



Resource Recovery and Environmental Protection in Wyoming's Greater Green River Basin Using Selective Nanostructured Membranes

DE-FE0031855

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November 3, 2020. Budget Period 1 Continuation Application



Project Goals and Objectives

This project will develop a working prototype of a two-part affinity based membrane separation process for recovering hydrocarbons, and separating particulates and organics, from produced water originating from the Greater Green River Basin in Wyoming. To this end we will:

- i. Synthesize superhydrophobic/oleophilic and superhydrophilic/oleophobic membranes to achieve high flux/selectivity for BTEX/oil and water filtration while being resistant to fouling from particulates and organics representative of GGRB produced waters, respectively.
- ii. Design and manufacture membrane spacers and channel geometries optimized for phase separation/recovery in spiral wound membrane element configurations.
- iii. Execute a techno economic assessment (TEA) of the implementation of the proposed membrane process in the GGRB to include economic benefits from resource (BTEX/oil) recovery, water savings, and reduced treatment costs.
- iv. Deliver two membrane prototype modules for BTEX/oil recovery and water filtration.



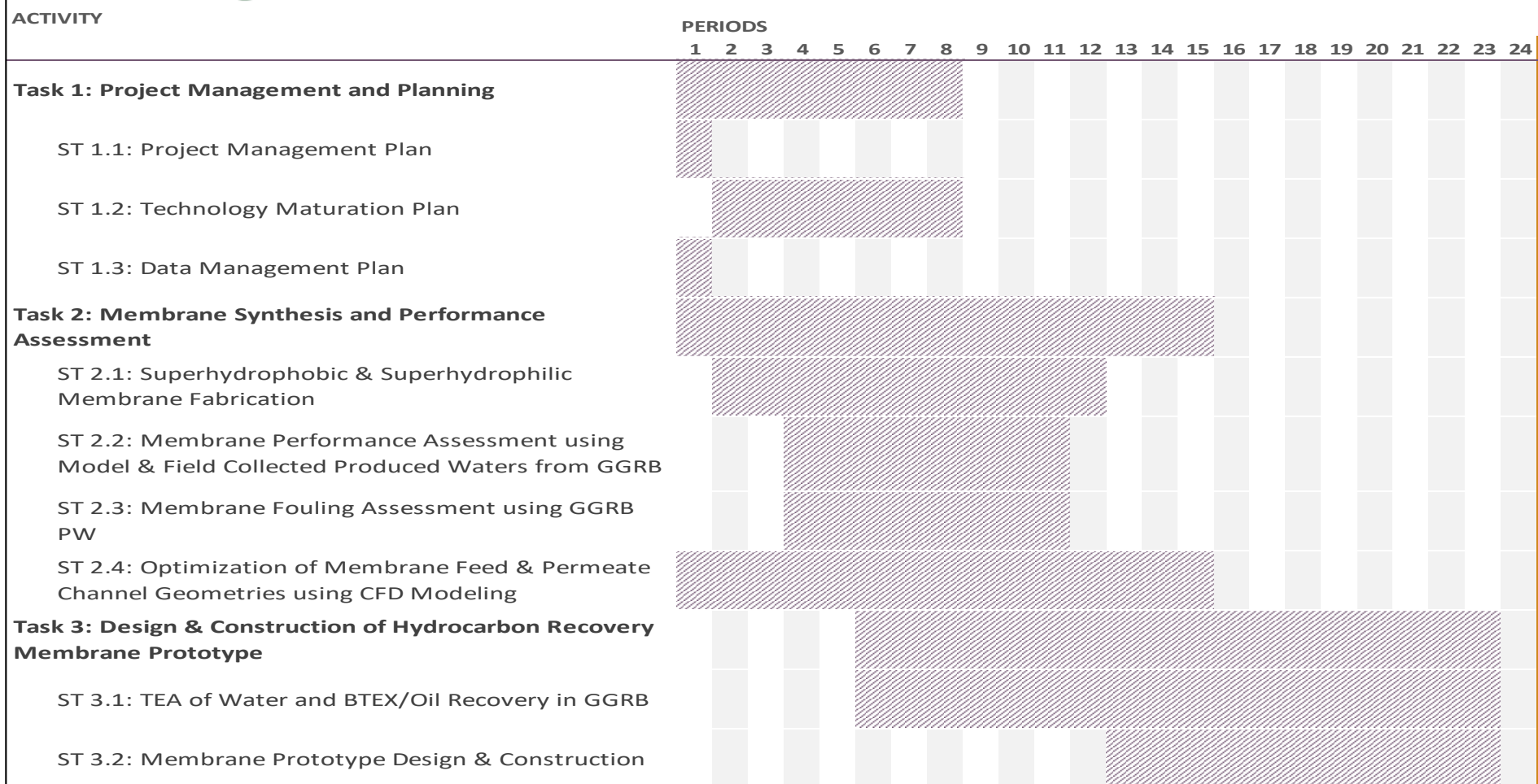
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Task/ Subtask	Milestone Title & Description	Planned Completion Date	Completion Date / % Complete
1.1	M1 - Project Management Plan	01/30/2020	01/30/20
1.2	M2 – Technology Maturation Plan (TMP)	09/01/2020	09/30/20
1.3	M3 – Data Management Plan (DMP)	01/30/2020	01/30/20
2.2, 2.3, 3.1	M4 – Water samples collected & characterized from 4 distinct stations in GGRB (70% of total sites)	09/01/2020	09/01/20
	M5 – Continuation Application	09/01/2020	09/01/20
2.1	M6 – Design of superhydrophobic & superhydrophilic membranes is complete	12/31/2020	45% complete
2.4	M7 – Completion of CFD modelling for membrane spacers & channel height	04/01/21	45% complete
3.1	M8 – TEA of BTEX/oil recovery process complete	12/31/2021	65% complete
3.2	M9 – Membrane prototype design and construction complete	12/31/2021	Pending





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Project Budget

	Budget Period 1		Budget Period 2		Total	
	DOE Funds	Cost Share	DOE Funds	Cost Share	DOE Funds	Cost Share
Applicant	\$746,743	\$0	\$459,520	\$0	\$1,206,263	\$0
H2O Systems	\$6,700	\$155,000	\$6,400	\$85,500	\$13,100	\$240,500
Triton Water	\$0	\$40,000	\$0	\$19,500	\$0	\$59,500
Total (\$)	\$753,443	\$195,000	\$465,920	\$105,000	\$1,219,363	\$300,000





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Aim #1 – Material optimization and performance evaluation of superhydrophilic/oleophobic and superhydrophobic/oleophilic membranes made using electrospinning/spraying.

Jonathan Brant (UW)





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Membrane Fabrication

- Superhydrophobic membranes made coating PVDF nanofibers w/ nano-carbon black
 - Spinning/spraying conditions manipulated to optimize fiber size → liquid entry pressure
 - Surface coatings explored for enhancing non-aqueous phase adhesion to fibers (enhanced permeation)
- Superhydrophilic membranes made using polyacrylonitrile (PAN)
- Synthesis conditions optimized for roll-to-roll production required for prototype construction





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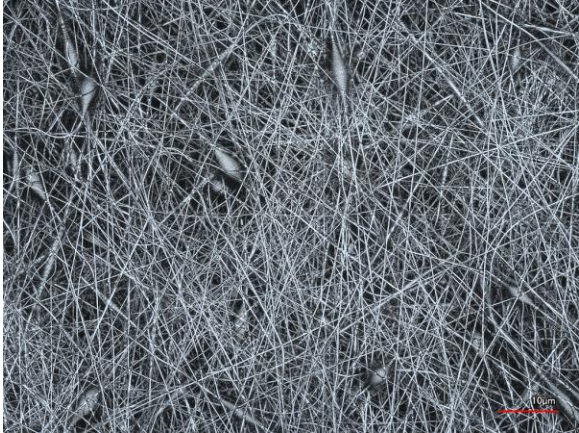
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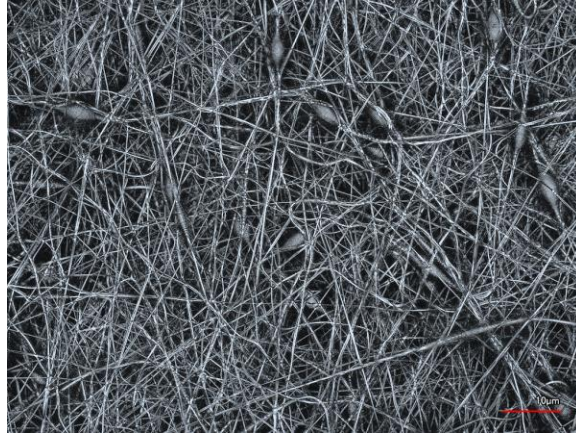


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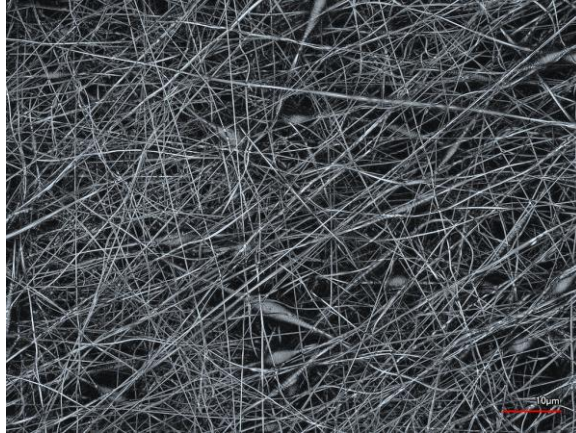
Superhydrophobic Membranes: Synthesis Conditions



Q = 0.8 mL/hr



Q = 1.0 mL/hr



Q = 1.3 mL/hr



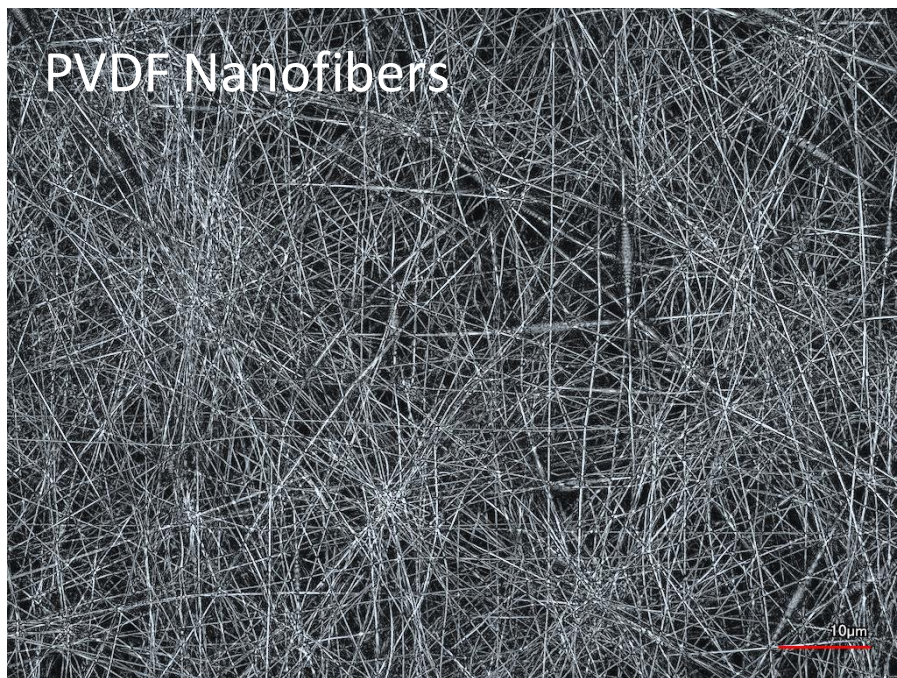
Q = 1.5 mL/hr

Optimum Conditions: Voltage Gradient = 19 kV, Tip to Collector = 25 cm, RH = 20%, Temp = 33°C

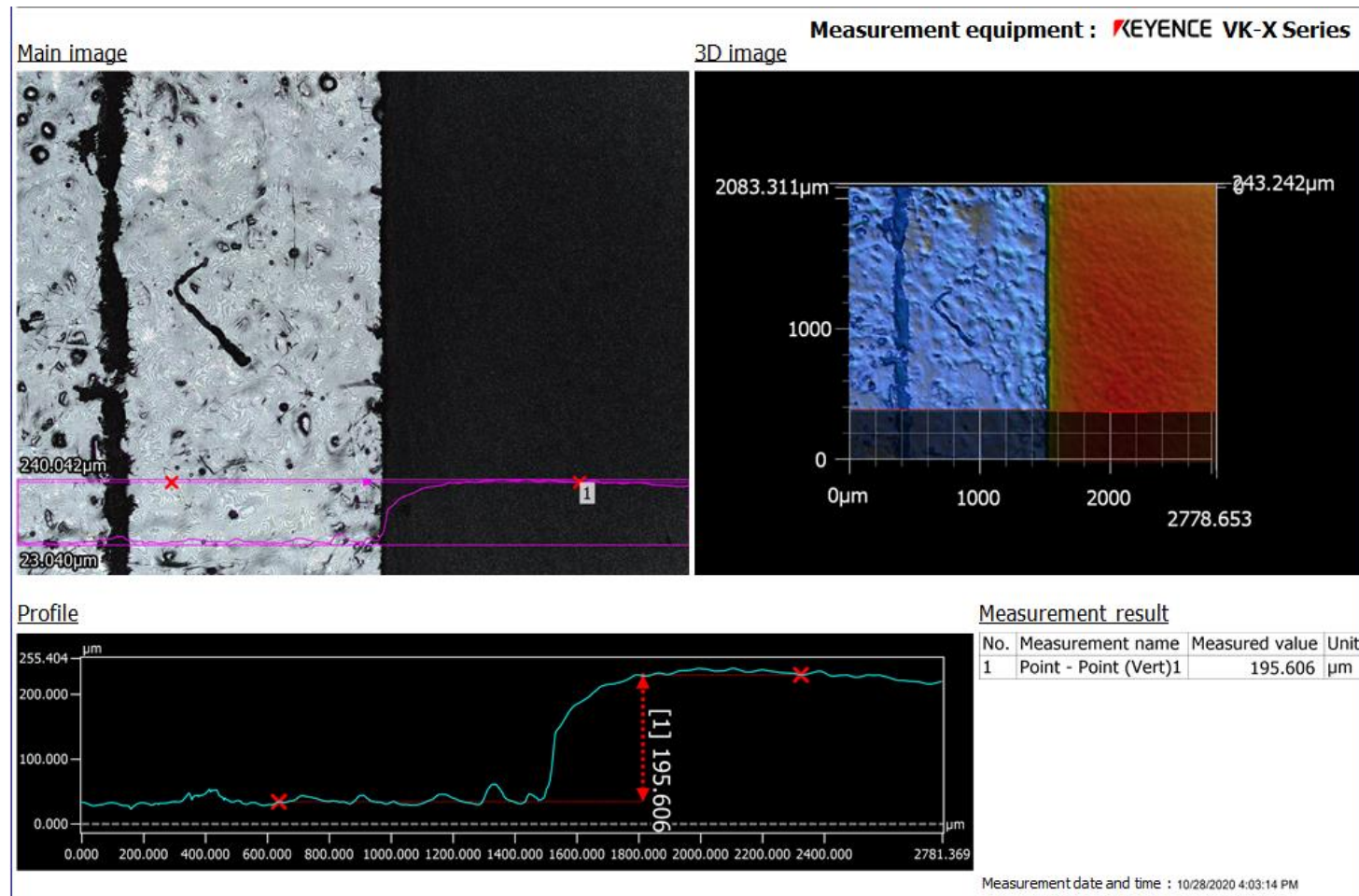


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Superhydrophobic Membranes



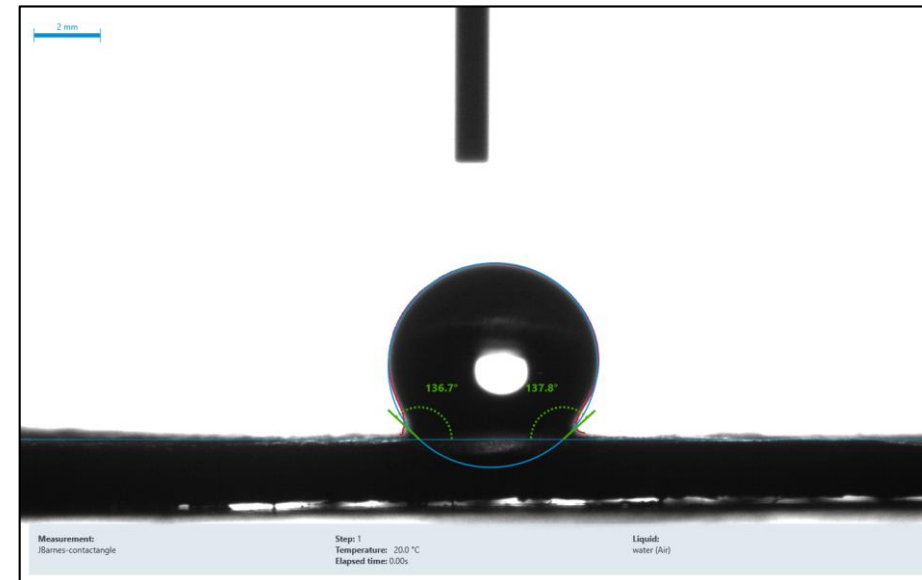
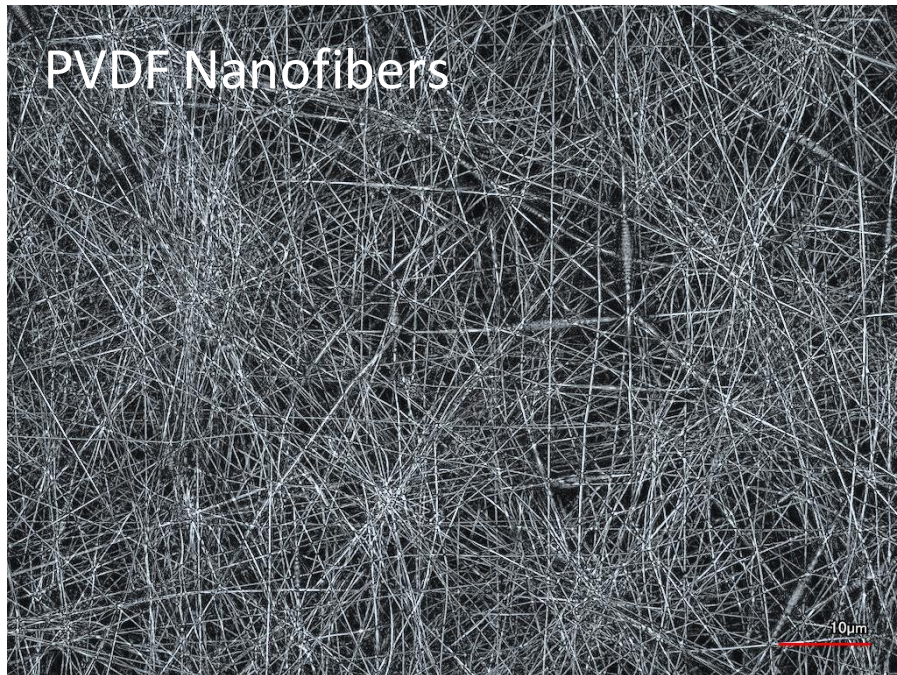
PVDF Nanofibers





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Superhydrophobic Membranes



Relevant properties:

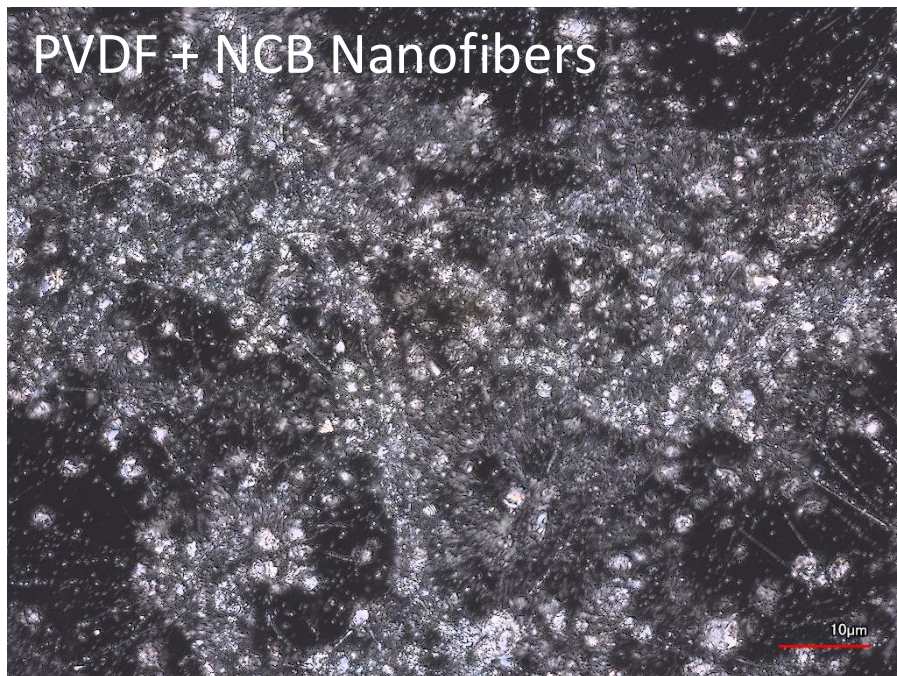
- Contact angle w/ water $\geq 135^\circ$
- LEP ≥ 20 psi
- Nominal pore diameter $\sim 0.4 \mu\text{m}$



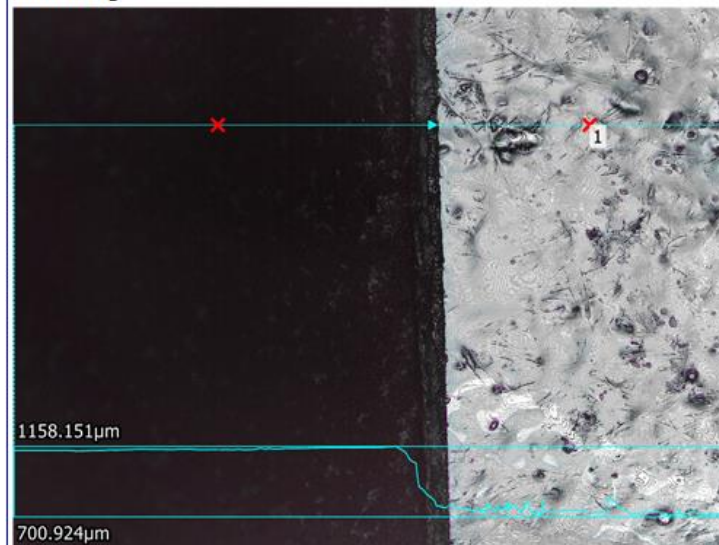
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Superhydrophobic Membranes

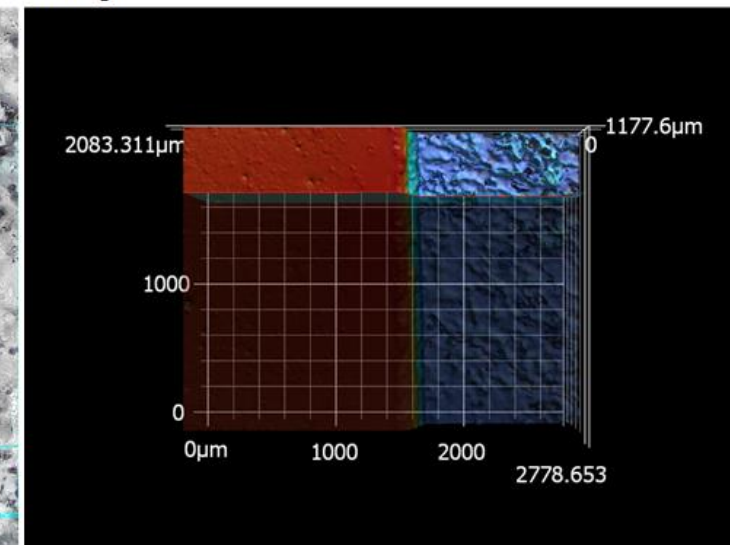
PVDF + NCB Nanofibers



Main image

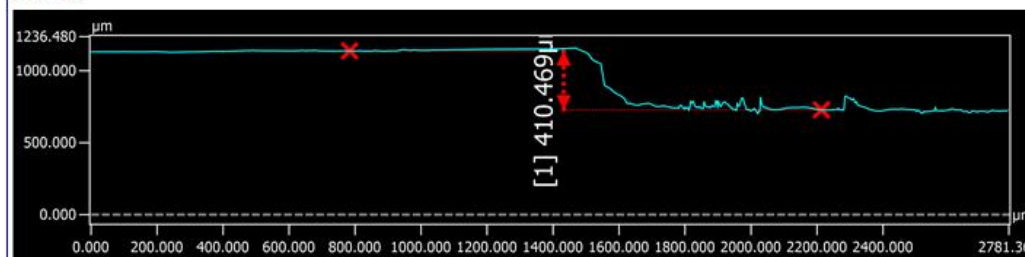


3D image



Measurement equipment : KEYENCE VK-X Series

Profile



Measurement result

No.	Measurement name	Measured value	Unit
1	Point - Point (Vert)1	410.469	µm

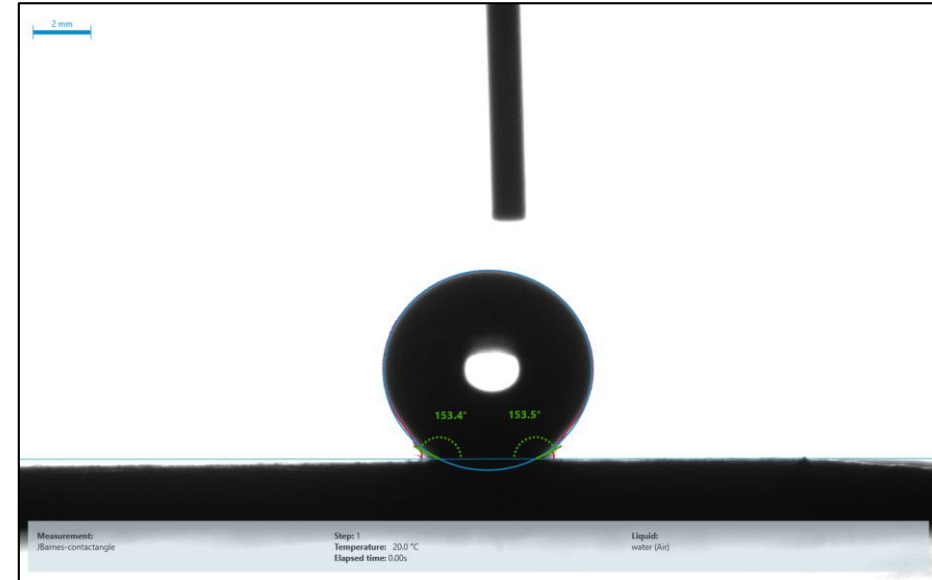
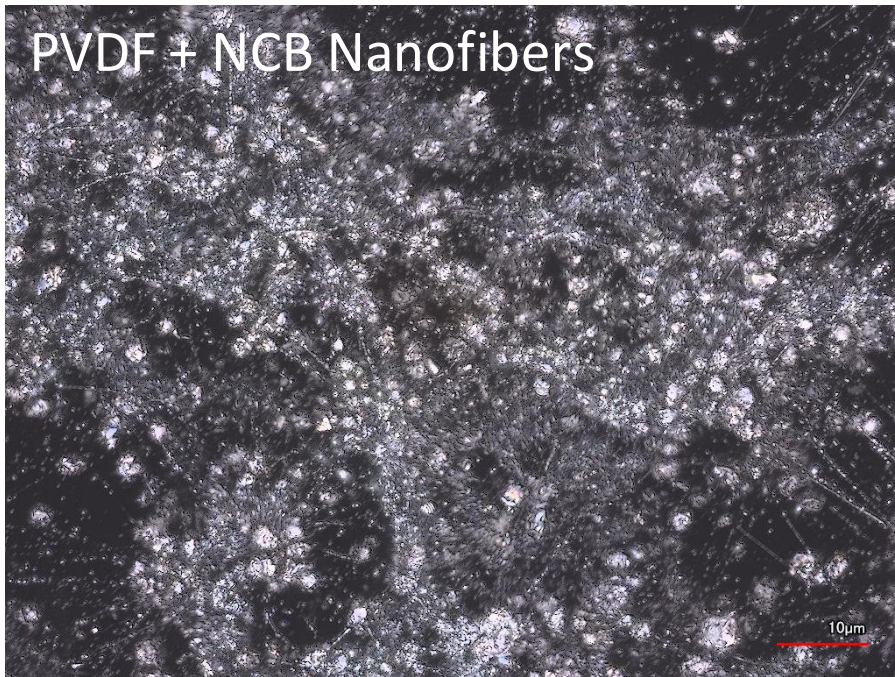
Measurement date and time : 10/22/2020 4:40:39 PM



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Superhydrophobic Membranes

PVDF + NCB Nanofibers



Relevant properties:

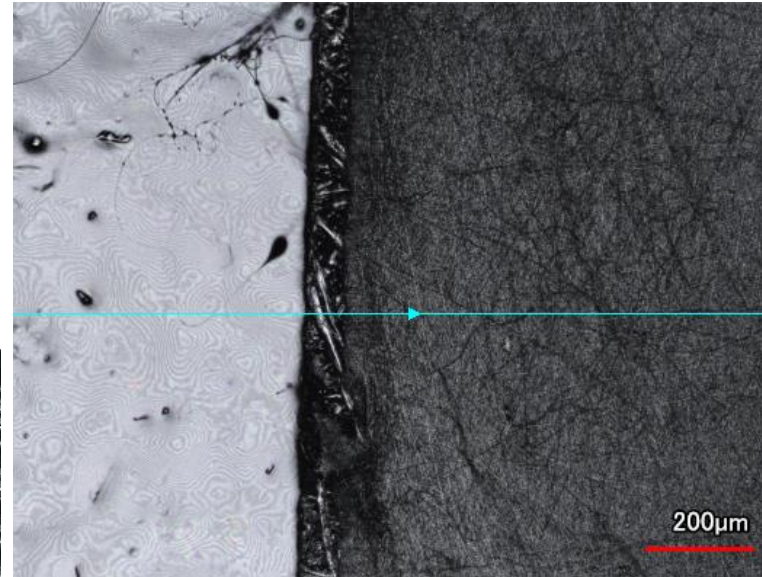
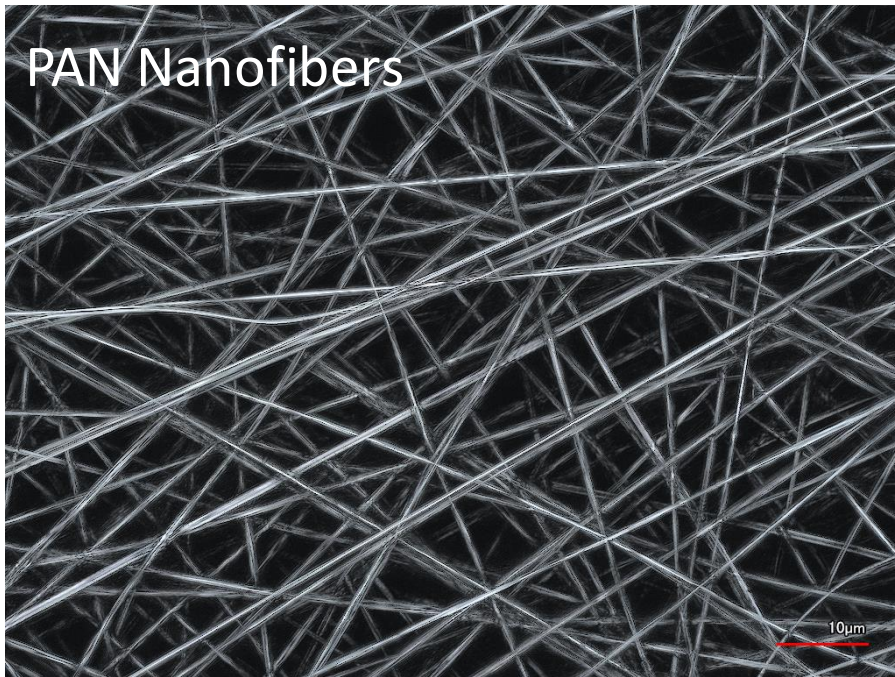
- Contact angle w/ water $\geq 155^\circ$
- LEP ≥ 30 psi
- Nominal pore diameter $\sim 0.35 \mu\text{m}$



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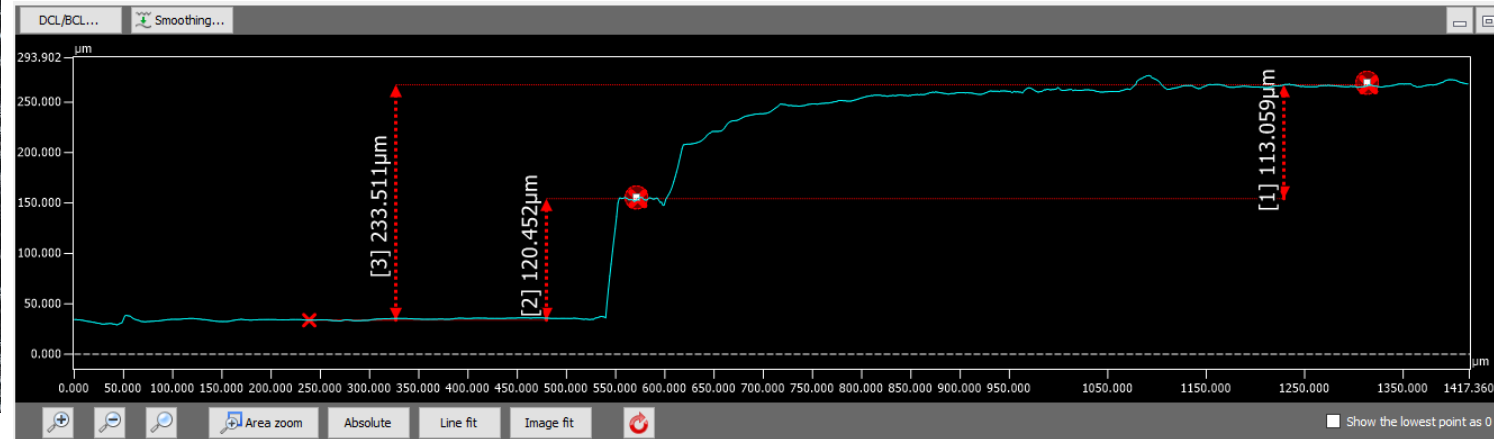
Superhydrophilic Membranes

PAN Nanofibers



Relevant properties:

- Contact angle w/ water $\sim 0^\circ$
- LEP = atmospheric
- Nominal pore diameter $\sim 0.4 \mu\text{m}$





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Aim #2 – Design and construction of crossflow membrane modules for selectively concentrating and then separating BTEX/oil from GGRB produced water

Jonathan Brant (UW)





- **Goals:** development of numerical simulations tools for the evaluation of
 - Membrane design options (spacer configurations)
 - Targeted flow variations (the effect of turbulence)
 - Up-scaling effects (use of design concepts for much larger domains)
- **Traditional (brute force) approach:** numerical solution of PDEs
 - Challenges: non-trivial boundary conditions (BC), range of model parameters
 - Implied issues: discretization errors, instabilities, convergence issues
 - Relatively high computational cost
- **Our strategy:** development of complementing analysis tools
 - Analytical tool (exact, highly efficient, applicable to simplified test cases)
 - Monte Carlo tool (general, flexible, more expensive, better than brute force)
 - Method validation, comparisons, design analysis

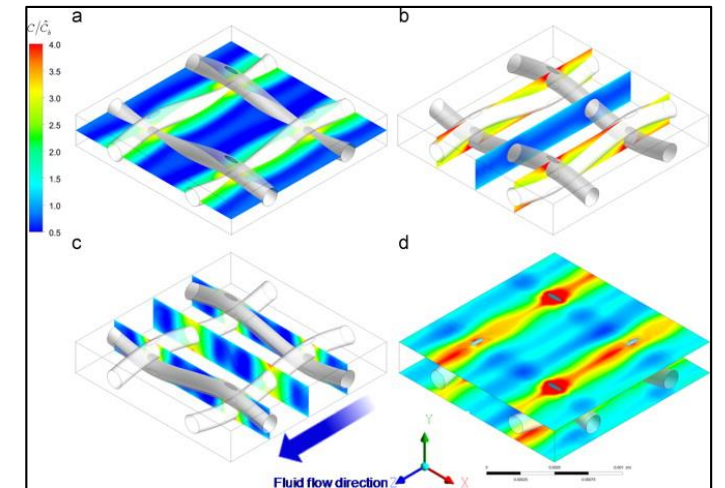


Image Credit: Gurreri et al. 2014.



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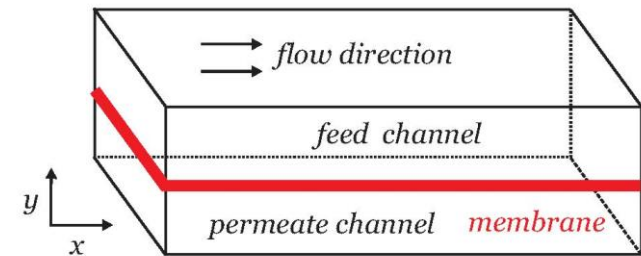
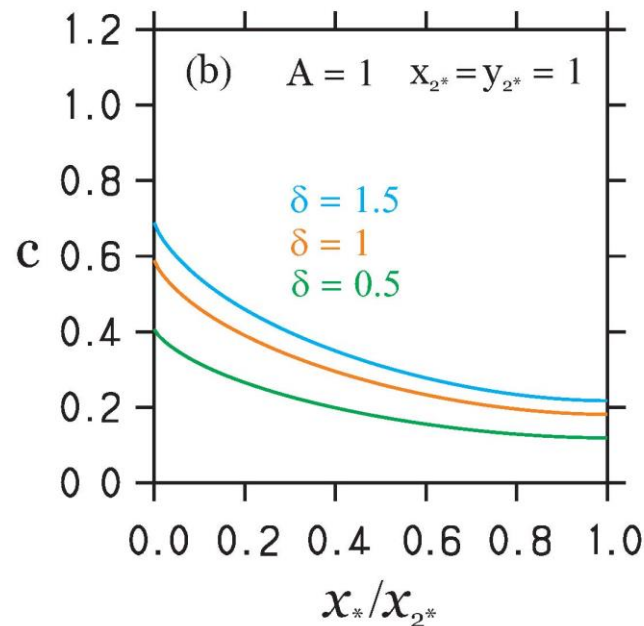
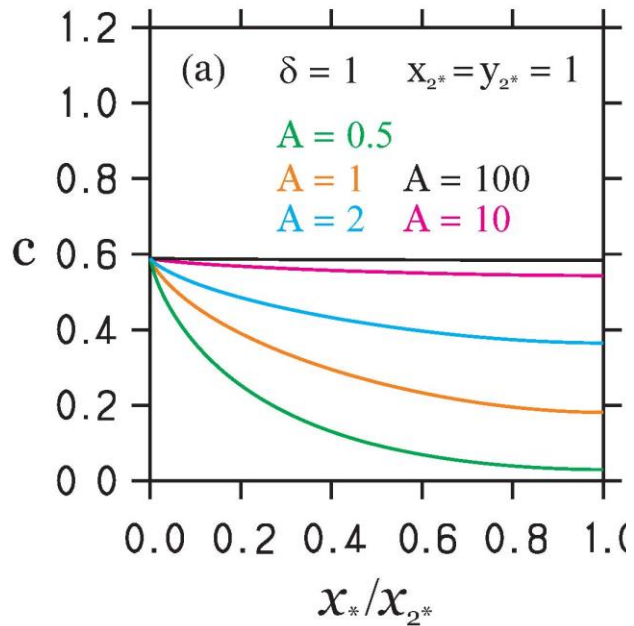
CFD – Analytical Flow Simulator (AFS)

PDE:
$$\frac{\partial c}{\partial t} + U c_x + V c_y = D_M (c_{xx} + c_{yy}), \quad \frac{\partial \varepsilon_p c}{\partial t} + U c_x + V c_y = D_M (c_{xx} + c_{yy})$$

IC, BC: $c(x, y, 0) = 0, \quad c(0, y, t) = c_0, \quad c_x(L, y, t) = 0.$

exact analytical solution
(Fourier series expansion)
– in less than one minute!

$c_y(x, y_1, t) = 0, \quad c(x, y_2, t)V / \delta - D c_y(x, y_2, t) = 0,$





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CFD: Monte Carlo Flow Simulator (MCS)

- Monte Carlo (MC) approach:

- Partial differential equations (PDEs) can be exactly reformulated as MC eqs.
- Math approach is hardly known (only some experts know about reformulation)
- Significant advantages compared to standard brute force tool (no instabilities)
- Significant advantage: flexible tool (enables study of spacer design effects)
- However, case considered is challenging (BC)

- Next steps:

- 1) Comparison of AFS predictions with experiments, publication
- 2) Monte Carlo Simulator (MCS) development (BC treatment)
- 3) MCS validation using AFS, experimental data
- 4) Computational reflection of spacer designs in MCS (channels)
- 5) Analysis and predictions: spacer design, up-scaling, BC



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Aim #3: Techno-economic assessment of BTEX/oil recovery, and clean water production, using superhydrophilic/oleophobic and superhydrophobic/oleophilic membrane separation for GGRB produced water.

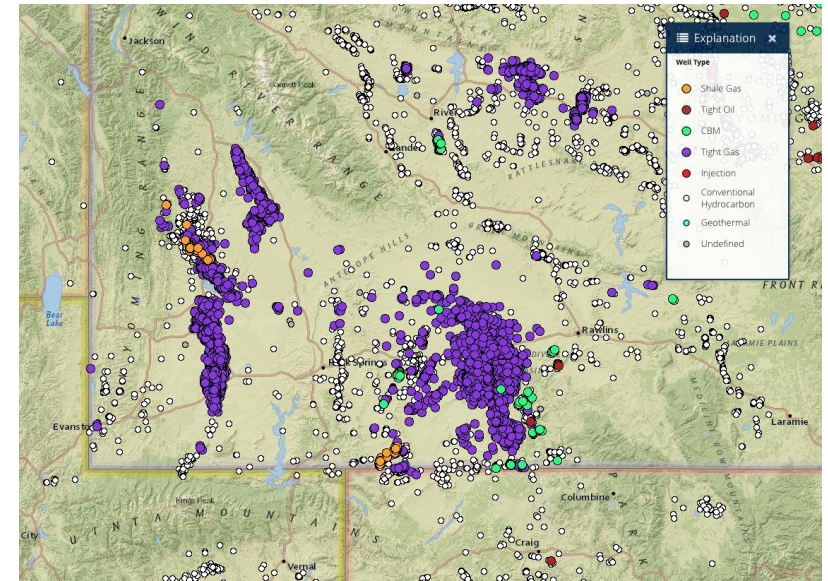
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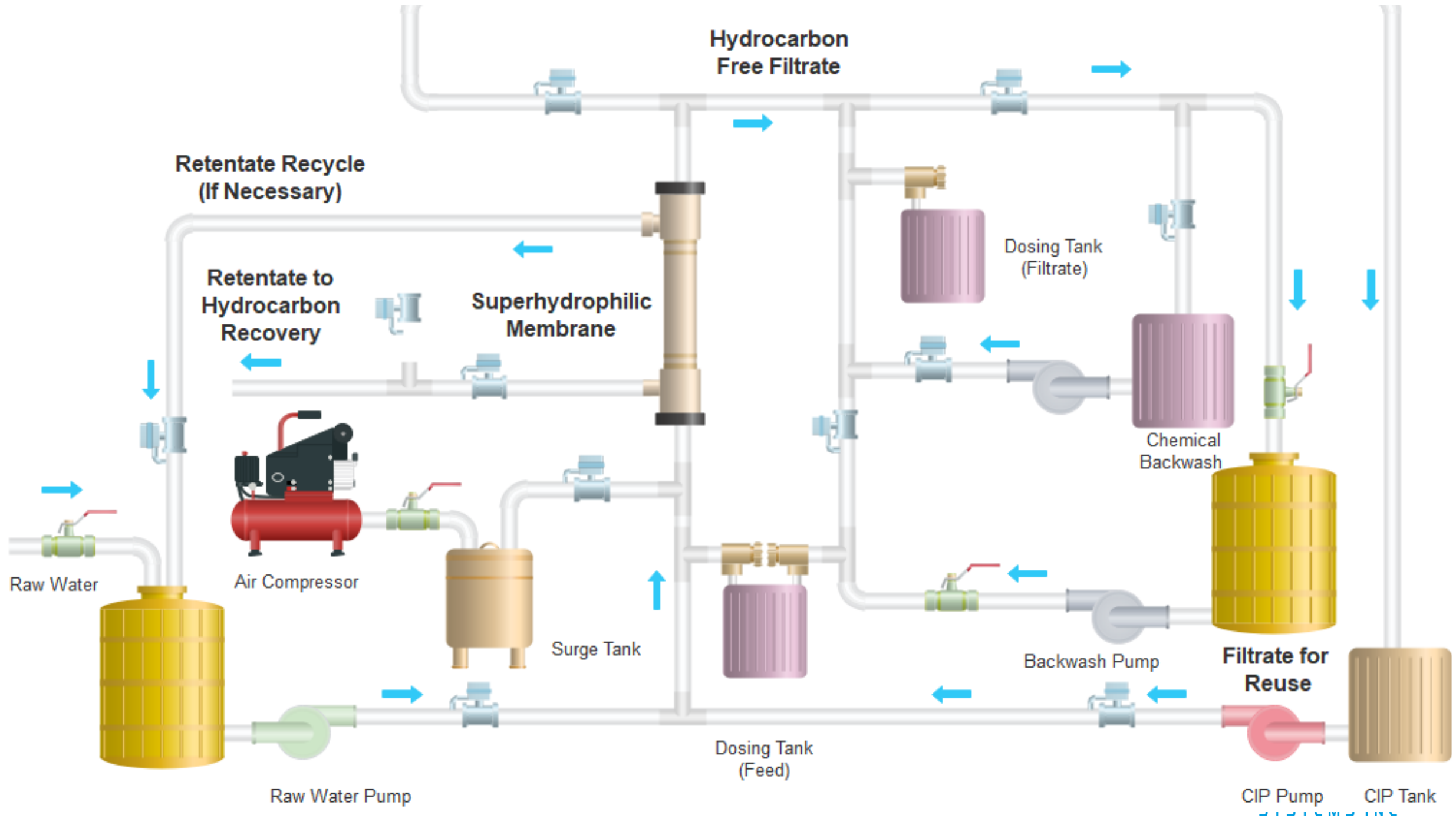


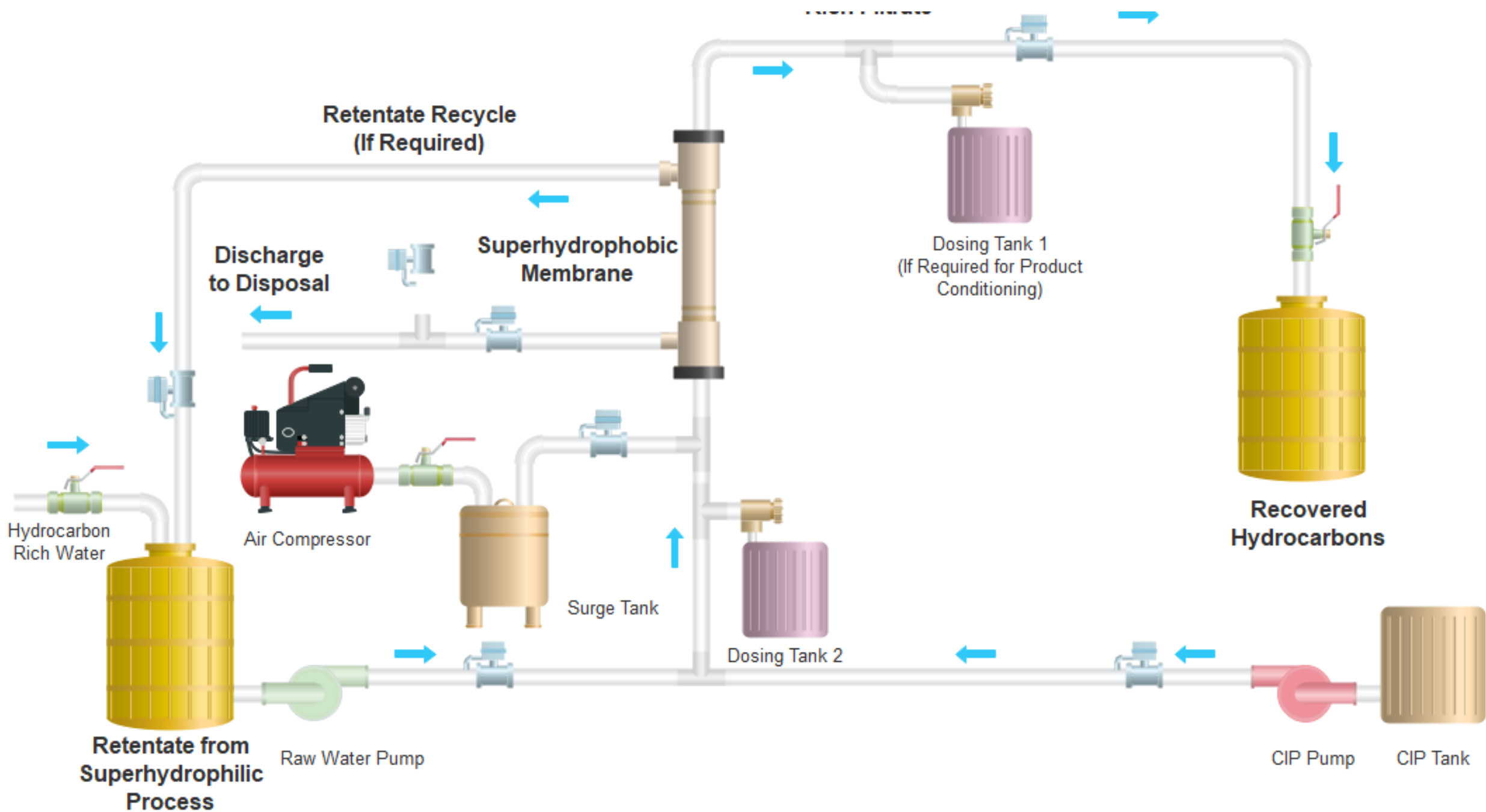
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Water Quality Parameter	Value
Turbidity, NTU	237
Total dissolved solids (TDS), mg/L	23,800
Chemical oxygen demand (COD), mg/L	682
Total hardness (TH), mg/L	704
Total organic carbon (TOC), mg/L	2,500



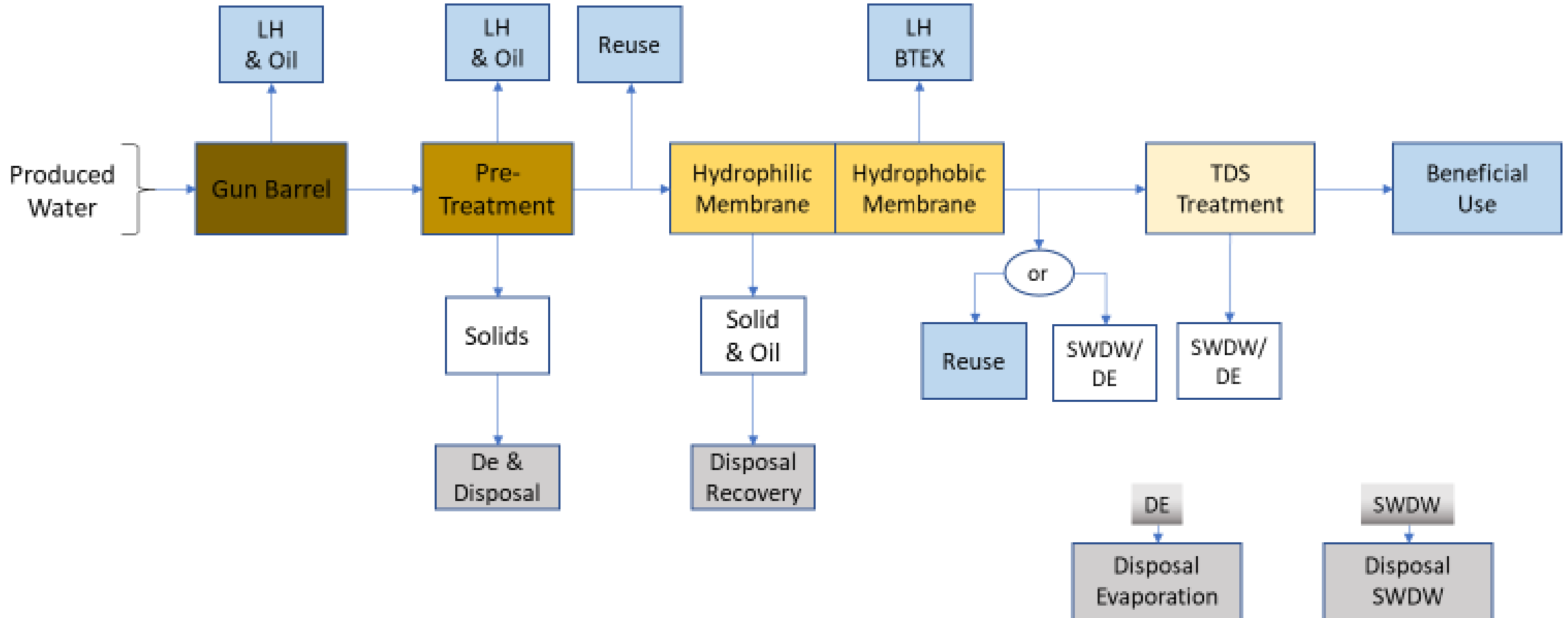
Sample	pH	EC (mS/cm)	Turbidity (NTU)	Total O&G mg/L	TSS (mg/L)	TDS (mg/L)
Canyon Creek	8.08	33.6	153	4,100	128	26,192
Trail	8.52	28.9	130	800	154	28,440
Kinney	8.20	119.0	49	2,400	658	103,482
Powder Wash	5.24	62.0	27	3,200	296	54,066
Church Buttes	5.74	23.8	>1,000	5,200	2,768	22,996

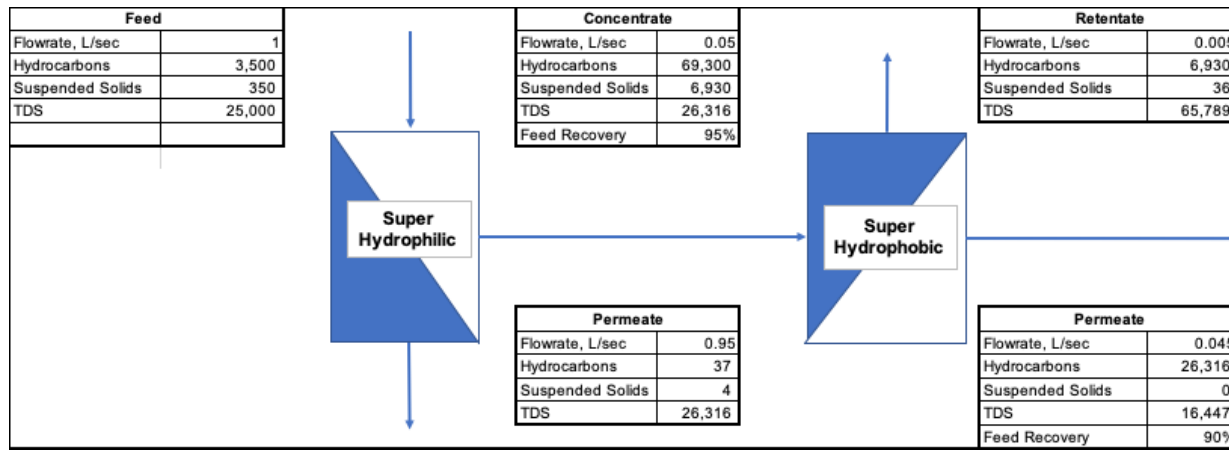






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Resource Recovery Parameters

- Water filtration using superhydrophilic/oleophobic membrane
 - Feed recovery ratio = 95%
 - Suspended solids rejection = 99%
 - Hydrocarbon rejection = 99%
 - Influent hydrocarbon (total O&G) concentration = 3,500 mg/L
- Hydrocarbon recovery superhydrophobic/oleophilic membrane
 - Feed recovery ratio = 90%
 - Hydrocarbon (total O&G) rejection = 1%
 - Water rejection = 99%

Economics

- Total PW Treated GGRB = 128 Mbbls
- Total O&G Recovered = 351,338 bbls/yr
 - Value = \$36/bbl (10% below market value)
- Economic recovery = \$12,648,183/yr
 - Payback period < 1 yr if 30 systems operating in GGRB