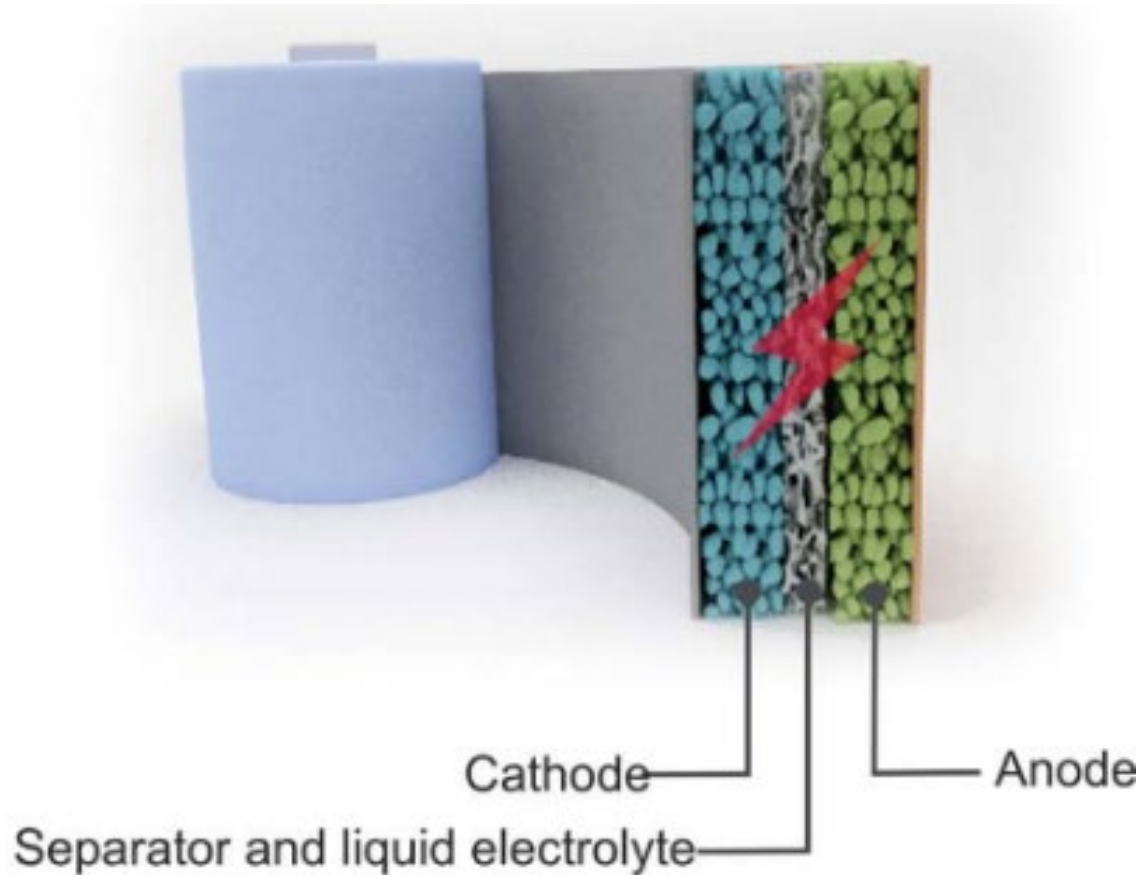


Dewatering Micro- and Nano-fibrillated Cellulose Membranes

Michael S. Reid, Widi Suganda, Emma Östmark, Anders Brolin, Lars Wågberg



Battery Separators



Separator Purpose

- Safety!
- Prevents short circuits and run-away reactions
- Facilitates ion flow
- Improves battery lifespan

Properties

Inert

- Do not influence battery chemistry

Thermally stable

- Operate at high temperatures (do not shrink)

Mechanically robust

- Good wet strength
- Puncture resistant (dendrites)

Porous

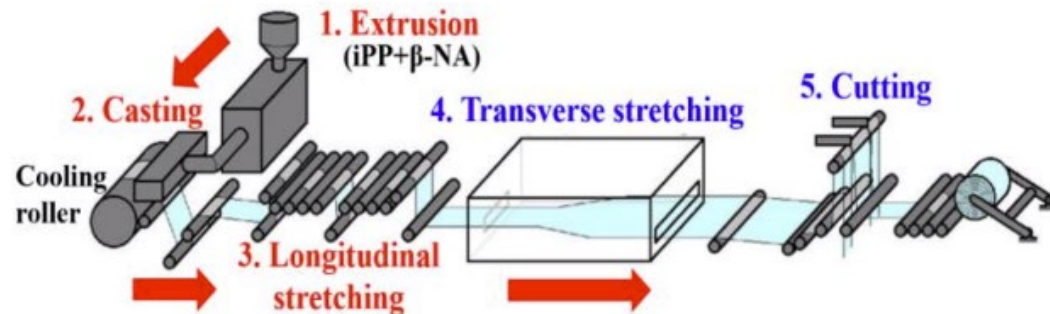
- Allow for ion flow

Thin

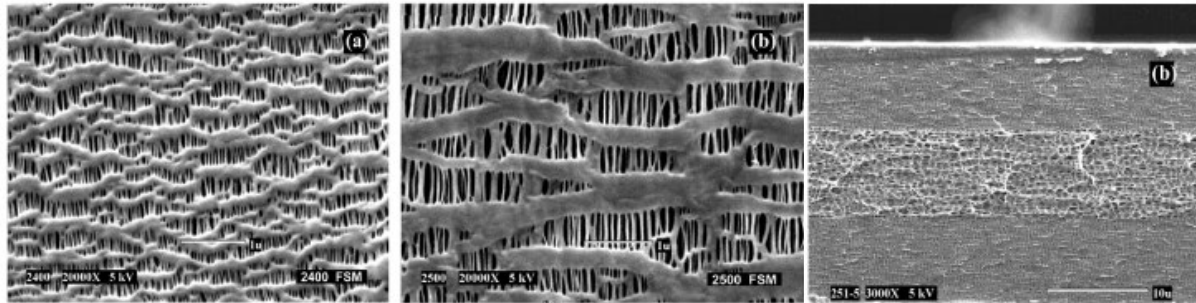
- More room for electrodes, higher power density



Battery Separators



Wu, et al. *Chin. J. Chem.* 2019, 37, 1207-1215



Arora, et al., *Chemical Reviews*, 2004, 104, 10

“The majority of the separators currently used in batteries were typically developed as spin-offs of existing technologies. They were usually not developed specifically for those batteries and thus are not completely optimized for systems in which they are used. One positive result of adapting existing technologies is that they are produced in high volume at relatively low cost. The availability of low-cost separators is an important consideration in the commercialization of batteries, because the battery industry traditionally operates with thin profit margins and relatively small research budgets.”

-Arora and Zhang *Chem. Rev.* 2004, 104, 4419–4462

Cellulose Battery Separators



Voltaic Pile

1820

Properties

- ✓ Inert
- ✓ Thermally stable
- ✓ Mechanically robust
- ✓ Porous
- ✓ Thin

Tailored for specific applications

- Cellulose can be utilized at numerous length scales as fibers microfibril, nanofibrils and polymers
- Functionalized chemically to optimize performance.

Cellulose (2017) 24:4103–4122
DOI 10.1007/s10570-017-1421-8



REVIEW PAPER

Recent developments of cellulose materials for lithium-ion battery separators

Jie Sheng · Shuhua Tong · Zhibin He · Rendang Yang

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Cellulose and its derivatives for lithium ion battery separators: A review on the processing methods and properties

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Research Questions

What dewatering behavior do MFCs and CNFs exhibit?

- Are there useful models?

What factors impact dewatering?

- Pressure, temperature, pH, ionic strength

How do mixtures affect dewatering and structure?

- Do CNFs fill gaps to slow dewatering?

Materials

MFC Grades

- Coarse – MFC-500
- Intermediate – MFC-50
- Fine – MFC-15

Carboxymethylated CNF

	Charge ($\mu\text{eq/g}$)	% Fines with Length <200 μm^a	% Fines with length <50 μm^a	Mean fiber distributions (μm) ^b		
				D _x (10)	D _x (50)	D _x (90)
MFC-500	10	51.5 $\pm$ 0.1	32.8 $\pm$ 0.5	-	-	-
MFC-50	20	79.2 $\pm$ 0.1	55.1 $\pm$ 0.2	12.7 $\pm$ 0.1	61.5 $\pm$ 0.4	226 $\pm$ 3
MFC-15	20	99.8 $\pm$ 0.1	96.5 $\pm$ 0.1	9.7 2 ± 0.03	20.1 $\pm$ 0.1	39.9 $\pm$ 0.3
CNF	560	100	100	-	-	-

MFC and CNF Morphology

Uncharged

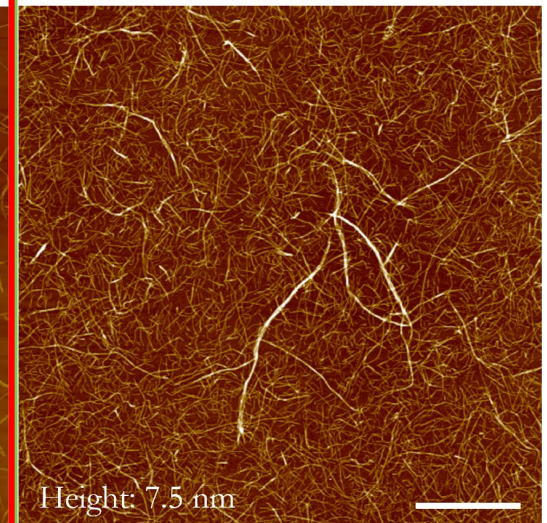
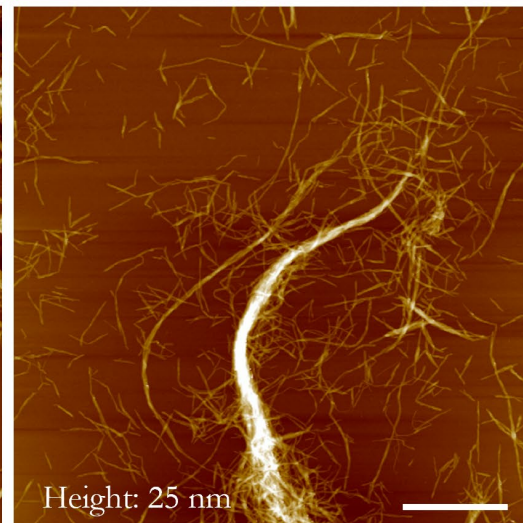
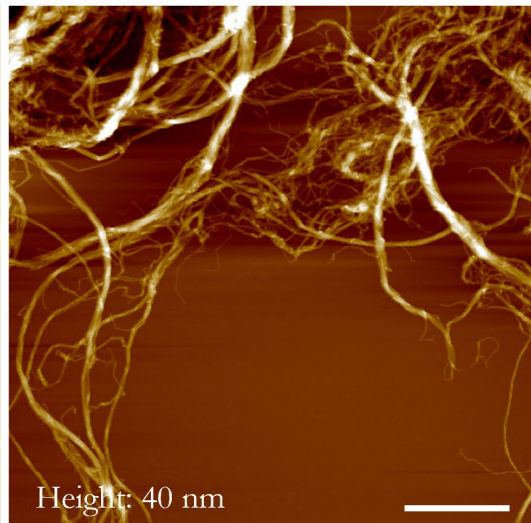
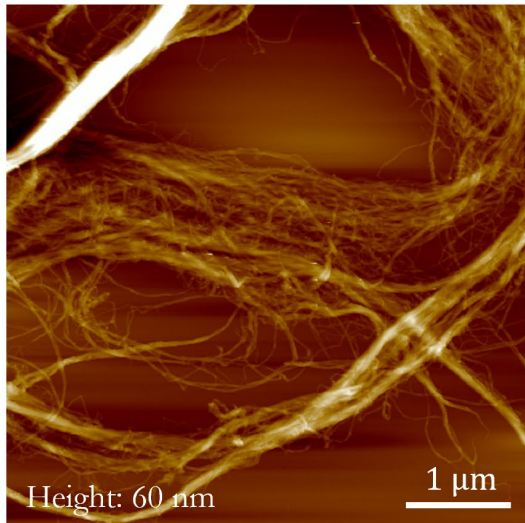
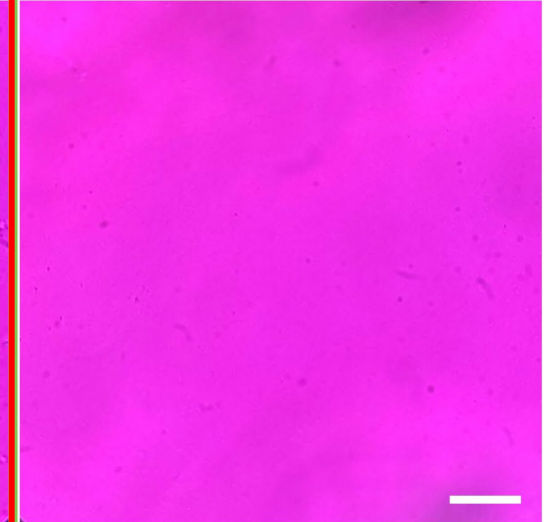
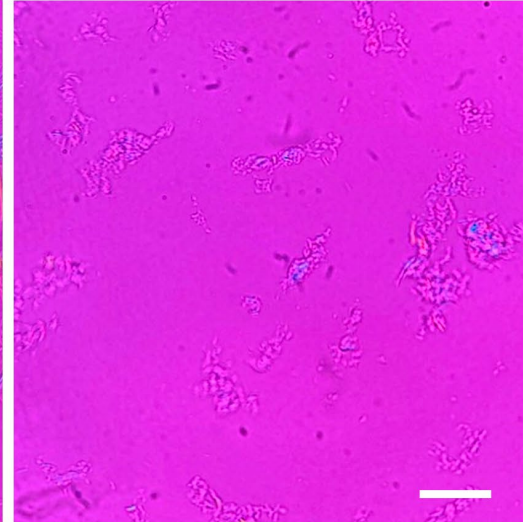
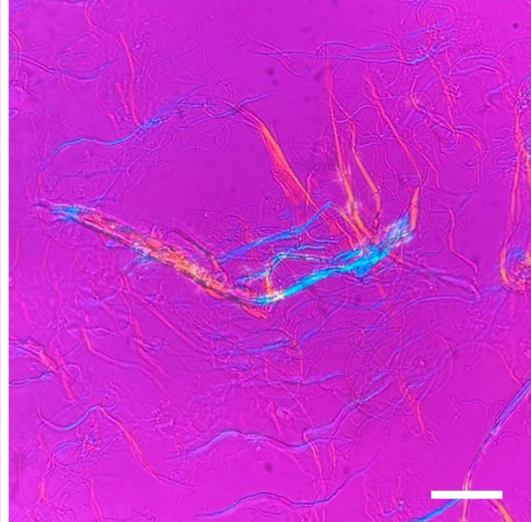
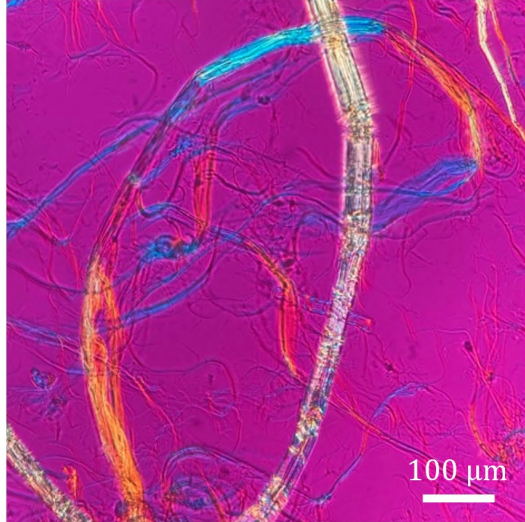
600 $\mu\text{eq/g}$

MFC-500

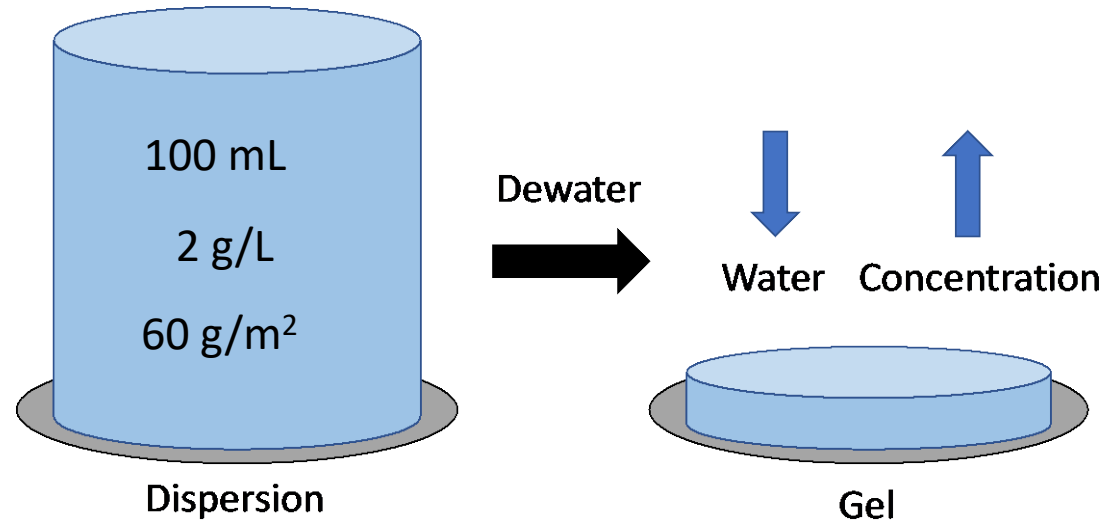
MFC-50

MFC-15

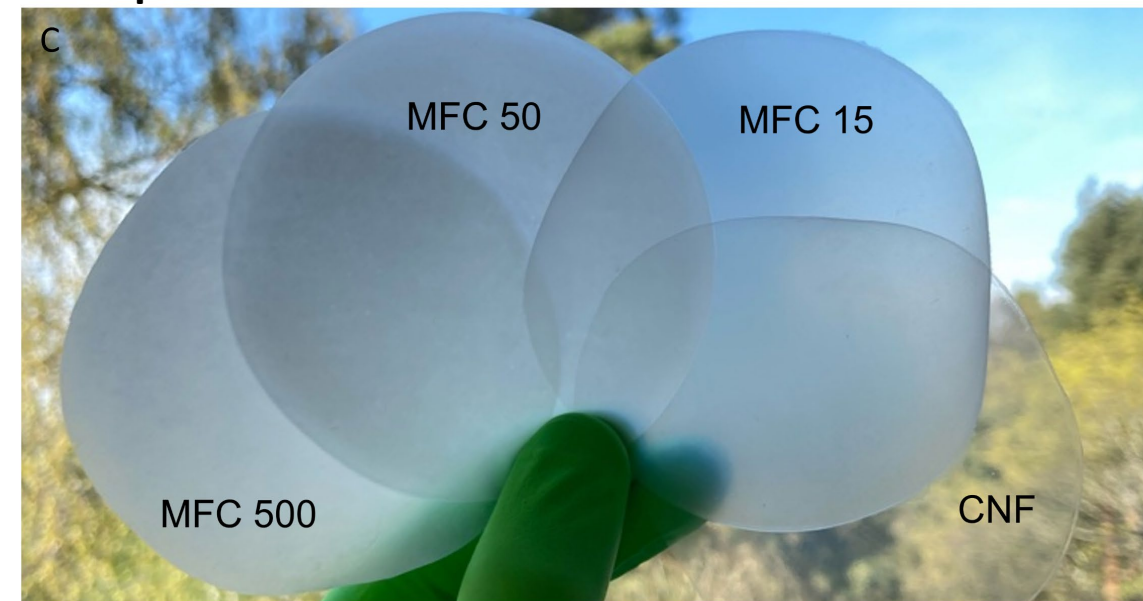
CNF



Dewatering Procedure



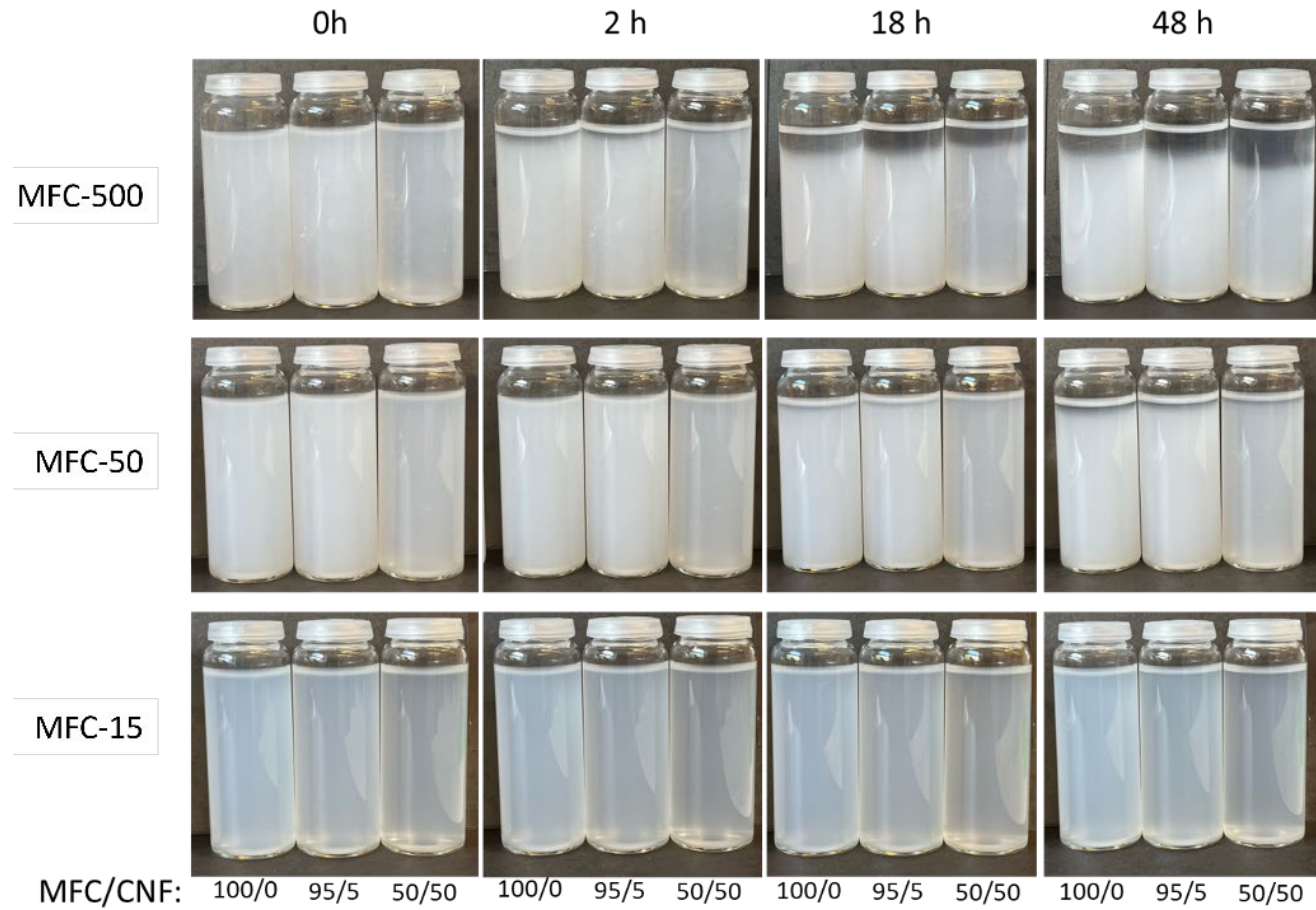
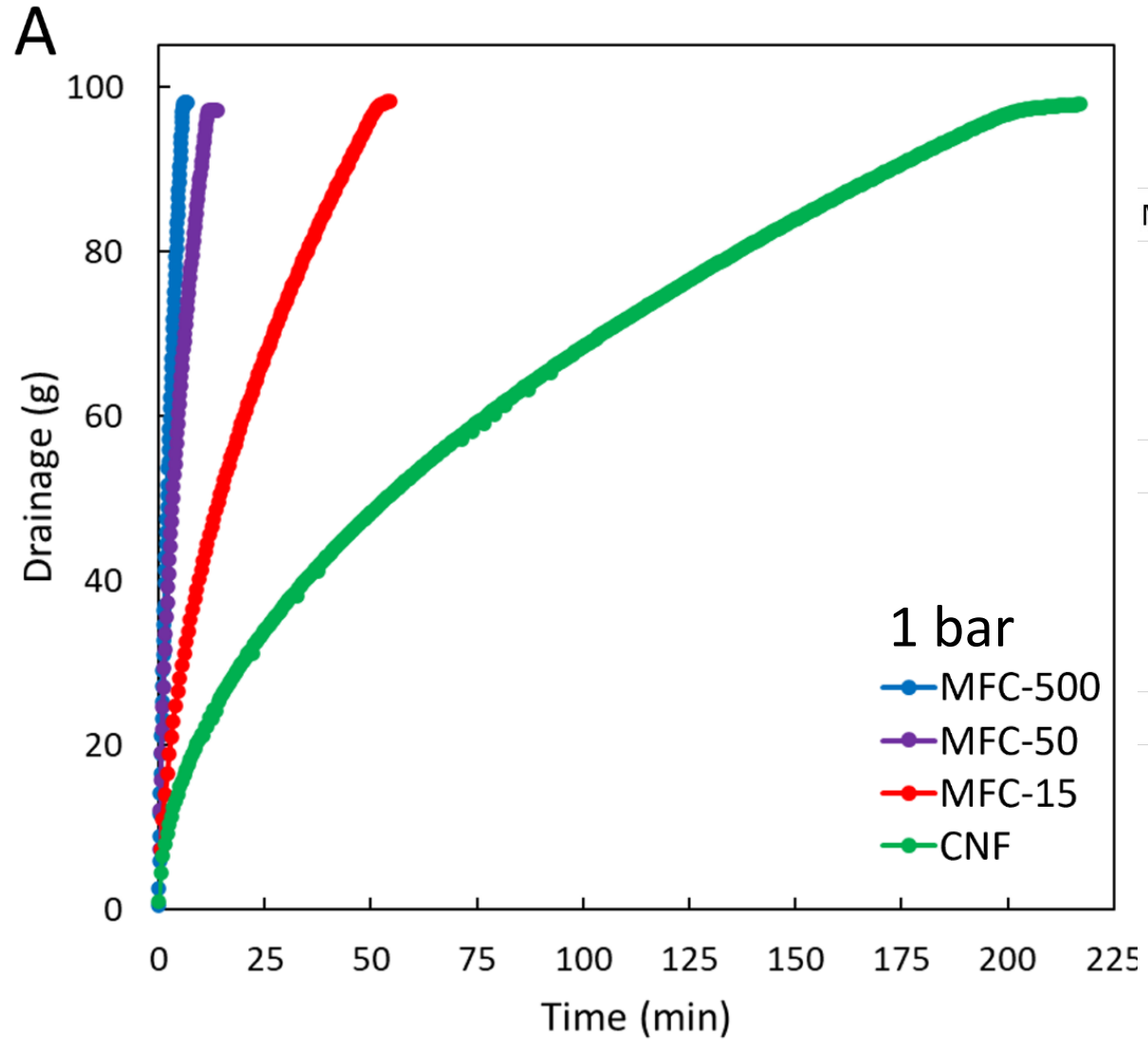
**Dewatering measured gravimetrically and stopped at 96-97 g.
Gels hot pressed at 94C for 15 min**



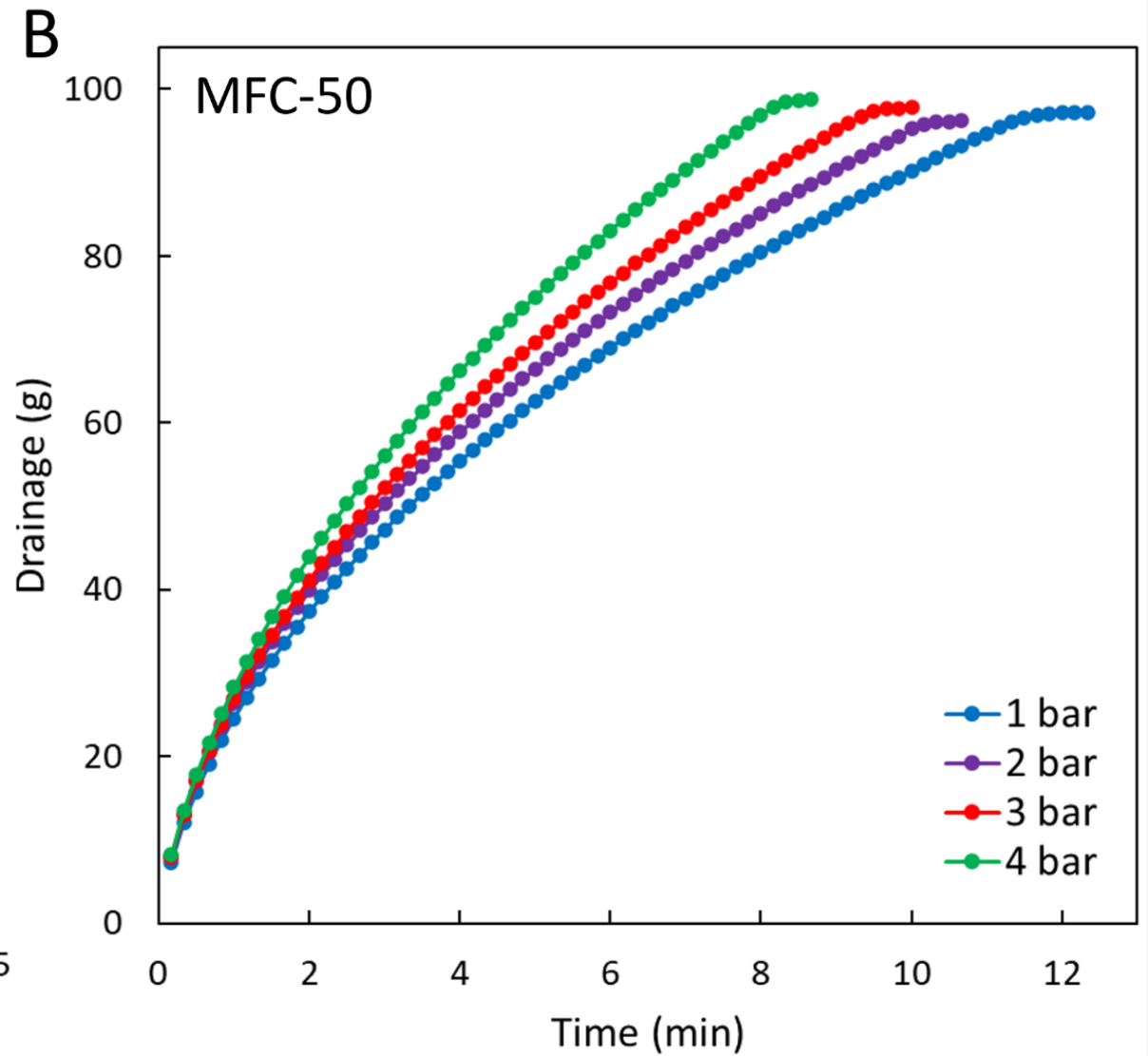
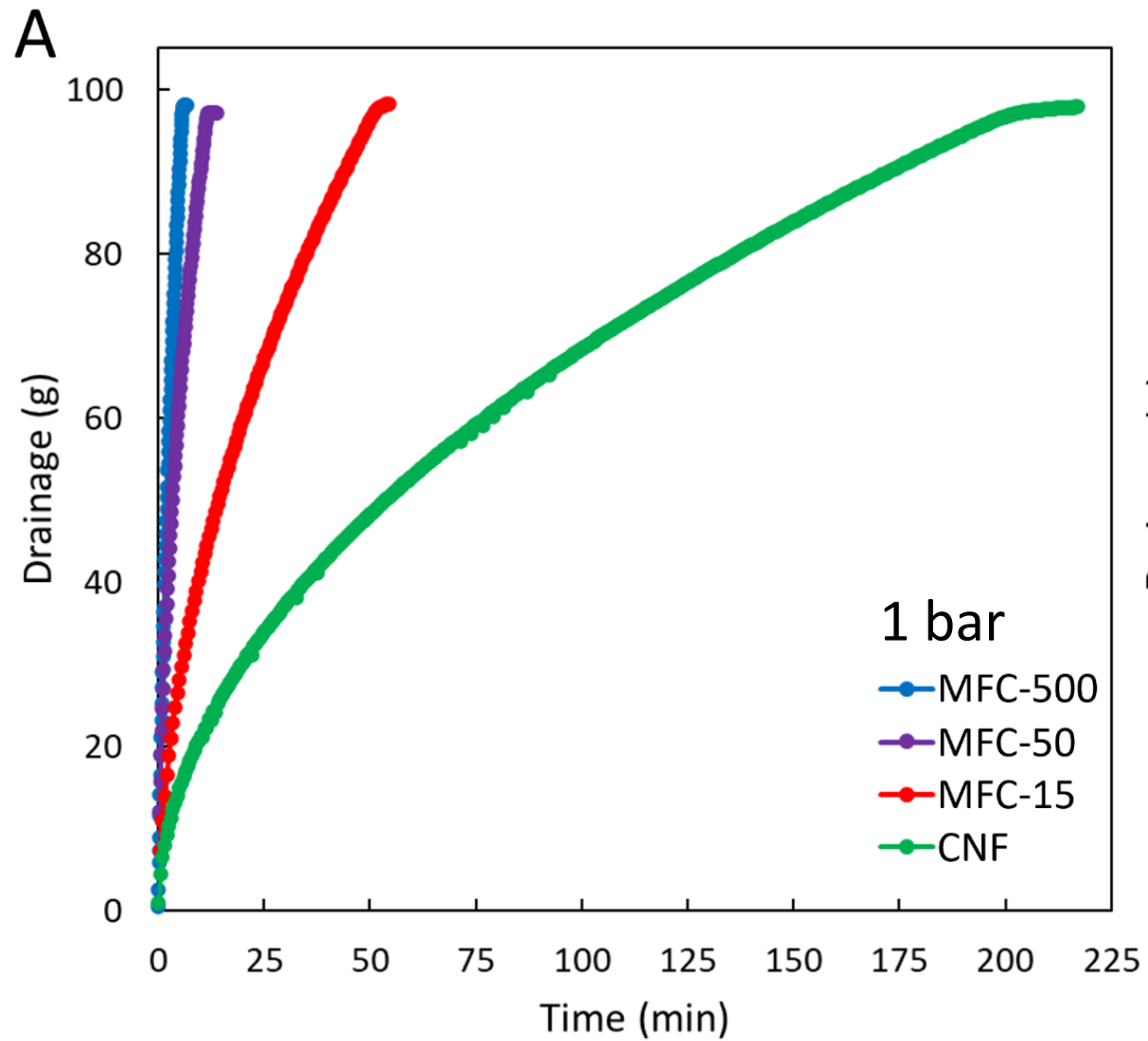
Film thickness: 35-50 μm



Dewatering

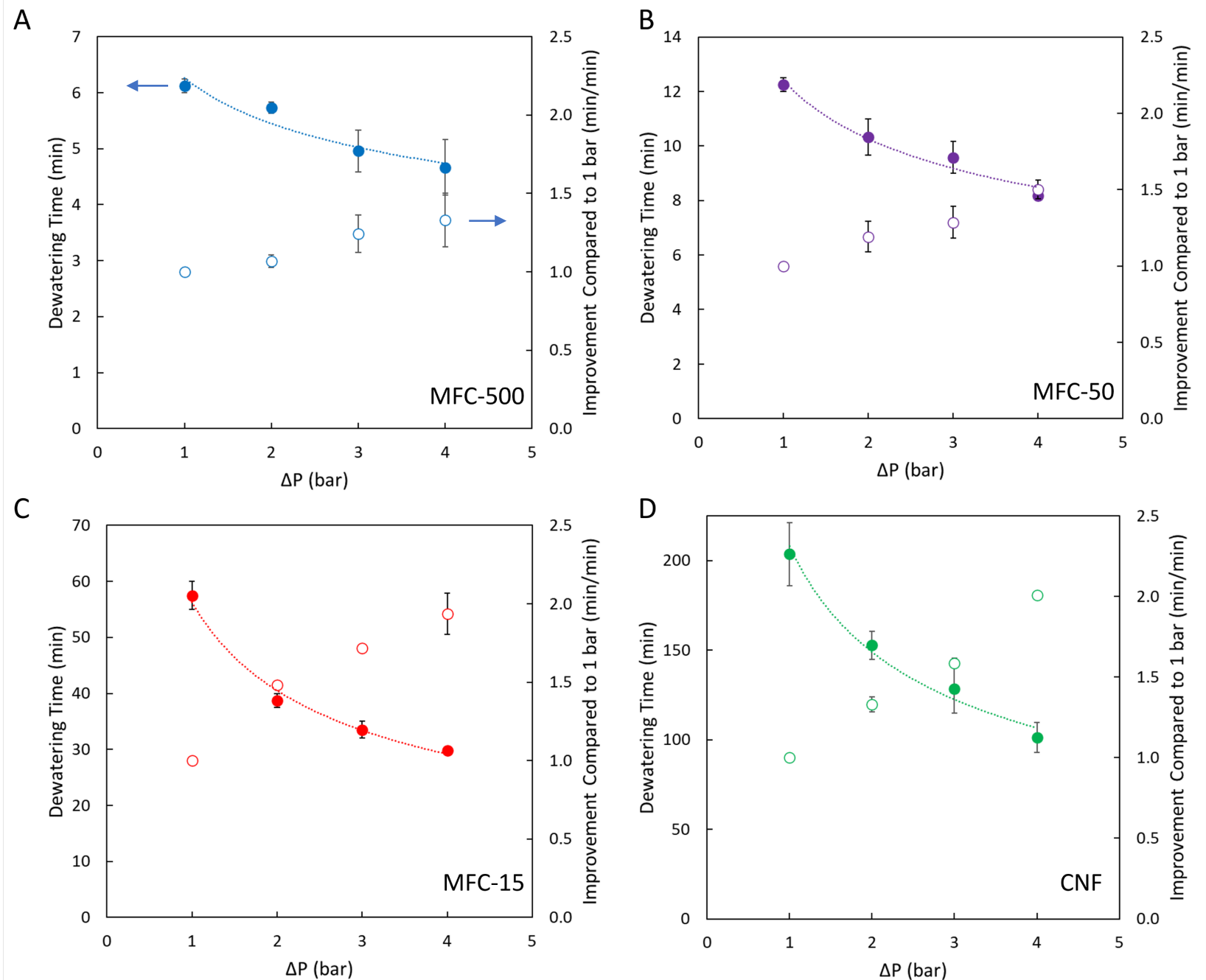


Dewatering

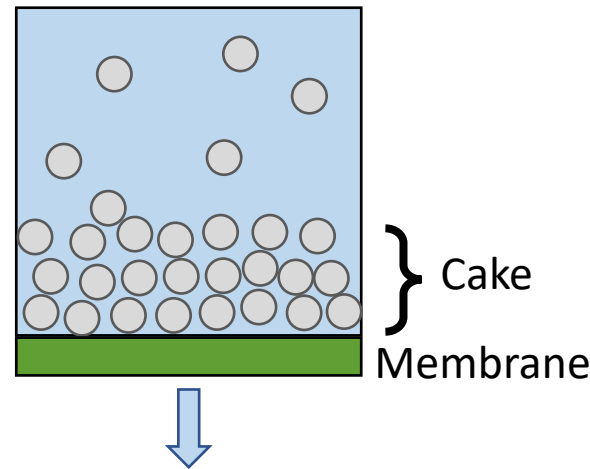


Dewatering

- Increasing pressure can significantly improve dewatering times
- Diminishing returns for coarser material. Can we explain this?



Dewatering



*Assume uniform pressure across the cake

$$\Delta P = \Delta P_{cake} + \Delta P_{membrane}$$

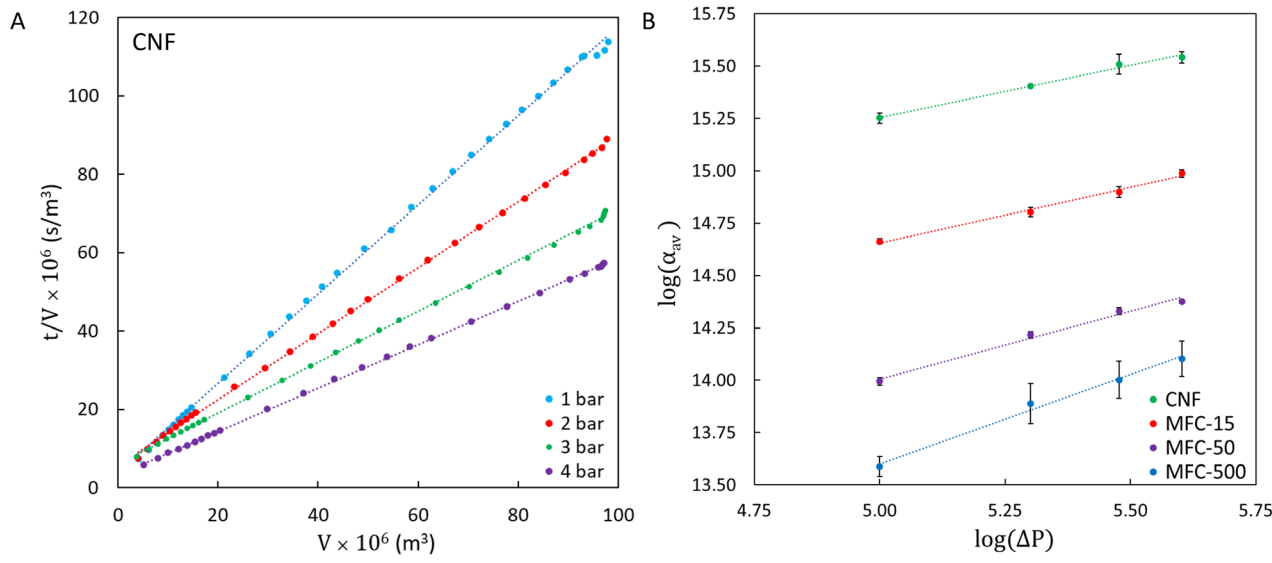
Darcy’s Law

$$v = K \frac{\Delta P}{\mu L} = \frac{1}{A} \frac{dV}{dt}$$

$$\frac{t}{V} = \frac{\alpha_{av} \mu S}{2A^2 \Delta P} V + \frac{\mu R_m}{A \Delta P}$$

Compressibility

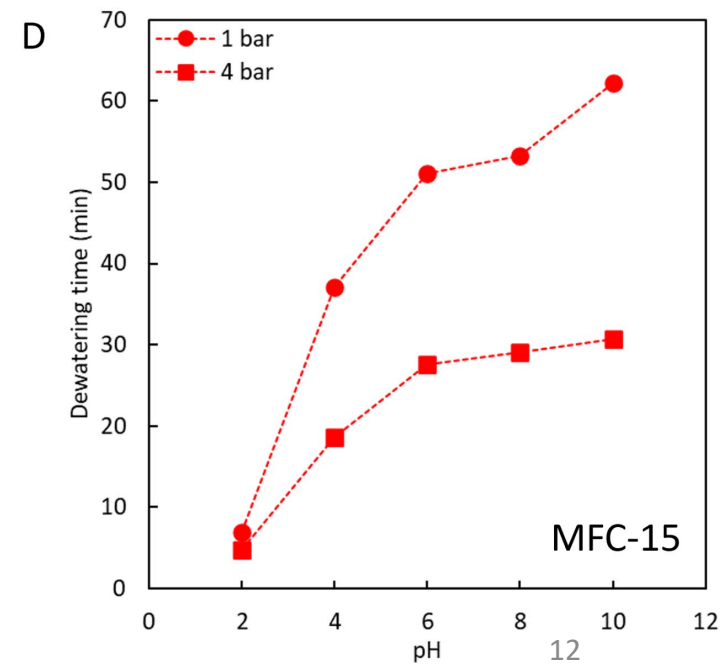
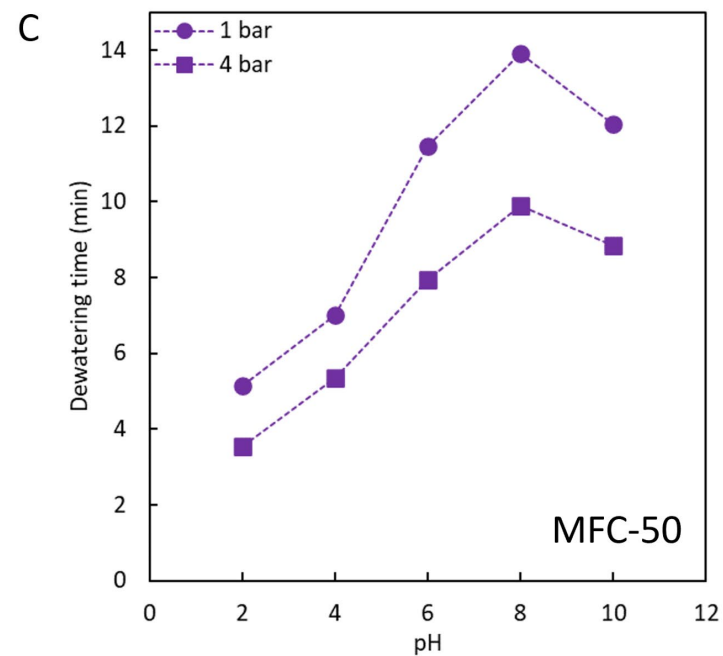
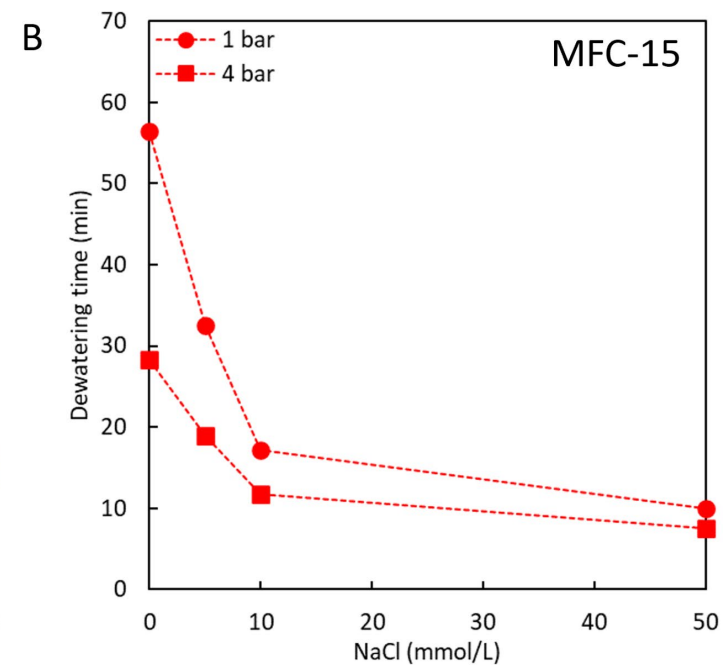
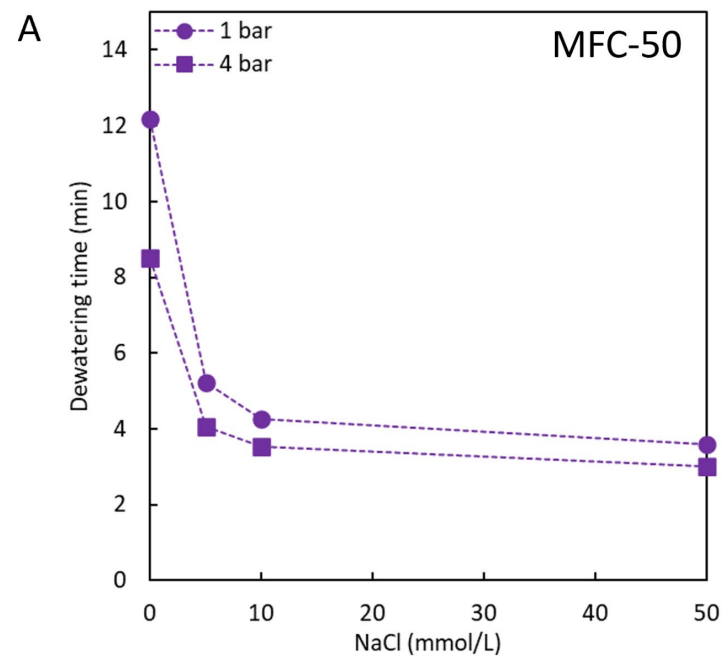
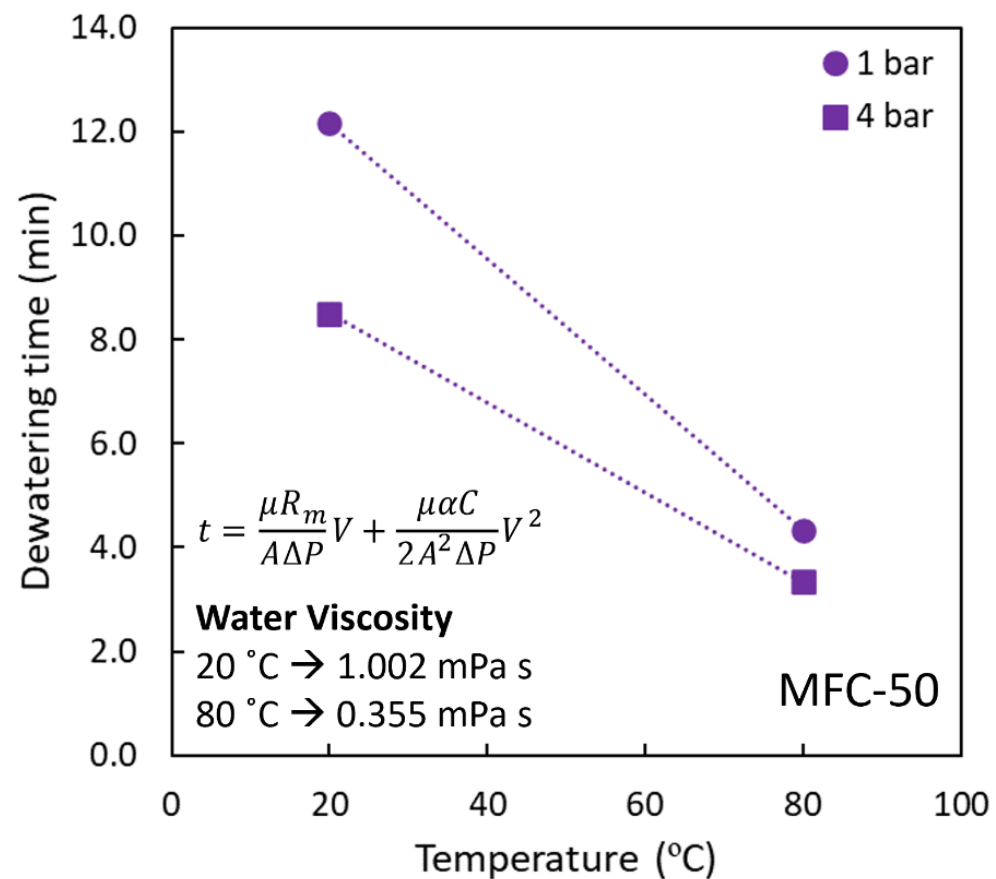
$$\alpha_{av} = a_i \Delta P^\eta$$



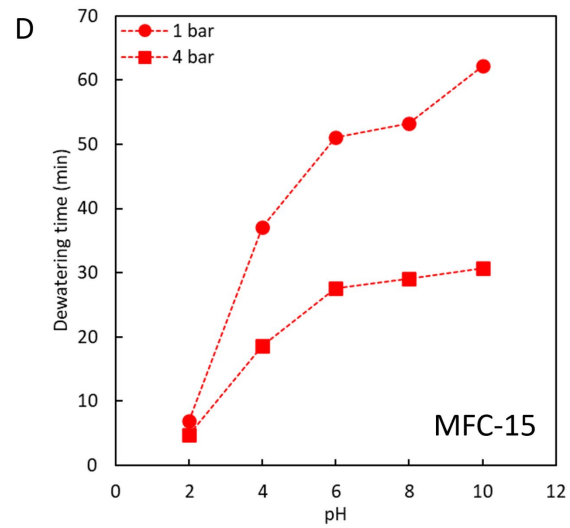
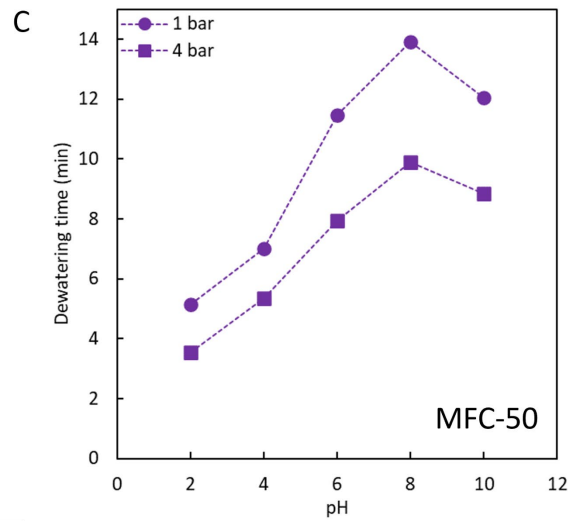
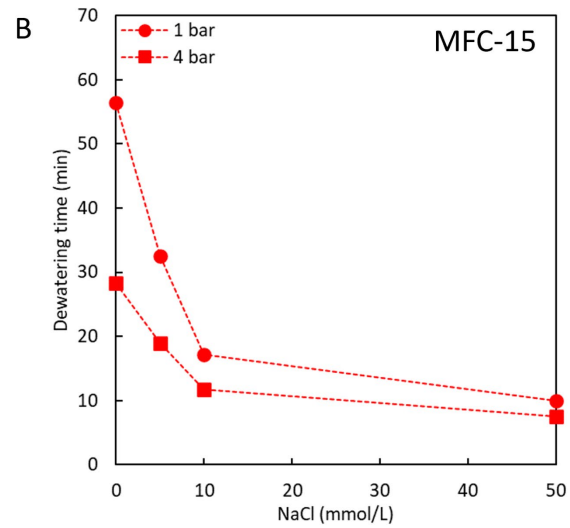
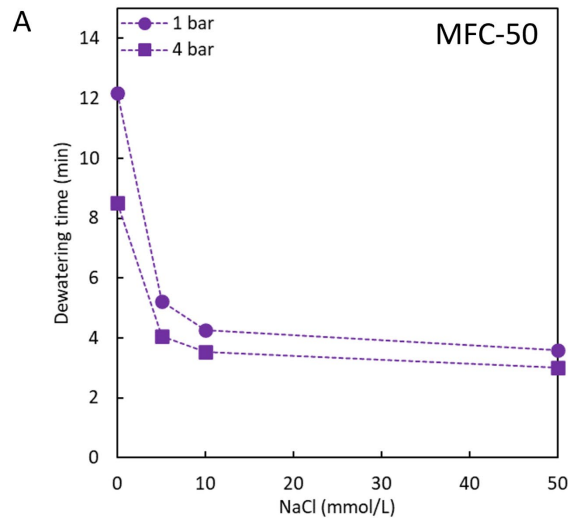
α_{av} cake resistance ($\times 10^{14}$) m/kg

Pressure (bar)	MFC-500	MFC-50	MFC-15	CNF
1	0.38 ±0.04	0.98 ± 0.04	4.60 ± 0.14	17.90 ± 1
2	0.79 ± 0.17	1.64 ± 0.06	6.36 ± 0.31	25.39 ± 0.47
3	1.0 ± 0.2	2.13 ± 0.08	7.94 ± 0.47	32.49 ± 3.6
4	1.29 ± 0.25	2.38 ± 0.04	9.73 ± 0.40	34.92 ± 2.1
n	0.85	0.64	0.53	0.50

Salt, pH and Temperature



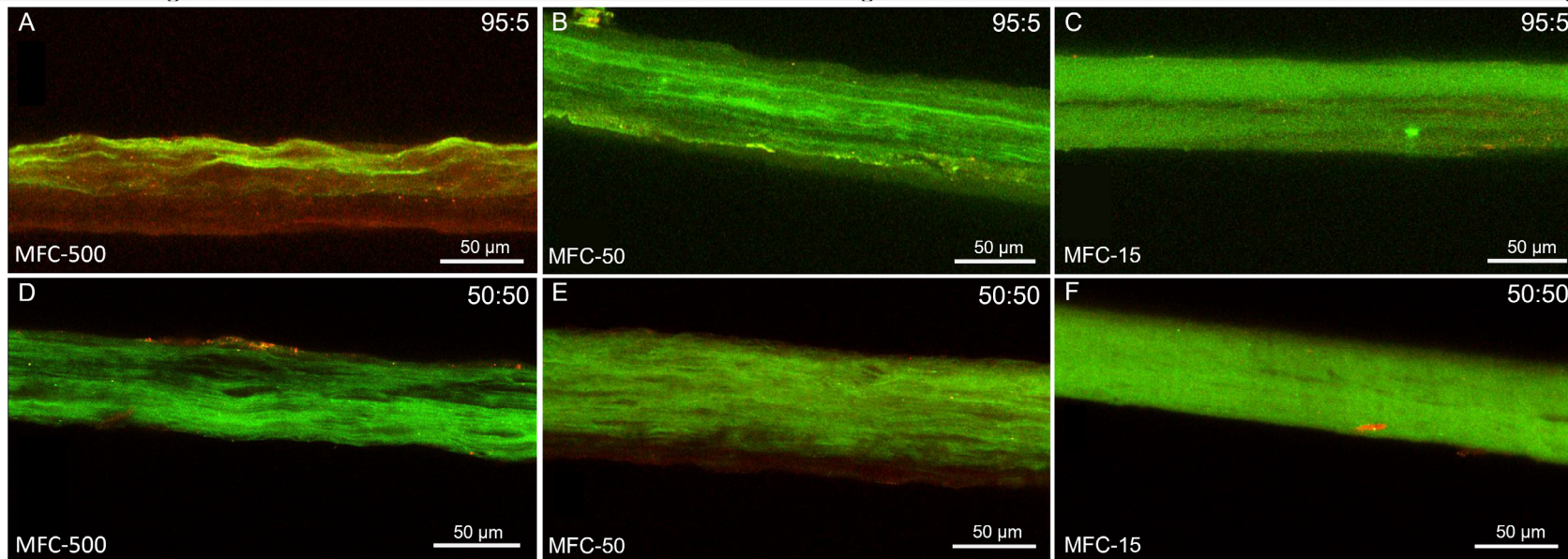
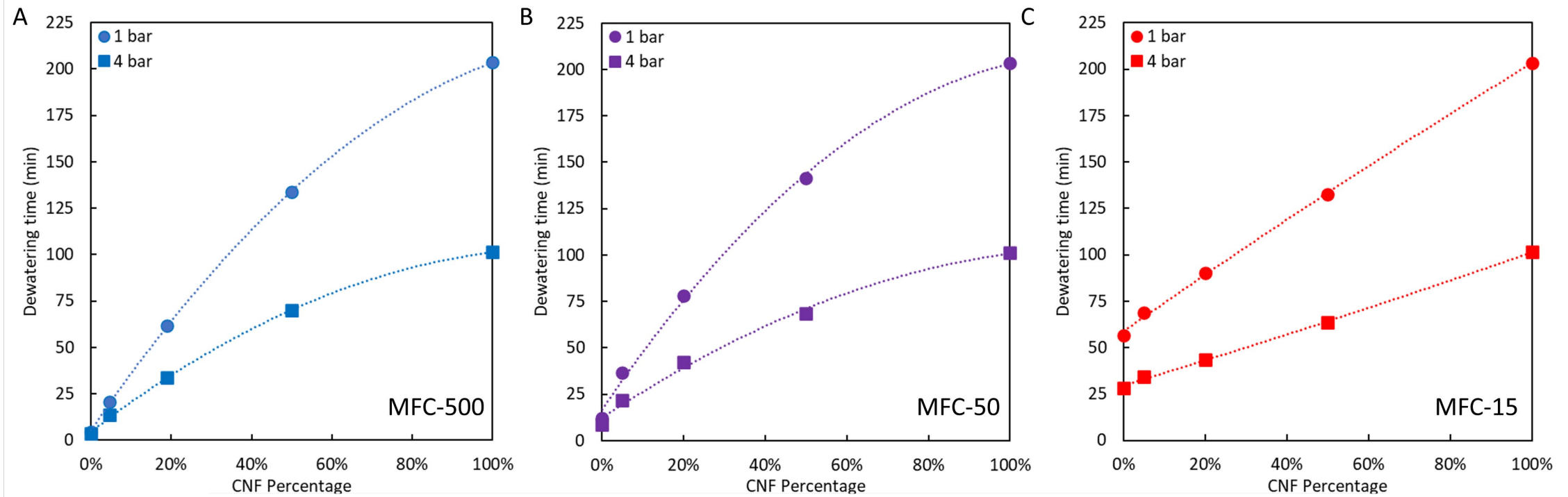
Salt, pH and Temperature



		α_{av} cake resistance ($\times 10^{14}$) m/kg			
		0 mM	5 mM	10 mM	50 mM
MFC-50	1	0.98 ± 0.04	0.52 ± 0.01	0.51 ± 0.01	0.51 ± 0.01
	4	2.38 ± 0.04	2.10 ± 0.03	1.98 ± 0.12	1.93 ± 0.01
	<i>n</i>	0.64	1.01	0.99	0.96
MFC-15	1	4.60 ± 0.14	2.76 ± 0.03	1.69 ± 0.01	1.08 ± 0.02
	4	9.73 ± 0.40	7.07 ± 0.05	4.29 ± 0.11	2.88 ± 0.07
	<i>n</i>	0.53	0.69	0.67	0.71

		α_{av} cake resistance ($\times 10^{14}$) m/kg				
		pH 2	pH 4	pH 6	pH 8	pH 10
MFC-50	1	0.48 ± 0.01	0.57 ± 0.02	0.86 ± 0.03	1.07 ± 0.02	1.01 ± 0.01
	4	1.66 ± 0.01	2.04 ± 0.05	2.61 ± 0.08	3.27 ± 0.01	3.07 ± 0.20
	<i>n</i>	0.89	0.91	0.80	0.80	0.80
MFC-15	1	0.95 ± 0.08	2.83 ± 0.03	4.43 ± 0.32	4.49 ± 0.10	5.14 ± 0.27
	4	1.78 ± 0.02	5.40 ± 0.12	8.44 ± 0.10	9.39 ± 0.01	9.58 ± 0.27
	<i>n</i>	0.45	0.47	0.47	0.53	0.45

Mixed MFC/CNF Membranes



Take Aways

- MFC/CNFs generally follow conventional dewatering theories
- Pressure is an effective way to reduce dewatering times. Particularly for highly fibrillated MFC/CNF
- Salt, pH, temperature can improve dewatering times, but at the cost of film properties
- Potential to control properties by mixing MFC/CNF membranes

Thanks!

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