

Supporting Information

Closing the Sustainable Life Cycle Loop of Membrane Technology via a Cellulose Biomass Platform

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Membrane fabrication with Green Solvents

Fabrication of cellulose acetate (CA) membranes with green solvents, such as Polarclean, methyl lactate, and triethyl phosphate (TEP), which have been reported as green alternatives to conventional solvents, verified the versatility of the proposed procedures.¹ SEM analysis (**Figure S1a**) was used to investigate the fabricated membranes for morphology, the viscosity of dope solution (**Figure S1b**), and permeance in ethanol (**Figure S1c**). Also, the viscosity of CA 20–25 wt% dope solutions and SEM images of CA 20–22 wt% are shown in **Figures S1, S3, and S4**, respectively.

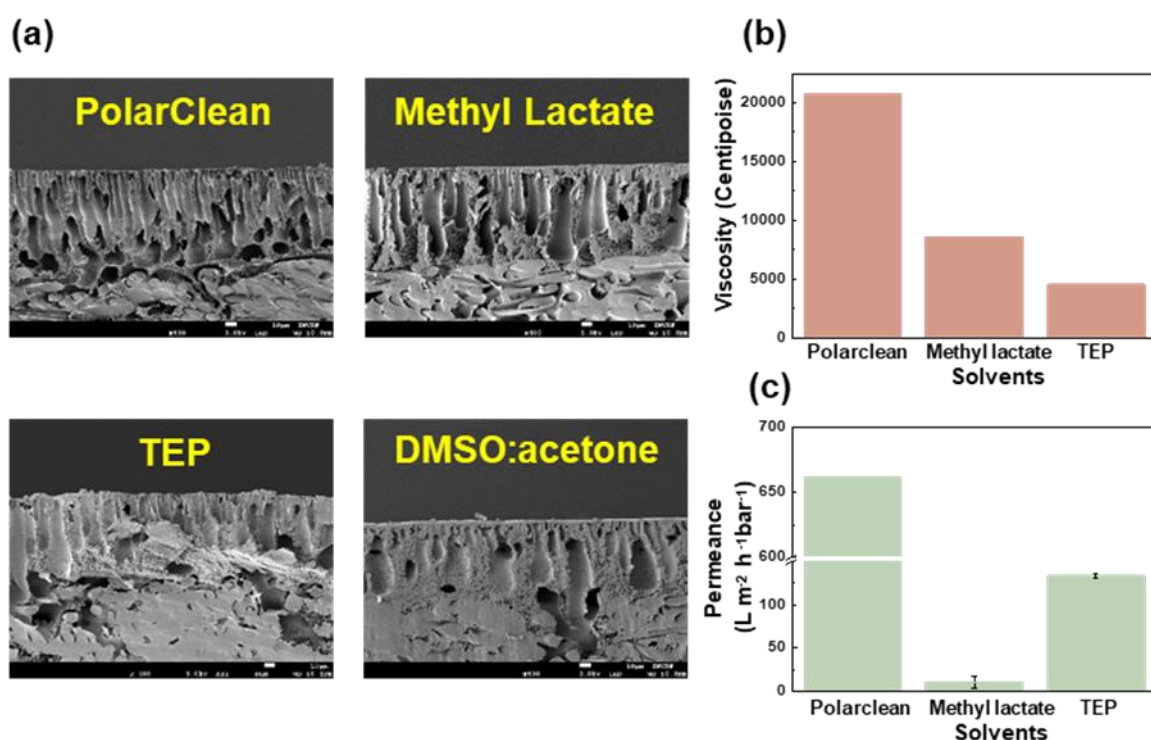


Figure S1. (a) SEM morphology of CA membranes fabricated using green solvents; (b) viscosity of the dope solution; and (c) CA15 membrane permeance in ethanol

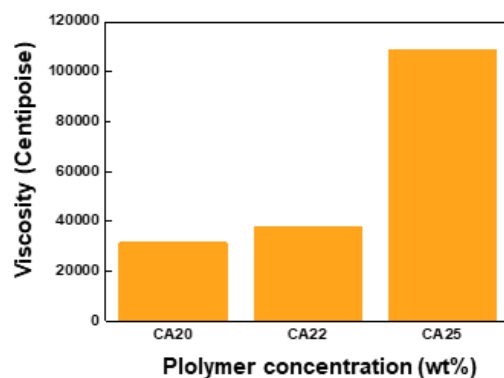


Figure S2. The viscosity of a dope solution containing 20 wt%, 22 wt%, and 25 wt% of CA fabricated from DMSO: acetone. Viscosity was measured using viscosity meter DV2TRVTJ0 (Ametek Brookfield, USA) at 25°C, speed of 2.5–8 rounds per minute (RPM), torque from 50 – 54%.

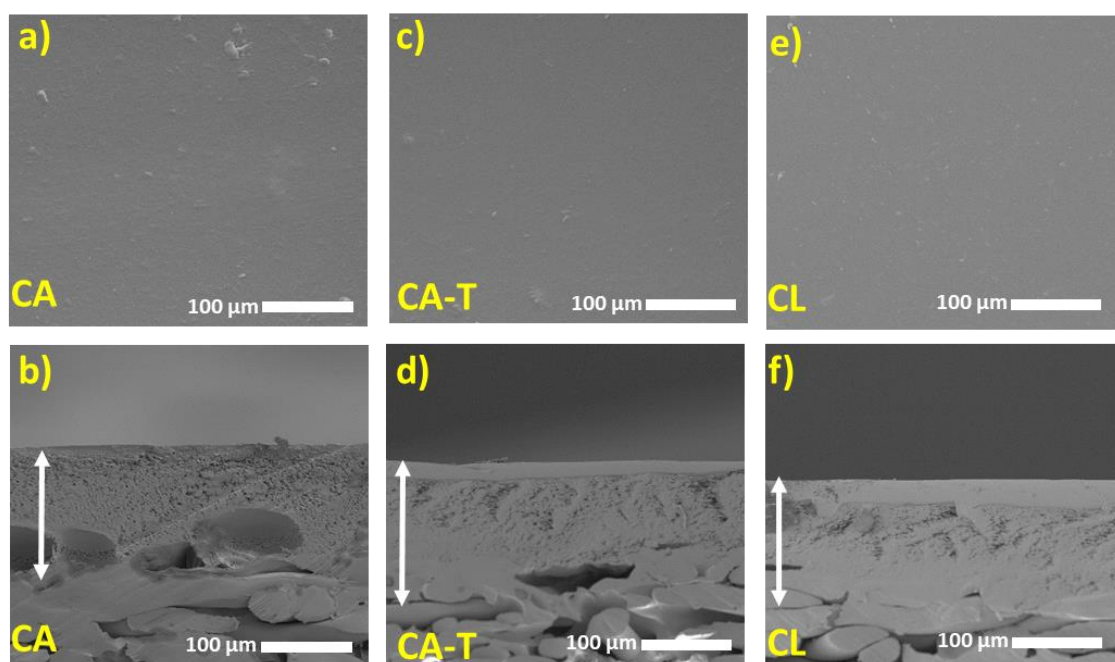


Figure S3. SEM images of cellulose acetate and cellulose membrane fabricated from a dope solution of CA 20 wt% and DMSO:acetone. a) CA surface image, b) CA cross-sectional image, c) CA-T surface image, d) CA-T cross-sectional image, e) CL surface image, f) CL cross-sectional image.

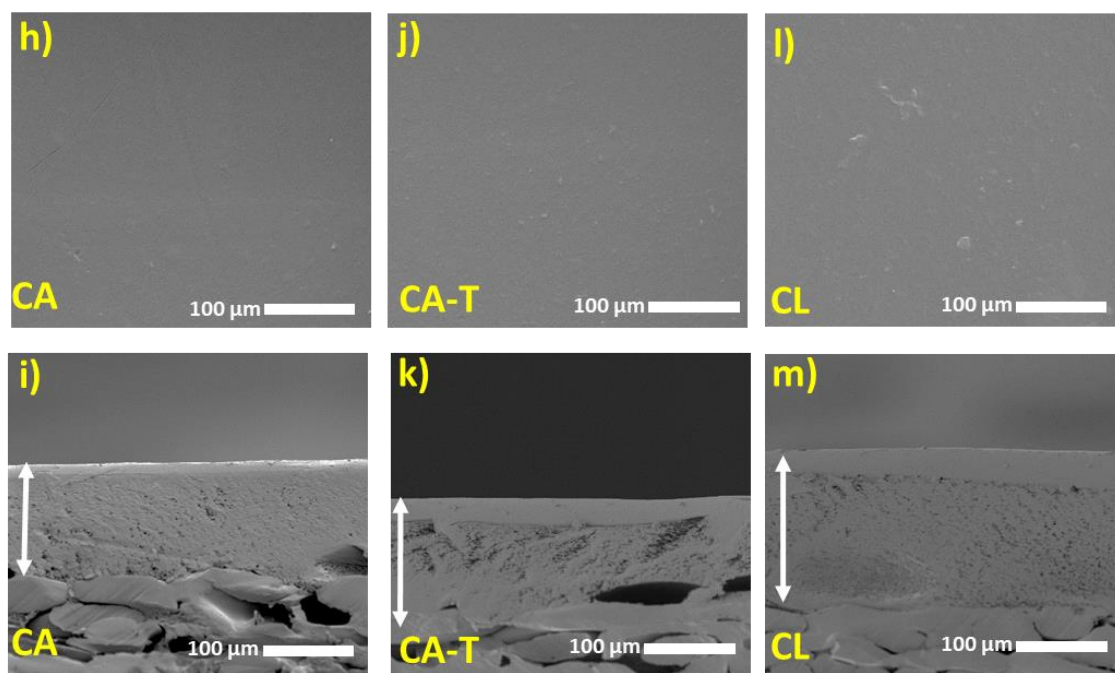


Figure S4. SEM images of cellulose acetate and cellulose membrane fabricated from a dope solution of CA 22 wt% and DMSO:acetone. h) CA surface image, i) CA cross-sectional image, j) CA-T surface image, k) CA-T cross-sectional image, l) CL surface image, m) CL cross-sectional image.

Deacetylation condition optimization

To control the deacetylation condition, we performed the experiment with NaOH aqueous solution ranging from 0–0.2 M. Deacetylation reaction was conducted with various intervals, from 0 to 24 h. We investigated the peak intensity related to the acetyl group employing IR data of cellulose acetate membrane (NaOH 0 M, 0 h reaction) and cellulose membrane (NaOH 0.2 M, 24 h reaction). The calibration region for CA and cellulose membrane of 0 % and 100 % deacetylation was then developed by relating absorbance intensity (x-axis) vs. degree of deacetylation (%) (y-axis) through corresponding peaks. **Figure S5** illustrates the deacetylation degree (%) of the as-prepared samples (confirmed by substituting the C=O peak ($\sim 1720\text{ cm}^{-1}$) and CH₃-C=O peak ($\sim 1230\text{ cm}^{-1}$) intensity values in the FT-IR data) in comparison with the prepared established curve.

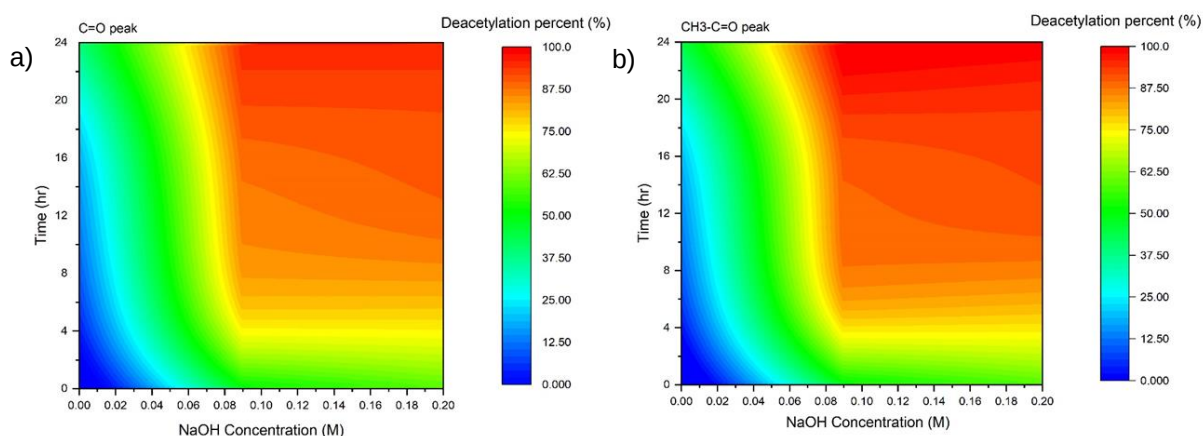


Figure S5. Deacetylation concentration/reaction time conditions deacetylation (%) contour map for C=O peak (a) and CH₃-C=O peak (b).

Mass change in stability experiment

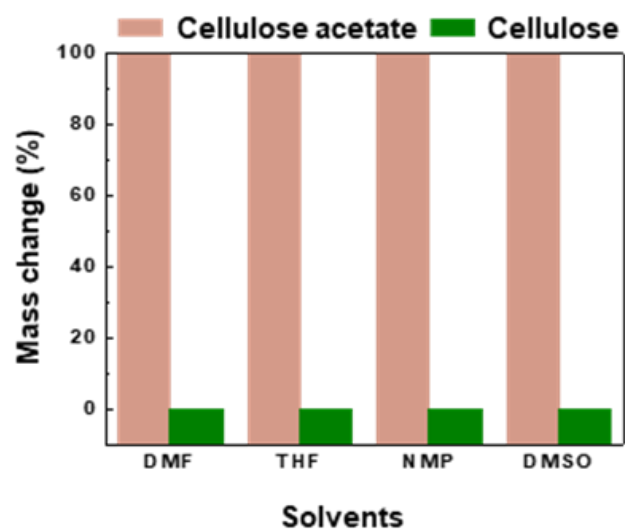


Figure S6. The difference in mass change of CA and cellulose membrane instability experiments with DMF, THF, NMP, and DMSO

Table S1. Mass Change Upon Exposure to Organic Solvents

Solvent	CA	Cellulose
DMF	100 ± 0 %	0.003 ± 0.00278%
THF	100 ± 0 %	0.0068 ± 0.002175%
NMP	100 ± 0 %	0.0036 ± 0.00274%
DMSO	100 ± 0 %	0.0038 ± 0.00261%

Membrane performance

The following figure indicates the rejection (%) of cellulose nanofiltration with added acetonitrile (MeCN). Acetonitrile is another polar aprotic solvent with significantly high solvent factor, which resulted in low PPG rejection.

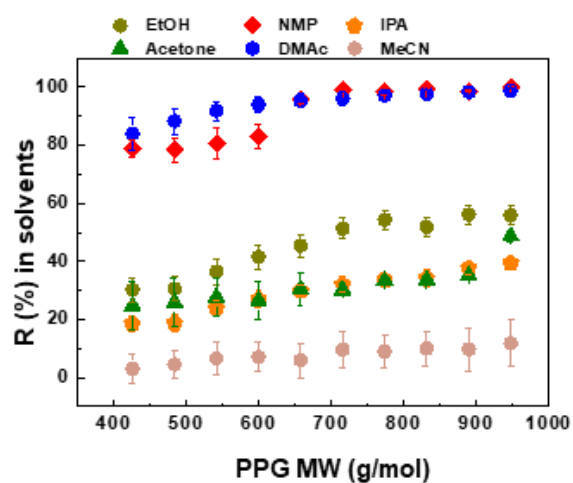


Figure S7. Nanofiltration of cellulose membrane in various solvents

Cross-compared membrane performance

Experiments were conducted to cross-compare the performance of pristine and assessed cellulose membranes. Cellulose membranes that were previously tested with several solvents, were re-tested under similar conditions with pristine cellulose membranes in crossflow utilizing DMAc and MeCN. The performance indicated that there was no significant difference between the two membrane batches, confirming the reliability and reproducibility of the cellulose membrane in OSN application.

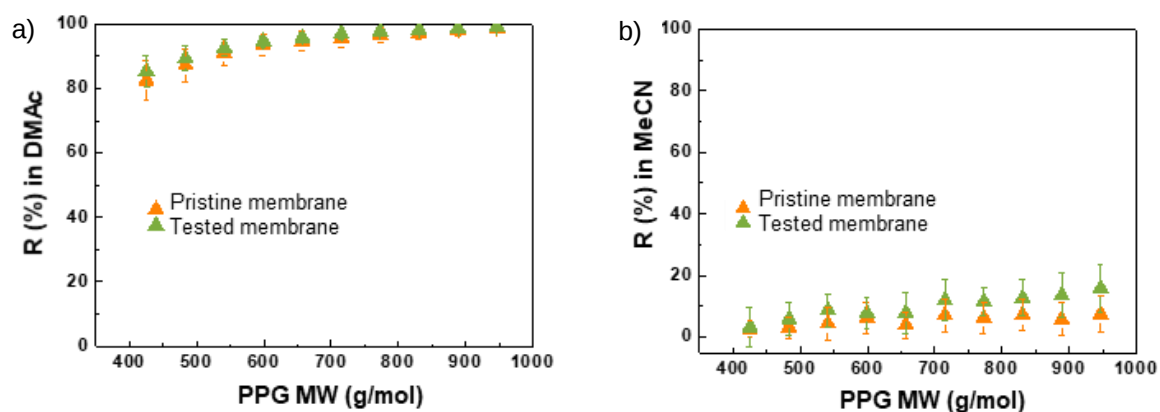


Figure S8. Performance of cellulose membrane (CA 25 wt%) in DMAc (a) and MeCN (b).

Nonpolar Solvent Solute Rejection

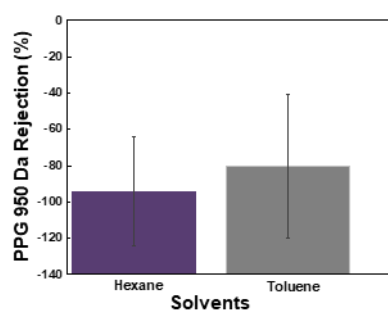


Figure S9. Nonpolar solvent solute rejection data

Solvent Properties and Analysis of Hansen Distance

Table S2. Hansen solubility parameter and physical properties of organic solvents used in nanofiltration study, ²⁻⁷ (Hansen solubility parameters were taken from available values in HSPiP software)

Solvent	Hansen solubility (MPa ^{1/2})			Polarity index (P')	Viscosity (η , cP), 25°C	Molar diameter (d_m , nm)	Dipole moment (D)
	δ_D	δ_P	δ_H				
Hexane	14.9	0	0	0.1	0.31	0.75	0.08
Toluene	18	1.4	2	2.4	0.55	0.70	0.31
IPA	15.8	6.1	16.4	3.9	1.96	0.62	1.66
Acetone	15.5	10.4	7	5.1	0.30	0.62	2.69
EtOH	15.8	8.8	19.4	5.2	1.07	0.57	1.66
DMAc	16.8	11.5	10.2	6.5	0.95	0.67	3.72
NMP	18	12.3	7.2	6.7	1.70	0.68	4.09
MeCN	15.3	18	6.1	5.8	0.37	0.55	3.44

Table S3. Ra between solute, solvent, and membrane⁴

Ra(PPG947-solvent)		Ra(Cellulose-PPG)	Ra(Cellulose-solvent)
NMP	8.81	32.03	27.06
DMAc	9.52		25.91

Octanol-water partition coefficient of PPG

We investigated its radical reactivity ($\log(\text{OHR})$), octanol/water partition coefficient ($\log(\text{Kow})$), and water solubility ($\log(\text{S})$) to see if there is any alteration in PPG's behavior along with higher molecular weight (MW) since the PPG molecule contains a wide range of -OH groups,. **Table S3** shows that the $\log(\text{OHR})$ of PPG also progressively increases with MW, signifying that larger PPG tends to divide into the organic phase than the water phase.

Table S4. Octanol-water partition coefficient of PPG⁴

PPG MW	$\log(\text{OHR})$	$\log(\text{Kow})$	$\log(\text{S})$
76.1	-11.03	-0.99	2
134.2	-10.33	-0.8	2
192.3	-10.12	0.44	-0.56
250.4	-9.49	1.28	2
308.5	-8.88	2.19	2
366.6	-8.29	3.14	2
424.7	-7.72	4.14	2
482.8	-7.15	5.17	2
540.9	-6.59	6.24	2
599	-6.03	7.33	2
657.1	-5.48	8.45	2
715.2	-4.93	9.59	2
773.3	-4.38	10.75	2
831.4	-3.84	11.92	2
889.5	-3.3	13.12	2
947.6	-2.76	14.33	2
1005.7	-2.22	15.55	2

Discussion on charge and different rejection of dyes

The as-fabricated cellulose membrane is super hydrophilic and partially negatively charged in water owing to the ionization of the –OH groups.⁸ The nanofiltration performance for dyes already exhibited high rejection of negatively-charged solutes and the low rejection of the positively-charged one, this can be attributed to the electrostatic interactions. This phenomenon was also identified in the study of F.M. Sukma et al.⁹ They reported negative rejection for positively charged solutes. Furthermore, in ethanol, which is in contrast to water, negatively charged dyes were rejected to a relatively low degree and the performance of positively charge solutes decreased also. Solute may have stronger interactions with the membrane leading to higher sorption in this case,¹⁰ resulting in a greater concentration of solute in the permeate compared with retentate and this would lead to negative rejection. In addition, there have been reports on solute-membrane interactions with dominant effect on solute retentions in literature.¹⁰⁻¹¹ There was another similarity discovered, under the case study conducted by Puspasari et al.:¹⁰ cellulose membranes fabricated by regenerating trimethylsilyl cellulose (TMSC) was able to separate molecules of very similar size but different charge and rejection of negatively-charged molecules by as-prepared membranes was attributed to electrostatic repulsion.

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