Valorization of heavy metal enriched phytoremediation biomass using deep eutectic solvent (DES)

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Captions

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Table S1 Effects of DES pretreatment on chemical composition of untreated poplar and pulp

			Composition of untreated poplar or pulp based on the original sample before pretreatment (%)		
		Pulp yield	Cellulose	Hemicellulose	Lignin
Poplar		N/A	48.1±0.6	16.0±1.5	28.2±1.0
	1 h	54.6±1.6	34.1±1.4	6.6±0.8	9.5±0.8
120 °C	3 h	43.8±1.5	31.1±1.6	4.4±0.5	4.1±0.3
	5 h	39.8±0.8	29.8±0.7	3.7±0.1	2.9±0.2
	1 h	44.6±1.6	33.0±1.5	4.9±0.4	4.9±1.1
130 °C	3 h	37.3±1.6	29.8±0.8	3.0±0.4	1.9±0.5
	5 h	36.1±1.2	29.5±0.6	2.0±0.4	2.0±0.1

Table S2 Content of Cd in biomass samples and liquid phase after poplar pretreatment

		Cd proportion (% of total)				Cd concentration (ppm)		
		Pulp	Lignin	Liquid	Loss	Pulp	Lignin	Liquid
Poplar		100	N/A	N/A	N/A	3.3±0.4	N/A	N/A
120 °C	1 h	4.5±0.8	N/A	88.9±1.6	6.5±1.9	0.3±0.1	N/A	0.3±0.0
	3 h	3.0±0.6	N/A	90.2±2.8	6.7±3.3	0.2±0.1	N/A	0.3±0.0
	5 h	2.4±0.4	N/A	94.5±2.5	2.8±2.2	0.2±0.0	N/A	0.3±0.0
130 °C	1 h	3.0±1.0	N/A	93.5±0.8	2.9±0.2	0.2±0.1	N/A	0.3±0.0
	3 h	2.1±0.5	N/A	91.3±1.3	6.4±0.9	0.2±0.0	N/A	0.3±0.0
	5 h	1.7±0.6	N/A	92.0±1.1	6.2±2.2	0.1±0.0	N/A	0.3±0.0

N/A: Below the detection limit.

Note: The loss mainly comes from the detection error and the loss in the experiment.

Table S3 Content of Cu in biomass samples and liquid phase after poplar pretreatment

		Cu proportion (% of total)				Cu concentration (ppm)		
		Pulp	Lignin	Liquid	Loss	Pulp	Lignin	Liquid
Poplar		100	N/A	N/A	N/A	9.5±0.72	N/A	N/A
120 °C	1 h	0.6±0.4	0.8±0.1	91.9±1.3	6.8±1.0	0.1±0.06	0.9±0.0	0.7±0.0
	3 h	0.5±0.7	2.2±0.1	89.5±2.1	8.0±1.7	0.1±0.05	1.3±0.0	0.7±0.0
	5 h	0.3±0.2	2.9±1.0	87.7±2.4	9.1±1.1	0.1±0.06	1.5±0.1	0.7±0.0
130 °C	1 h	0.4±0.4	1.2±0.3	88.3±1.4	10.2±1.2	0.1±0.11	0.8±0.0	0.7±0.0
	3 h	0.4±0.4	3.8±0.1	85.5±1.9	10.4±1.5	0.1±0.11	1.8±0.0	0.7±0.0
	5 h	0.4±0.2	6.0±0.2	82.9±1.0	10.4±0.6	0.1±0.05	2.4±0.0	0.6±0.0

N/A: Below the detection limit.

Note: The loss mainly comes from the detection error and the loss in the experiment.

Table S4 Semi-quantitative information for subunits and interunit linkage in lignin

		β-O-4 %	β-β %	β-5 %	S/G
MWL		50.1	8.4	4.7	0.9
	1 h	10.4	2.6	3.1	1.4
120 °C	3 h	3.0	2.0	1.0	1.6
	5 h	2.3	3.1	1.5	1.7
	1 h	2.4	1.0	N/A	1.9
130 °C	3 h	2.2	1.7	N/A	1.6
	5 h	1.7	2.5	N/A	1.8

N/A: Below the detection limit.

Table S5 Functional group contents of lignin from different pretreatment conditions (mmol/g)

		Aliphatic OH	C_5 substituted OH	Guaiacyl OH	P-hydroxy OH	Carboxylic acid OH	Total phenolic OH
MWL		4.95	0.07	0.84	0.43	0.08	1.34
	1 h	2.21	1.13	0.73	0.20	0.50	2.06
120 °C	3 h	1.78	1.54	0.79	0.23	0.45	2.56
	5 h	1.40	1.72	0.86	0.19	0.57	2.76
	1 h	1.93	1.51	0.90	0.20	0.36	2.51
130 °C	3 h	1.75	1.75	0.90	0.24	0.75	2.90
	5 h	0.73	1.87	0.99	0.20	0.51	3.05

Table S6 The influence of the water content on the electrochemical properties of DES

Water contents wt%	Conductivity (ms/cm)	Cathodic limiting potential (V)	Anodic limiting potential (V)	Electrochemical window
0	0.5	-1.91	1.64	3.53
10	1.8	-1.83	1.59	3.42
20	4.0	-1.76	1.56	3.32
30	4.9	-1.63	1.56	3.19

Table S7 Content of HMs in biomass samples and liquid phase after *Sedum alfredii* pretreatment

		HMs proportion (% of total)			**HMs concentration (ppm)**		
		Cd	Pb	Cu	Cd	Pb	Cu
Sedum alfredii		100	100	100	599.2±0.9	166.1±2.4	5.3±0.1
	Pulp	3.5±0.5	22.7±2.6	14.7±1.6	90.8±7.8	165.9±14.9	3.4±0.5
130	Lignin	N/A	0.2±0.0	55.8±2.5	N/A	3.8±0.4	28.2±2.9
°C 3 h	Liquid	93.1±0.7	76.7±0.3	22.7±2.9	44.7±0.3	10.2±0.1	0.1±0.0
	Loss	3.3±0.8	0.6±0.2	8.6±1.6	N/A	N/A	N/A

N/A: Below the detection limit.

Note: The loss mainly comes from the detection error and the loss in the experiment.

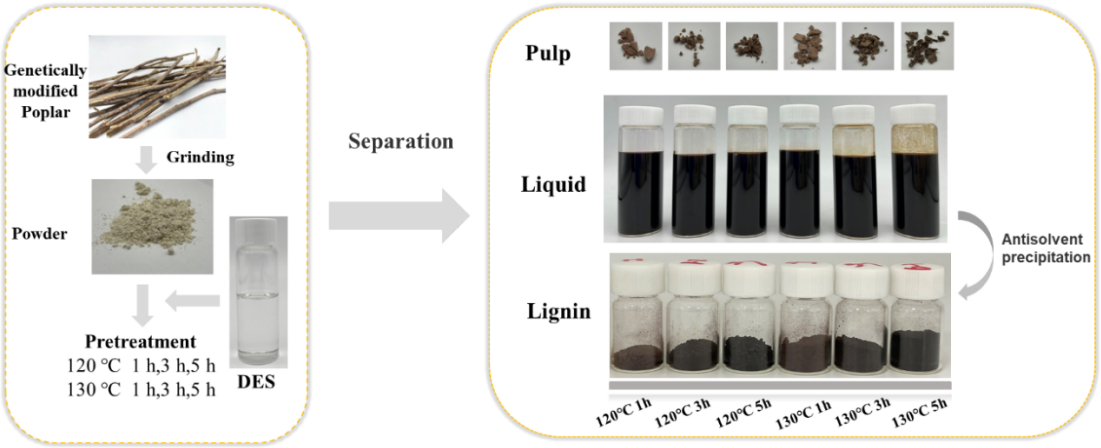

Fig. S1 Procedure for the pretreated genetically modified poplar and extracted lignin.

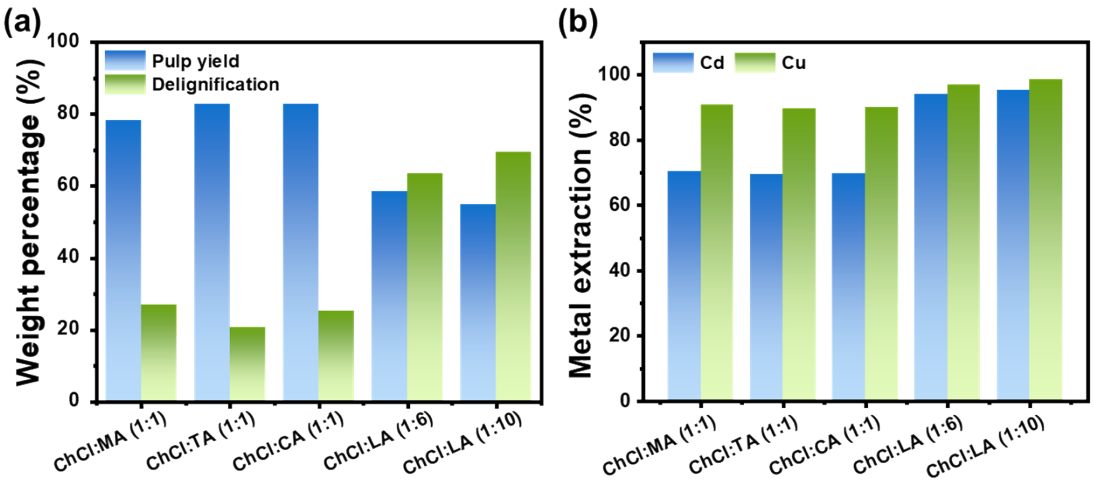

Fig. S2 Pretreatment of genetically modified poplar with different DES at 120 °C for 1 h. (a) Pulp yield and lignin removal efficiency; (b) Effect of different DES on heavy metal extraction efficiency in the gene modified poplar.

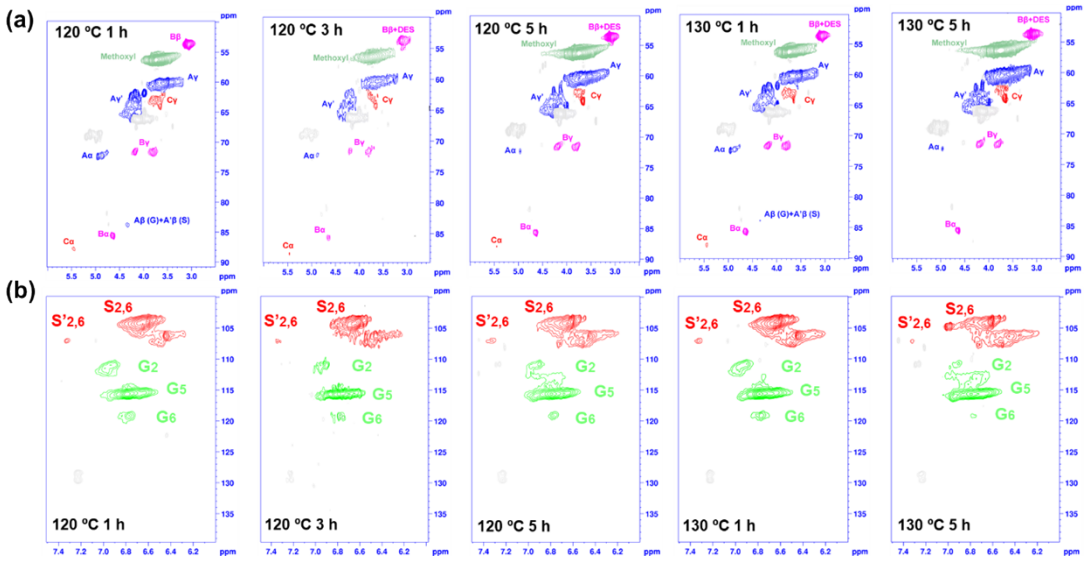

Fig. S3 2D HSQC NMR characterization of lignin obtained with different pretreatment conditions: (a) Side-chain regions; (b) Aromatic regions.

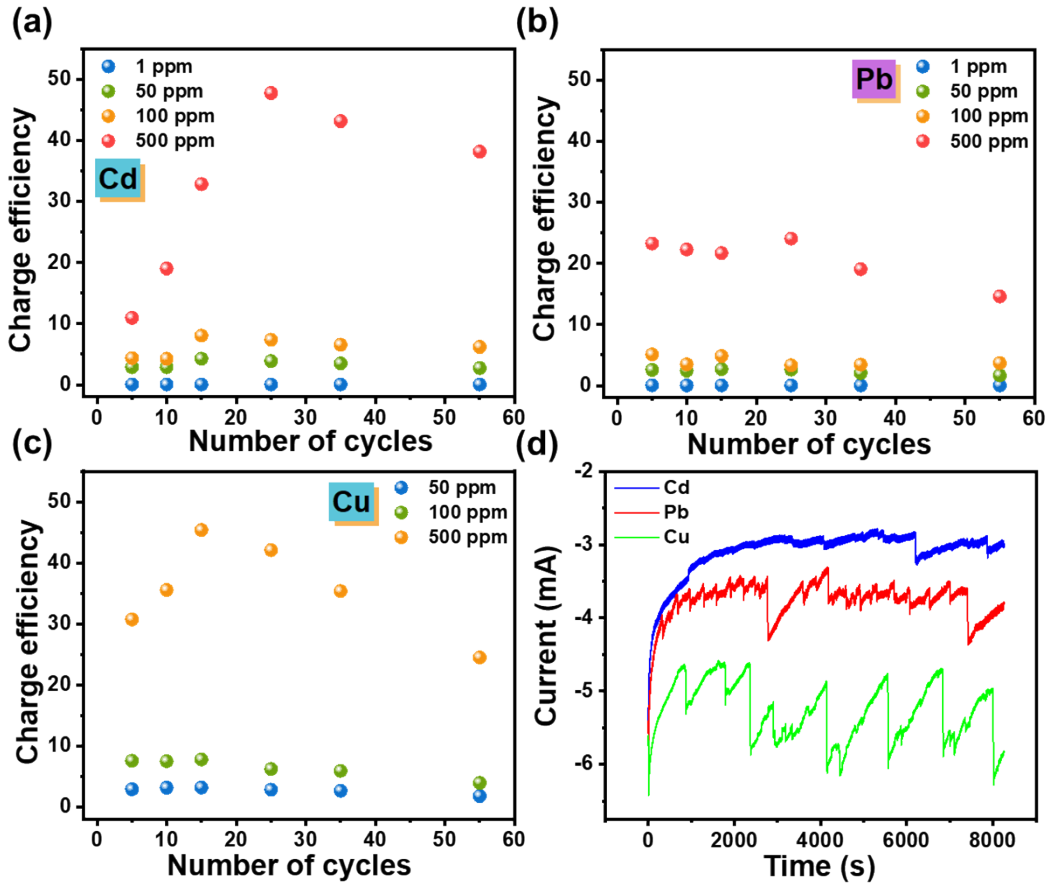

Fig. S4 (a-c) The charge efficiency of Cd, Pb and Cu from DES (20 wt% H_2O) with different content pollution by electrochemical deposition. All three solutions only contain a single contaminant. Potential applied -1.4 V vs Ag/AgCl; (d) Current curve of Cd, Pb and Cu of 100 ppm initially from DES (20 wt% H_2O) using electrodeposition method.

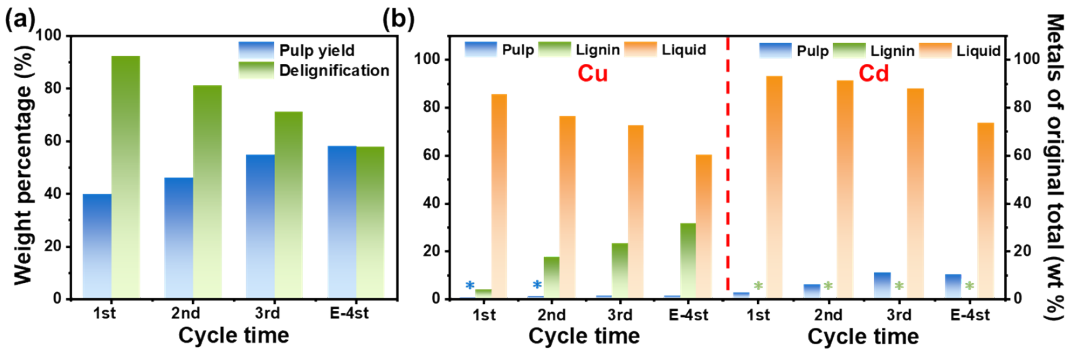

Fig. S5(a) Pulp yield and delignification efficiency after various cycles of DES treatment at 130 °C for 3 h; (b) Distribution of heavy metals in various components of poplar after DES pretreatment. *: not detected. E-4st refers to the DES treatment of poplar at 130 °C for 3 h using electrodeposited DES (Electrodeposited DES was obtained from the 3rd DES after electrodeposition).

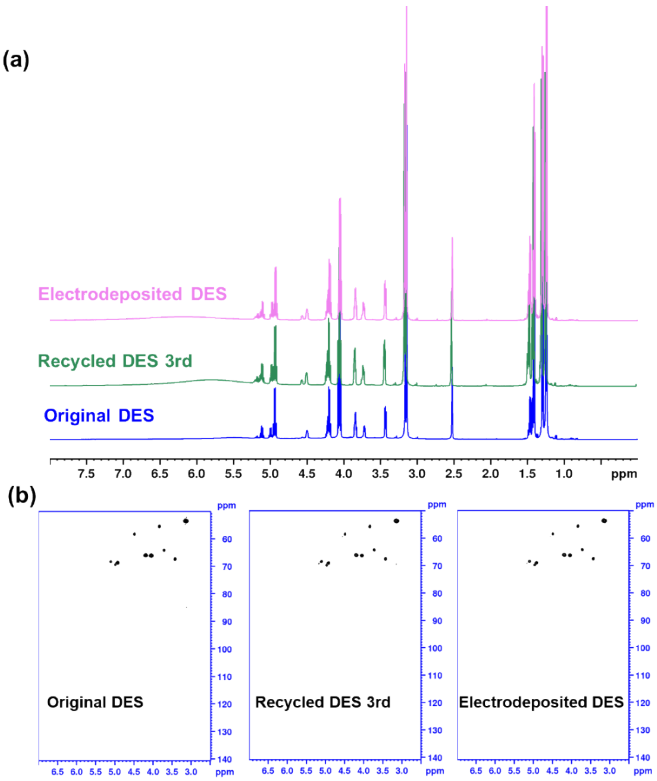

Fig. S6 (a) ^{1}H NMR spectra of original, the recycled DES and electrodeposited DES. (b) 2D-HSQC NMR spectra of the original, recycled DES after three cycles and electrodeposited DES.