Supplementary Information (SI) for Green Chemistry.
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Waste to Worth: A Circular Solution through Lignin Engineering

Supplementary Data

1. Chemicals.

1.1 Chemicals for particle synthesis.

Citric Acid (99%), Oxalic Acid (99%), and Fumaric Acid (99%) were purchased from Sigma Aldrich Co. LLC (USA). Glutaric Acid (99%), Ammonium Chloride (99%), Succinic Acid (99%), Methylene Blue (99%), and Sodium Hydroxide (99%) were purchased from TCI America (USA). Deionized water was used to prepare all the solutions.

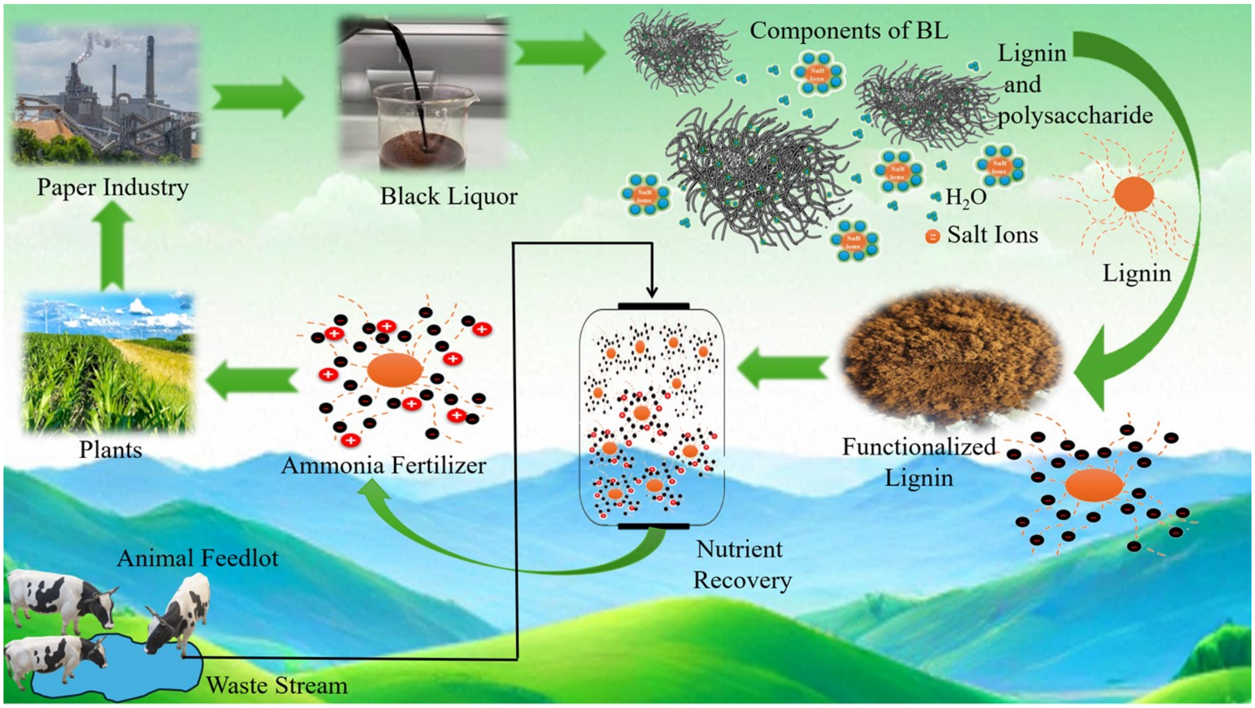
1.2 Solvents.

Ethanol (99%) was purchased from Sigma Aldrich Co. LLC (USA).

1.3 Dyes.

MB (98%) was purchased from TCI America (USA).

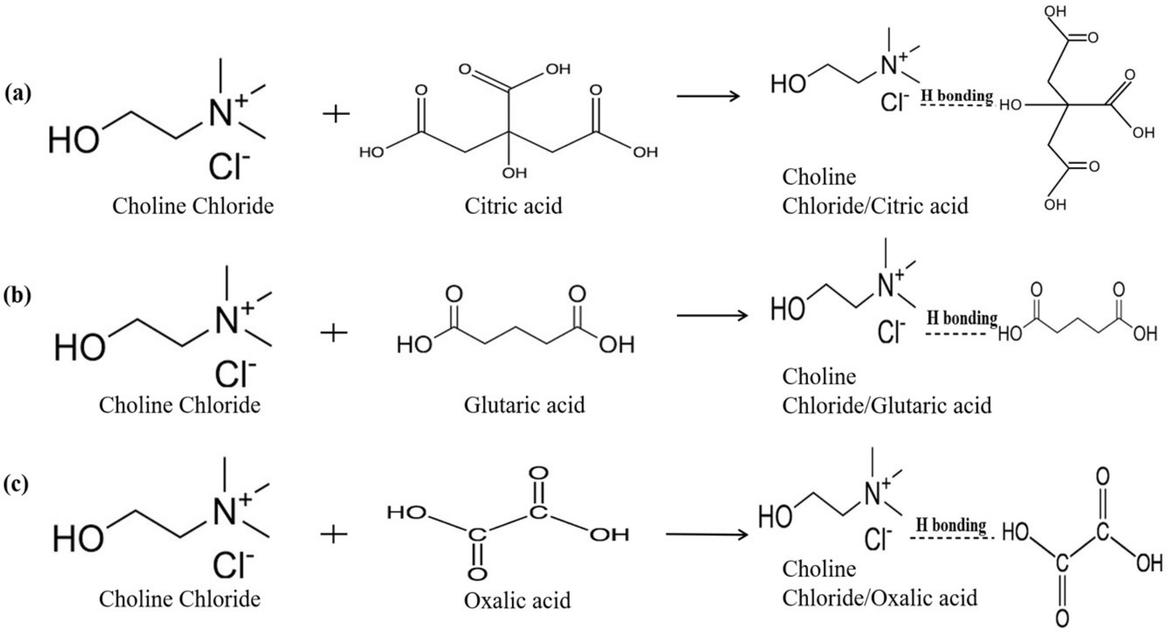
2. Summary Figure



Supplementary Fig. 1. The figure highlights a sustainable closed-loop system that integrates waste recovery, lignin functionalization, nutrient recycling, and agricultural productivity.

3. Synthesis and characterizations of Organic Solvents.

3.1 Synthesis of Organic Solvents



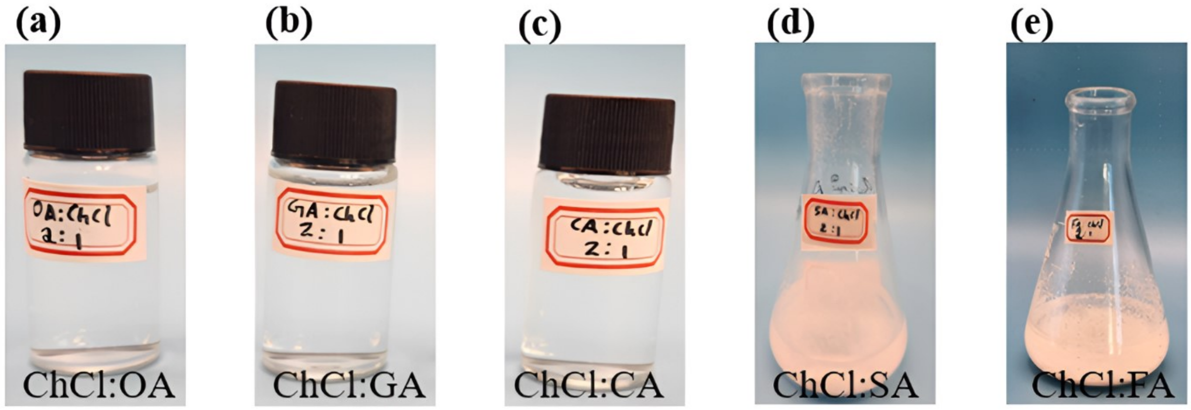
Supplementary Fig. 2. A schematic illustration of the hydrogen bonding interactions between the hydrogen bond providers (oxalic acid, citric acid, and glutaric acid) and the acceptor (choline chloride). The formation of these stable eutectic mixtures is driven by strong hydrogen bonding interactions between the -OH group of choline chloride and the -COOH groups of the acids, suitable for lignin functionalization.

For the synthesis of the solvents the ratio between choline chloride and HBD were varied between 1M and 3M. The other systems which were investigated include choline chloride as a HBA and various organic acids as HBDs including oxalic acid, fumaric acid, glutaric acid, succinic acid and Citric acid. Among these combinations the Choline chloride, Fumaric acid and succinic acids did not form a stable eutectic system (Supplementary Figure 2 b and c). The reaction conditions are detailed in the table below. By employing different organic acids as HBDs, the impact of molecular structure on solvent interactions and subsequent lignin functionalization were assessed. These formulations serve as green solvents for lignin modification, enhancing its surface properties and adsorption capabilities for wastewater treatment applications.

Table 1. Composition and preparation conditions of choline chloride-based solvent systems with different hydrogen-bond donors at varying molarities.

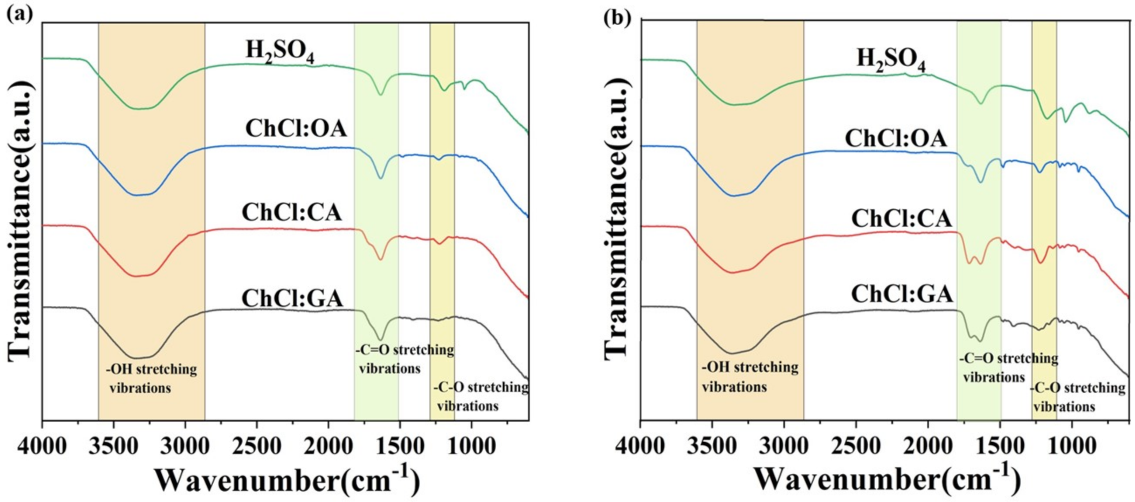
Quaternary ammonium salt	**Hydrogen-bond donors**	**Molarity (M)**	**Molar ratio of salt to HBD**	**Temperature (^oC)**	**Time (hour)**
Choline Chloride	Oxalic Acid	3	1:2	80	3
Choline Chloride	Citric Acid	3	1:2	80	3
Choline Chloride	Glutaric Acid	3	1:2	80	3
Choline Chloride	Oxalic Acid	1	1:2	80	3
Choline Chloride	Citric Acid	1	1:2	80	3
Choline Chloride	Glutaric Acid	1	1:2	80	3

Furthermore, succinic and fumaric acid-based system (ChCl:SA, ChCl:FA) were also prepared. However, they failed to form a stable eutectic mixture likely due to the strong self-association of these dicarboxylic acids through cyclic hydrogen bonded dimers and their high melting points, which makes their crystalline lattice difficult to disrupt [1]. As a result, the interaction between choline chloride (HBD) and these acids were insufficient to produce the stable liquid at room temperature. Experimentally, this behavior resulted as a clear melt at high temperature that recrystallized on cooling into granular solids (Supplementary fig. 3).



Supplementary Fig. 3. Green solvent system prepared with different combinations between Choline chloride and various organic acids: (a) ChCl:OA, (b) ChCl:GA, (c) ChCl:CA, (d) ChCl:SA, and (e) ChCl:FA

3.1 Characterization of Organic Solvents



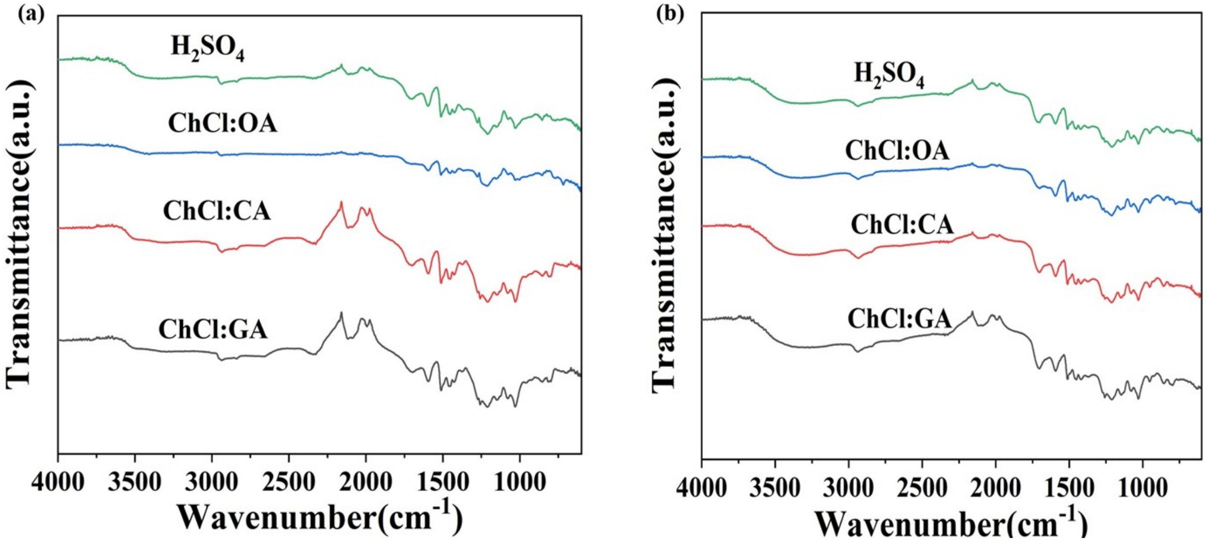
Supplementary Fig. 4. FTIR spectra of solvent systems used for lignin functionalization. Figure (a) and (b): FTIR spectra of solvents (H_2SO_4, ChCl:GA, ChCl:CA, and ChCl:OA) treated lignin at (a) 1 M and (b) 3 M concentrations. Key functional group regions are highlighted: -OH stretching (3200-3600 cm^{-1}), C=O stretching (~1700 cm^{-1}), and C-O stretching (~1200-1000 cm^{-1}).

The FTIR spectra reveal significant structural differences between the organic solvents at 1M and 3M concentrations, particularly in the carboxylic acid functional region near 1700 cm^{-1}, corresponding to C=O stretching. In the case of H_2SO_4, the C=O band is extremely weak. In contrast, organic solvents, especially at higher concentrations, show a significant enhancement in the intensity and definition of the C=O peak. In Figure 4(a) at 1M concentrations, there is a noticeable but still weak shoulder near 1700 cm^{-1}, indicating lower concentration of carbonyl groups. However, when the concentration is increased to 3M in Figure 4(b), the spectra display a sharp, intense peak in the 1700 cm^{-1} region, with the citric acid-based DES (ChCl:CA) showing the most prominent peak, followed by oxalic acid (ChCl:OA) and glutaric acid (ChCl:GA). This indicates a much higher level of carboxylic acid incorporation, likely due to the greater availability of proton donors and carboxylic acid groups in the 3M systems [2]. Additionally, the broadening and increased intensity in the -OH region (3200-3500 cm^{-1}) and shifts in C-O vibrations (around 1100-1300 cm^{-1}) further suggesting stronger hydrogen bonding and a higher abundance of hydroxyl and carbonyl groups. These differences confirm that increasing the concentration of the organic acid in the solvent matrix enhances the presence of reactive acid functionalities. This increased functional group density is expected to play a crucial role in lignin modification, as these groups can participate in esterification or hydrogen bonding during lignin treatment. Overall, the FTIR analysis demonstrates that the 3M solvent is chemically richer in functional groups capable of interacting with lignin, making it a more effective medium for subsequent functionalization.

Between the synthesized solvents (ChCl:OA, ChCl:CA, and ChCl:GA), FTIR spectrum highlighted the superior functionalization potential of ChCl:CA. The broad absorption band in the 3200-3600 cm^{-1} region, corresponding to -OH stretching vibrations, is most intense in ChCl:CA, indicating strong hydrogen bonding interactions due to its three carboxyl (-COOH) groups [3]. Additionally, the prominent peaks around 1600 cm^{-1} and 1200 cm^{-1}, associated with C=O and C-O stretching, respectively, are more pronounced in ChCl:CA, confirming enhanced interactions between choline chloride and citric acid [4]. Compared to oxalic acid and glutaric acid, citric acid forms a more stable eutectic mixture, likely contributing to improved dissolution properties and increased surface functionality. These findings suggest that ChCl:CA is the most effective organic solvent for lignin modification and adsorption applications, making it a promising candidate for wastewater treatment and other functionalization processes.

4. Lignin Precipitation at different temperatures.

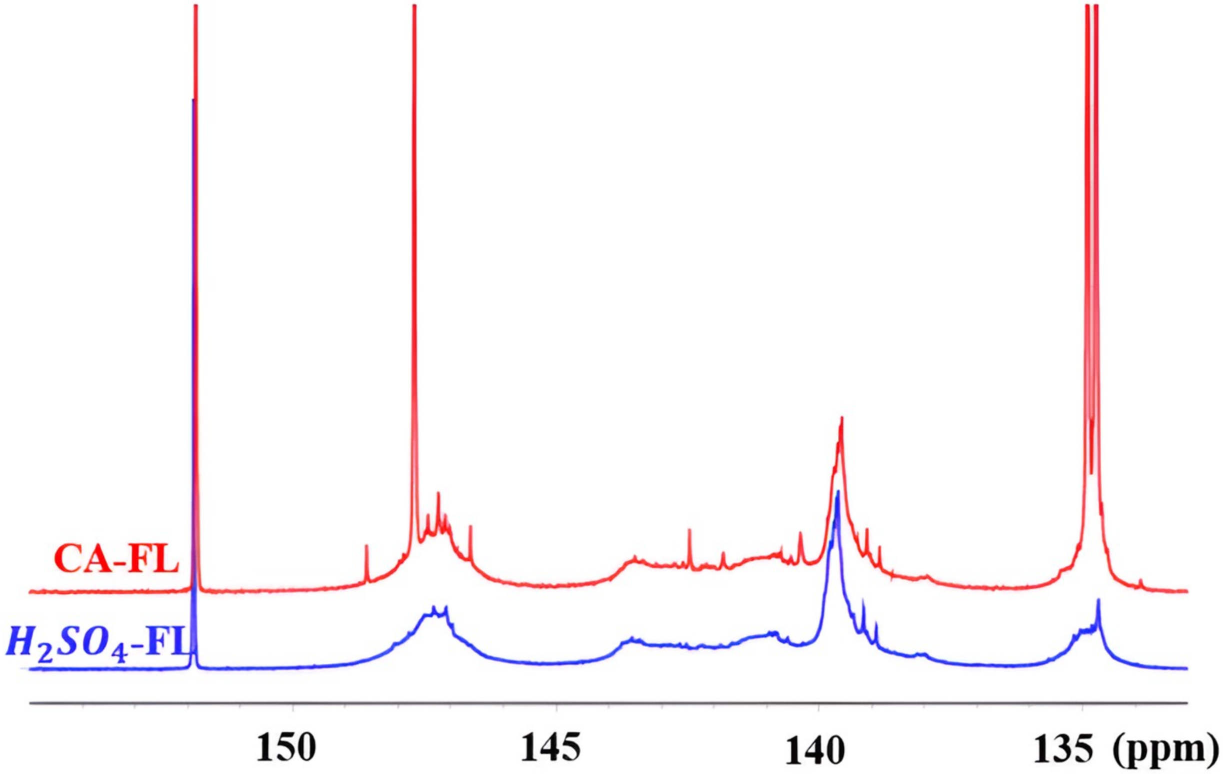
Lignin precipitation was carried out under three different reaction temperatures: 25 °C (room temperature), 60 °C, and 80 °C.



Supplementary Fig. 5. FTIR spectra of lignin precipitated at (a) 25 °C and (b) 60 °C using H_2SO_4 and choline chloride-based organic acid solvent systems (ChCl:OA, ChCl:CA, ChCl:GA).

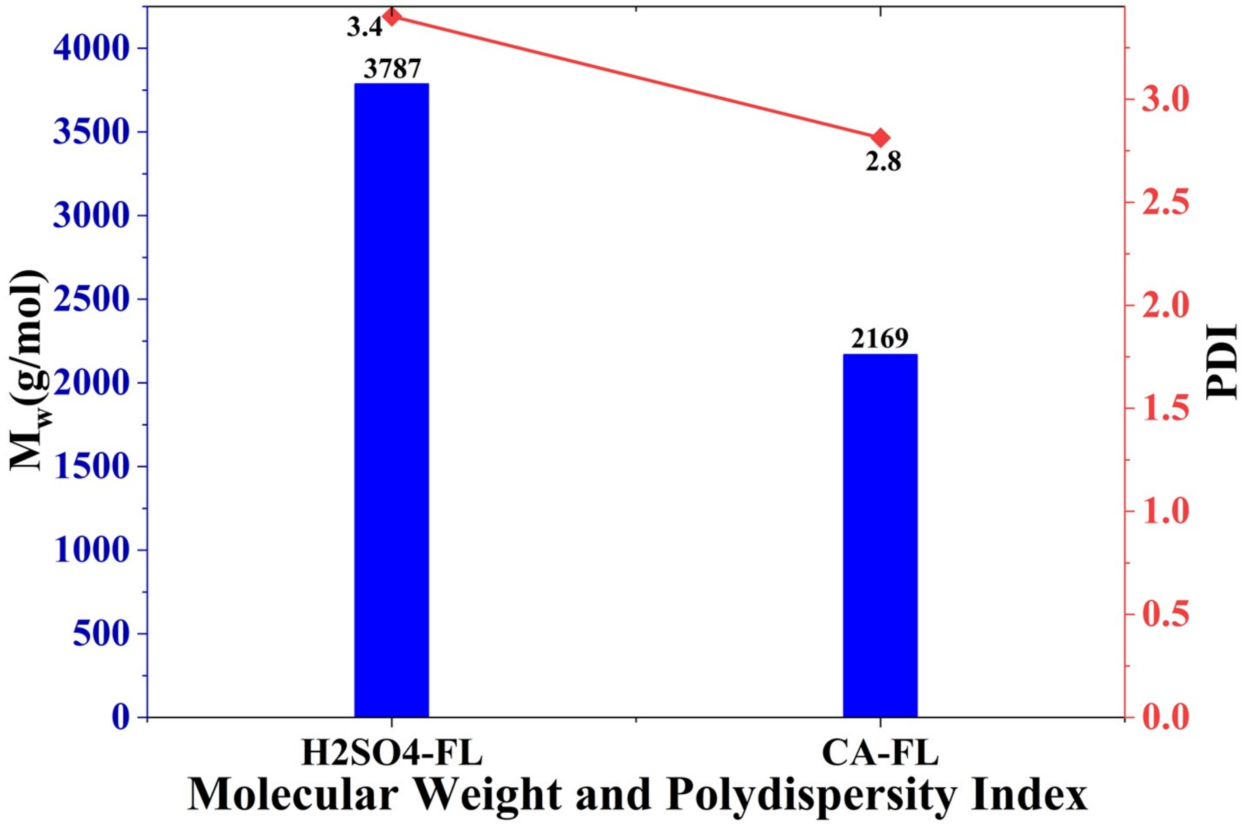
The FTIR spectra of lignin precipitated at 25 °C (a) and 60 °C (b) using different solvent systems show clear temperature-dependent differences in peak intensity and resolution. At 60 °C, most characteristic peaks, particularly in the fingerprint region (1800-1000 cm^{-1}), are sharper and more intense compared to 25 °C, indicating a more defined functional group structure. The C=O stretching band around ~1720 cm^{-1} is notably stronger for the ChCl:CA and ChCl:GA systems, suggesting enhanced carbonyl or carboxylic group presence due to increased solubilization and re-precipitation of oxidized lignin fragments at higher temperature [5]. Aromatic skeletal vibrations between 1600-1500 cm^{-1} are also better resolved, reflecting reduced structural heterogeneity. Additionally, the broad O-H stretching band near 3400 cm^{-1} becomes slightly narrower at 60 °C, implying more uniform hydrogen bonding arrangements. Overall, precipitation at 60 °C results in lignin with more pronounced and well-defined functional groups, highlighting the stronger lignin-solvent interactions and structural reorganization achieved at elevated temperature. The FTIR spectra of FLAMs precipitated at 80 °C are presented and discussed in the main manuscript (Fig. 2).

5. ^{31}P NMR spectra of H_2SO_4-FL and CA-FL



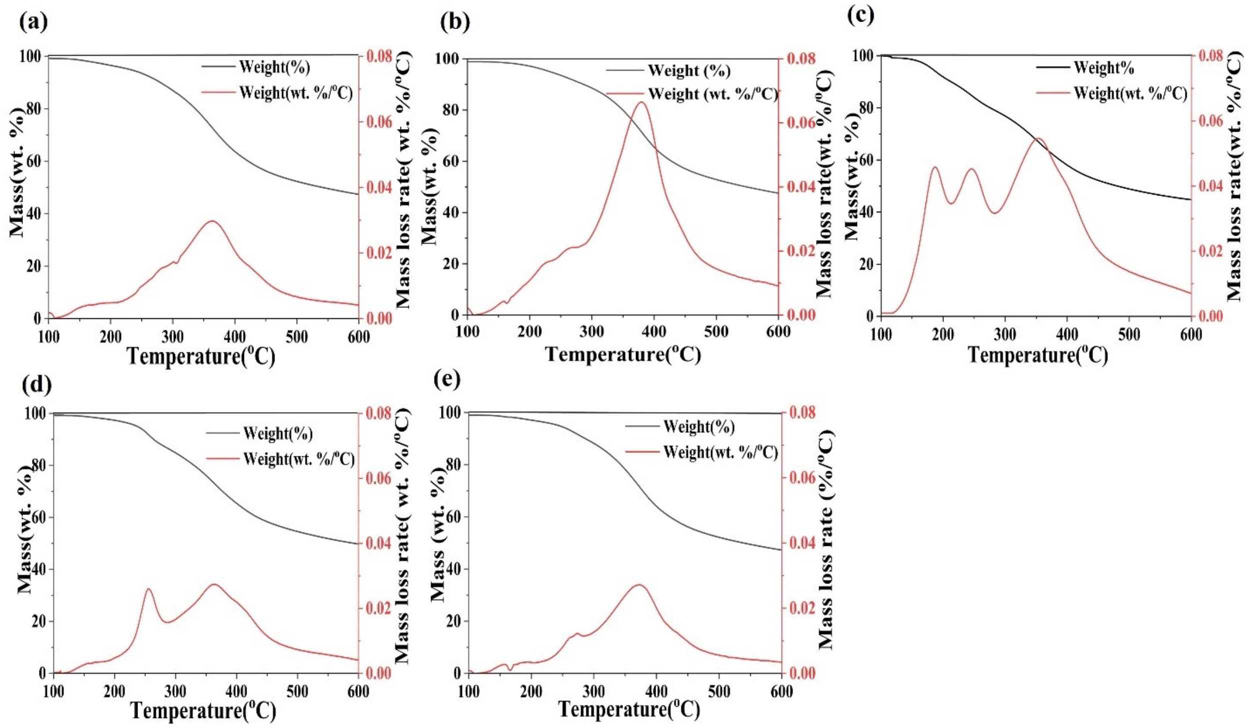
Supplementary Fig. 6. ^{31}P NMR spectra of H_2SO_4-FL and CA-FL

6. Gel permeation chromatography (GPC) of H_2SO_4-FL and CA-FL



Supplementary Fig. 7. Molecular weight and polydispersity index of H_2SO_4-FL and CA-FL

7. Thermal Gravimetric Analysis of FLAM

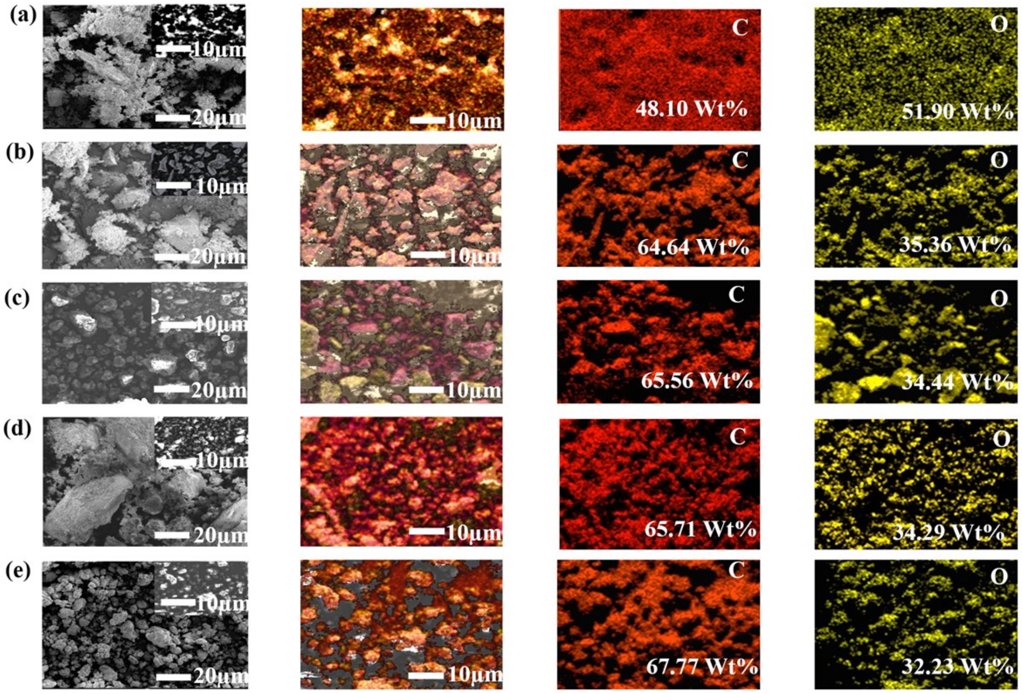


Supplementary Fig. 8. TGA and DTG curves of lignin precipitated using different solvent systems: (a) H_2SO_4, (b) Kraft Lignin, (c) ChCl:CA, (d) ChCl:GA, and (e) ChCl:OA. The thermograms show the weight loss (%) and corresponding mass loss rate (wt. %/°C) as a function of temperature, revealing distinct thermal degradation patterns for each treatment. Samples treated with choline chloride-organic acid systems exhibit varied thermal stability compared to Kraft lignin and H_2SO_4-precipitated lignin, with shifts in decomposition onset and maximum degradation temperatures, indicating the influence of the solvent system on lignin's structural and thermal properties.

The thermal behavior and degradation of Kraft and functionalized lignin were identified using thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) was performed on different samples of lignin using a TA Instruments TGA Q500 (V20.13 Build 39) equipped with an EGA furnace and a platinum pan. Nitrogen was used as both balance gas (10.0 mL/min) and sample gas (90.0 mL/min) to maintain an inert atmosphere. The temperature program consisted of heating from 20 °C to 105 °C at 20 °C/min, followed by a 10 min isothermal hold, then heating to 800 °C at 10 °C/min with another 10 min isothermal period. The system was subsequently cooled to 50 °C at 40 °C/min and equilibrated. The instrument recorded time, temperature, sample weight, derivative weight (DTG), and second derivative weight signals, with a data sampling rate of 0.5 s.

The kraft lignin showed greater thermal stability with single major DTG peak at higher temperatures. In contrast, ChCl:CA treated lignin showed multiple DTG peaks and an earlier onset of mass loss, showing the presence of thermally liable and low molecular weight fractions. The DTG peaks for ChCl:CA at 135 ^{o}C, 250 ^{o}C, and 320 ^{o}C, can be attributed by the oxygenated groups by the modification of citric acid on the lignin surface.

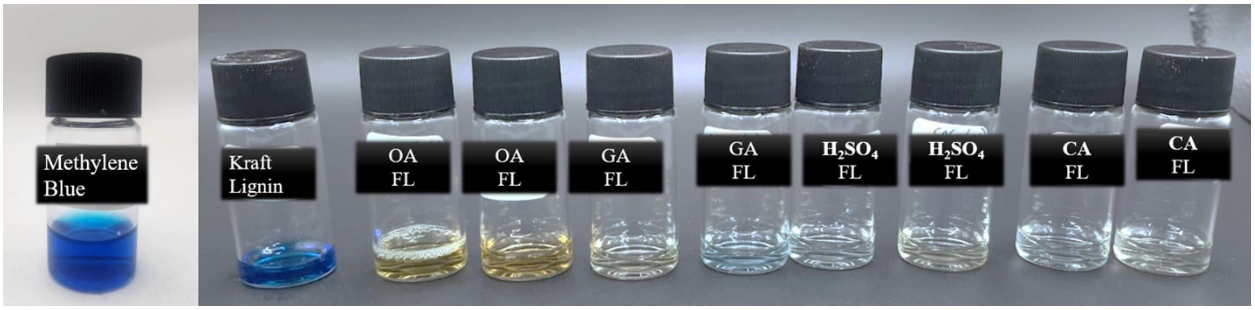
8. SEM and EDS Images of the FLAM and Kraft Lignin



Supplementary Fig. 9. The morphologies of different functionalized lignin (a)ChCl:CA, (b) ChCl:GA, (c) ChCl:OA, (d) H_2SO_4-Lignin, and (e) Kraft lignin with element analysis, respectively. The result demonstrated that the content of oxygen element significantly increased in modified lignin compared with kraft lignin, which indicated the carboxyl group was successfully grafted on lignin. The CA: FL showed the highest amount of oxygen weight percentage indicating superior adsorption capacity.

9. Comparison of Dye Removal Experiments

The efficiency of dye removal was analyzed by treating 10 mL of 10 mg/L of Methylene Blue solution with 5mg of CA-FL, GA-FL, OA-FL, H_2SO_4-Lignin and Kraft Lignin.



Supplementary Fig. 10. Comparison between different FLAM with CA-FL showing superior performance.

10. Adsorption Kinetic Model

(a) Pseudo First Order Kinetics

Model	Pseudo First Order Kinetics
Equation	y = a*(1 - exp(-b*x))
Plot	\b (Experimental Value)
a	688.53009 ± 15.6496
b	0.72861 ± 0.06217
Reduced Chi-Sqr	794.69495
R-Square (COD)	0.98689
Adj. R-Square	0.9847

(b) Pseudo Second Order Kinetics

Model	Pseudo Second Order Kinetics
Equation	qe^2*k2*t/(1+k2*qe*t)
Plot	\b(Experimental Value)
qe	766.12335 ± 18.90326
k2	0.00124 ± 1.52075E-4
Reduced Chi-Sqr	616.64409
R-Square (COD)	0.99983
Adj. R-Square	0.99813

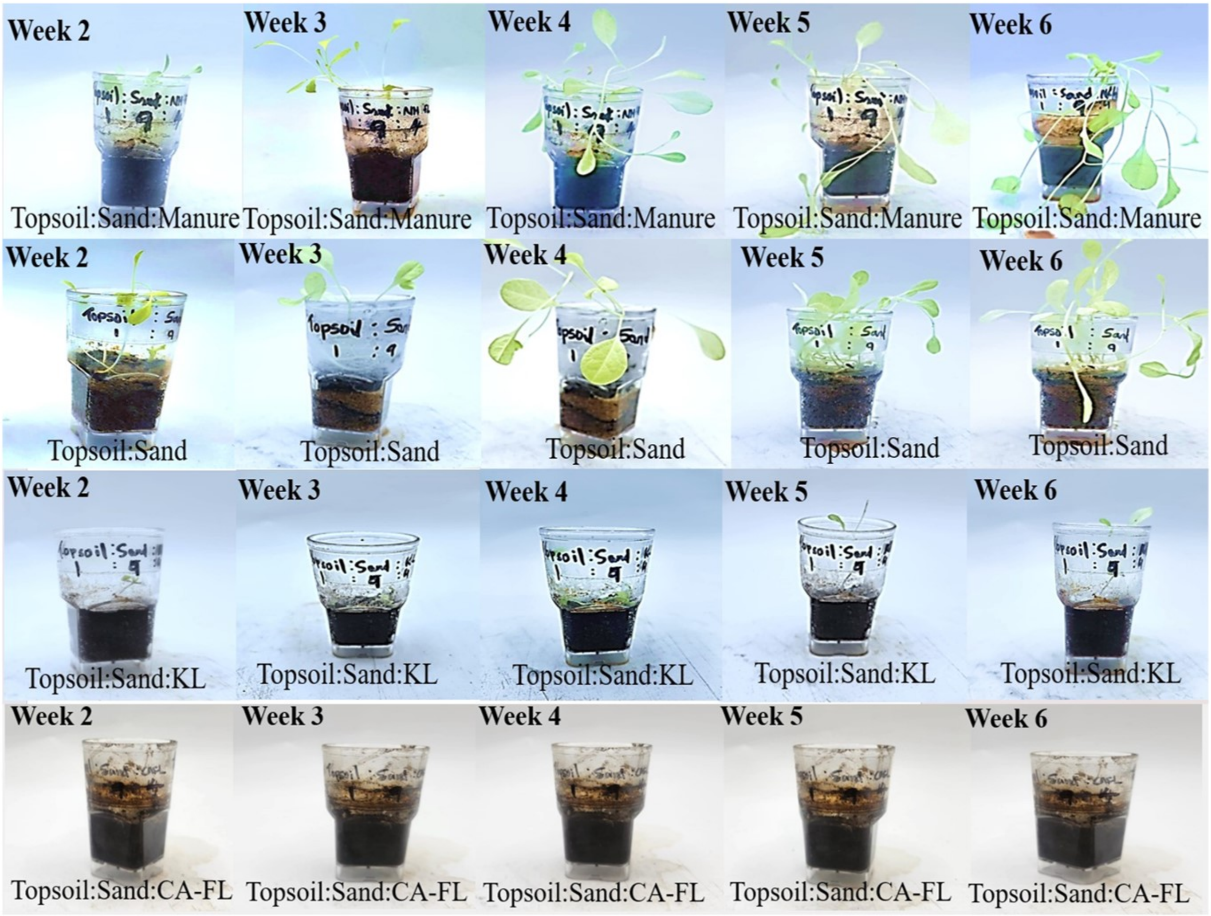
11. Adsorption Isotherm Models

(a) Freundlich Adsorption Isotherm

Model	Freundlich Asdsorption isotherm
Equation	y = a*x^b
Plot	\b(Experimental Value)
a	44.40203 ± 9.38632
b	0.52833 ± 0.04226
Reduced Chi-Sqr	988.56687
R-Square (COD)	0.98701
Adj. R-Square	0.98442

12. Plant Growth Analysis

To compare the efficiency of the manure treated CA-FL as a slow-release fertilizer different combinations of mixes were prepared including CA-FL: Topsoil: Sand, Kraft Lignin: Topsoil: Sand, Topsoil: Sand and Manure-CA-FL: Topsoil: Sand. Topsoil: Sand mix was kept as the control for comparison. The plant height and number of leaves were recorded every 14 days. The ratios were kept constant across the samples as 1:9:4(Topsoil : Sand : Lignin).



Supplementary Fig. 11. Comparison between the efficiency of lignin as slow-release fertilizer for plant growth.

Reference

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