Data Analytics for Membrane Material Innovations

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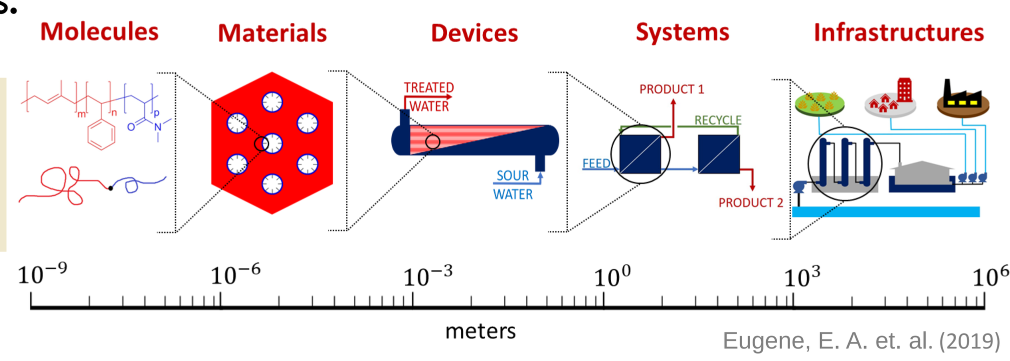
Introduction

Background

Structure-property-performance relationships provide the fundamental knowledge to guide both the inverse material design and the large-scale process design for novel membrane applications.

Molecular-to-Infrastructure Design

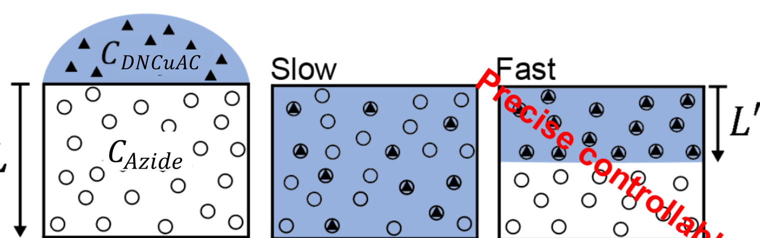


Eugene, E. A. et. al. (2019)

Purpose

How data analytics help facilitate membrane innovations?

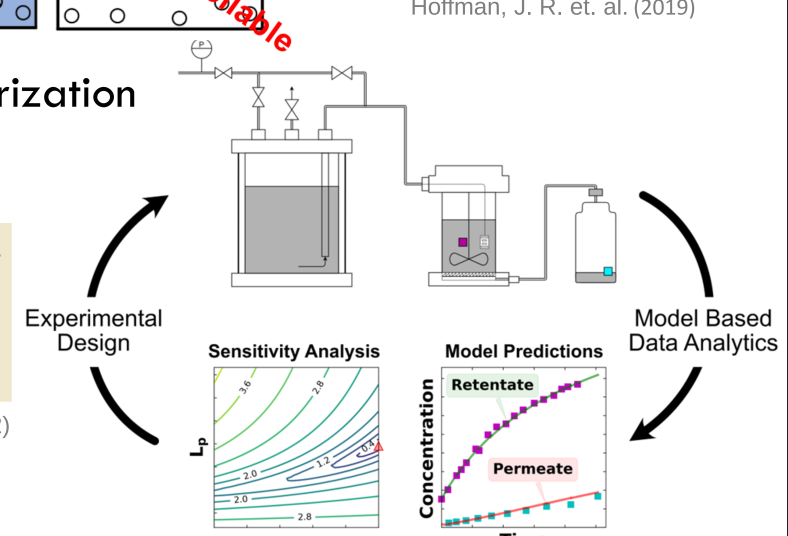
- Membrane Functionalization



Precise Control of the Structure

Hoffman, J. R. et. al. (2019)

- Membrane Characterization

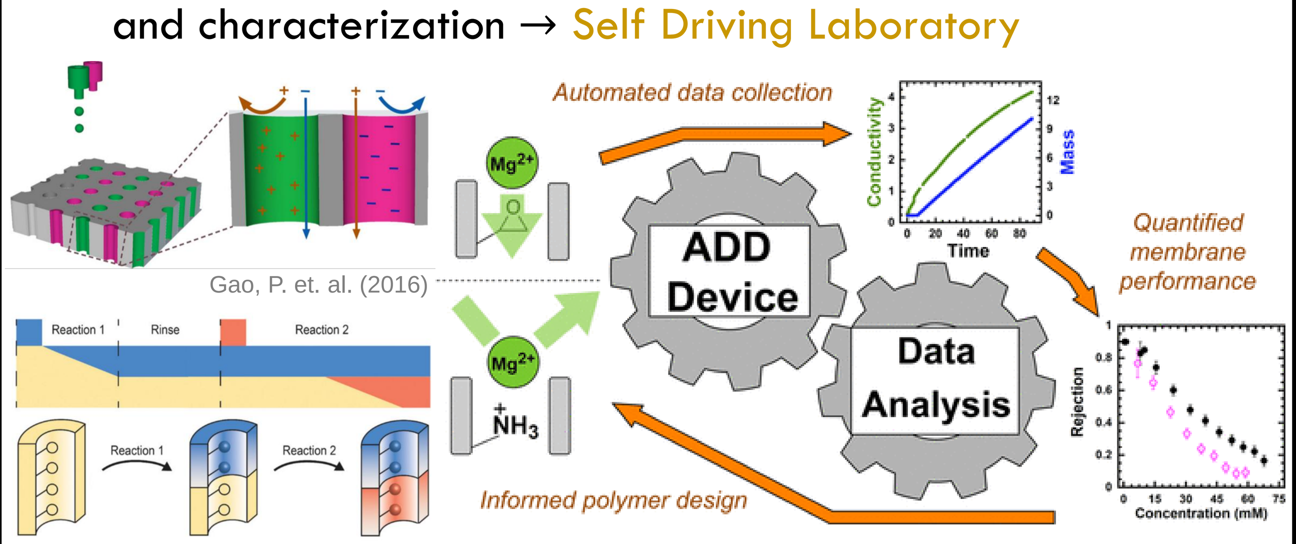


DATA: Diafiltration Apparatus for high-Throughput Analysis

Ouimet, J. A. et. al. (2022)

Future Work

- ❑ MBDoE for model discrimination, with 1000+ build from model hierarchy
- ❑ System automation for both membrane functionalization and characterization → Self Driving Laboratory



Gao, P. et. al. (2016)

Hoffman, J. R. et. al. (2020)

Muetzel, Z. W. et. al. (2022)

References & Additional Information

Reactive Inks	DATA	MBDoE	Dowling Lab	Email Contact
Liu, X., et. al. (2022)	Ouimet, J. A. et. al. (2022)	Liu, X., et. al. (2022)		

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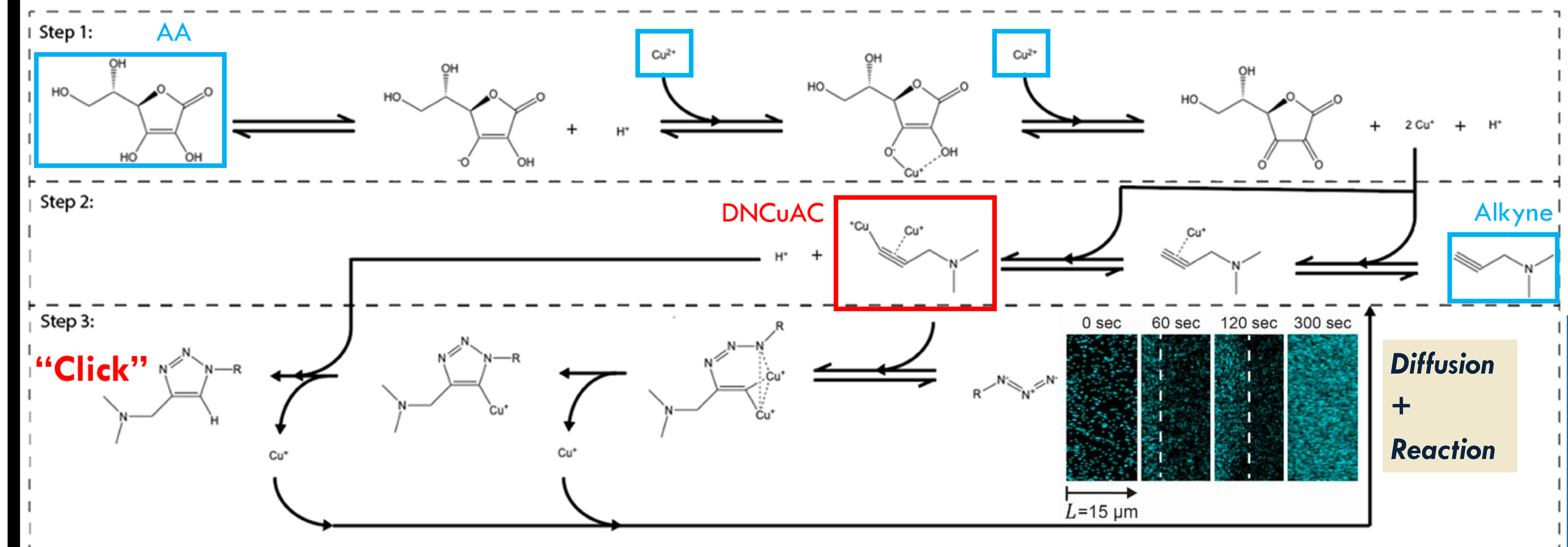
Precise Controllable Membrane Functionalization

"Click" reaction



Diffusion + Reaction

Experimentalists loaded excess harmful components (i.e., copper) to achieve a high concentration of DNCuAC for fast reaction.

Visually observe the functionalization process by Scanning Electron Microscopy−Energy Dispersive X-ray Spectrometry (SEM-EDX)

Hoffman, J. R. et. al. (2019)

Optimize reactive ink formulation

$$\min_x \; w^T x \quad \text{- Cost of ink}$$

$$s.t. \quad \theta(t_{end}) \geq \theta^*$$

- Fast conversion requirements

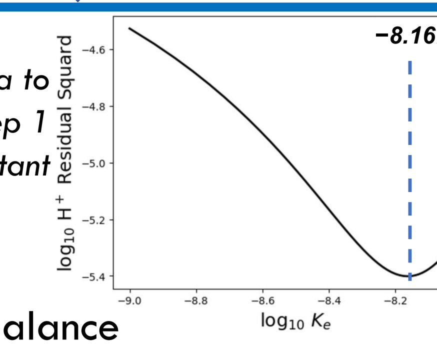
$$\theta(t_{end}) = f_3(C_{D0}, C_{A0})$$

- Step 3 model

$$C_{D0} = f_{1,2}(x)$$

- Step 1&2 model

Use pH data to identify step 1 equilibrium constant



Equations:

- Charge balance
- Reaction (main + side) equilibriums
- Component conservations

Diffusion-reaction

$$\frac{\partial C_D}{\partial t} = D\frac{\partial^2 C_D}{\partial z^2} - k_{az} C_A \cdot C_D$$

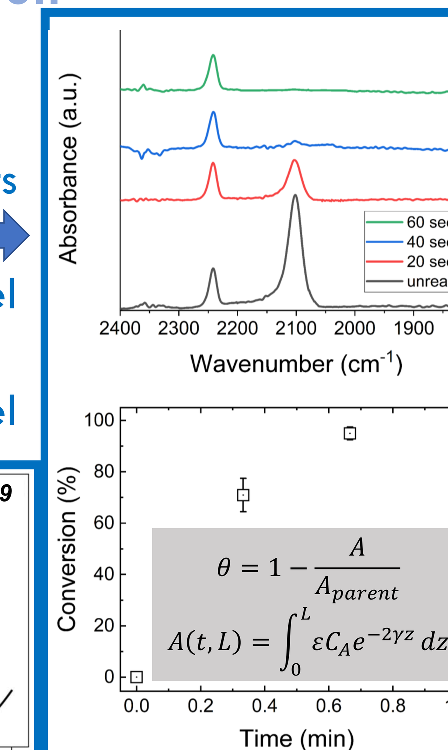
$$\frac{\partial C_A}{\partial t} = -k_{az} C_A \cdot C_D$$

I.C. $C_D(0,z) = 0, \forall z > 0$

$C_A(0,z) = C_{A0}, \forall z \geq 0$

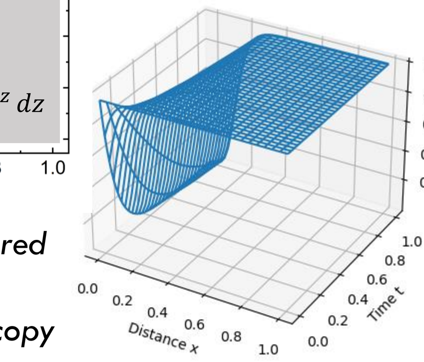
B.C. $C_D(t,0) = C_{D0}, \forall t \geq 0$

$\frac{\partial C_D}{\partial z}(t,L) = 0, \forall t \geq 0$



$$\theta = 1 - \frac{A}{A_{parent}}$$

$$A(t, L) = \int_0^L \varepsilon C_A e^{-2\gamma z} dz$$



Azide Conversion Monitered with Fourier Transform Infrared (FTIR) Spectroscopy

Hoffman, J. R. et. al. (2019)

High-Throughput Membrane Characterization Exploring Structure-Property-Performance Relationships

Diafiltration model & parameter estimation

Parameters

- L_p: hydraulic permeability
- B : solute permeability coefficient
- σ : reflection coefficient

Solution-Diffusion

Water flux across the membrane

$$J_w = L_p \Delta P - \sigma \Delta \pi$$

$$\Delta \pi = nRT(c_{in} - c_h)$$

Solute flux across the membrane

$$J_s = B(c_{in} - c_h)$$

Concentration Polarization

$$\frac{c_{in} - c_h}{c_f - c_h} = exp\left(\frac{J_w}{k}\right)$$

$$\frac{kb}{D} = 0.23\left(\frac{bc^0}{\nu}\right)^{0.57}\left(\frac{\nu}{D}\right)^{0.33}$$

DAEs	Time steps	Diafiltration reservoir	Stirred cell	Hold-up	Collecting vial
Start-up ("Lag" mode)	Hold-up volume filled	$\frac{dm_d}{dt} = 0$	$\frac{dm_f}{dt} = -A_m\rho J_w$; $\frac{d(c_f m_f)}{dt} = -c_d\frac{dm_d}{dt} - A_m\rho J_s$	$\frac{dm_h}{dt} = A_m\rho J_w$; $\frac{d(c_h m_h)}{dt} = A_m\rho J_s$	-
	No diafiltrate induced			$\frac{dm_h}{dt} = 0$; $\frac{d(c_h m_h)}{dt} = A_m\rho J_s - c_h A_m\rho J_w$	$\frac{dm_v}{dt} = A_m\rho J_w$; $\frac{d(c_v m_v)}{dt} = \frac{dm_v}{dt}c_h$
	First drop of diafiltrate	$\frac{dm_d}{dt} = -S - A_m\rho J_w$	$\frac{dm_f}{dt} = S$; $\frac{d(c_f m_f)}{dt} = -c_d\frac{dm_d}{dt} - A_m\rho J_s$		
Vial collection	First drop in vial				

$$\hat{\theta} = \arg\min_{\theta} \sum_i w_{m,i}(m_{v,i} - \hat{m}_{v,i})^2$$

Mass collected

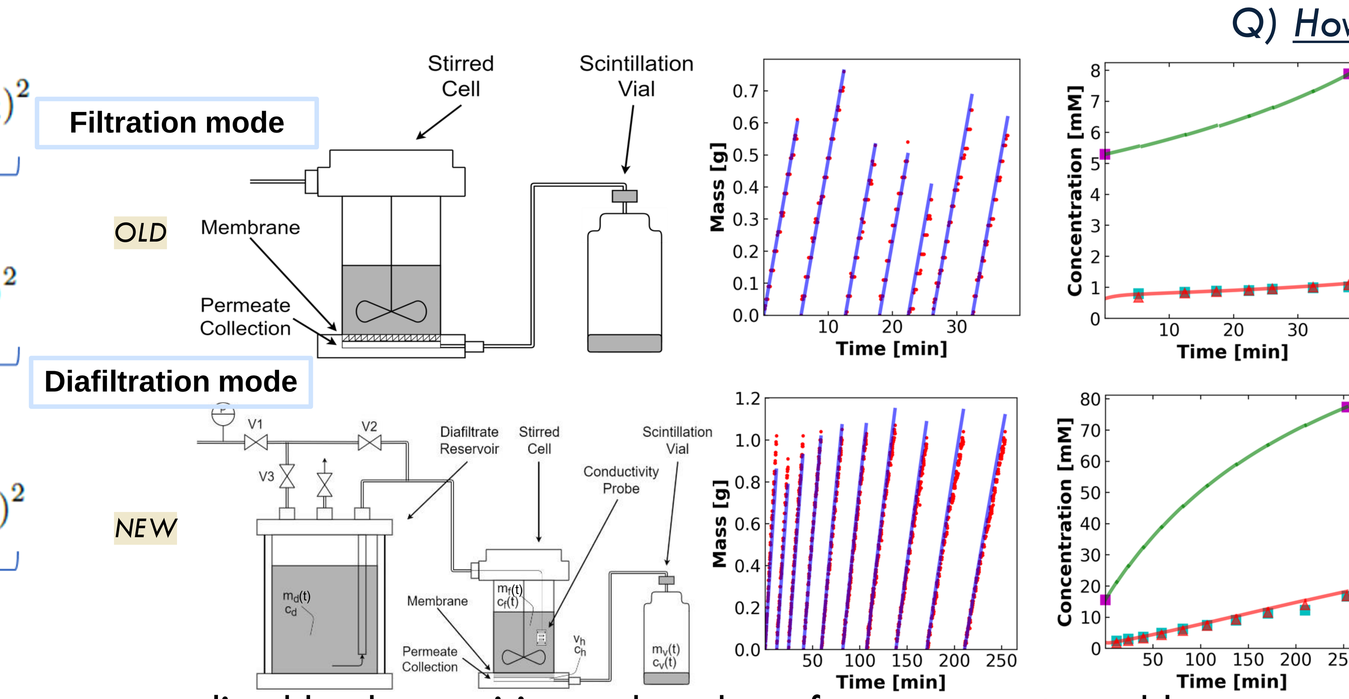
$$+ \sum_j w_{c_v,j}(c_{v,j} - \hat{c}_{v,j})^2$$

Vial concentration

$$+ \sum_k w_{c_f,k}(c_{f,k} - \hat{c}_{f,k})^2$$

Retentate concentration

s.t. DAE constraints



A) Weighted least-square normalized by the precision and number of measurements enables nonlinear parameter estimation from different type of data in dynamic systems.

Q) *How to use different types of data to calibrate the model parameters?*

Fitted parameters

L_p	B	σ
4.30 L/(m²-hr-bar)	0.67 μm/s	0.83 dimensionless
3.25 L/(m²-hr-bar)	0.31 μm/s	1 dimensionless

Fisher Information Matrix (FIM) Analyses

Q1) *Are the parameters reliable?*

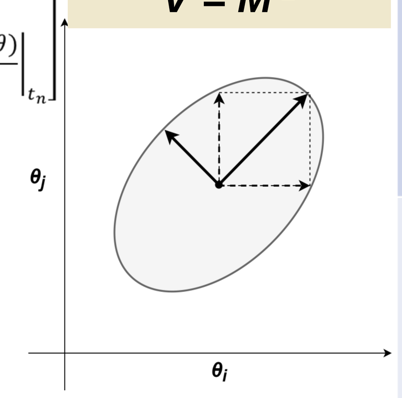
$$M = V_{\hat{\theta}}^{-1} = Q^T \Sigma^{-1} Q$$

$$Q(\theta) = \begin{bmatrix} \frac{\partial f(x_1,\theta)}{\partial \theta_1}\Big|_{t_1} & \cdots & \frac{\partial f(x_1,\theta)}{\partial \theta_m}\Big|_{t_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial f(x_n,\theta)}{\partial \theta_1}\Big|_{t_n} & \cdots & \frac{\partial f(x_n,\theta)}{\partial \theta_m}\Big|_{t_n} \end{bmatrix}$$

$$\Sigma = \begin{bmatrix} \sigma_{x_1}^2 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \sigma_{x_n}^2 \end{bmatrix}$$

- M - Fisher information matrix
- $V_{\hat{\theta}}$ - Covariance matrix for $\hat{\theta}$
- Q - Sensitivity matrix
- Σ - Output error matrix
- $\hat{\theta}$ - Best fit parameters

Confidence Ellipse for Covariance Matrix $V = M^{-1}$

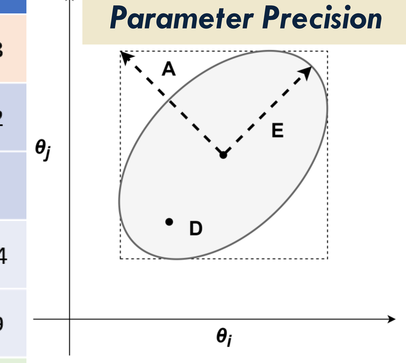


Mode	Eigenvalues of M	Eigenvectors of M		
		L_p	B	σ
Filtration	4.85E+03	0.086	0.0033	0.9963
	1.63E+05	0.002	-1	0.0032
	4.37E+07	-0.9963	-0.0017	0.086
Diafiltration	1.96E+06	-0.1405	-0.9468	-0.2894
	1.27E+08	0.9503	-0.211	0.2289
	8.18E+08	-0.2778	-0.2429	0.9294

A1) Eigen decomposition of FIM reveals diafiltration contains more information to infer the parameters, especially σ.

Q2) *Does the investment in new instrument and additional data collection worth it?*

FIM-Based Metrics for Parameter Precision

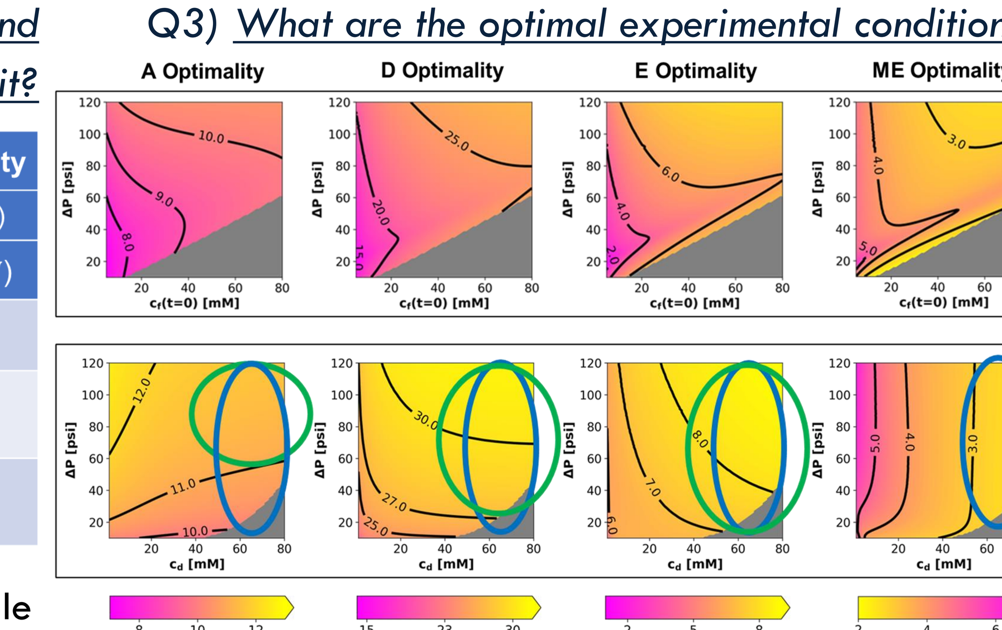


- A - Dimensions of the enclosing box
- D - Area or volume
- E - Size of major axis

min $g(V)$ ⇕ max $g(M)$	A-optimality	D-optimality	E-optimality
	trace(V)	det(V)	max eig(V)
	trace(M)	det(M)	min eig(M)
Initial	9.87E+08	9.12E+22	3.93
Incorporate New Sensor	2.06E+10 1E2↑	1.93E+24 1E2↑	9.55 143%↑
Model Start-up	1.95E+13 1E3↑	2.76E+30 1E6↑	207.91 1E2↑

A2) FIM-based metrics indicate valuable experiment modifications.

Q3) *What are the optimal experimental conditions?*



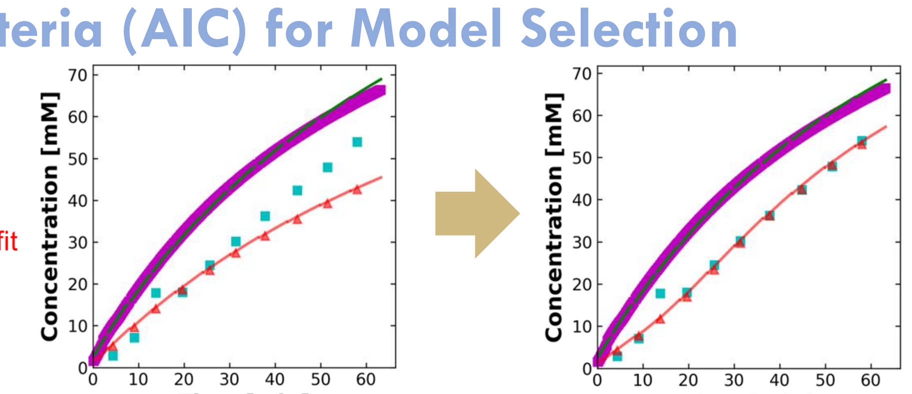
A3) Diafiltration experiments should be performed with $c_d \geq 50$ mM and $\Delta P \geq 50$ psi.

Akaike Information Criteria (AIC) for Model Selection

$$\Delta AIC = N \cdot \ln\left(\sum_i w_i (y_i - \hat{y}_i)^2\right) + 2n_p$$

Quality of fit — Penalty of overfit

- N - Number of measurements
- n_p - Number of model parameters
- y - Model predictions
- $\hat{y}$ - Measurements



$B = constant$ → $B = \sum_{i \in I} b_i c_f^{\,i}$

Predictions from Empirical Models for Charged Membrane

Q) *What are the dominant phenomena & mechanisms?*

A) For charged membrane NF270, B shows a quadratic dependence on feed side concentration.

The calibrated model is ready to be embedded in the scale-up, design, and optimization of membrane-based separation systems with high computing performance. It also can be applied to inform and filter the phenomenological models imported into model discrimination problems.

Science-Based Data Analytics Workflow