

Supporting information

Integration of lignin microcapsule pesticide production into lignocellulose biorefinery through FeCl₃-mediated deep eutectic solvents pretreatment

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Six tables (Table S1, S2, S3, S4, S5 and S6)

Four figs (Fig S1, S2, S3 and S4)

Table S1. Residual carbohydrates content in regenerated lignins of FeCl₃-mediated DESs extraction.

Carbohydrates (%)	ChCl/LA-FeCl ₃	ChCl/Gly-FeCl ₃	K ₂ CO ₃ /Gly-FeCl ₃
Glucose	0.59	0.86	5.26
Xylose	0.01	0.28	0.95
Total	0.60	1.04	6.21

Table S2. The content Fe element of obtained substrates pretreated by FeCl₃-mediated DESs

Sample	Fe (mg g ⁻¹)
Bamboo	0.21
ChCl/LA-FeCl ₃ (cellulose)	0.54
ChCl/LA-FeCl ₃ (lignin)	0.41
ChCl/Gly-FeCl ₃ (cellulose)	1.51
ChCl/Gly-FeCl ₃ (lignin)	0.51
K ₂ CO ₃ /Gly-FeCl ₃ (cellulose)	7.02
K ₂ CO ₃ /Gly-FeCl ₃ (lignin)	4.59

Table S3. Assignment of main ¹³C-¹H cross-signals in HSQC spectra of these DES lignins.

label	δ_C/δ_H (ppm)	assignment
B _{β}	53.5/3.06	C _{β} -H _{β} in β - β (resinol) substructures (B)
-OCH ₃	55.6/3.73	C-H in methoxyls
A _{γ}	59.5/3.20–3.63	C _{γ} -H _{γ} in β -O-4 substructures (A)
L ₂	66.0/4.21	C ₂ -H ₂ in lactic acid (L)
A _{α}	71.8/4.86	C _{α} -H _{α} in β -O-4 linked to S units (A)
A _{β(G)} / A' _{β(S)}	83.9/4.29	C _{β} -H _{β} in β -O-4 substructures linked to G and H units (A)
B _{α}	84.8/4.65	C _{α} -H _{α} in β - β (resinol) substructures (B)
A _{β(S)}	85.9/4.12	C _{β} -H _{β} in β -O-4 substructures linked to S units (A)
C _{α}	86.8/5.46	C _{α} -H _{α} in phenylcoumaran substructures (C)
S _{2,6}	103.8/6.71	C _{2,6} -H _{2,6} in etherified syringyl units (S)
S' _{2,6}	106.2/7.32	C _{2,6} -H _{2,6} in oxidized (C _{α} =O) syringyl units (S')
G ₂	110.9/6.98	C ₂ -H ₂ in guaiacyl units (G)
PCE ₈	114.2/6.27	C ₈ -H ₈ in <i>p</i> -coumarate (PCE)
G ₅	114.9/6.77	C ₂ -H ₂ in guaiacyl units (G)
G ₆	119.0/6.80	C ₆ -H ₆ in guaiacyl units (G)
H _{2,6}	127.9/7.19	C _{2,6} -H _{2,6} in <i>p</i> -hydroxyphenyl units (H)

PCE _{2,6}	130.2/7.48	C _{2,6} -H _{2,6} in <i>p</i> -coumarate (PCE)
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Table S4. Major covalent bond content of lignins quantified by 2D-HSQC spectra (results expressed as the number of moieties per 100 Aromatic rings).

Covalent bond	β -O-4	β - β	β -5	S/G
MWL	52.08	8.53	7.31	1.21
ChCl/LA	21.23	3.52	<0.1	2.37
ChCl/LA-FeCl ₃	<0.1	<0.1	<0.1	–
ChCl/Gly	44.29	7.01	8.73	1.28
ChCl/Gly-FeCl ₃	15.86	<0.1	<0.1	1.66
K ₂ CO ₃ /Gly	40.32	5.92	4.16	2.24
K ₂ CO ₃ /Gly-FeCl ₃	8.52	<0.1	<0.1	–

Table S5. Assignment and quantification of signals of ¹³C NMR spectra (results expressed as number of moieties per Aromatic ring).

Chemical shift (ppm)	58-54	124-102	140-124	156-140	125-102
Assignment	-OCH ₃	C _{Ar-H}	C _{Ar-C}	C _{Ar-O}	degree of condensation ^a
MWL	2.08	2.07	1.9	1.86	0.94
ChCl/LA	2.03	1.76	1.98	2.04	1.27
ChCl/LA-FeCl ₃	1.29	1.40	1.95	2.22	1.57
ChCl/Gly	1.83	1.99	1.96	1.88	1.04
ChCl/Gly-FeCl ₃	1.13	2.33	2.35	1.59	1.12
K ₂ CO ₃ /Gly	2.45	2.06	1.49	2.04	0.91
K ₂ CO ₃ /Gly-FeCl ₃	1.98	1.83	1.73	2.07	1.13

^aCalculated from $3.00 - I_{125-102}$

Table S6. AVM loading and encapsulation efficiency of AVM-loaded lignin nanospheres.

Shell material	Encapsulation efficiency (%)	AVM loading (%)
LNS-ChCl/LA-FeCl ₃	80.72	20.18
LNS-ChCl/Gly-FeCl ₃	81.83	20.46
LNS-K ₂ CO ₃ /Gly-FeCl ₃	44.10	11.21

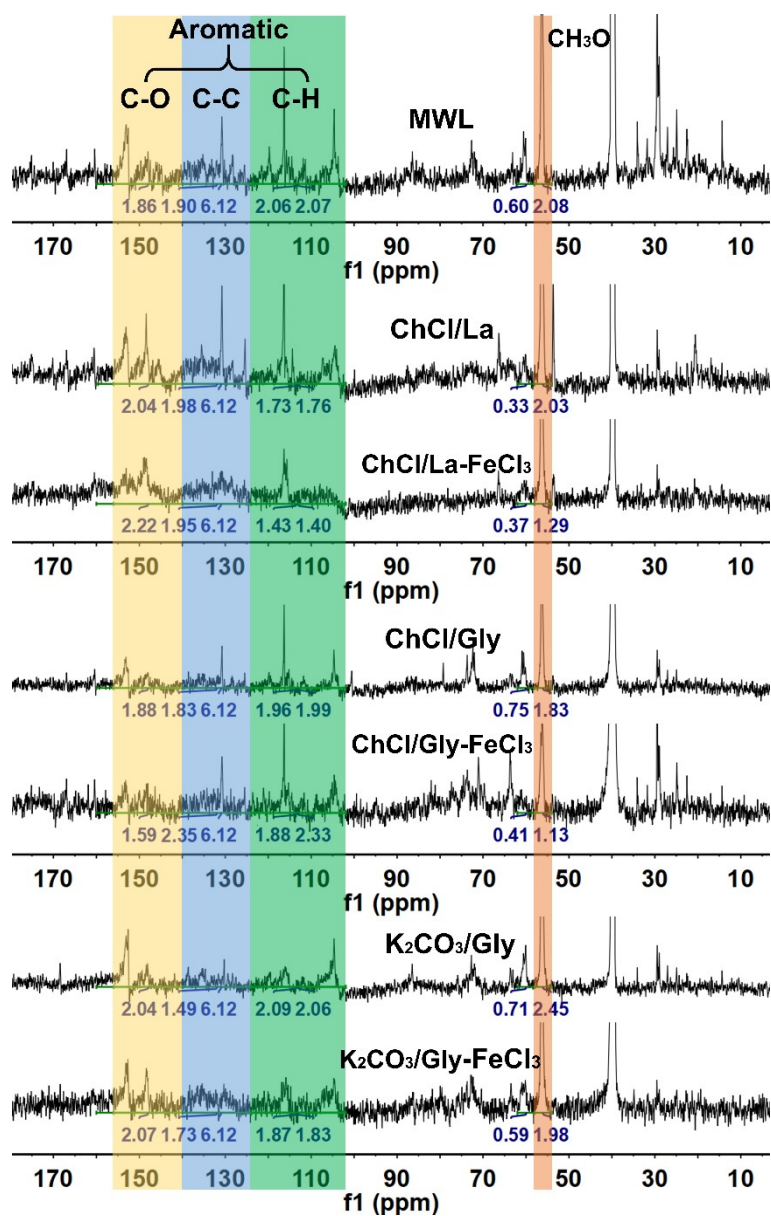


Fig. S1. Quantitative ^{13}C NMR spectra of MWL and DES lignins.

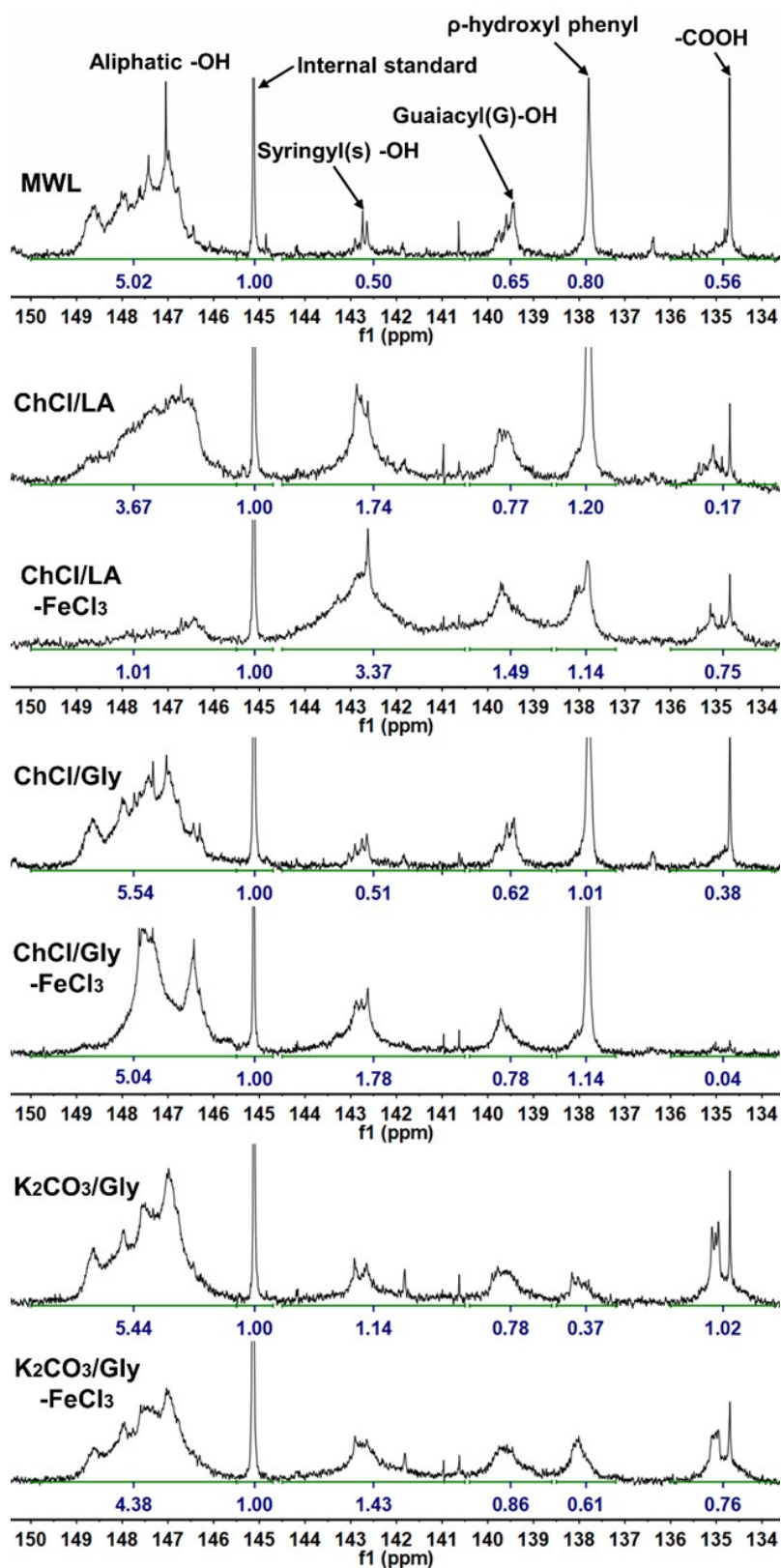


Fig. S2. Quantitative ^{31}P NMR spectra of MWL and regenerated lignins.

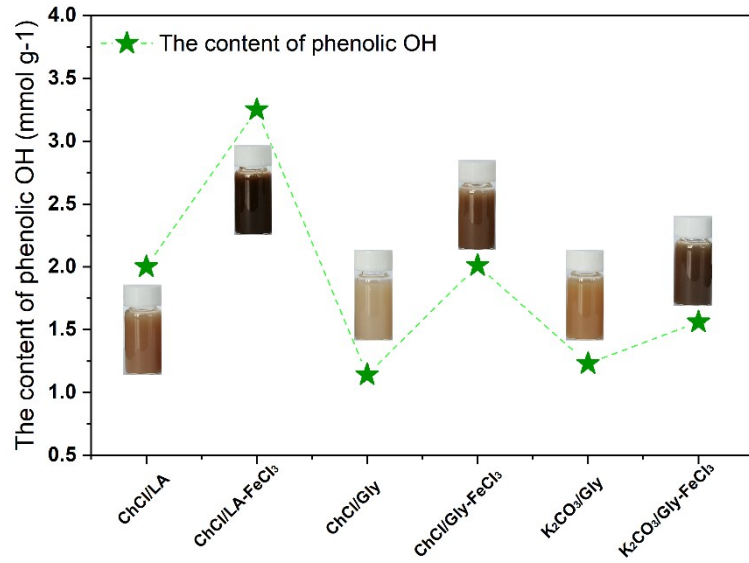


Fig. S3. The content of phenolic-OH and its corresponding digital photo of these DES lignin nanospheres.

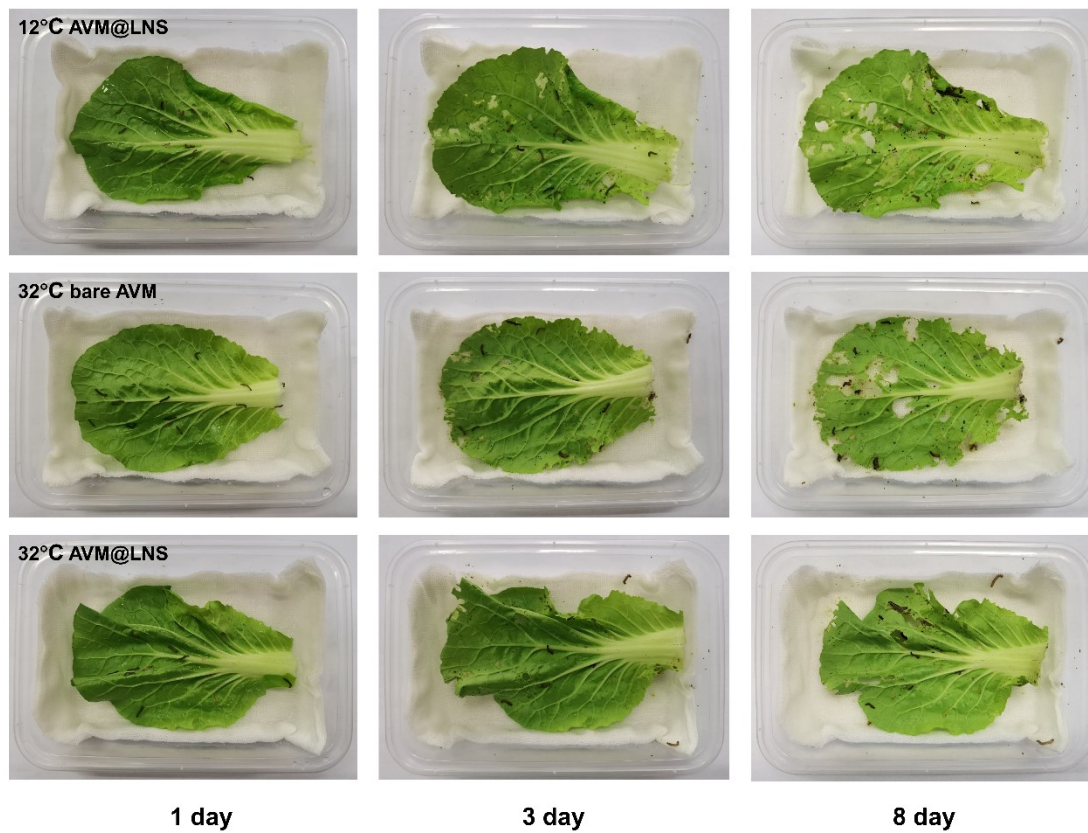


Fig. S4. Photographs of Baby Bok Choy after feeding *Mythismna separata* at different times.