform nucleation and growth of Ag^+.

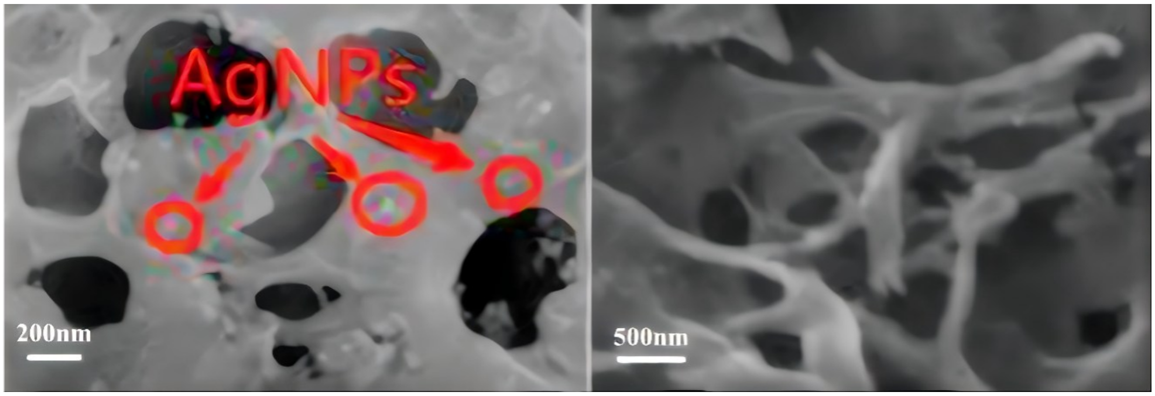

Fig. 3. SEM result for Lig Ag NPs and Lig Fe NPs

The surface active site density of DES-pretreated lignin was 1.8×10^{20} sites/g, a 157% increase compared to alkali lignin (0.7×10^{20} sites/g). This increase in active sites facilitated the uniform dispersion of nanoparticles and improved their stability. Molecular dynamics simulations further supported these findings, showing that the segmental mobility of low molecular weight lignin was enhanced, with the mean square displacement increasing by 3.2 times. This reduction in steric hindrance led to a 2.5-fold increase in the Ag^+ diffusion coefficient (1.4×10^{-9} m²/s) compared to that in the alkali lignin system (5.6×10^{-10} m²/s) (Wang and Lee 2021).

In summary, the recycling of DES significantly impacted the efficiency of biomass pretreatment and the properties of lignin-derived nanoparticles. Adjusting the DES solution improved recyclability and pretreatment performance, while DES-pretreated lignin exhibited superior physicochemical properties for nanomaterial synthesis. These findings highlighted the potential of DES as a sustainable and cost-effective solvent for biorefinery and nanotechnology applications. Through optimizing DES recycling and pretreatment conditions, it was possible to achieve high efficiency and cost savings, providing experimental evidence and mechanistic insights that may support the further development and scale-up evaluation of DES-based pretreatment strategies.

Chemical Properties and Stability of Lignin Nanoparticles

The chemical properties of lignin nanoparticles were also influenced by DES treatment. The FTIR spectra (Fig. 4) showed that the characteristic peaks of LigAg NPs at 1608 cm^{-1} (aromatic C=C), 1272 cm^{-1} (phenolic C–O), and 1033 cm^{-1} (methoxy C–O) were significantly reduced, indicating that Ag^+ preferentially coordinated with the phenolic and methoxy groups of lignin (Wang *et al.* 2022). The XPS analysis further confirmed the chemical bonding mechanism, with the Ag $3d_{5/2}$ binding energy observed at 367.8 eV, corresponding to the formation of Ag–O–C bonds.

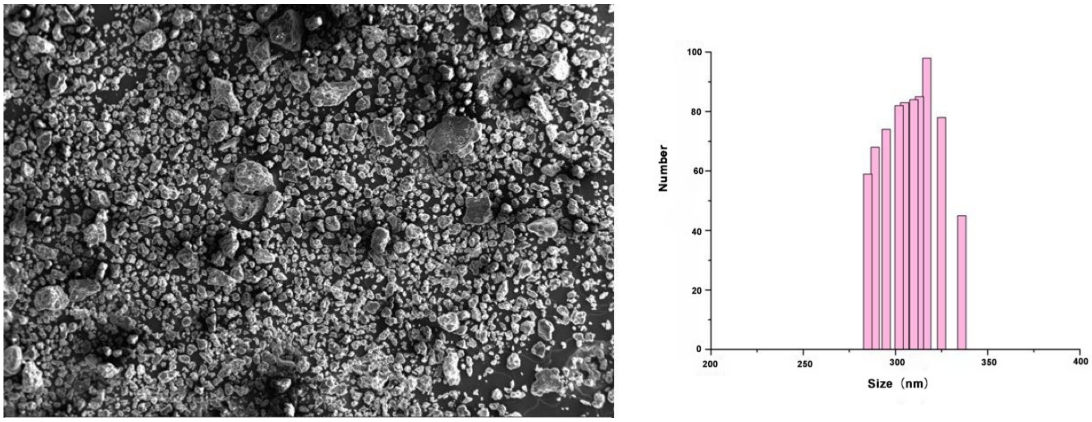

Fig. 4. Nanoparticle size of LigAg NPs

In contrast, no characteristic peak was detected in the Fe 2p spectrum, suggesting that Fe^{3+} failed to bind effectively due to the lack of suitable coordination sites in lignin. This selective binding difference was attributed to the soft acid nature of Ag^+, which exhibited strong coordination affinity with the phenolic groups of lignin (soft base), whereas the hard acid nature of Fe^{3+} was less compatible with lignin functional groups (Zhu *et al.* 2021). The inherent heterogeneity of lignin could, in principle, broaden the nanoparticle size distribution. However, the mild acidity and internal dispersant role of lactic acid in the DES system suppress agglomeration. Dynamic light scattering revealed a narrow PDI (0.21) and SEM showed uniform spherical morphology. The zeta potential of –29.5 mV confirmed strong electrostatic stabilization, indicating that DES viscosity did not adversely affect performance.

The stability of LigAg NPs was evaluated using zeta potential measurements, which revealed a value of –29.5 ± 0.3 mV. This high negative charge, originating from the deprotonated phenolic groups on the lignin surface, provided strong electrostatic repulsion that inhibited particle aggregation. After 30 days, the particle size increased only slightly from 318.8 to 319.1 nm (Δ < 0.3%), demonstrating excellent long-term stability.

Table 3. Zeta Potential and Average Particle Size of LigAg NPs Before and After 30 Days

Samples	Zeta Potential (mV)	Average Particle Size (nm)
Raw LigAgNPs	29.5	318.8
LigAgNPs after 15 days	29.6	319.1
LigAgNPs after 30 days	29.4	318.9

The UV-Vis (UV) spectrum of LigAg NPs displayed a surface plasmon resonance absorbance peak at 417 nm, with a narrow full width at half maximum (FWHM = 32 nm). This narrow peak indicated a uniform particle size distribution, further confirming the advantages of DES-pretreated lignin in nanoparticle synthesis. Compared to conventional alkali lignin, DES-pretreated lignin exhibited superior performance in nanoparticle synthesis. The Ag^+ reduction efficiency increased from 40.1% to 92.4%, while the nanoparticle polydispersity index (PDI) improved from 0.58 to 0.21. Additionally, the phenolic hydroxyl retention in DES-pretreated lignin was significantly higher (1.92 mmol/g) than in alkali lignin (0.87 mmol/g).

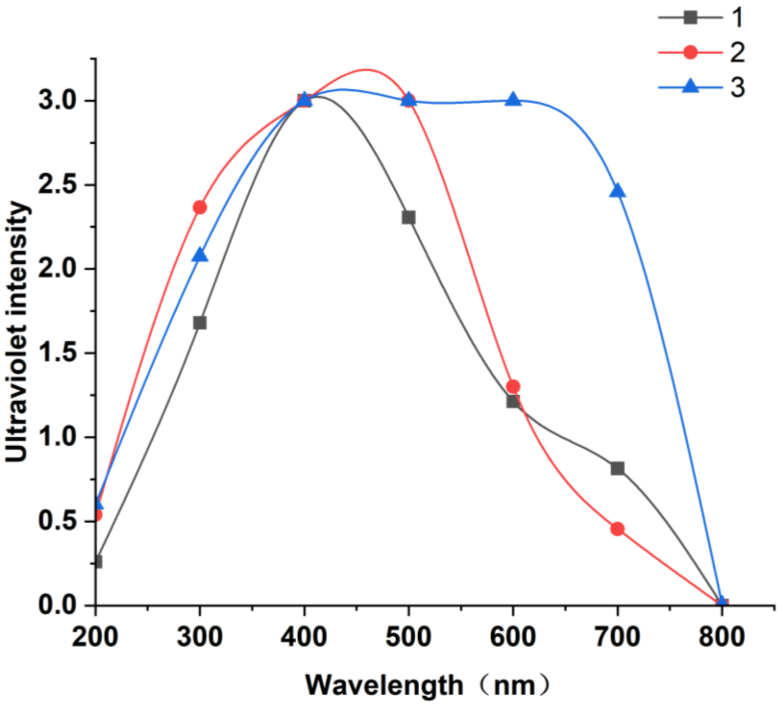

Fig. 5.Ultraviolet Spectral Curve of DES-LigAg Nanoparticles

These improvements were attributed to the mild acidic conditions of DES (pH = 1.36), which prevented irreversible oxidation of phenolic groups under strong alkaline environments (Chen *et al.* 2020b). The specific surface area of LigAg NPs derived from DES-pretreated lignin was 18.7 m^2/g, significantly higher than that of alkali lignin-derived nanoparticles (11.2 m^2/g). This increase in surface area enhanced the catalytic and adsorption properties of the nanoparticles, making them suitable for a wide range of applications. Moreover, DES treatment not only enhanced the efficiency of biomass deconstruction, but it also provided a versatile platform for the synthesis of high-performance lignin nanoparticles. The combination of economic and environmental benefits made DES a promising candidate for largescale applications in biorefineries and nanotechnology.

CONCLUSIONS

1. This study demonstrated that dynamic hydrogen bond regulation *via* dropwise addition of 5 to 10 DES droplets significantly enhanced lignin dissolution efficiency, reducing solid recovery from 81.4% to 59.0% and extending DES recyclability from 2 to 4 cycles.
2. The lignin-derived LigAg NPs (320 nm) were 36% smaller than conventional 500 nm particles, leading to a 67% increase in specific surface area. In lignin-PVA composites, improved molecular chain mobility and enhanced modulus highlighted the role of DES hydrogen bond equilibrium in lignin dissolution.

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