Latulippe
RESEARCH GROUP

CWWA ACEPU

Bridging the gap at the water-energy nexus:

Treating wastewater byproducts from biogas production processes via hybrid filtration technology

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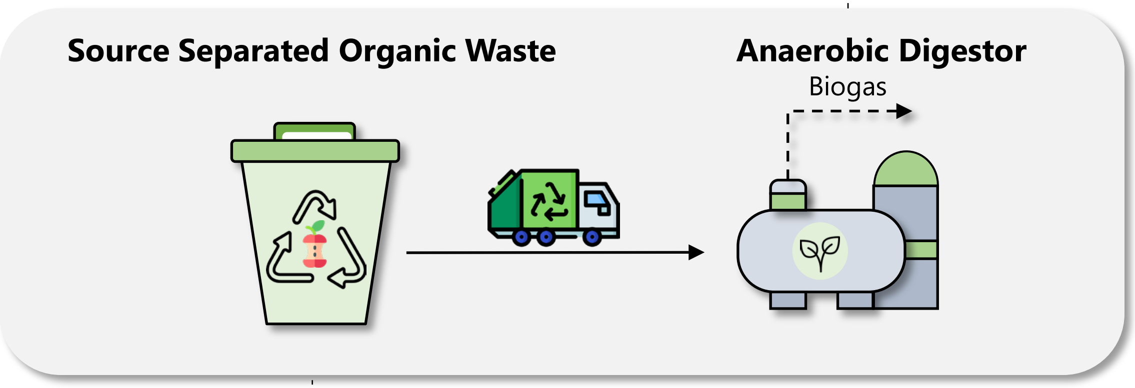
ENGINEERING | McMaster University

Biogas is a clean energy resource

Anaerobic digestion of organic matter creates a CO_2 and CH_4 rich mixture known as biogas



Source Separated Organic Waste

Anaerobic Digestor

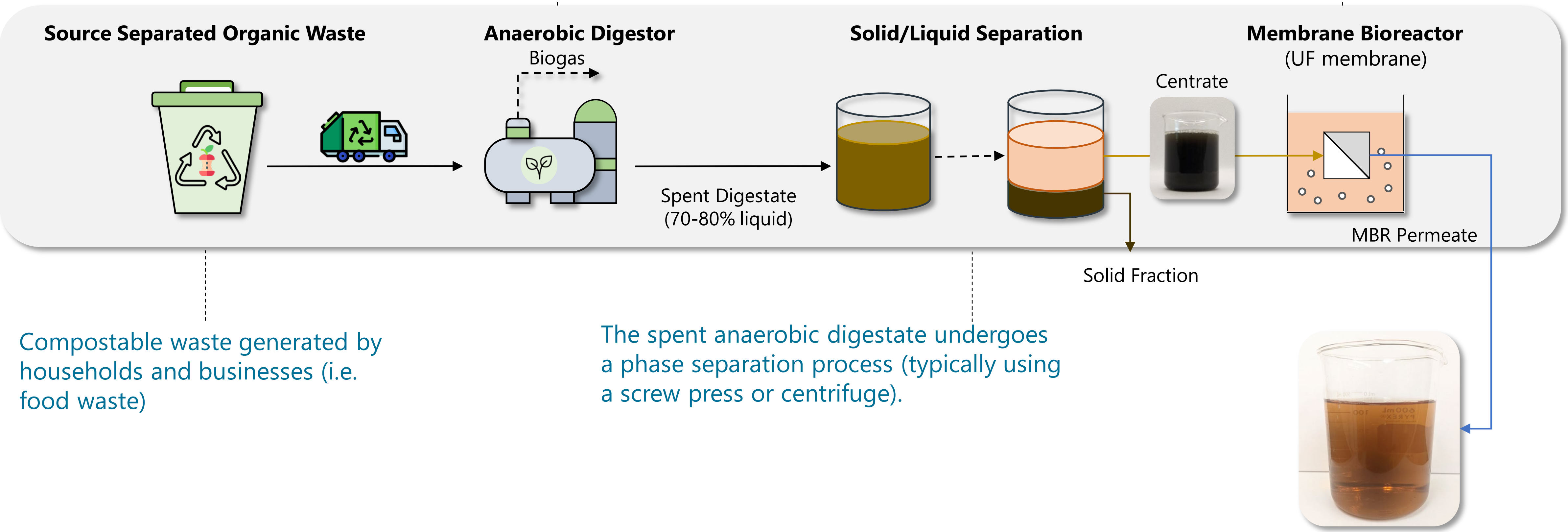
Biogas

Compostable waste generated by households and businesses (i.e. food waste)

Biogas is a clean energy resource, however treating downstream liquid waste by-products can be challenging

Anaerobic digestion of organic matter creates a CO_2 and CH_4 rich mixture known as biogas

Combines biological and physical treatment to treat liquid fraction



Source Separated Organic Waste

Anaerobic Digestor

Biogas

Spent Digestate
(70-80% liquid)

Solid/Liquid Separation

Centrate

Solid Fraction

Membrane Bioreactor
(UF membrane)

MBR Permeate

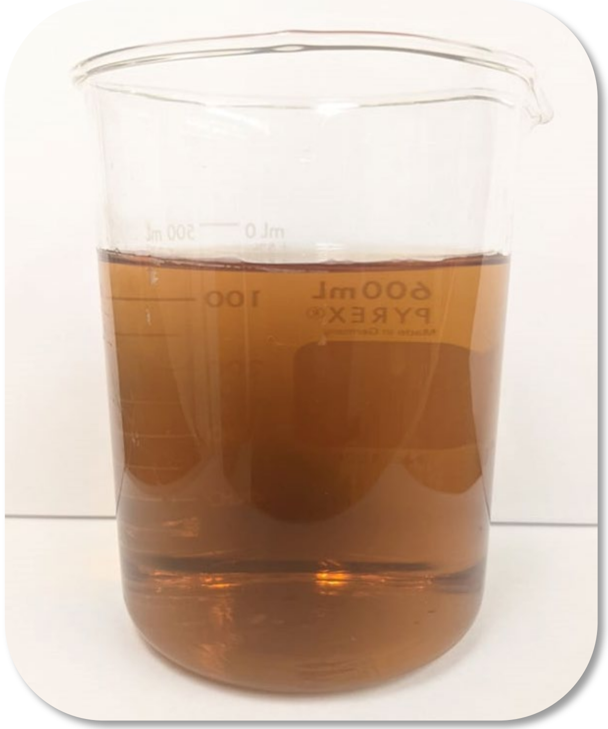
Compostable waste generated by households and businesses (i.e. food waste)

The spent anaerobic digestate undergoes a phase separation process (typically using a screw press or centrifuge).

The MBR centrate has significantly higher concentrations of select measured values, **but what does this mean for a membrane process?**

MBR Centrate (What goes into the MBR)

MBR Permeate (What comes out of the MBR)

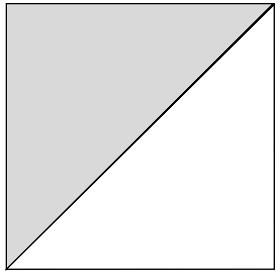


Parameter	Units	MBR Centrate	MBR Permeate
Chemical Oxygen Demand	mg/L	4800 – 7900	300 – 700
Zeta-Potential	mV	~-17	~-15
Electrical Conductivity	mS/cm	18 – 23	19 - 21
pH		8.2 - 8.8	7.7 – 8.3
Total Dissolved Solids	mg/L	7500 - 13000	10000 - 15000
Nitrate as N	mg/L	<1.4	34 – 59
Nitrite as N	mg/L	<1.1	1640 – 1770
Ammonia as N	mg/L	1700 - 2300	0.5 – 134
Total Organic Carbon	mg/L	800 – 1300	200 – 230
True Colour	TCU	2800 – 7000	1630
Turbidity	NTU	680 – 4300	0 - 10
Total Calcium	mg/L	30 – 200	40 – 100
Total Magnesium	mg/L	49 – 123	40 – 80
Total Potassium	mg/L	1000 - 1800	1300 – 1500
Total Sodium	mg/L	1200 – 3200	2800 – 4400
Total Iron	mg/L	9 - 52	0.2 – 0.5

The process is dynamic, and there is variability in process measurements

Our previous work in this collaboration has shown that membrane performance depended on the membrane used and batch-to-batch variation

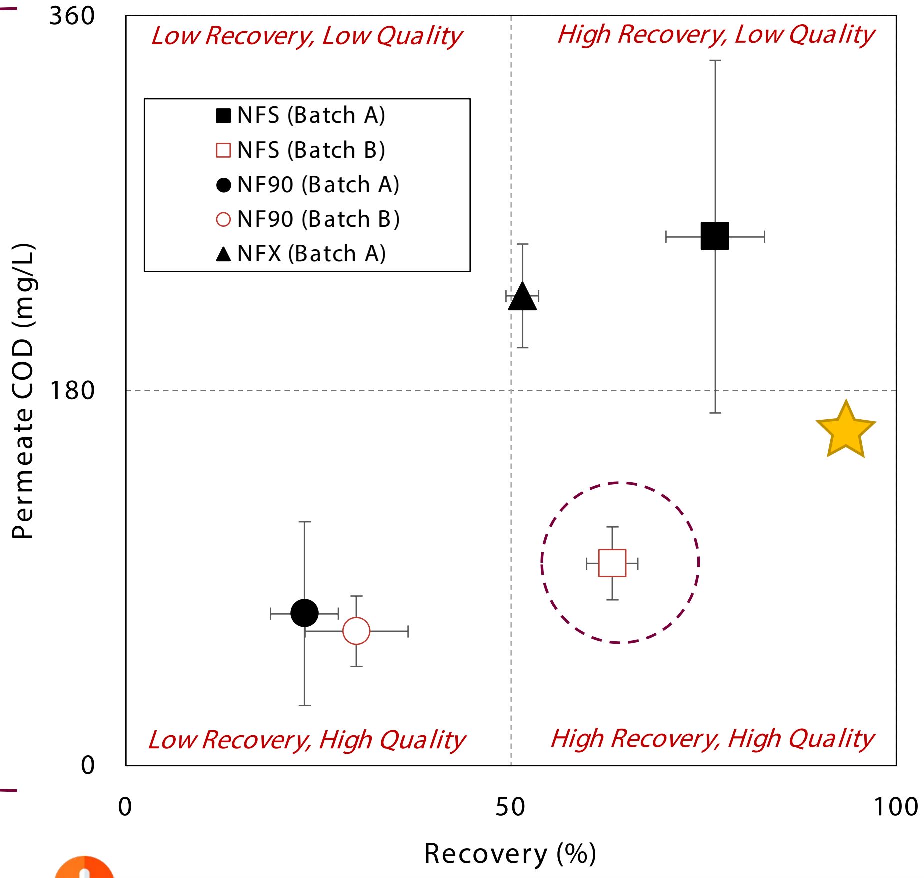
Our previous work



Nanofiltration polishing process

Performance was **batch** and **membrane dependent**

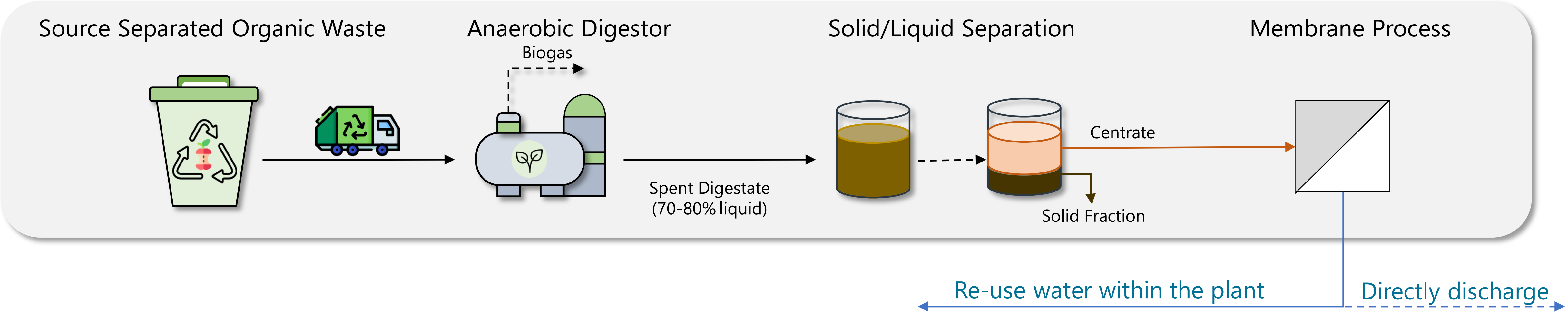
Premachandra et al., *Journal of Water Process Engineering* (2022)



Can we take a membrane that performs well and use in a 'tougher' upstream treatment application?

Replacing the MBR with nanofiltration processes may improve treatment and enable water re-use within the facility

Can we ***replace*** a membrane bioreactor with a nanofiltration membrane to produce a high-quality permeate?



Source Separated Organic Waste

Anaerobic Digestor

Biogas

Spent Digestate (70-80% liquid)

Solid/Liquid Separation

Centrate

Solid Fraction

Membrane Process

Re-use water within the plant

Directly discharge

'Ultrafiltration' Membrane

Physical Treatment (10 - 40 nm)

\+

Bioreactor

Biological Treatment

Smaller Pore Size →

Remove more contaminants

'Nanofiltration' Membrane

Physical Treatment (0.2 – 2 nm)

Replacing th… w better treatment ar…

Source Separate…

…on Process

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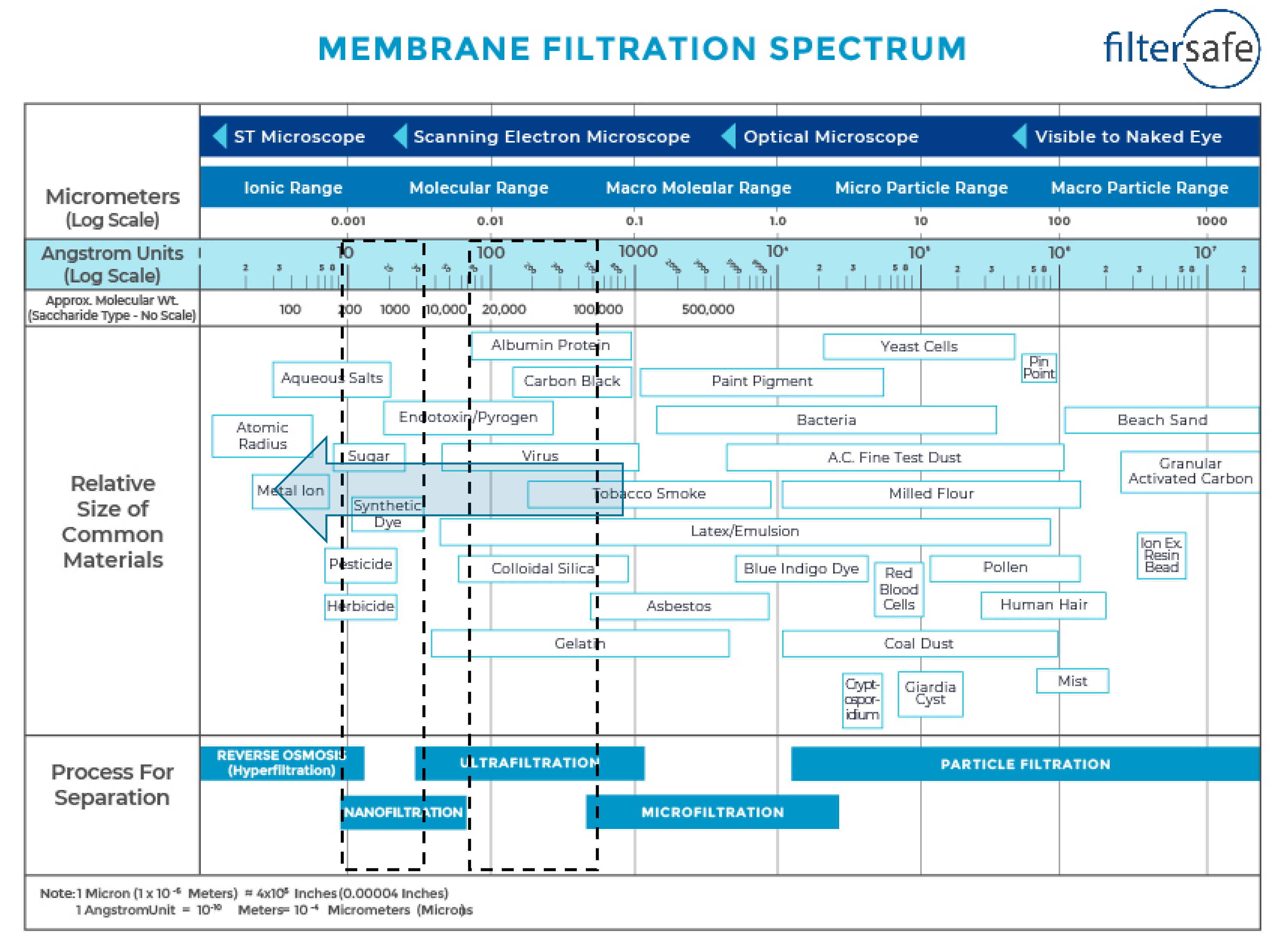
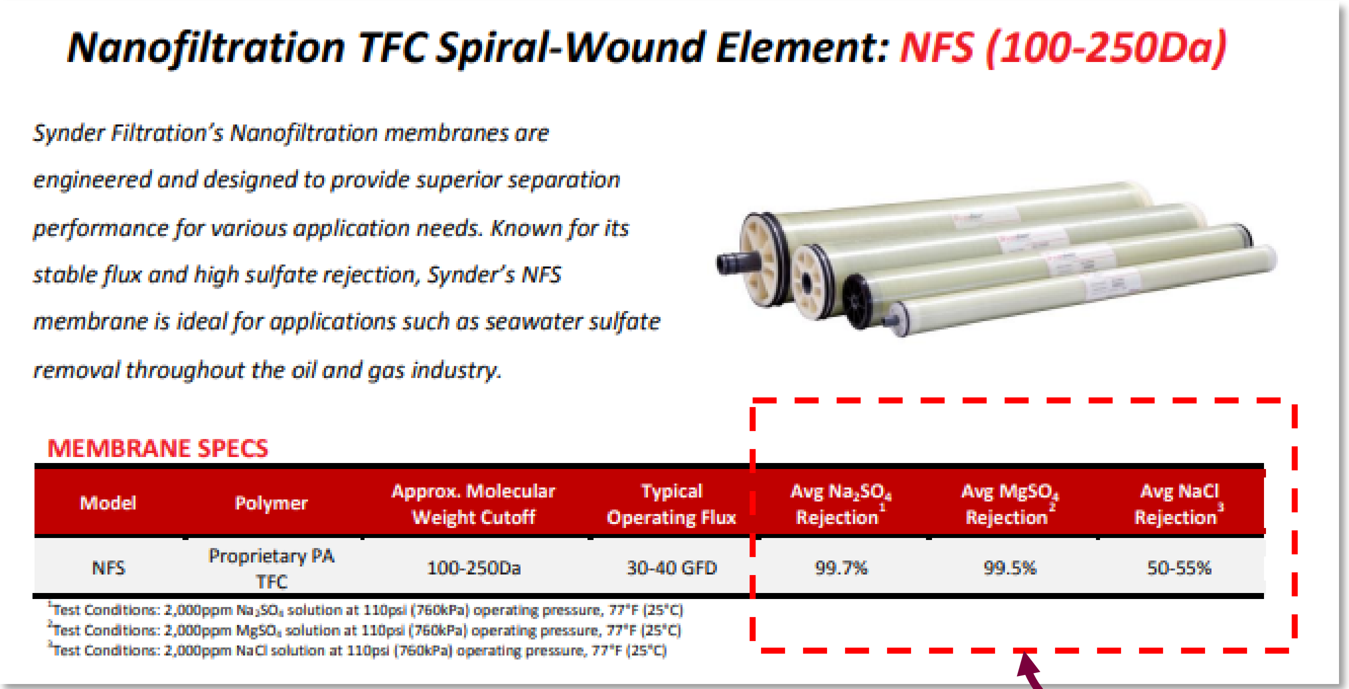


NF membranes are rated based only on monovalent and divalent salt rejection, making it difficult to predict their performance when filtering complex mixtures



Nanofiltration TFC Spiral-Wound Element: NFS (100-250Da)

Synder Filtration's Nanofiltration membranes are engineered and designed to provide superior separation performance for various application needs. Known for its stable flux and high sulfate rejection, Synder's NFS membrane is ideal for applications such as seawater sulfate removal throughout the oil and gas industry.

MEMBRANE SPECS

Model	Polymer	Approx. Molecular Weight Cutoff	Typical Operating Flux	Avg Na_2SO_4 Rejection[1]	Avg $MgSO_4$ Rejection[2]	Avg NaCl Rejection[3]
NFS	Proprietary PA TFC	100-250Da	30-40 GFD	99.7%	99.5%	50-55%

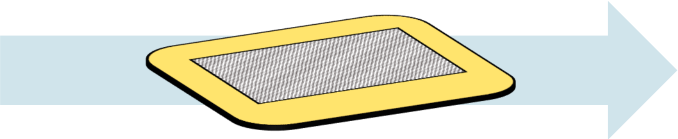
[1] Test Conditions: 2,000ppm Na_2SO_4 solution at 110psi (760kPa) operating pressure, 77°F (25°C)
[2] Test Conditions: 2,000ppm $MgSO_4$ solution at 110psi (760kPa) operating pressure, 77°F (25°C)
[3] Test Conditions: 2,000ppm NaCl solution at 110psi (760kPa) operating pressure, 77°F (25°C)

Parameter	Units	MBR Centrate
Chemical Oxygen Demand	mg/L	5883
Zeta-Potential	mV	-17.1
Electrical Conductivity	µS/cm	21400
pH		8.29
Total Dissolved Solids	mg/L	8940
Nitrate as N	mg/L	<1.4
Nitrite as N	mg/L	<1.1
Ammonia as N	mg/L	2220
Total Organic Carbon	mg/L	874
True Colour	TCU	6990
Turbidity	NTU	689
Total Calcium	mg/L	97.0
Total Magnesium	mg/L	48.6
Total Potassium	mg/L	1020
Total Sodium	mg/L	1230
Total Iron	mg/L	9.69

The centrate has a higher concentration of *natural organic matter,* that can lead to organic & colloidal fouling on a membrane surface

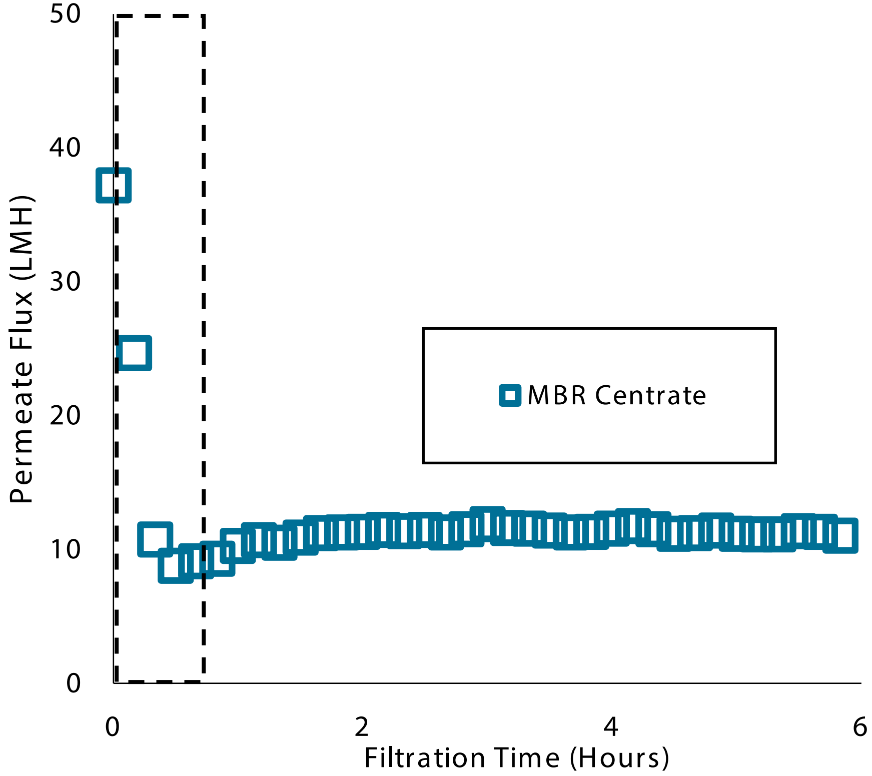
Turbidity: 1420 NTU
Color: 2830 TCU
COD: 7730 mg/L

NFS membrane [Synder]



Molecular weight cut off: 100-250 Da

Turbidity: <0.5 NTU
Color: 5 TCU
COD: 567 mg/L



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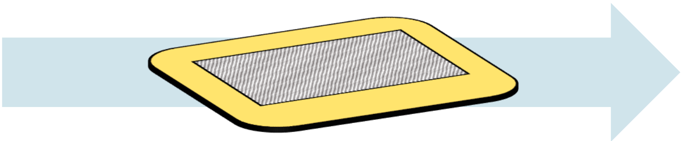

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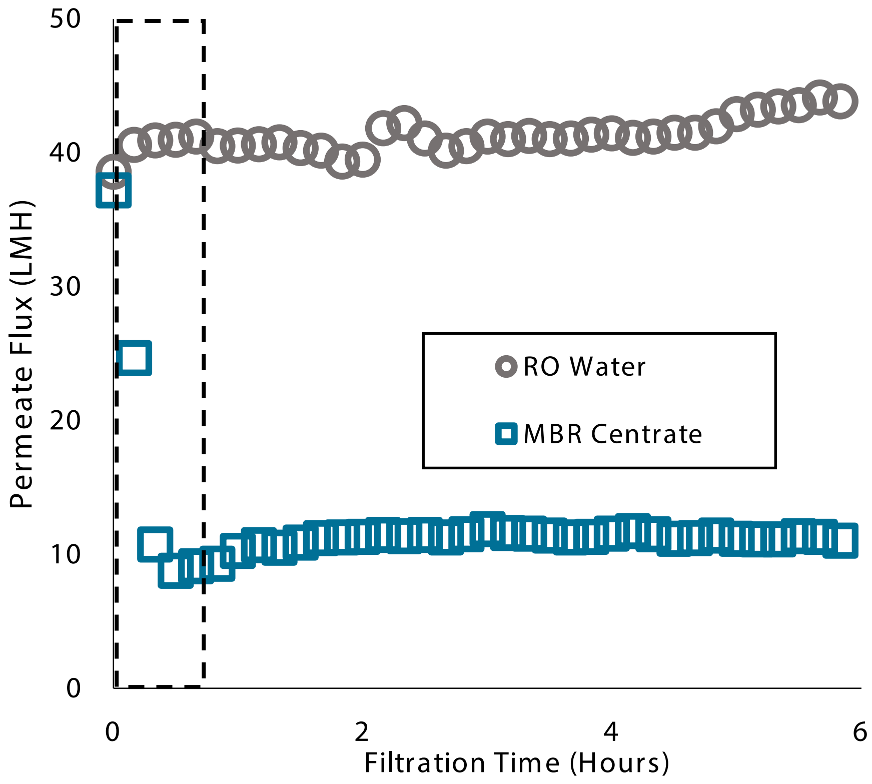

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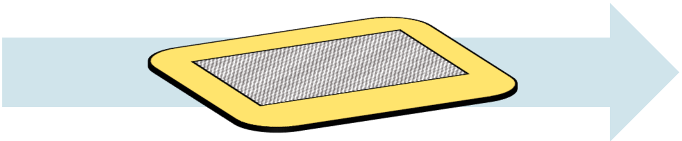

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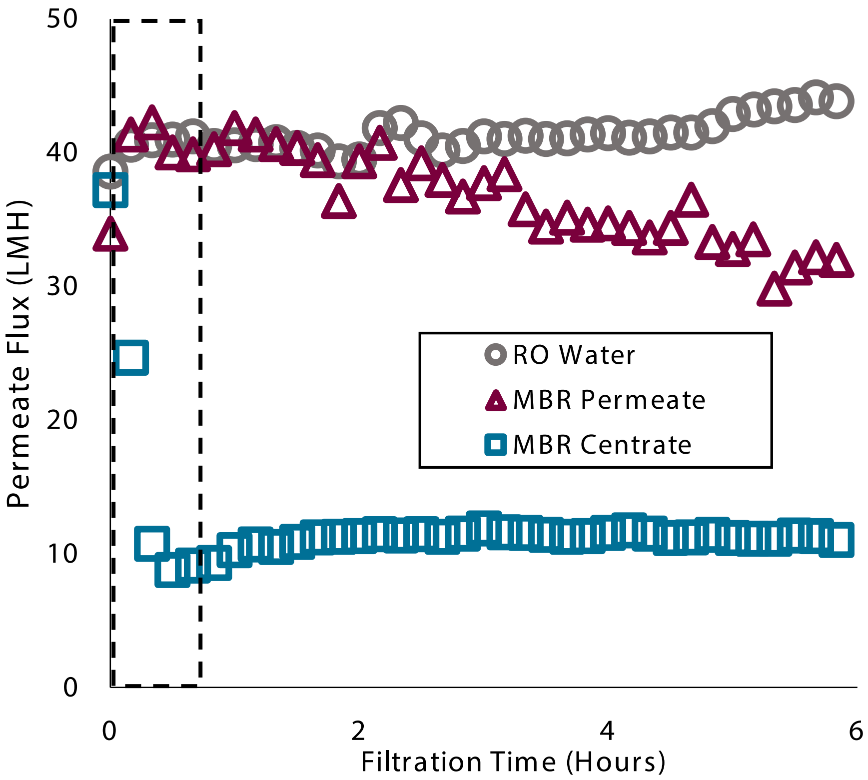
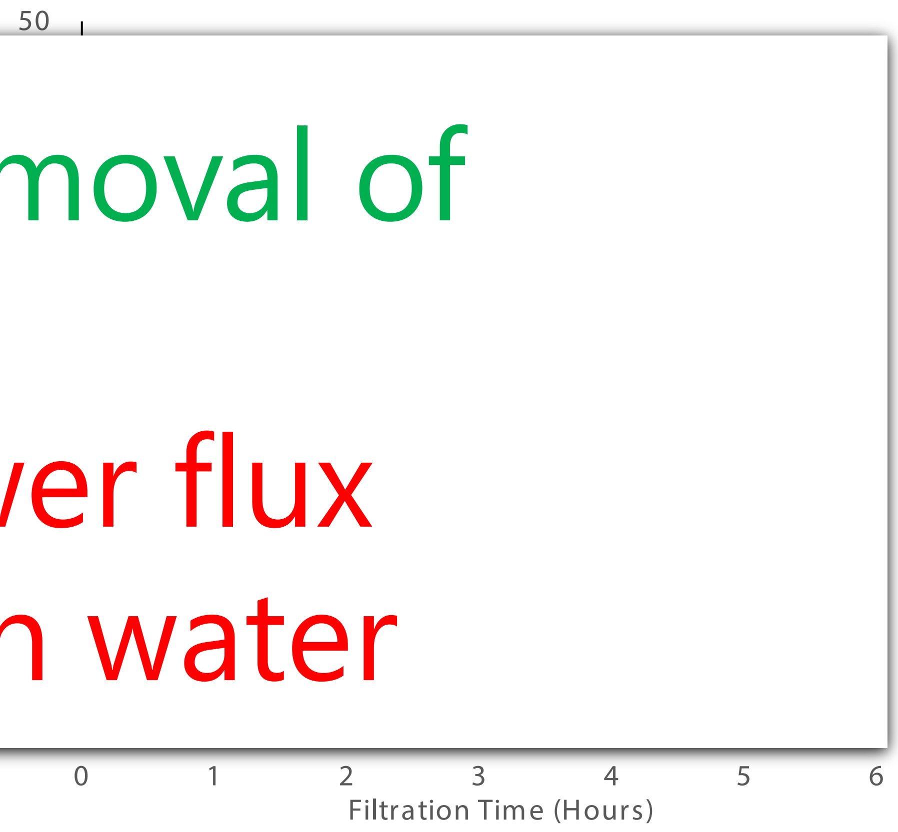


The centrate has a higher concentration of *natural organic matter,* that can lead to organic & colloidal fouling on a membrane surface

Turbi
Col
COD

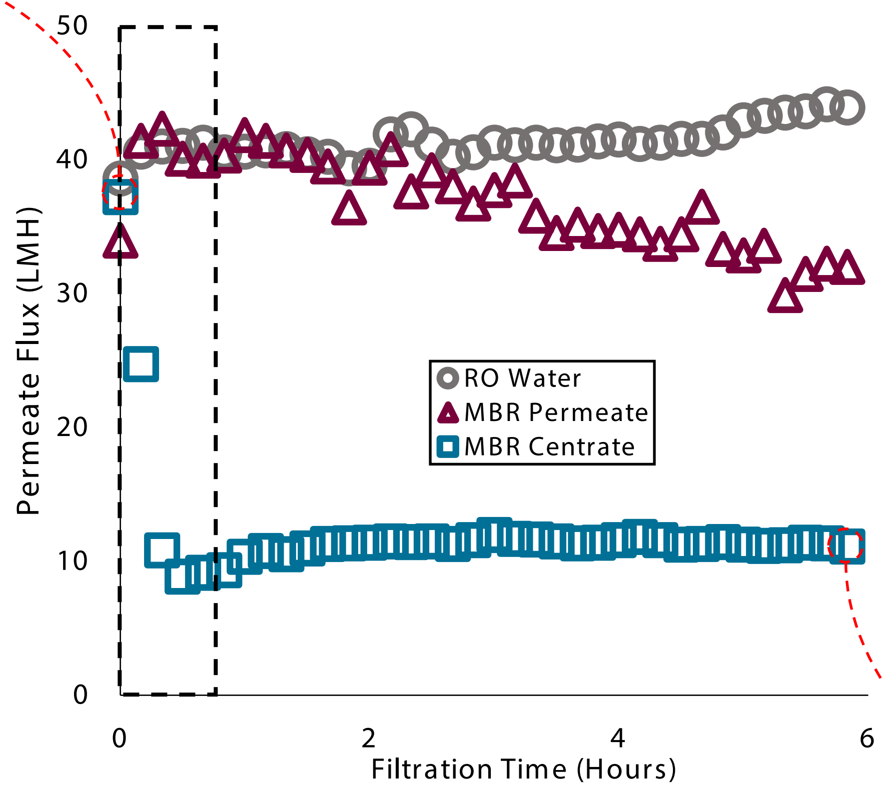
✓ **Quality:** 93 % Removal of COD

✗ **Efficiency:** 4X lower flux compared to clean water

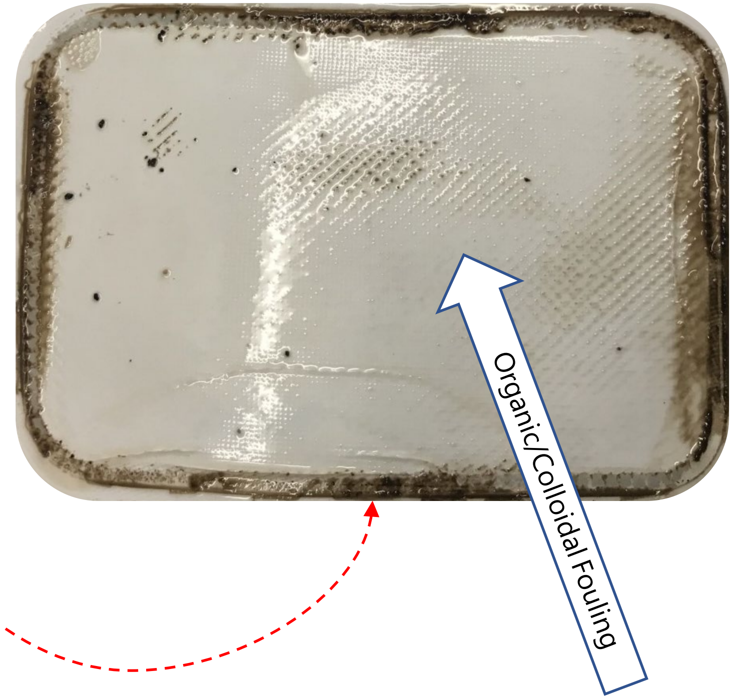


Colloids that are much larger than the pore size of the membrane causes a cake layer to form on the surface of the membrane

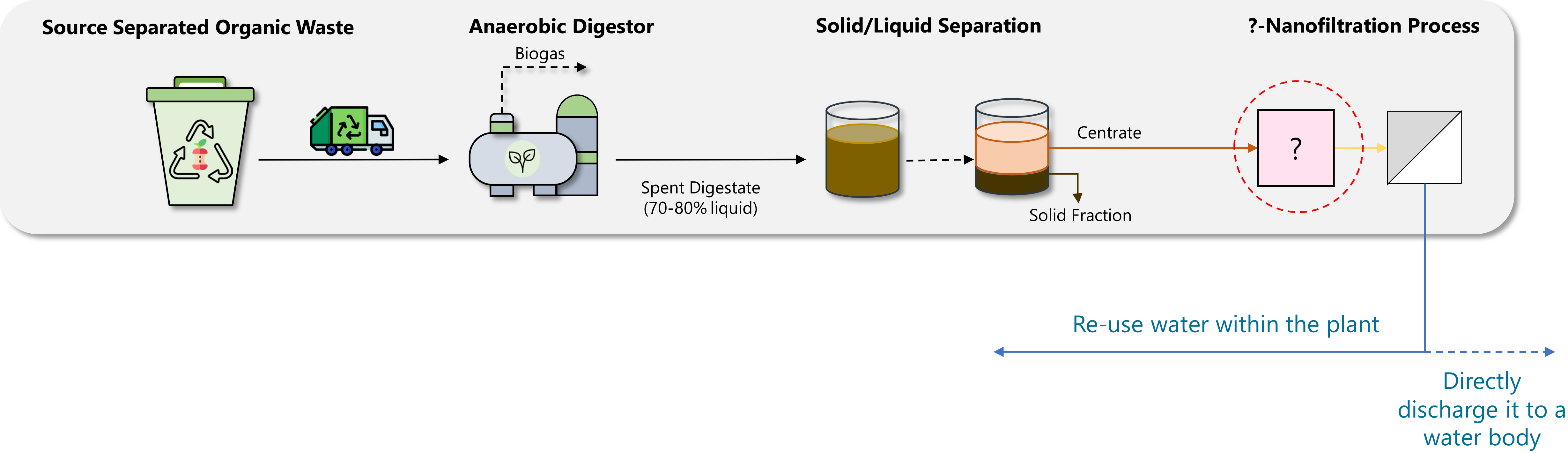
Before Filtration



After Filtration



An intermediary treatment process that is scalable and energy efficient is needed to target colloidal removal prior to nanofiltration



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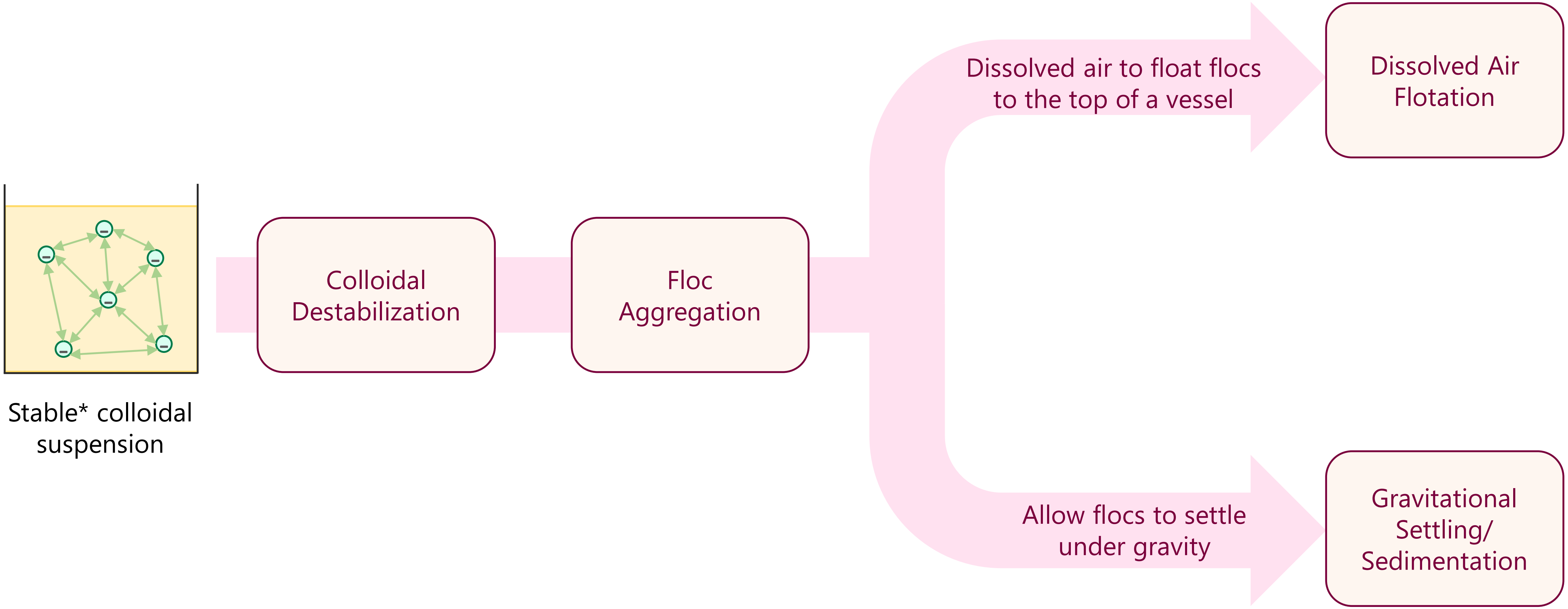
How are colloids removed in wastewater treatment processes?

An intermediary treatment process that is scalable and energy efficient is needed to target organics removal prior to nanofiltration



Stable* colloidal suspension

Colloidal Destabilization

Floc Aggregation

Dissolved air to float flocs to the top of a vessel

Dissolved Air Flotation

Allow flocs to settle under gravity

Gravitational Settling/ Sedimentation

*Zeta-Potential = -17.1 mV

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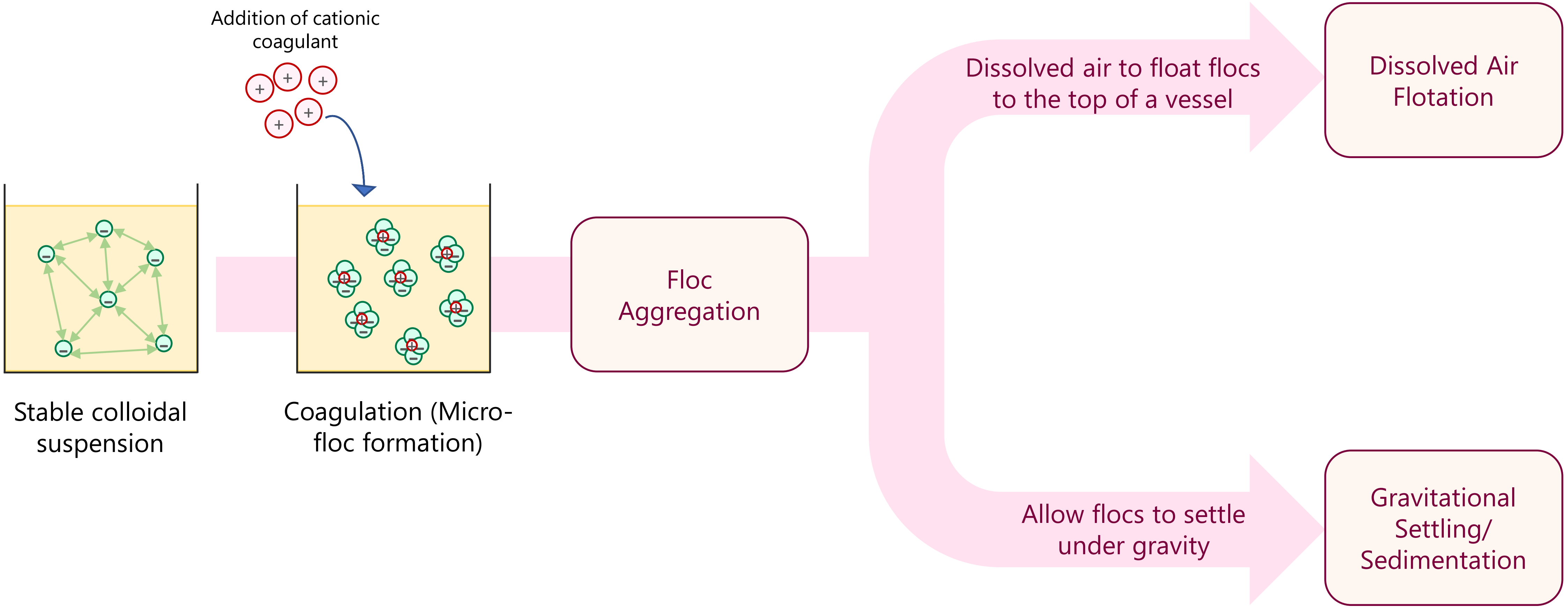

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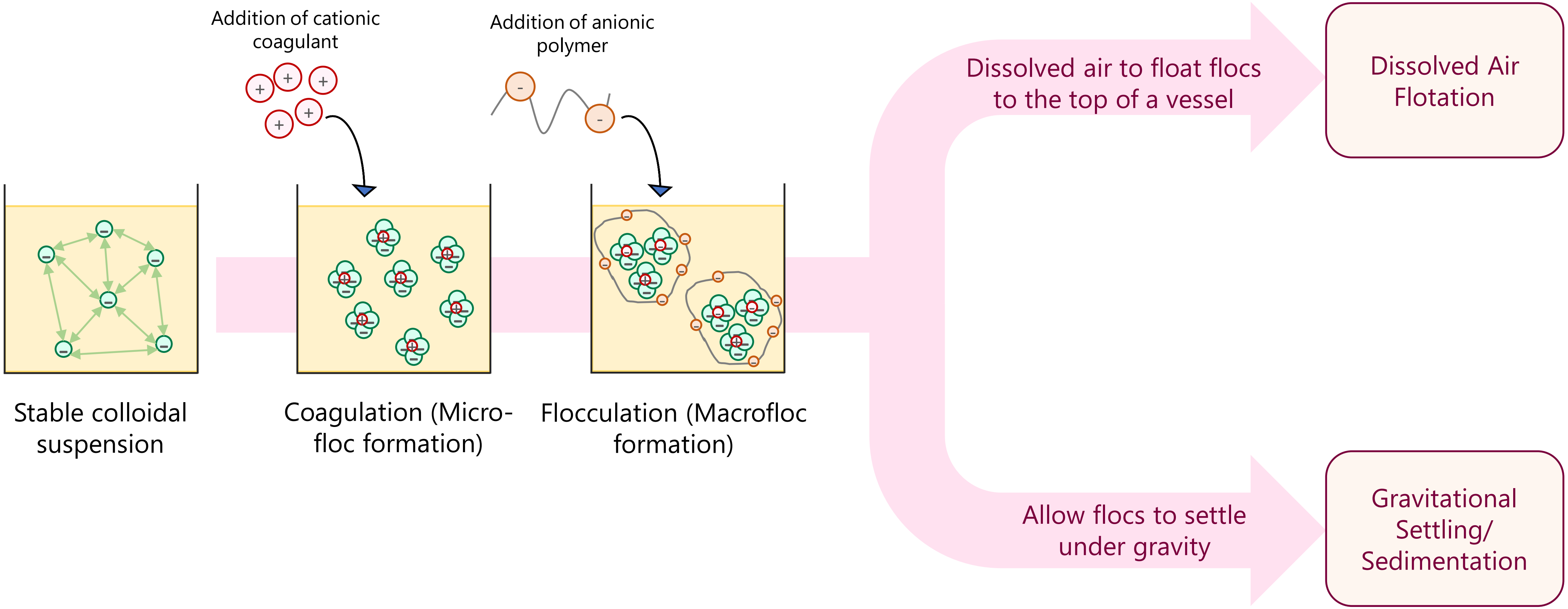

Addition of cationic coagulant

Addition of anionic polymer

Stable colloidal suspension

Coagulation (Micro-floc formation)

Flocculation (Macrofloc formation)

Dissolved air to float flocs to the top of a vessel

Dissolved Air Flotation

Allow flocs to settle under gravity

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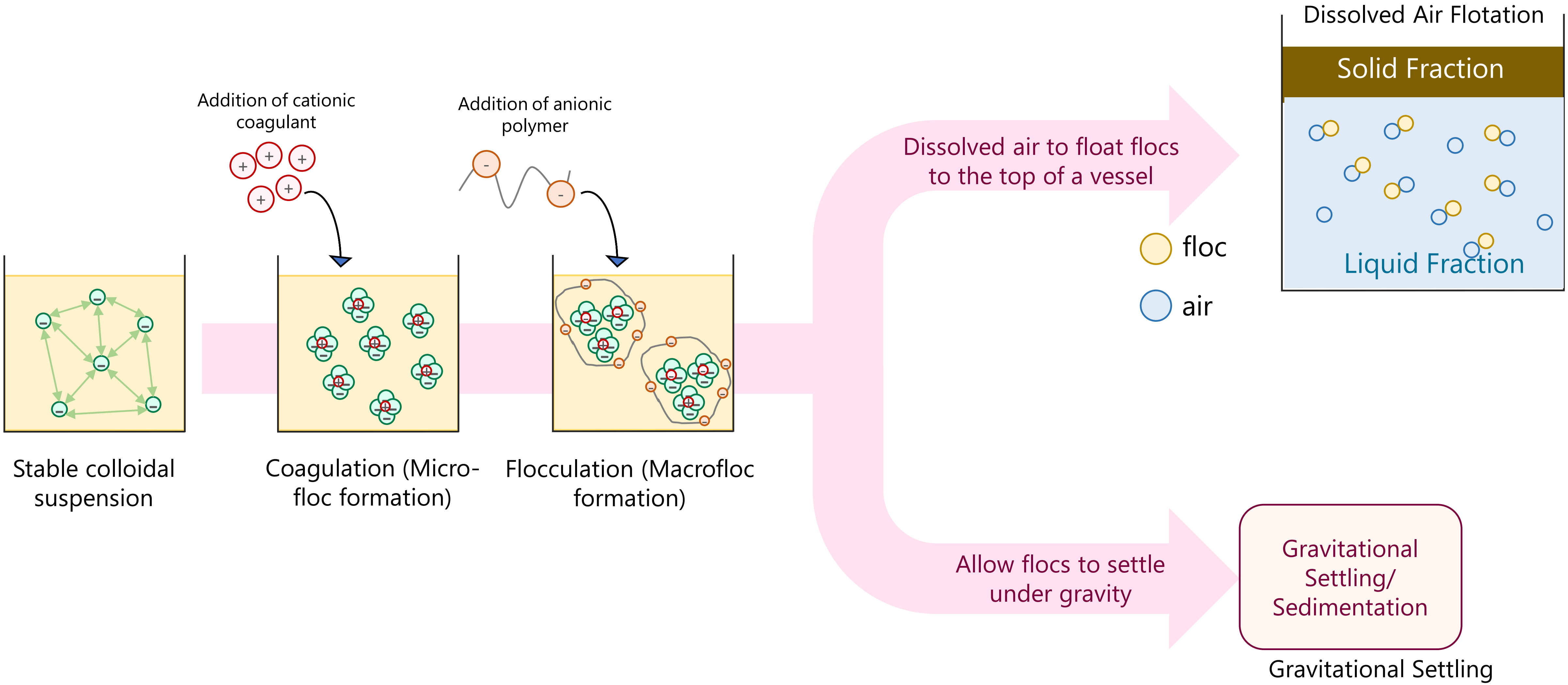

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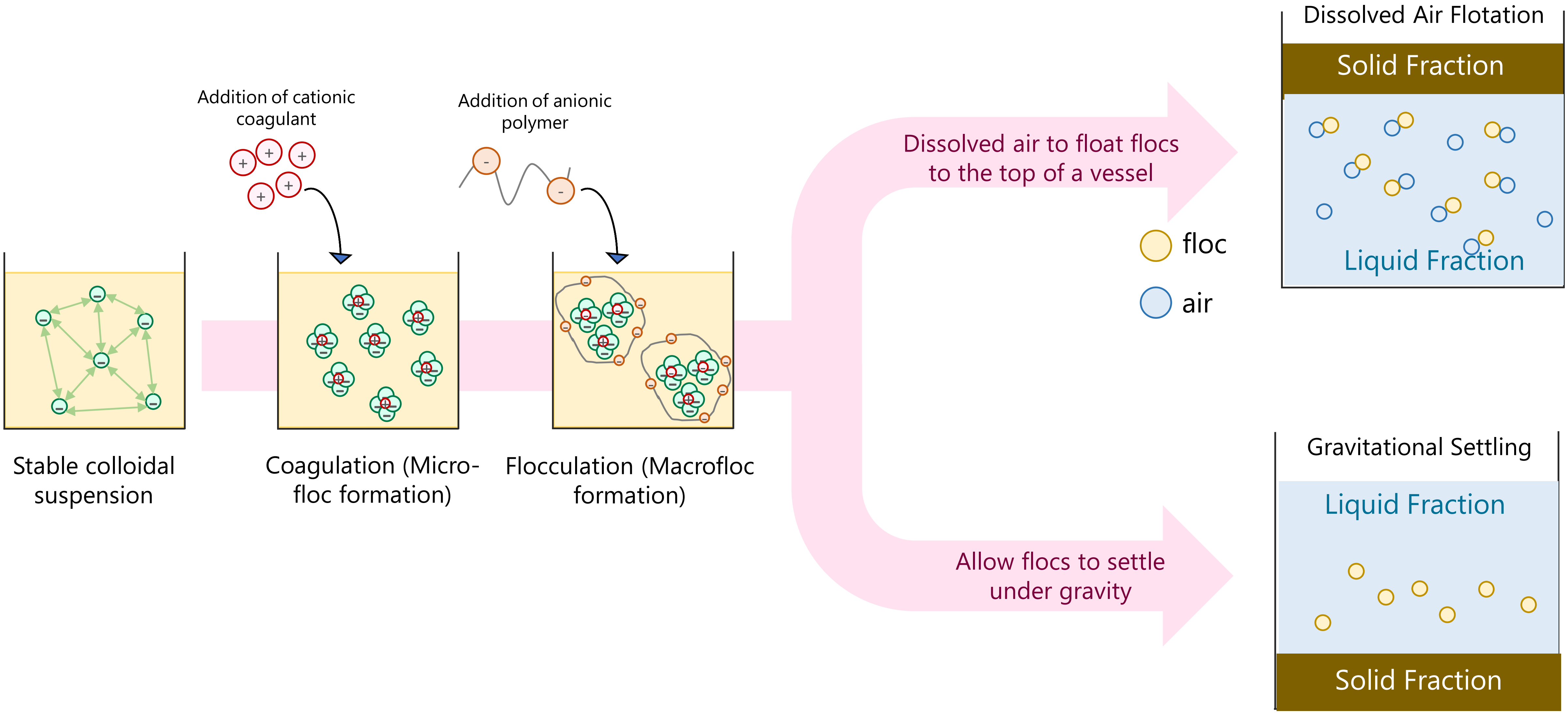

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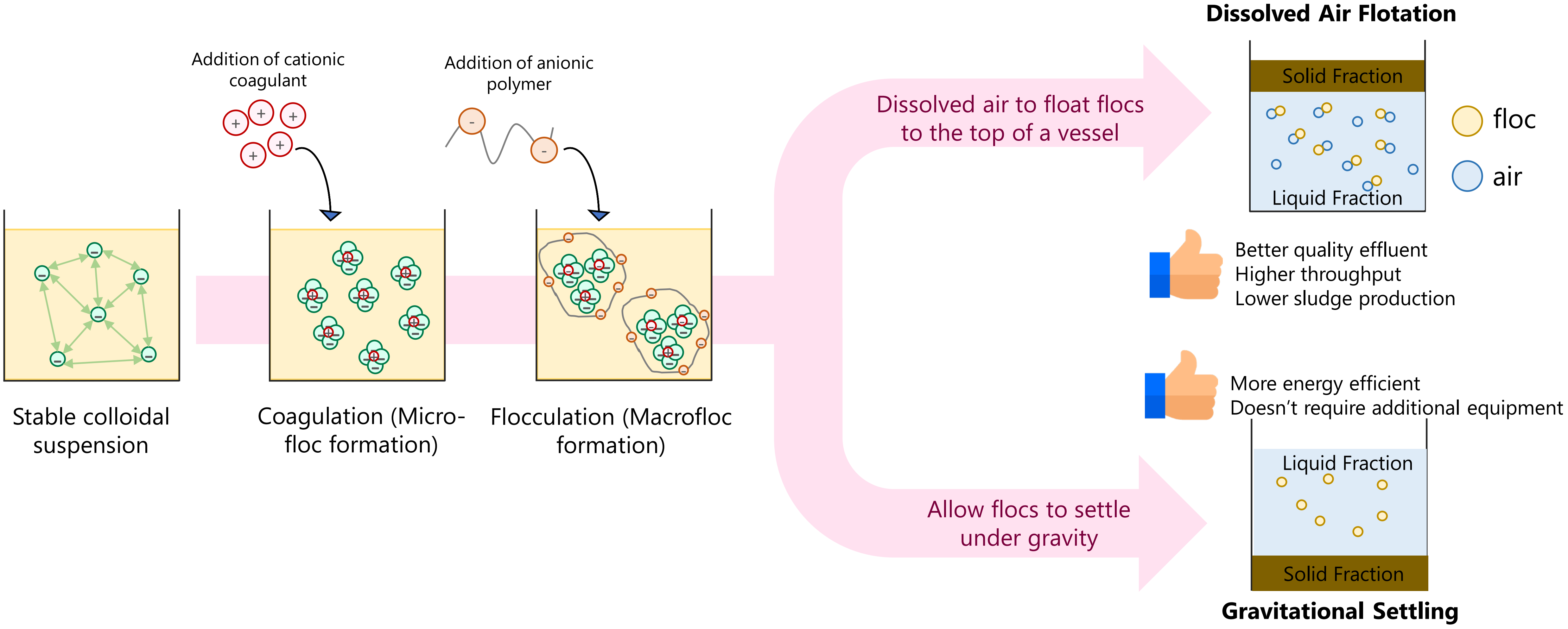


Addition of cationic coagulant

Addition of anionic polymer

Stable colloidal suspension

Coagulation (Micro-floc formation)

Flocculation (Macrofloc formation)

Dissolved air to float flocs to the top of a vessel

Allow flocs to settle under gravity

Dissolved Air Flotation

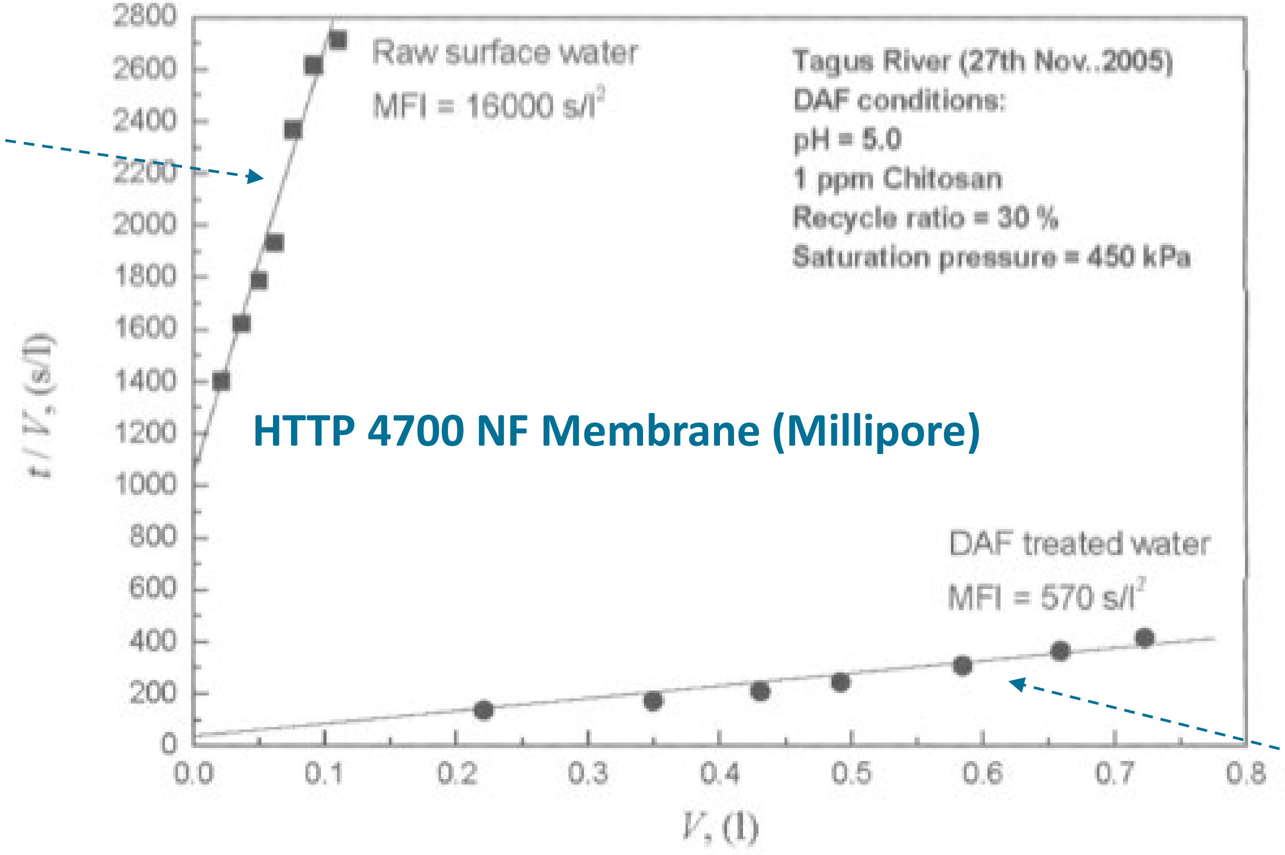
Better quality effluent
Higher throughput
Lower sludge production

More energy efficient
Doesn’t require additional equipment

Gravitational Settling

Previous studies have shown that DAF pre-treatment can significantly reduce the fouling rate of NF processes

Time required to filter set volume increases as more permeate is recovered when **raw surface water** is filtered

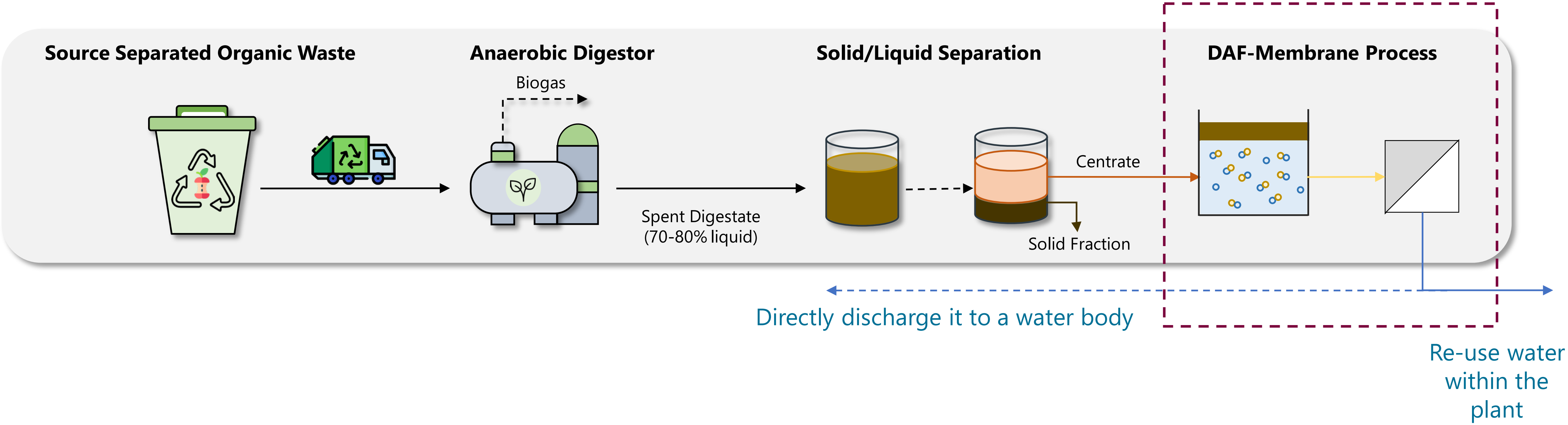


HTTP 4700 NF Membrane (Millipore)

Time required to filter set volume **increases as a slower rate** as more permeate is recovered when **DAF treated surface water** is filtered

Geraldes et al. *Desal.* (2018)

DAF pre-treatment to remove colloids prior to membrane filtration can improve nanofiltration performance



DAF pre-treatment to remove colloids prior to membrane filtration can improve nanofiltration performance

How *can* we quantify colloidal destabilization?

An analytical centrifuge provides more qualitative information about the performance of coagulation/flocculation process than traditional jar testing

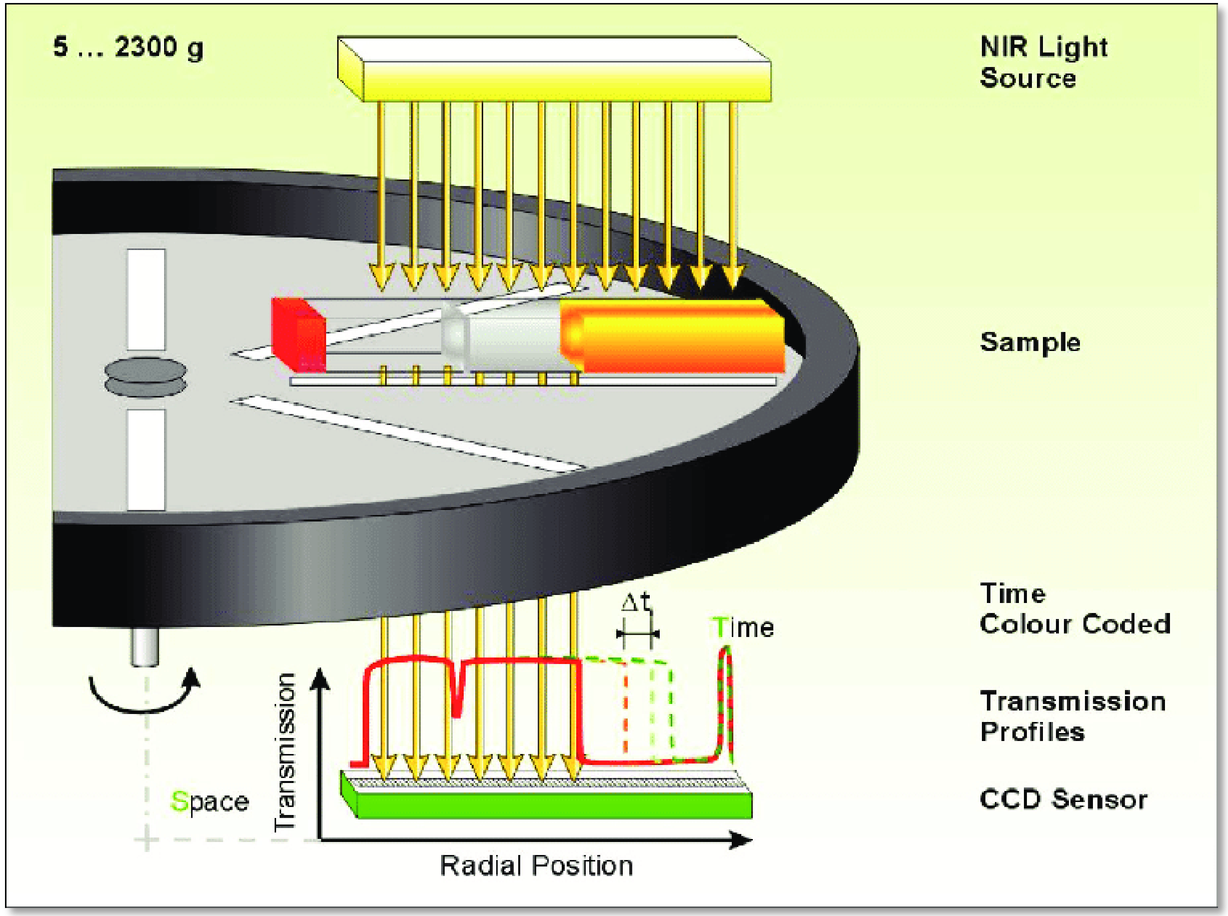
Traditional: Jar Tester

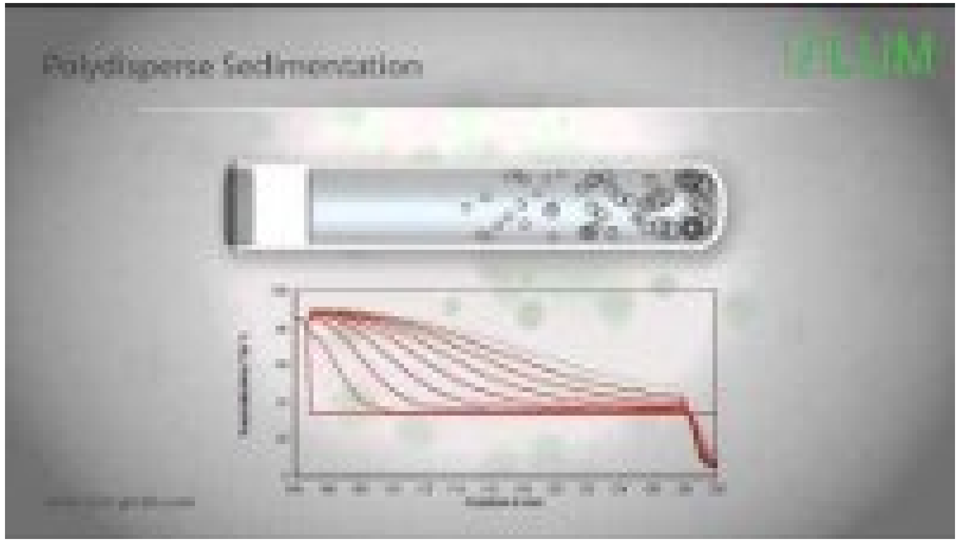
- 👍 Large volume chemistry
- 👍 Parallel testing of multiple conditions
- 👎 **Limited information about colloidal stability and settling time**
- 👎 Testing times can be long (if settling times are long)
- 👎 Large volume required (typical 1-2L per jar)

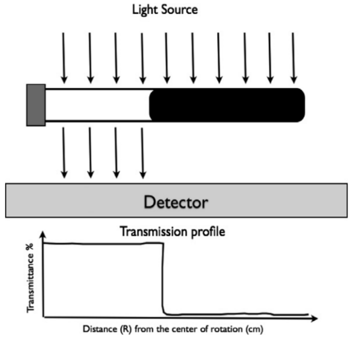
Novel: Analytical Centrifuge

- 👍 **Provides quantitative information about settling time and colloidal stability**
- 👍 Small volumes required (1.6mL per test/99% less wastewater per test).
- 👍 Parallel testing of 8 solutions
- 👎 Small volume chemistry (scale-up challenges)
- 👎 **Cost ($60,000 vs. $3000 for jar tester)**

The analytical centrifuge measures the change in position of a solids-liquids phase boundary over time, and the *stability* of a colloidal suspension







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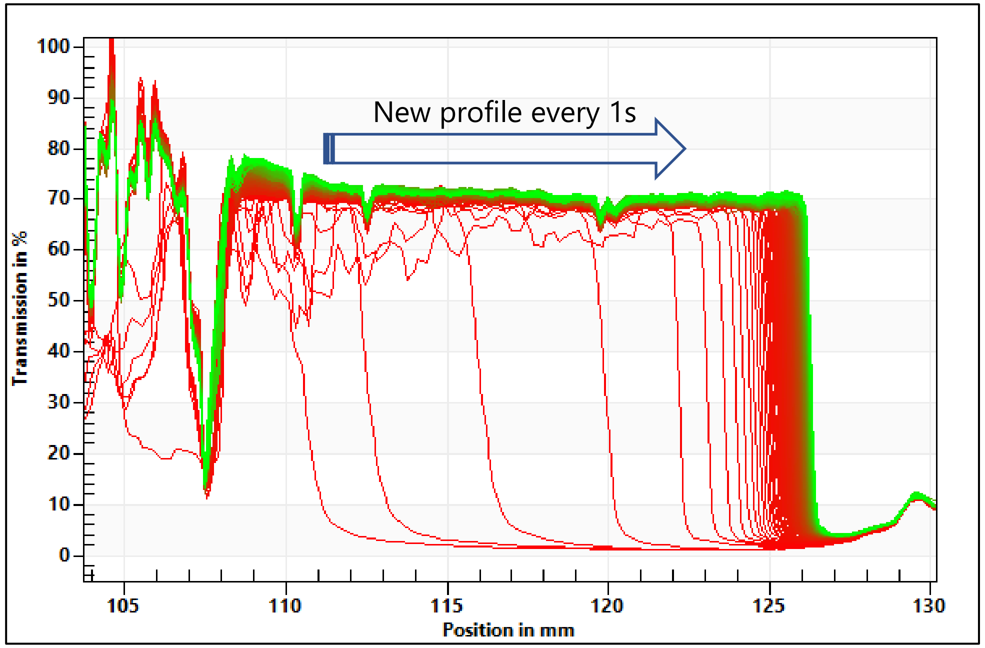
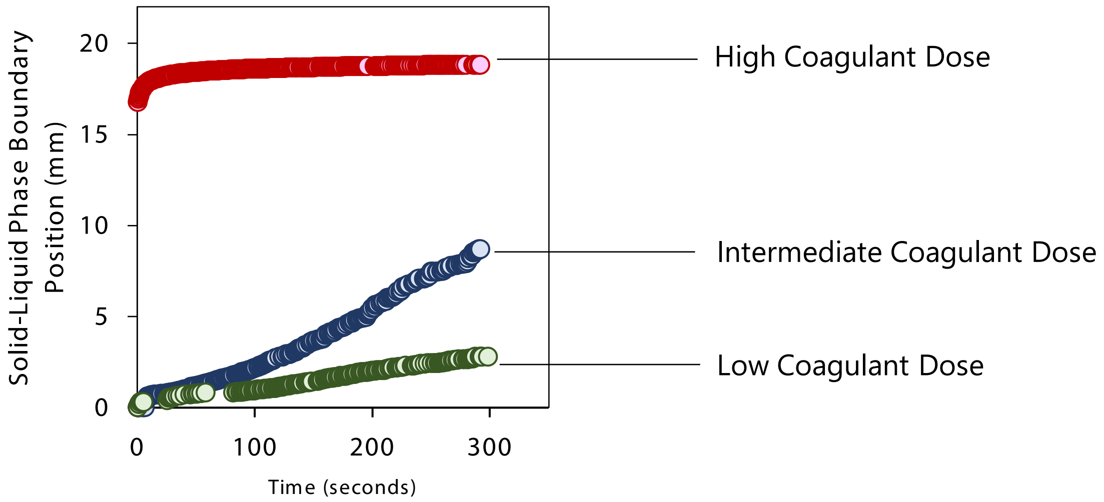
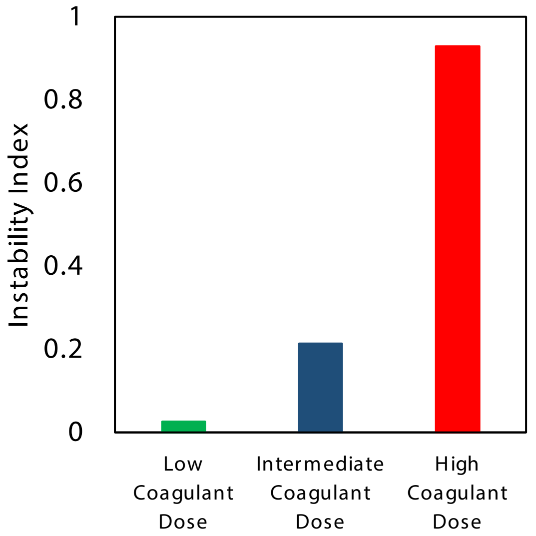


1. Front Tracking



2. Stability Analysis



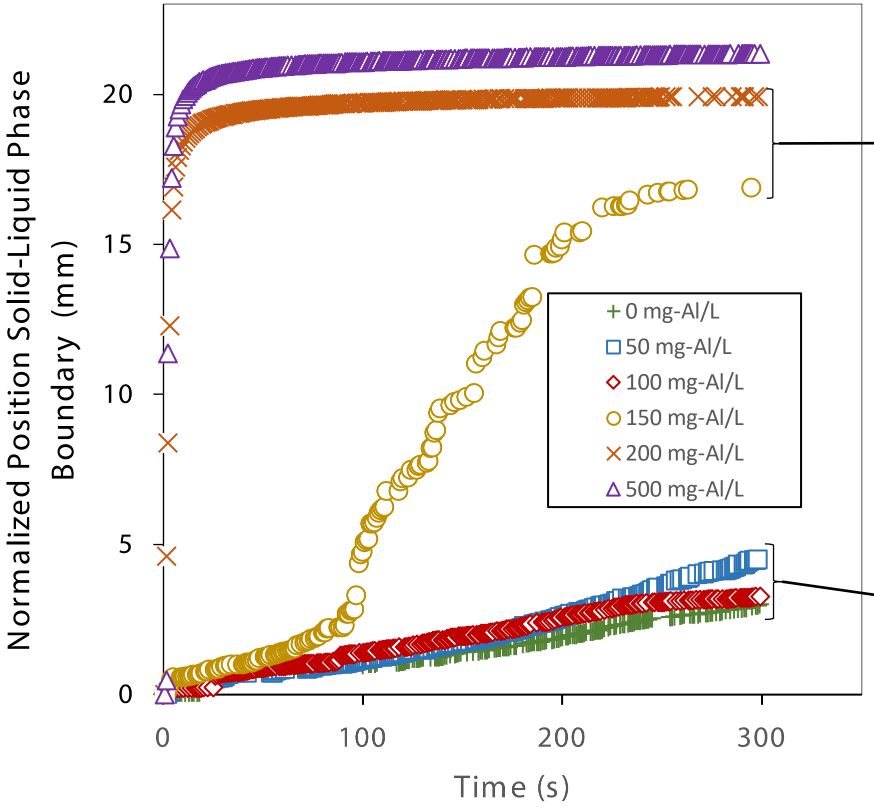
$$\text{Instability Index} = \frac{\Delta T_i}{\Delta T_{max}}$$

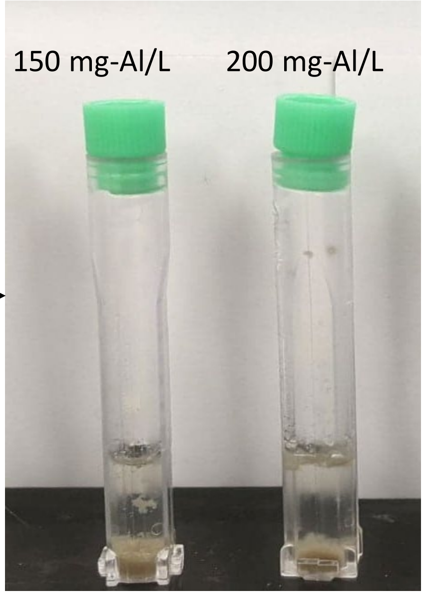
Key Takeaway:

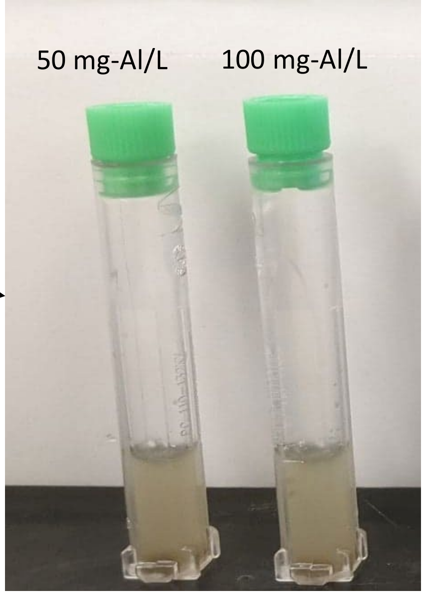
↑ Instability index ↑ Better Settling

Results 1: Phase-boundary profiles and instability indexes enable us to determine the lowest coagulant concentration required for rapid colloid settling

Varying *polyaluminum chloride* dosages at a solution pH of 6.







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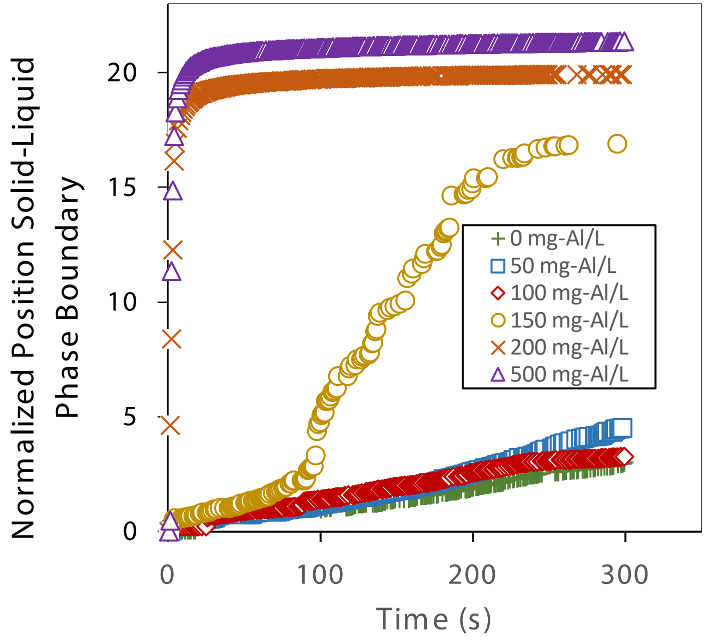
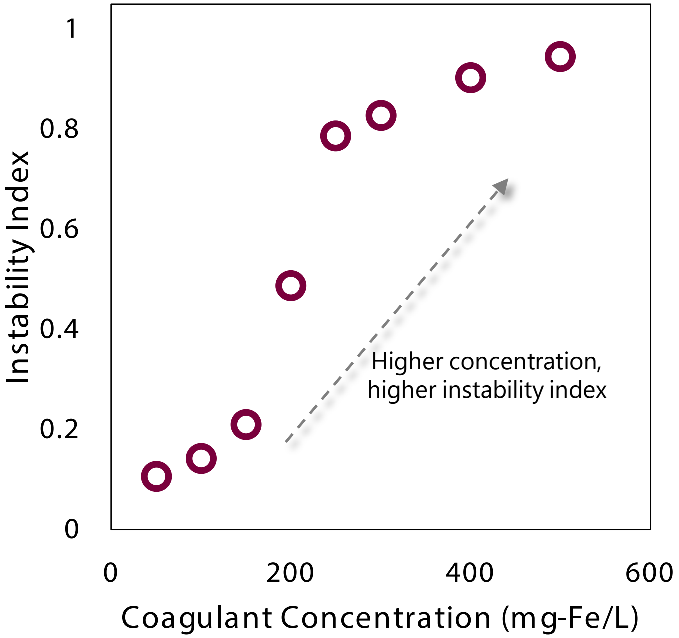
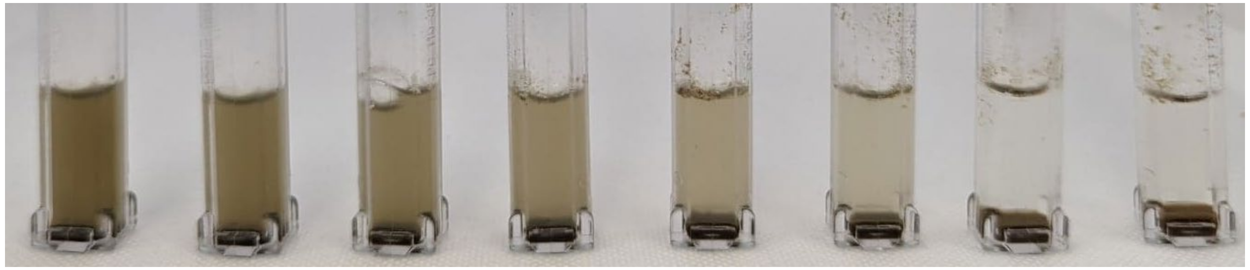


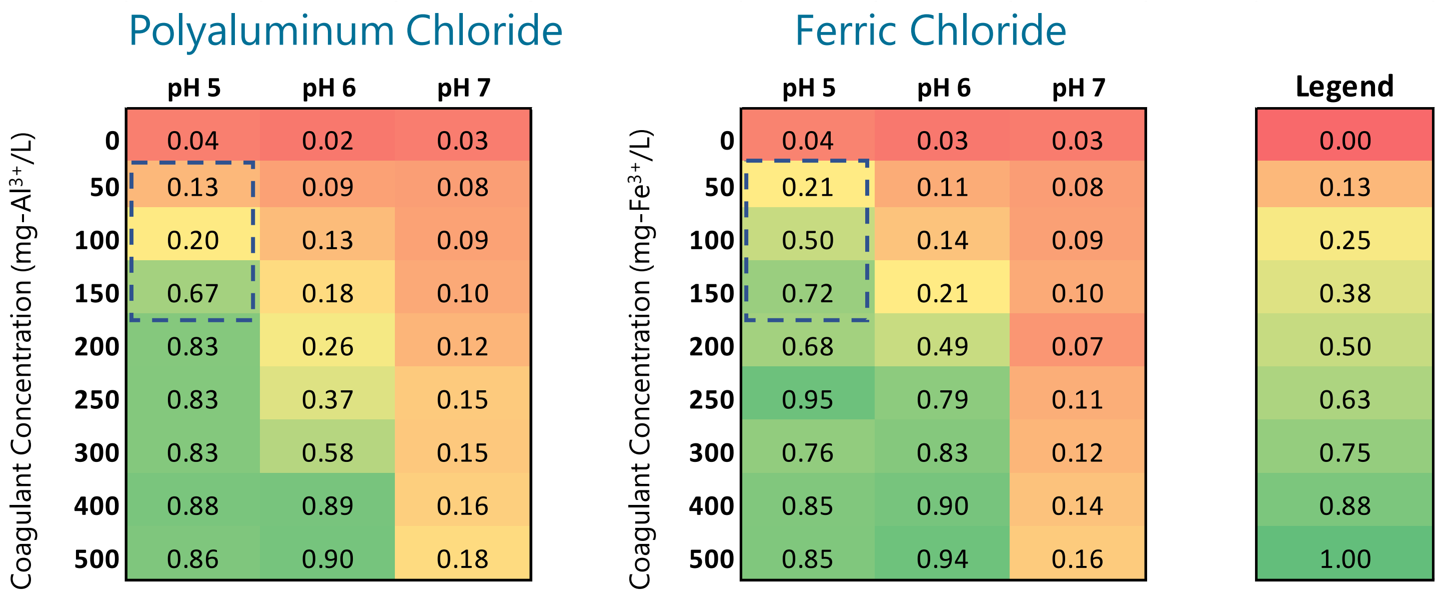




Key Takeaways

- Identify coagulant dosage needed to achieve high colloidal instability

Results 2 & 3: Instability index values allow us to rapidly identify conditions that provide rapid colloid destabilization & compare coagulants head-to-head



Polyaluminum Chloride

Coagulant Concentration (mg-Al^{3+}/L)

	pH 5	**pH 6**	**pH 7**
0	0.04	0.02	0.03
50	0.13	0.09	0.08
100	0.20	0.13	0.09
150	0.67	0.18	0.10
200	0.83	0.26	0.12
250	0.83	0.37	0.15
300	0.83	0.58	0.15
400	0.88	0.89	0.16
500	0.86	0.90	0.18

Ferric Chloride

Coagulant Concentration (mg-Fe^{3+}/L)

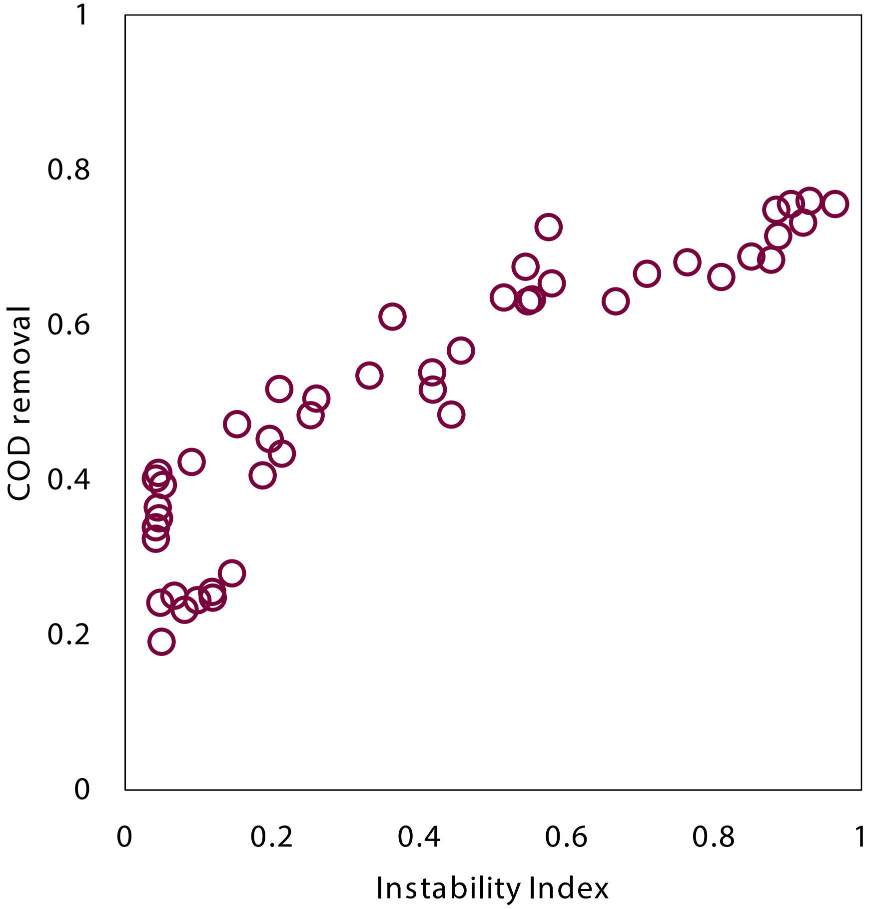
	pH 5	**pH 6**	**pH 7**
0	0.04	0.03	0.03
50	0.21	0.11	0.08
100	0.50	0.14	0.09
150	0.72	0.21	0.10
200	0.68	0.49	0.07
250	0.95	0.79	0.11
300	0.76	0.83	0.12
400	0.85	0.90	0.14
500	0.85	0.94	0.16

Legend
0.00
0.13
0.25
0.38
0.50
0.63
0.75
0.88
1.00

Key Takeaways

- Identify coagulant dosage needed to achieve high colloidal instability
- Higher instability index values achieved at lower pHs
- Higher instability index values achieved with ferric chloride

Results 4: When comparing all 48 experiments, positive relationship between COD removal and instability index was identified



COD measured from
LUMiFuge supernatant

Key Takeaways

- Identify lowest **concentration** and stability index needed for rapid settling at a single **pH**
- Higher instability achieved at lower pHs
- Greater instability was achieved with ferric chloride
- The higher the instability index, the higher the COD removal

The LUMiFuge can effectively quantify colloidal instability, but can it be used to select pre-treatment conditions for DAF treatment?

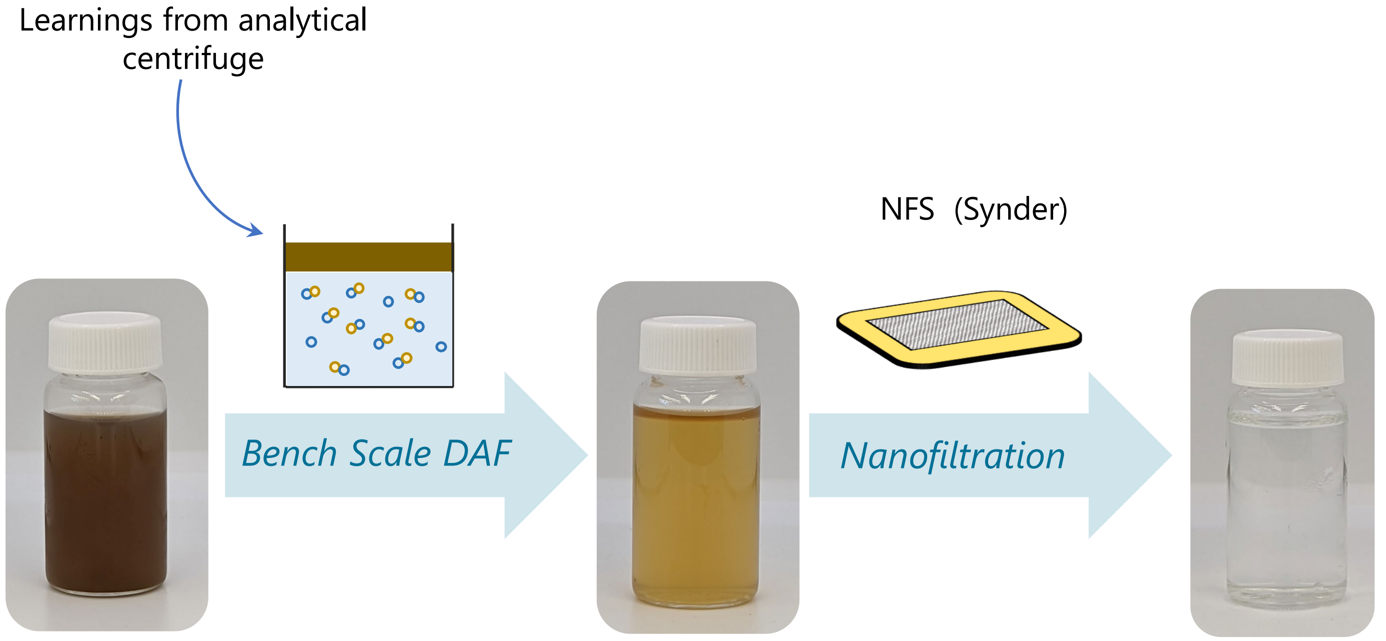
✓ **LUMiFuge** can quantify instability

? Can it select conditions for DAF treatment?

Key Takeaways

- Identify lowest **concentration** and stability index needed for rapid settling at a single **pH**
- Lowering the solution pH (making it more acidic), requiring less coagulant to achieve destabilization
- Ferric chloride was able to produce greater instability and at lower coagulant dosages
- The higher the instability index, the higher the COD removal

DAF treating the centrate enabled 2-fold increase in permeate flux as compared to the untreated centrate



Learnings from analytical centrifuge

NFS (Synder)

Bench Scale DAF

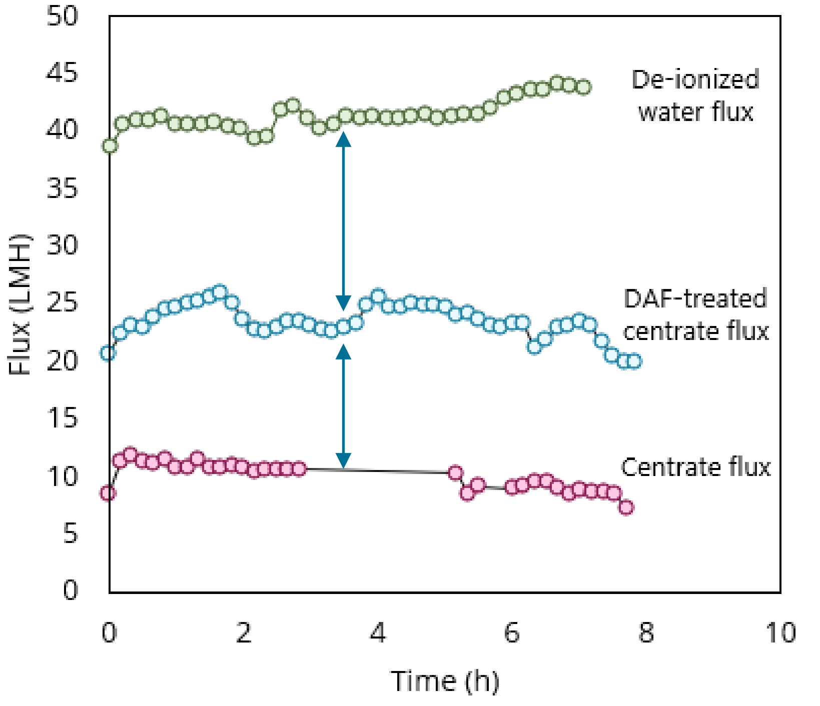
Nanofiltration

Turbidity: 1420 NTU
Color: 2830 TCU
COD: 4778 mg/L

Turbidity: 44.4 NTU
Color: 647 TCU
COD: 2219 mg/L

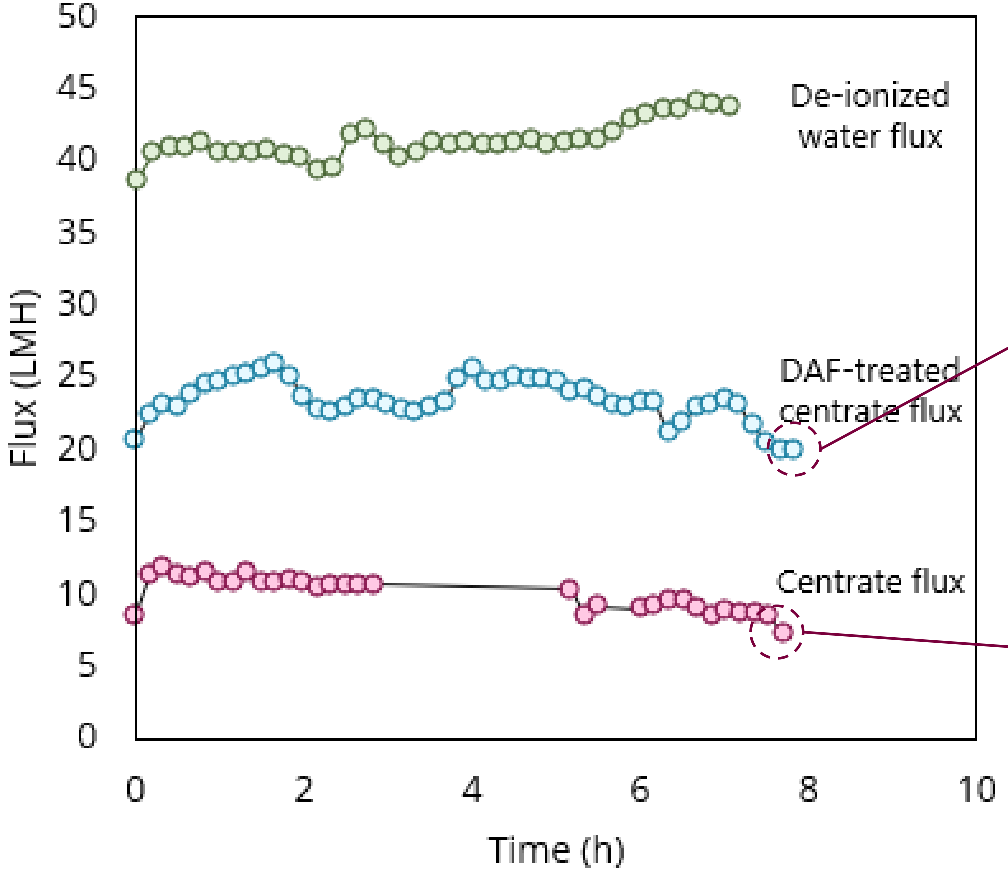
Turbidity: <0.5 NTU
Color: 5 TCU
COD: 1020 mg/L

DAF-Treated flux ~2x the centrate flux



DAF resulted in excess residual iron in the wastewater, which resulted in inorganic (mineral) fouling

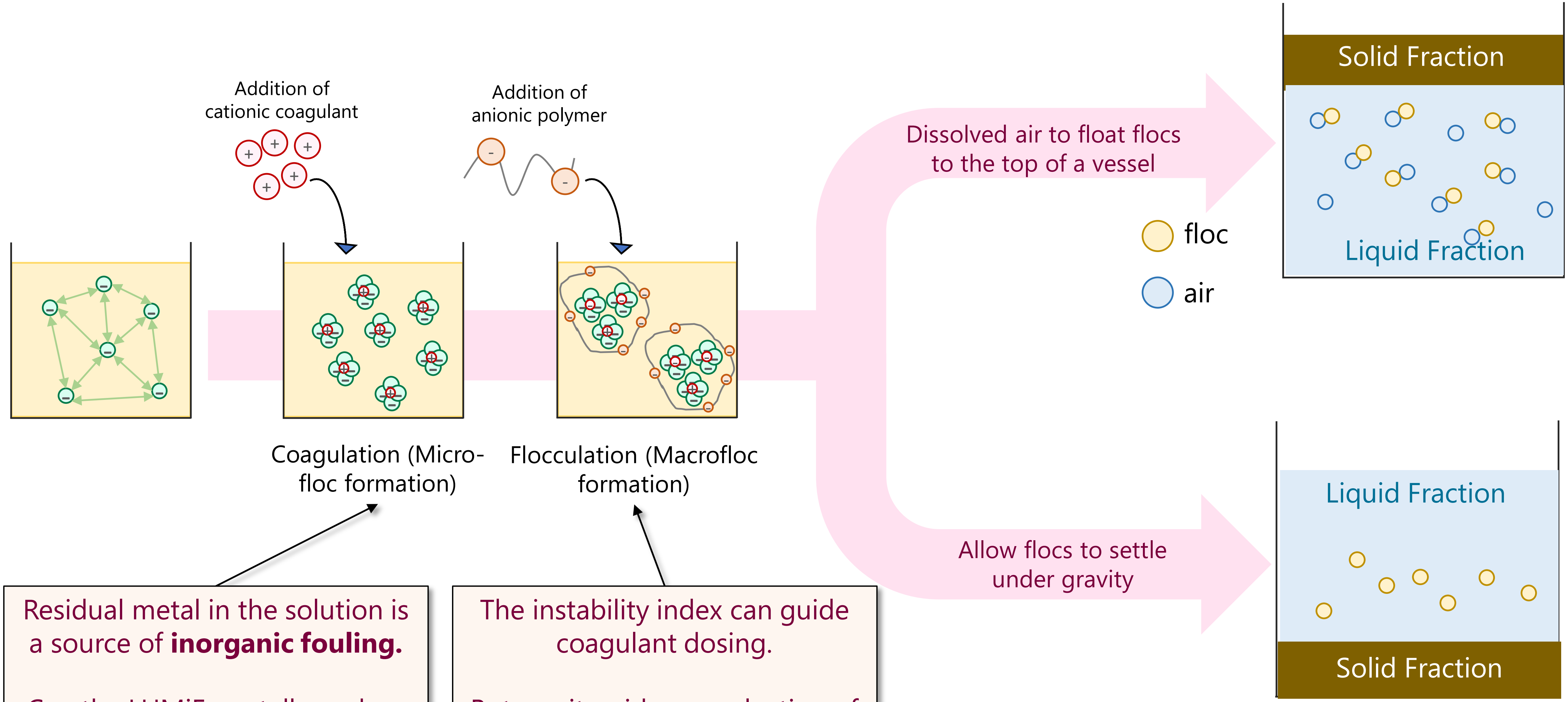
DAF-Treated flux ~2x the centrate flux



Centrate with DAF treatment

Centrate

Forming large flocs using a flocculant is crucial for DAF treatment, while excess iron can lead to inorganic fouling in downstream membrane filtration processes



Addition of cationic coagulant

Addition of anionic polymer

Coagulation (Micro-floc formation)

Flocculation (Macrofloc formation)

Dissolved air to float flocs to the top of a vessel

Allow flocs to settle under gravity

floc

air

Solid Fraction

Liquid Fraction

Liquid Fraction

Solid Fraction

Residual metal in the solution is a source of **inorganic fouling.**

Can the LUMiFuge tell us when we dosed in too much metal?

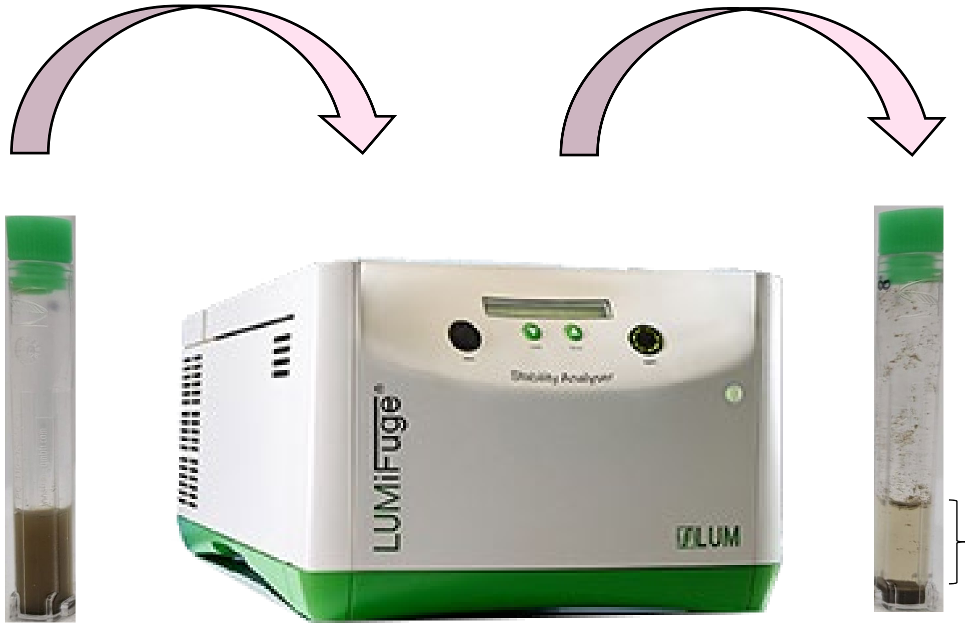
The instability index can guide coagulant dosing.

But can it guide our selection of flocculant dosage?

We measured the COD removal and residual iron in the supernatant fraction of the LUMiFuge vial

Residual metal in the solution is a source of **inorganic fouling.**

Can the LUMiFuge tell us when we dosed in too much metal?

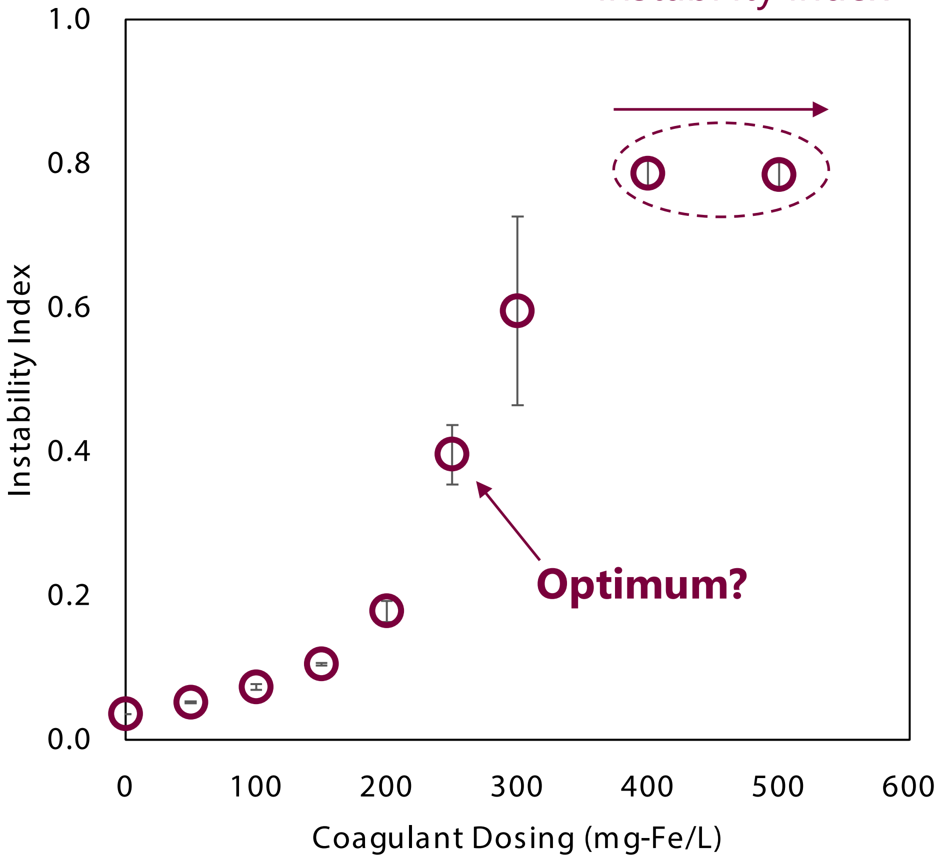


COD REMOVAL
RESIDUAL IRON (ICP-OES)

INSTABILITY INDEX
FRONT TRACKING

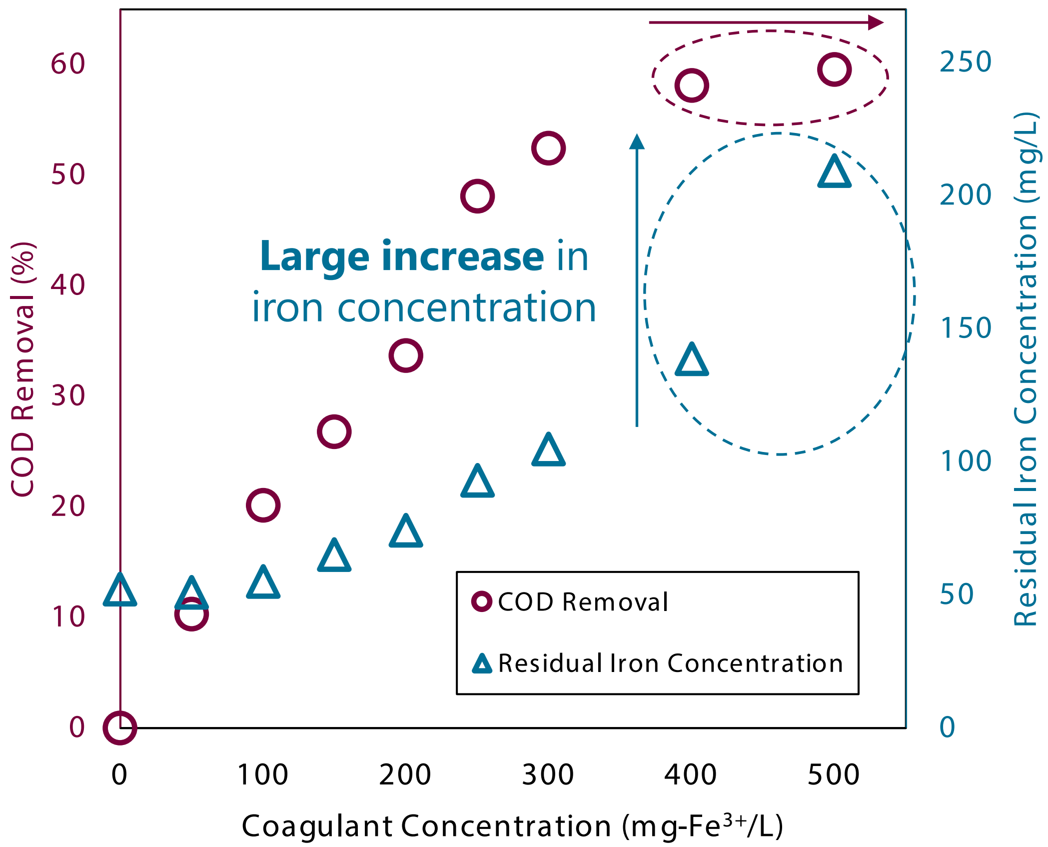
Parameter	Units	Aug-2022
Chemical Oxygen Demand	mg/L	7739
Zeta-Potential	mV	-17.1
Electrical Conductivity	µS/cm	23600
pH		8.34
Total Dissolved Solids	mg/L	10600
Nitrate as N	mg/L	<1.4
Nitrite as N	mg/L	<1.1
Ammonia as N	mg/L	2900
Total Organic Carbon	mg/L	1280
True Colour	TCU	6000
Turbidity	NTU	249
Total Calcium	mg/L	201
Total Magnesium	mg/L	83.2
Total Potassium	mg/L	1730
Total Sodium	mg/L	2419
Total Iron	mg/L	52.2

Plateauing regions of instability index can indicate when additional coagulant will not improve COD removal and increase residual iron



No increase in instability index

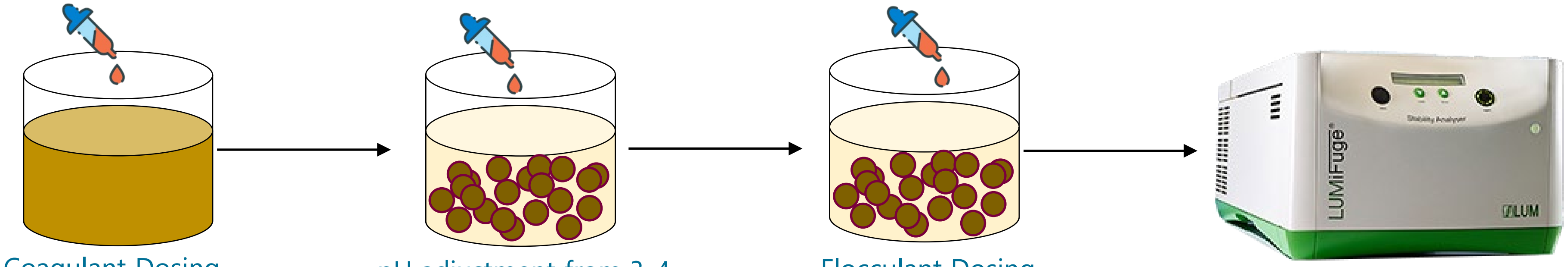
Optimum?



No increase in COD removal

Large increase in iron concentration

Low, intermediate and high coagulant dosages were selected for further treatment with a polyacrylamide anionic polymer



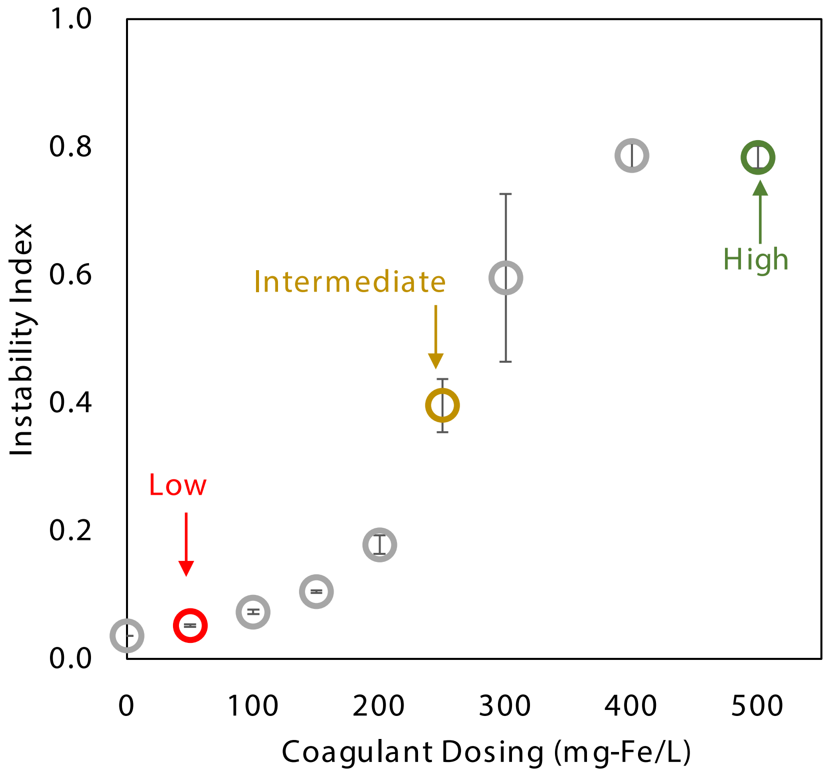
Coagulant Dosing
(300 rpm, 3 minutes)

pH adjustment from 3-4
to 7 – 7.5 with NaOH
(50 rpm, 1 minute)

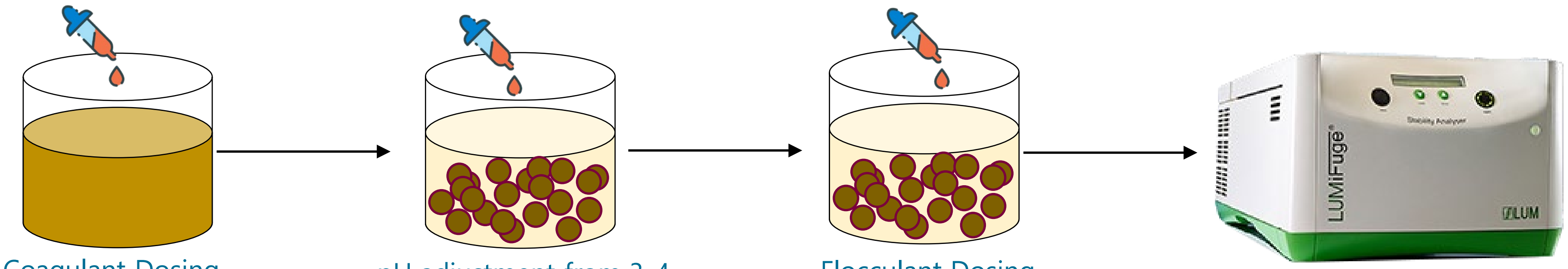
Flocculant Dosing
(50 rpm, 3 minute)

The instability index can guide coagulant dosing.

But can it guide our selection of flocculant dosage?



Flocculant dosing increased settling velocity, however, did not have an impact on in the instability index



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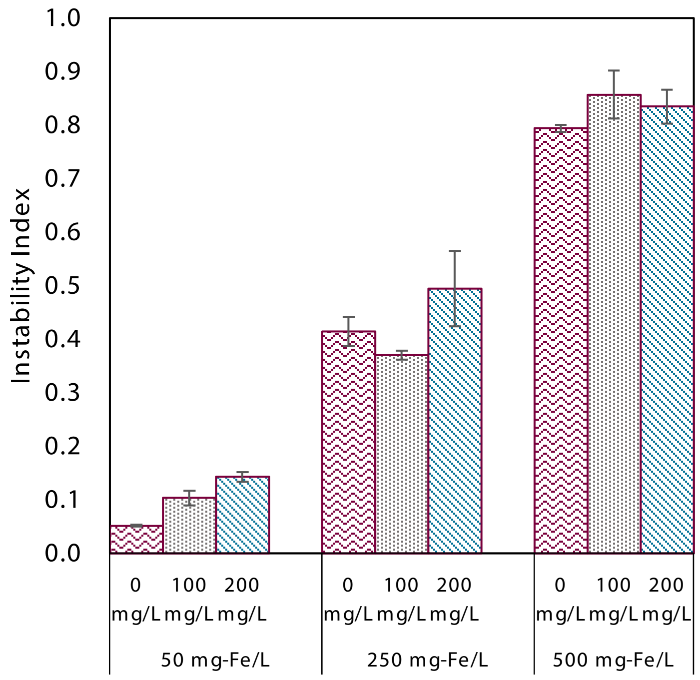
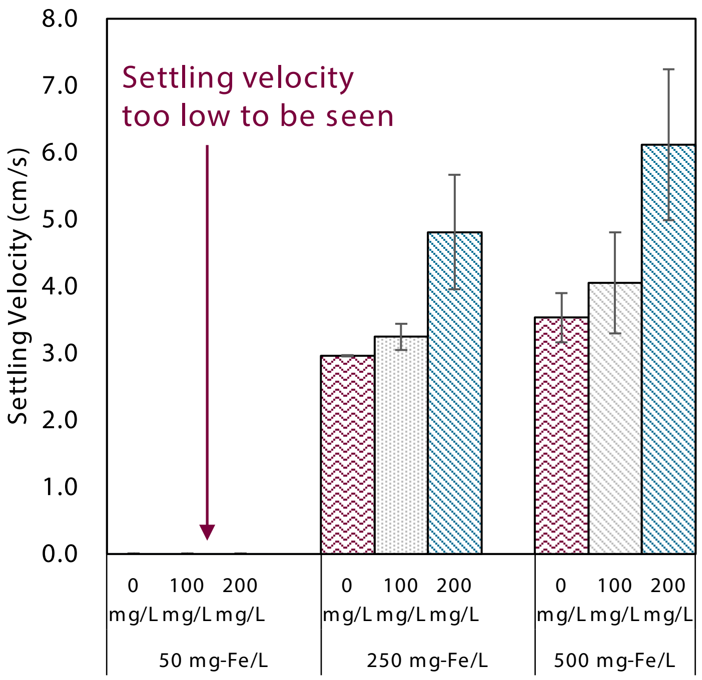
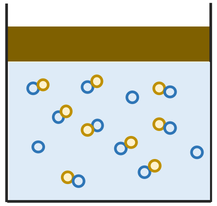




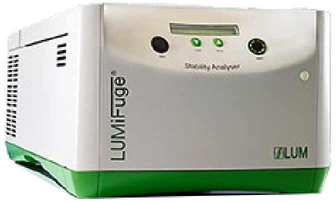
Settling velocity
too low to be seen

DAF-NF process enables on-site water reuse or direct discharge, and the LUMiFuge enables rapid screening of coagulants and flocculants

What did we learn?



A DAF-NF process can enable wastewater re-use within a biogas plant, thereby ***bridging the gap*** in the water energy nexus



The LUMiFuge is a fast an effective alternative that can be used to determine the ideal solution conditions for DAF treatment

Where do we go from here?

Pilot-scale DAF System

Pilot-scale NF system

Thank you!

Mitacs

Anaergia
Fueling a Sustainable World™

JNE Environmental

DUPONT™

Bridging the gap at the water-energy nexus:

Treating wastewater byproducts from biogas production processes via hybrid filtration technology

Abhishek Premachandra[1], Yves McKay[1], Indranil Sarkar[2], Kevin Lutes[2], Sasha Rollings-Scattergood[2] & David Latulippe[1]
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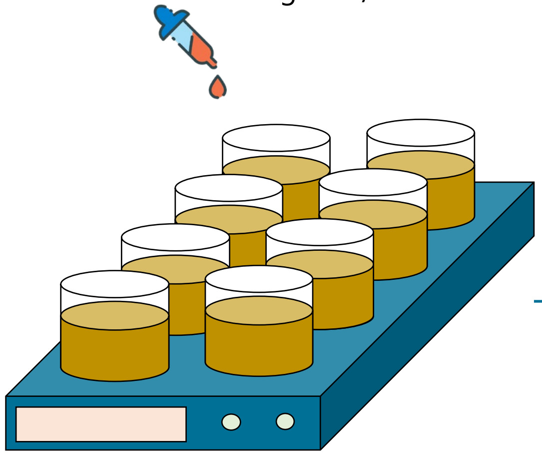
[1]McMaster University, Hamilton, ON, Canada
[2]Anaergia, Burlington, ON, Canada

Results 1: Phase-boundary profiles and instability indexes enable us to determine the best conditions for coagulation

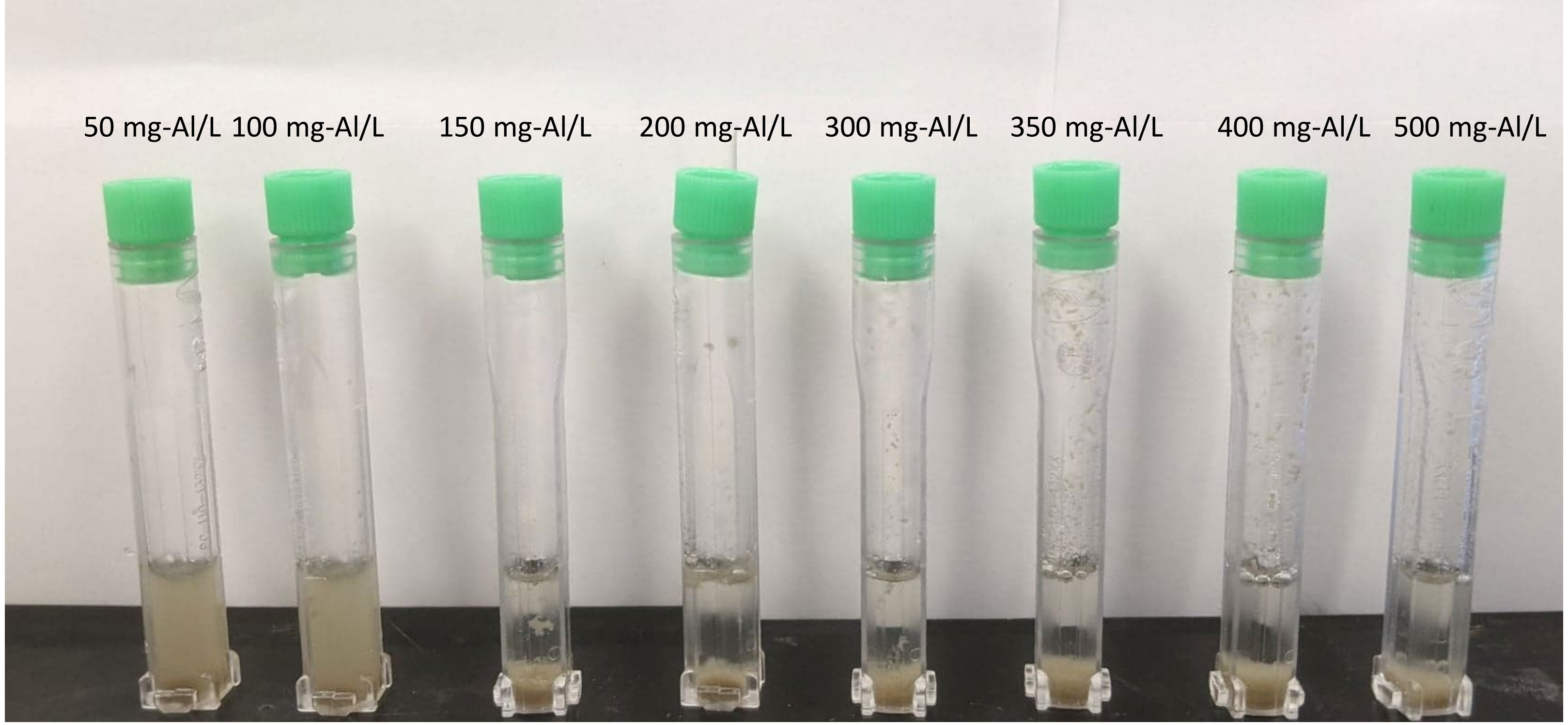
The Process:

Coagulant/Flocculant Dosing, pH adjustment



Transfer to LumiFuge Vial

Centrifugation at 2000 RPM with front tracking every second


50 mg-Al/L
100 mg-Al/L
150 mg-Al/L
200 mg-Al/L
300 mg-Al/L
350 mg-Al/L
400 mg-Al/L
500 mg-Al/L