Protocol for Preparing Synthetic Solutions Mimicking Produced Water from Oil and Gas Operations

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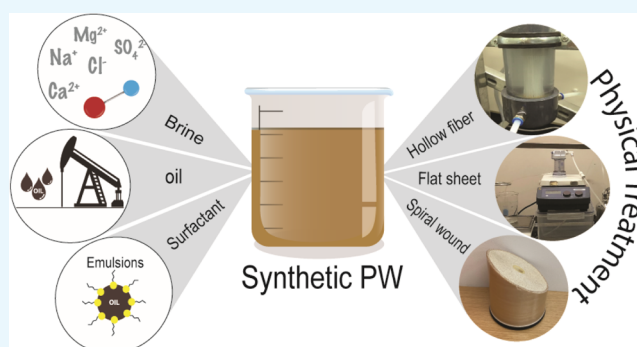
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ABSTRACT: Produced water (PW) is the water associated with hydrocarbons during the extraction of oil and gas (O&G) from either conventional or unconventional resources. Existing efforts to enhance PW management systems include the development of novel membrane materials for oil−water separation. In attempting to evaluate these emerging physical separation technologies, researchers develop various formulations of test solutions aiming to represent actual PW. However, there is no clear scientific guideline published in the literature about how such a recipe should be prepared. This article develops a protocol for preparing synthetic solutions representing the characteristics and behavior of actual PW and enabling the performance comparisons of different oil−water separation membranes at the bench scale level. In this study, two different brine recipes were prepared based on salts present in actual PW, crude oil was used as the hydrocarbon source, and a surfactant was added to disperse the oil into the aqueous phase. The recipe is accessible to the wider scientific community and was proven to be reproduceable, homogenous, stable, and comparable to actual PW field samples through analytical monitoring measurements and bench scale evaluations.

1. INTRODUCTION

1.1. Water in the Oil and Gas Industry. Water is an integral part of oil and gas (O&G) operations; it is produced and used in both upstream and downstream facilities within the O&G industry (Figure 1). In upstream applications, most of the water involved is referred to as produced water (PW), which is the water associated with hydrocarbons during the extraction of O&G from either conventional or unconventional resources. Water is also generated as a byproduct during the subsequent processing of hydrocarbons and in this setting, it is referred to as process water. In terms of PW production volumes, on average,
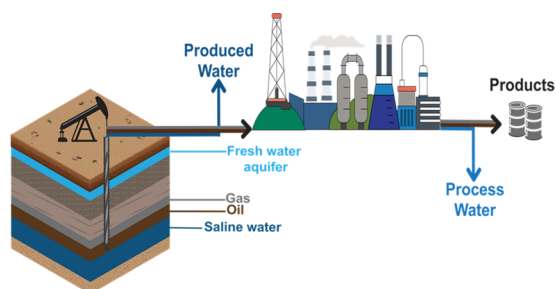
3−4 barrels of water are produced with every barrel of conventional oil extracted.[1] This value depends on several factors including the type, age, and geological features of a formation and may reach up to 10 barrels of water per barrel of oil for aging reservoirs.[2,3] The expansion of O&G production from unconventional resources was greatly dependent upon technologies, which utilize large volumes of water such as hydraulic fracturing for O&G extraction from shale plays.[4−7] Thus, based on the above estimates, it can be stated that on average O&G companies manage more volumes of water than hydrocarbons on a day-to-day basis making cost-effective water management a necessity for sustainable O&G operations.[8−10]

1.2. PW Characteristics. Unlike seawater, the chemical characteristics of PW cannot be generalized as they depend greatly on the age and location of the geological formation in addition to the type of hydrocarbon being produced.[1,11] The bulk characteristics of PW can be classified into organic and

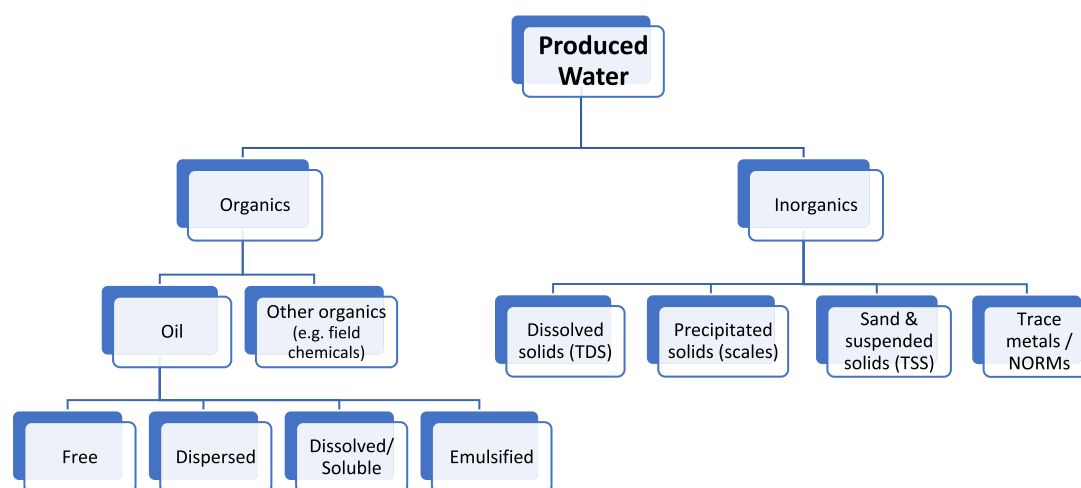**Figure 1.** Produced and process water in the O&G industry.

Figure 2. Main constituents of PW.

Table 1. Summary of Selected Synthetic Oil-In-Water Recipes Used in the Literature

references	oil source	surfactant	aqueous phase	method of mixing
Hu et al.[32]	machine oil	Tween 80 and Span 80	DI water	blended at 20,000 rpm for 5 min
Ghulam et al.[33]	hexadecane	SDS or $C_{23}H_{42}ClN$	NaCl solution	ultrasound at 50% amplitude for 30 min
Cherukupally et al.[34,35]	Texas Raw Crude	none added	water (not specified if tap/DI/other source)	continuous stirring of feed during the experiment
Cha et al.[36]	Rangely crude oil	none added	DI water	stirred at 500 rpm for 30 min
Ibrahim et al.[37]	canola oil	emulsifier (Ajax, Colgate-Palmolive, Australia)	water (not specified if tap/DI/other source)	blended at high speed for 15–20 min (milky white solution)
Almarouf et al.[38]	Catenex Oil 11 (shell)	Armac T. (solid phase)	100,000 ppm NaCl brine	mixed at 2500 rpm for 30 min
da Silva et al.[39]	crude oil from Potiguar Basin (Brazil)	ethoxylated surfactant derived from fatty acid	brine containing: NaCl, NaSO$_4$, MgCl$_2$, CaCl$_2$ (based on composition of PW)	stirred at 33,000 rpm for 25 min then left for 50 min for free oil separation
Jiang et al.[40]	motor oil	none added	water (not specified if tap/DI/other source)	mixed at 2240 rpm for 30 s–1 min then used immediately

inorganic fractions (Figure 2). The inorganic fraction includes dissolved, precipitated (scales), and suspended solids. A widely used metric to quantify part of the PW's inorganic fraction is the total dissolved solids (TDS) in a sample. This can vary from values well below 10,000 mg/L for water accompanying gas production up to 300,000 mg/L for oil-field PW.[12,13] Ions composing these dissolved solids are predominantly sodium and chloride but also include calcium, magnesium, iron, barium, carbonate, and other dissolved salts.[14] The organic fraction on the other hand is typically classified into free, dispersed, dissolved, and emulsified oil. Other organic components that could also be present in PW result from the addition of field chemicals. For instance, corrosion inhibitors contain surfactants, which contribute to the organic content of the water and aid in the formation of emulsified oil.[15]

The organic content of PW is strictly monitored by environmental regulations around the world and hinders reuse opportunities in some cases.[16] Hence, a detailed classification of the different organic fractions is needed to develop fit-for-purpose treatment technologies. The types of oil present in PW (Figure 2) can be classified based on average oil droplet size as free (>150 μm), dispersed (20–150 μm), emulsified (5–20 μm), and dissolved/soluble oil (<5 μm).[17,18] An emulsion is defined as a suspension of two immiscible liquids (in PW those are oil and water). When an emulsifying agent (e.g., surfactant) is present, it maintains the interfacial film between the two phases forming what is called a stable emulsion. In the absence of

any emulsifying agents, this interfacial film breaks quickly, and the oil droplets coalesce forming suspended droplets, which are classified as dispersed oil. Dissolved or soluble oil refers to hydrocarbons and organics, which are soluble in water to some extent such as benzene, toluene, ethyl benzene, and xylene (BTEX). Finally, free oil refers to the bulk oil phase, which can be easily separated from the water phase using conventional gravitational means.[15]

1.3. Analytical Methods for Measuring Oil-In-Water. The various forms of oily compounds present in PW are usually quantified as mg/L of "total oil and grease" (TOG), the analytical definition of which is a class of hydrocarbons with a low affinity to water.[19] The exact concentration of TOG in a water sample is also dependent upon the extraction solvent used in the method of chemical analysis. Substances usually categorized as TOG include aliphatic and aromatic hydrocarbons, and other organics.[20] Advanced measurement techniques are also applied in portable devices that can be used in both field and lab applications such as the TD-560 (Turner Designs oil-in-water analyzer). Similar to traditional approaches, this instrument enables determining the concentration of hydrocarbons in PW samples by targeting the fluorescent aromatic compounds in a given hydrocarbon and their response to ultraviolet light based on concentration.[21]

1.4. Synthetic PW Recipes. Recently, there have been significant efforts made in developing novel membrane materials for enhanced oil–water separation and removal of organics from

water using advanced membrane technologies.[22−26] The challenge in evaluating these emerging technologies is obtaining a characteristic PW sample, which enables equating the outcomes of different bench scale studies and comparing them to existing technologies applied in full scale systems.[27,28]

Previous studies evaluating oil−water separation technologies have formulated different recipes to mimic the characteristics of oily wastewater.[29−31] The general approach was based on producing a uniform oil-in-water emulsion. Formulations varied in the type of oil used, the amount and type of surfactant, and properties of the aqueous phase. Hu et al. prepared a 1 g/L emulsion by mixing machine oil and two surfactants (Tween-80 and Span-80) in distilled water with a weight ratio of 4:1:1 (oil to surfactants). This mixture was blended for 5 min at 20,000 rpm, stored at room temperature, and used within 24 h. To assess the stability of the emulsion, the size distribution of oil droplets in the feed solution was evaluated when prepared and 2 h later with no significant changes in the droplet size of 1.8 μm.[32] In another attempt, Ghulam et al. prepared oil−water emulsions with the aim of mimicking real PW. In their recipe, they added 2400 mg/L of hexadecane (oil source), 240 mg/L of a surfactant (anionic: sodium dodecyl sulfate, i.e., SDS, or cationic: benzyl-dimethyl-tetradecyl ammonium chloride), and 10 g/L of sodium chloride to distilled water. The solution was mixed and then ultrasound was applied to stabilize the emulsion, the average particle size measured was 0.3 μm.[33] These two examples highlight the variance in recipes where the type of oil used, surfactants, aqueous matrix, and even mixing procedures were different. All these parameters affect the properties and behavior of the test solution, making comparison of the results between various synthetic recipes or even benchmarking against performance of actual oily wastewaters not possible. Table 1 presents a summary of different recipes and approaches used in the literature.

While some formulas were based on the use of crude oil, others used motor oil, vegetable oil, or an organic solvent as the hydrocarbon source for the mixture. The addition of surfactants or stabilizers seemed to be a common approach to assure homogeneity and sufficient mixing between the oil and aqueous phase. However, the type and amount of surfactant used did not follow a clear rule or any particular reasoning. Finally, some researchers used DI/tap water to mimic the aqueous phase of PW while others added one or more salts to better resemble the inorganic fraction. These variabilities in the recipe of synthetic solutions affect the analytical properties of the mixture as well as its stability and reliability.

For instance, motor oil, machine oil, and gasoline do not represent the organic moieties present in PW. This is because in addition to hydrocarbon type molecules, there are many polar compounds in PW that are not present in gasoline or motor oil. These polar compounds affect separation efficiencies of various technologies such as resins or membranes. The chemical additives present in such oils for enhanced commercial performance also have negative impacts on the synthetic solutions formulated using this approach as they partition into the water phase to some extent and interfere with analytical techniques that measure organics in the water such as chemical oxygen demand (COD) and total organic carbon (TOC). Furthermore, the use of DI or tap water does not represent brine as salinity influences the partition of organics into the aqueous phase and interactions of the solution with solid resins or oil removal media. Although the addition of a surfactant enhances blending and dispersion of the mixture, it changes the extent of dispersed organics in the aqueous phase and hence the

concentration and type of surfactant used must be carefully determined, clearly stated, and fixed for a given oil−water emulsion recipe.

1.5. Objective. Based on the above information, there is a clear need to develop a protocol for synthetic PW solutions that is based on solid scientific grounds and accessible to researchers from different institutes around the world. Hence, the objective of this study is to:

- Develop a protocol for preparing synthetic PW solutions that represent the characteristics and behavior of actual PW and can be used for screening evaluations of emerging physical separation processes, specifically novel membranes.
- Conduct an extensive analytical characterization to examine both organic and inorganic fractions of the synthetic solution and evaluate how these different moieties interact.
- Evaluate the homogeneity, reproducibility, and stability of the synthetic recipe and compare those analytical aspects to a synthetic solution prepared using different oil sources.
- Validate the performance of the synthetic PW solution in bench scale oil−water membrane separation testing by comparing its behavior to actual PW and other synthetic recipes.

2. MATERIALS AND METHODS

2.1. Reagents. *2.1.1. Salts.* Sodium chloride (NaCl, 99%), calcium chloride dihydrate (CaCl$_2$·2H$_2$O, 99%), magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O, 99%), potassium chloride (KCl, 99%), sodium sulfate (Na$_2$SO$_4$, 99%), ammonium chloride (NH$_4$Cl, 99%), sodium bicarbonate (NaHCO$_3$, 99%), and strontium chloride hexahydrate (SrCl$_2$·6H$_2$O, 99%) were all purchased from Sigma-Aldrich and used without any modifications or treatment.

2.1.2. Surfactant. Sodium dodecyl sulfate (NaC$_{12}$H$_{25}$SO$_4$, 99%) was purchased from Thermo Fischer Scientific and used as received.

2.1.3. Water Phase. DI water was generated in the lab using a Milli-Q ultrapure water system (Integral 10, Millipore) with an installed 0.2 μm microfilter (Millipak, Millipore); resulting water resistivity was approx. 18 MΩ am.

2.1.4. Oil Source. Three different crude oil samples were sourced from O&G operations and commercially available motor oil SAE 10W30 was purchased from ACDelco (General Motors, USA) with specifications highlighted in Table 2.

Table 2. Crude Oil Sample Properties

sample name	deg API	density (g/mL) @ 25 °C
crude #1	28.7	0.875
crude #2	38.7	0.825
crude #3	54.9	0.750
[a]motor oil	32.1	0.865

[a]Density of motor oil is reported at 15 °C.

2.2. Laboratory Analyses. Table 3 below summarizes the analytical methods used in characterizing both the actual and synthetic PW samples.

2.3. Validation and Comparison Testing. *2.3.1. Bench Scale Setup.* An Amicon cell (Millipore, USA) was used for the filtration evaluation in verifying the performance of the synthetic PW solution compared to actual PW. This filtration cell

Table 3. Analytical Methods

parameter	method	instrument
total organic and inorganic carbon and total nitrogen (TOC, IC, and TN)	combustion method	TOC Analyzer (TOC-V, Shimadzu)
conductivity/pH	immersing conductivity/pH probes in the sample	Orion 3 Star meter
turbidity	applies nephelometry to measure turbidity using a calibrated turbidimeter	Hach turbidimeter
TOG−Horiba extraction	US EPA test method 413.2 solvent extraction and absorbance measurement using a spectrophotometer	Horiba OCMA-350 spectrophotometer
TOG−TD560	ultraviolet fluorescence detection	oil in water analyzer TD-560 by Turner Designs Hydrocarbon Instruments
UV254	absorbance of ultraviolet light at 254 nm	UV/vis spectrometer
microscope	light microscope	Olympus BX51 Fluorescence Microscope
particle size instrument	light scattering phenomenon by use of a multi wavelength light	Beckman and Coulter Analyzer, Model LS 13320

possesses an area of 13.4 cm^2 and is capable of testing flat sheet membranes at different pressures (1−5 bar) achieved using a nitrogen gas cylinder. In each trial, the Amicon cell was loaded with a 0.2 μm polyether sulfone (PES) commercial micro-filtration (MF) membrane (Sterlitech, USA). The bench scale unit can filter variable volumes of feedwater, and the flux is measured in real-time during the experiment through a weighing balance connected to a LabVIEW acquisition system.

2.3.2. Testing Protocol. Fouling and chemical cleaning tests were conducted to evaluate the flux performance of MF PES membranes using different feed solutions (real PW, synthetic PW-crude oil, and synthetic PW-motor oil). Each test was conducted in duplicates using two different membrane coupons to assure reproducibility of the results. The clean membrane sheet was first soaked overnight in DI water. After that, the membrane was compacted using DI water at a pressure of 0.5 bar and stirred at 560 rpm for 2 h until a stable water flux measurement is obtained. The experiment stages can then be divided into four main parts all carried out at 0.5 bar under the same stirring speed of 560 rpm:

2.3.2.1. Clean Membrane Flux. An initial baseline test measuring the clean membrane water flux was performed using DI water and used as the benchmark water flux for the fouling evaluation.

2.3.2.2. Actual/Synthetic PW Test. The membrane was then tested using PW (actual or synthetic) targeting 50% feed volume reduction. Feed and permeate samples were collected for TOC, turbidity, and O&G measurements.

2.3.2.3. Fouled Membrane Flux. Another baseline experiment using DI water was conducted to measure the fouled membrane flux.

2.3.2.4. Chemical Cleaning Flux. The fouled membrane was then cleaned with NaOH solution for 15 min at 560 rpm, followed by SDS cleaning under similar conditions. A final baseline test was subsequently performed to measure the membrane's final water flux and the total flux loss associated with the experiment.

3. RESULTS AND DISCUSSION

3.1. Synthetic PW Recipe. Several PW samples from oil and gas field operations were analyzed in our laboratories to develop the basis of this synthetic PW recipe. Table 4 summarizes the key constituents of these water samples. It is understood that the salinity of PW can be higher than 40,000 mg/L, however at such higher salinities (more than seawater), water treatment using membrane processes would likely not be cost efficient.

Table 4. Analytical Properties of the Actual PW Samples

parameter	PW 1 (gas field) low salinity	PW 2 (oil field) intermediate salinity	PW 3 (oil field) high salinity
chloride (Cl⁻), mg/L	2265	15,916	23,300
sodium (Na⁺), mg/L	1000	9405	6735
calcium (Ca²⁺), mg/L	300	668	7740
magnesium (Mg²⁺), mg/L	62	87	492
sulfate (SO₄²⁻), mg/L	50	96	770
potassium (K⁺), mg/L	50	167	234
ammonium (NH₄⁺), mg/L	10	206	
bicarbonate (HCO₃⁻), mg/L	100		
bromide (Br⁻), mg/L		140	
strontium (Sr²⁺), mg/L		197	90
total cations, mEq	65.4	470	728
total anions, mEq	67.2	451	673
total ion balance, mEq	−1.8	+19	+54
TDS, mg/L	3800	27,000	40,000
pH	4.3	7.41	6.9
conductivity (μS/cm)	7200	40,500	67,000

Because the composition of PW is greatly dependent on the age and location of the geological formation in addition to the type of hydrocarbon being produced. Table 4 demonstrates variations in the dissolved ions present in two oil field PW samples. Namely, PW 3 and PW 4. This variation is because PW 2 is from an unconventional formation in the lower 48 while PW 3 is from an offshore conventional oil production field in the North Sea. For example, PW 3 contains much higher calcium of 7740 mg/L compared to PW 2 only of 668 mg/L. This value is within typically reported calcium concentrations for offshore oilfield PW.[41]

A scientific approach was developed for preparing the synthetic PW. The use of a representative aqueous phase, hydrocarbon source, and surfactant was all considered in addition to assuring the applicability of this method for researchers working in different laboratories around the world. Specific salts were used in preparing the brine that mimics actual PW TDS while crude oil was added at various concentrations depending on the desired TOC to be evaluated. Figure 3 below depicts general preparation procedures of the synthetic PW solution followed by detailed explanations of each step.

Step 1 → prepare synthetic brine targeting either low salinity (gas-field PW) or high salinity (oil-field PW). The exact salinity and brine composition may be modified depending on the
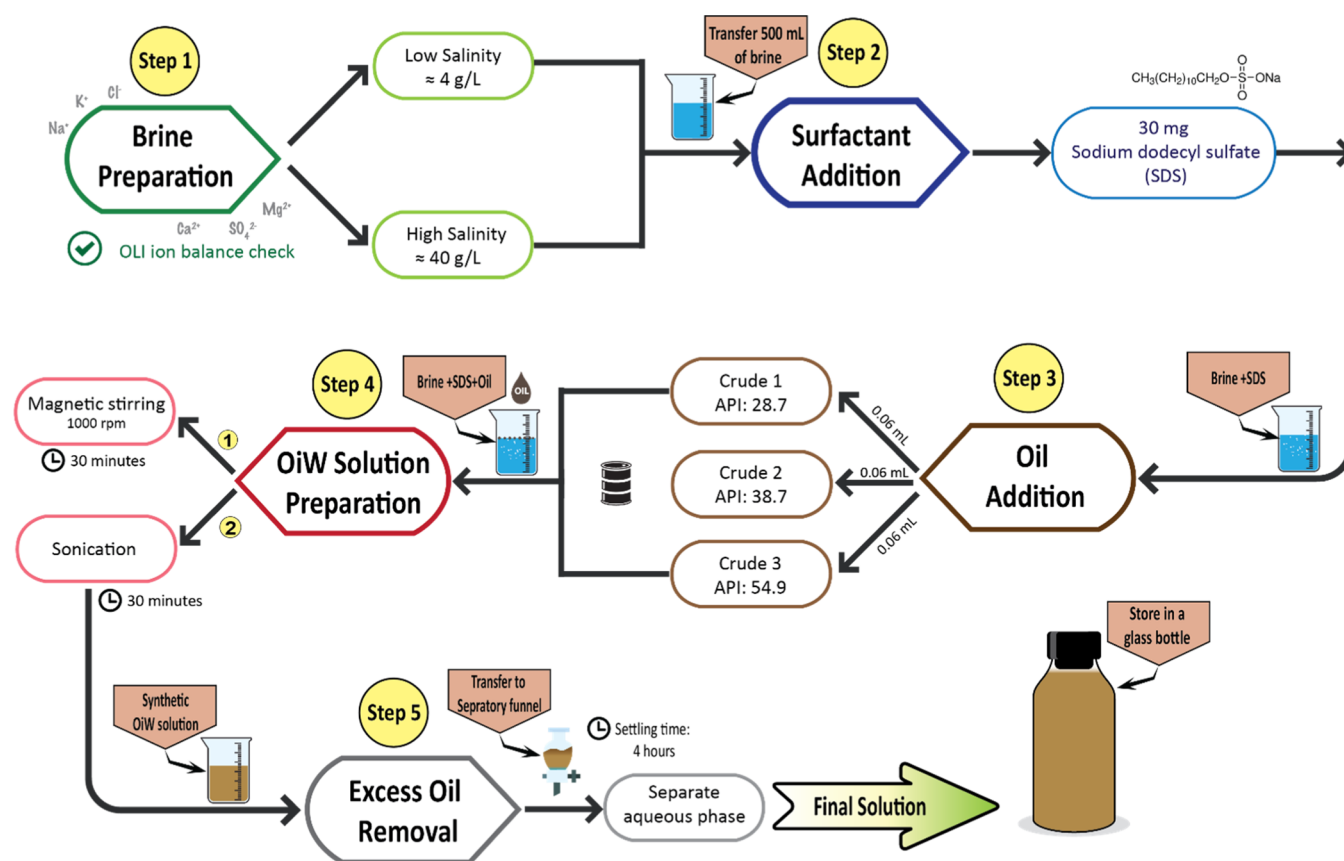
Figure 3. Synthetic PW preparation protocol.

application and characteristics of the PW being mimicked for testing. In this study, two different formulations were evaluated, as examples, one at ∼4000 mg/L TDS (low salinity) and the other at ∼40,000 mg/L TDS (high salinity), based on ionic compositions of actual PW samples listed in Table 4. OLI was used to model the brine characteristics, assuring a balanced formula and avoiding any precipitation or scaling issues in the solution. The use of such brine is more representative than DI or tap water because it reflects the effect of salinity on the partition of organics into the aqueous phase as is the case in actual PW. Table 5 below lists the salts used in the recipe.

Table 5. Salts Added to Prepare Synthetic Brines

actual salts added	low-salinity brine	high-salinity brine
	(g/L)	
NaCl	2.39	16.75
CaCl$_2$·2H$_2$O	1.10	28.39
MgCl$_2$·6H$_2$O	0.52	4.12
KCl	0.10	0.45
Na$_2$SO$_4$	0.07	1.14
NH$_4$Cl	0.03	0.00
NaHCO$_3$	0.14	0.00
SrCl$_2$·6H$_2$O		0.34

Step 2 → transfer 500 mL of the brine into a 1 L beaker and add sodium dodecyl sulfate (SDS) to the solution to get an oil to surfactant weight ratio of 5:1. This ratio, based on literature references, was slightly modified to optimize the balance between solution stability and forming emulsions that are too difficult to break.[33] Thus, in the 500 mL sample, 30 mg of SDS

was added based on the precalculated oil amounts. In the absence of surface-active agents, it is not possible to produce a homogenous stable oil−water mixture because most of the oil coalesces into larger droplets and comes out of the solution after some time. In addition, field chemicals present in PW typically contain surfactants, which implies that a synthetic PW solution should also contain a defined concentration of surfactants to model this behavior and stabilize part of the oil in solution.

Step 3 → add a total of 0.18 mL of crude oil. In the synthetic solution prepared for this evaluation, equal amounts of each of the three crudes (#1 to #3) listed in Table 2 were added to 500 mL brine (3 × 0.06 mL i.e., total of 0.18 mL, which translates to 150 mg for the given densities). These amounts were calibrated through experimental trials, which determined the volume of oil to be added that results in a solution with TOC of approximately 100 mg/L. This concentration was targeted as a baseline as it is typical for the feed to oil−water physical separation processes.

Step 4 → stir the mixture at 1000 rpm for 30 min then sonicate for another 30 min to stabilize the emulsion.

Step 5 → transfer the test solution to a separatory funnel and allow it to settle for 4 h to separate any free oil layer. This step mimics primary skimming or phase separation done in the field and ensures that the final solution is a homogenous sample avoiding analytical uncertainty associated with free oil randomly dispersed in the mixture. Finally, transfer the aqueous layer to a glass bottle and store in a refrigerated environment at 4 °C.

This recipe provides a general guideline for preparing a solution mimicking actual PW with a key focus on using a representative brine, a suitable oil source, and adequate amounts of dispersants with defined oil to surfactant ratios. The recipe can also be modified based on the target salinity and oil-in-water

content where different amounts of added oil would result in different total organic contents. Several synthetic PW samples were prepared to assess the repeatability, homogeneity, and stability of the recipe through various analytical techniques as described in Sections 3.2−3.4.

The protocol described in this section is not proposed to replace actual PW but rather provides a baseline recipe for synthetic PW solutions that can be used in the screening evaluations of physical separation processes, specifically novel materials and membranes introduced into the O&G industry. This method is designed to be accessible to researchers from different institutes around the world without the complication of transporting large volumes of PW to laboratories. Because of limited access to O&G operations in some cases and potential environmental risks associated with the shipment of large PW volumes, the transfer of much smaller volumes of crude oil is more feasible and represents less safety concerns from the perspective of O&G producers. Alternatively, lab grade crude oil can be purchased from chemical vendors making this method accessible to the wider scientific community. A potential improvement under consideration for the recipe includes adding known amounts of soluble organic solvents, namely BTEX, to enable evaluation of technologies for dissolved organics removal.

3.2. Characterization of Synthetic PW. Initial characterization analyses were conducted on synthetic PW samples prepared using the low and high salinity brines. The surfactant used in this recipe (SDS) is a synthetic organic compound with chemical formula $CH_3(CH_2)_{11}SO_4Na$. Hence, it is expected to contribute to the TOC and a control sample of brine and SDS was prepared and characterized for comparison purposes.

Based on the analytical parameters presented in Table 6, the following remarks can be highlighted about each synthetic solution:

Table 6. Synthetic PW-Initial Characterization

		synthetic PW	
parameter	brine + SDS (control)	low salinity	high salinity
temperature (°C)	18	18	21
pH	7.8	7.8	5.9
conductivity (μS/cm)	7,060	7,037	63,490
turbidity (NTU)	<1	261	105
TOC (mg/L)	28	128	80
IC (mg/L)	18	18	<1
TN (mg/L)	8.3	8.3	<1
UV254	0.005	1.03	0.75

3.2.1. Brine + SDS (Control). TOC attributed to SDS addition is approximately 28 mg/L for the model solution as prepared in Section 3.1. The inorganic carbon and total nitrogen are attributed to the bicarbonate and ammonium added to the low-salinity brine recipe. In terms of physical appearance, the solution is clear with no turbidity, color, or precipitation. Finally, the conductivity of 7060 μS/cm confirms solution salinity of approximately 4000 mg/L.

3.2.2. Synthetic PW (Low Salinity). TOC of this solution was measured to be 128 mg/L. After deducting background TOC attributed to SDS, it can be estimated that 100 mg/L of TOC present in solution results from the added mixture of crudes. The physical appearance of this synthetic PW (Figure 4) represents the color of actual PW with a brownish/yellowish shade and a

turbidity of 261 NTU, again no precipitation is observed at this salinity.

Figure 4. Synthetic PW solutions (left: high salinity and right: low salinity).

3.2.3. Synthetic PW (High Salinity). Although the added amount of oil was identical to that of the low-salinity solution, the TOC of this mixture was slightly lower at 85 mg/L. Assuming the same amount of TOC would be attributed to SDS (28 mg/L) that leaves approximately 57 mg/L of TOC resulting from the different forms of oil present. The turbidity of solution was also less at 105 NTU and it had a slightly clearer appearance (Figure 4). This is because of the fact that higher salinity hinders the partitioning of organics into the aqueous phase and hence, in order to obtain the same final organic content, additional amounts of oil must be added to the higher salinity sample. The conductivity of this solution was measured at 63,490 μS/cm indicating a salinity of around 40,000 mg/L as prescribed in the brine. Both physical appearance and OLI modeling confirmed no precipitation at this salinity. This phenomenon of salinity hindrance to organics is observed to be a function of bulk salinity of the brine and formation of precipitates.

The last analytical parameter listed in Table 6 is UV 254, which is defined as a measurement of the amount of ultraviolet (UV) light absorbed by organic compounds, specifically aromatics, in a water sample at a specific wavelength.[42] UV light at a wavelength of 254 nm is passed through a quartz cell containing the water sample. Previous literature studies have highlighted the correlation between UV 254 and other parameters such as TOC, COD, and BOD (chemical and biological oxygen demand).[43] In this analysis, UV 254 was also found to track TOC measurements of different oil-in-water emulsions containing aromatic type oils as demonstrated in Table 7.

3.3. Calibrating the Oil Content. Further calibration assessments were carried out to confirm the applicability of the synthetic PW recipe in preparing solutions of lower oil content that can then be used to evaluate tertiary treatment technologies, especially membrane separation. Knowing the amount of oil added in a certain batch, its resulting TOC, and the intended TOC of the new batch can help estimate the amount of oil needed to prepare a new synthetic PW batch. The relation

Table 7. Crude Oil Versus Motor Oil

		synthetic PW[a]	
parameter	brine + SDS (background)	crude oil	motor oil
conductivity (μS/cm)	7060	7084	7031
TOC[b] (mg/L)	28	136	134
TOG−Horiba (mg/L)		155	205
TOG−Turner (mg/L)		150	1,450
UV254	0.005	1.88	1.04

[a]Solution preparation followed the steps described in Section 3.1 using the low-salinity brine. [b]TOC reported for synthetic PW samples is after subtracting brine + SDS background.

between those parameters was translated into a simple formula developed for calculating amounts of oil and surfactant required to prepare new synthetic PW solutions with different TOC concentrations. Eq 1 presents the correlation between the oil added in a sample of known TOC and the oil amounts required to achieve a lower TOC. The amount of SDS is then determined using eq 2 that simply depends on an oil to surfactant ratio of 5:1.

$$L_i = \frac{L_T \times \frac{C_0 \times T_n}{T_0}}{3 \times 1000 \times D_i} \qquad \text{for } i = 1, \ 2, \ 3, \ \text{etc.} \tag{1}$$

$$S_n = \frac{C_0 \times T_n}{5 T_0} \tag{2}$$

where: D_i is the crude oil density in g/mL, L_T is the synthetic solution batch volume (i.e., 0.5 L), L_i is the crude oil required volume for the new solution in mL, C_0 is the oil concentration in the basic solution in mg/L, S_n is the surfactant (SDS) concentration in the new solution in mg/L, T_0 is the TOC concentration in the basic solution in mg/L, and T_n is the TOC concentration in the new solution in mg/L.

These formulas (eqs 1 and 2) were validated and used to prepare a new synthetic PW solution having a TOC concentration of 50 mg/L utilizing the data obtained from the basic batch (TOC = 128 mg/L) as a reference. It is estimated that a total of 0.071 mL of oil and 11.5 mg of SDS are required to prepare the new low TOC solution. This solution was prepared using a low-salinity brine and following the same preparation protocol outlined in Section 3.1. Resulting TOC and TOG were found to be ∼66 and 53 mg/L, respectively. These results were comparable with targeted concentrations and within acceptable experimental error deviations. The formulas were further validated and used to prepare another synthetic PW solution having a TOC concertation of 25 mg/L using this time only one crude oil type (crude #2—38.7 °API). For that, eq 1 was slightly modified to account for only one crude oil type instead of three as illustrated in eq 3 below. Approximately 0.035 mL from crude #2 was added along with 5.7 mg of SDS to 500 mL of synthetic low-salinity brine. This new solution also showed equivalent results to targeted concentrations of TOC and TOG at 25 and 27 mg/L, respectively, making it suitable for tertiary treatment evaluations via membrane filtration processes.

$$L_2 = \frac{L_T \times \frac{C_0 \times T_n}{T_0}}{1000 \times D_2} \tag{3}$$

3.4. Analytical Comparison: Crude Oil Versus Motor Oil. Several analytical tests were conducted to evaluate the effect

of using motor oil compared to crude oil as the hydrocarbon source in a synthetic PW recipe (Figure 5). Those include

Figure 5. Synthetic PW solutions (left: motor oil and right: crude oil).

- Corelating TOC and TOG measurements
- Evaluating the particle size distribution
- Evaluating the variation of properties with time

3.4.1. Organic Content: TOC Versus TOG. While TOC reports the TOC in a water sample, it is not possible to distinguish whether the source of that organic carbon is oil present in the water or other additives. Thus, further analysis was conducted to verify the source of TOC in the synthetic PW recipe prepared using crude oil and compare that result with other hydrocarbon sources. Motor oil was selected as the hydrocarbon source for comparison because it is among the most widely referenced in literature trials for preparing synthetic PW. All crude oils are a variation of the hydrocarbon base CH_2, the ultimate composition of which generally shows ∼86% carbon, 10−14% hydrogen and smaller percentages of sulfur, nitrogen, and oxygen depending on the type and source of crude.[44] Although the 86% carbon content is an approximation that may differ from one crude oil to another, it is a good order-of-magnitude indication as to whether much additives are contributing to the organic content of a synthetic PW sample. Table 7 below shows a comparison between two synthetic PW samples prepared in an identical manner, one using crude oil and another using motor oil as the hydrocarbon source.

TOC values of both crude oil and motor oil samples are 136 and 134 mg/L, respectively, which seem to be within reasonable agreement with recipe expectations. However, taking a closer look at the TOG values fails the motor oil sample in two aspects. For one, 86% of 205 mg/L TOG recorded using the Horiba extraction method should result in a TOC of 177 mg/L, which is 32% higher than the reported value of 134 mg/L. This indicates that some Horiba extractable compounds that contribute to the sample absorbance and TOG measurement are not carbon-containing oil molecules but rather other chemical additives. In addition, the recorded TOG value using Turner TD560 was at an unreasonable value of 1450 mg/L, which is approximately five times higher than the initial concentration of oil added to the sample even before the phase separation and settling step. The above measurements represent two examples of how chemical additives present in commercial motor oil interfere with analytical methods typically used to determine the oil content

in PW samples. This interference was observed even though the instrument had been previously calibrated using the exact same motor oil added to the synthetic PW recipe.

On the other hand, 86% of the 155 mg/L TOG reported for the synthetic PW sample prepared using crude oil corresponds to an expected 134 mg/L TOC, which is only 1% lower the actual analytical measurement. In addition, TOG values measured using both Horiba extraction (150 mg/L) and Turner TD560 (155 mg/L) methods agree with only a 3% difference. Finally, the higher UV254 value of the crude compared to the motor oil PW sample confirms that more aromatic type compounds are present in the crude oil PW.

3.4.2. Evaluating the Particle Size Distribution. A common tool used to evaluate stability of oil-in-water emulsions is the particle size distribution of the oil droplets in solution and the pace at which that distribution changes over time as the emulsion starts to break. Figure 6 below shows the oil droplet
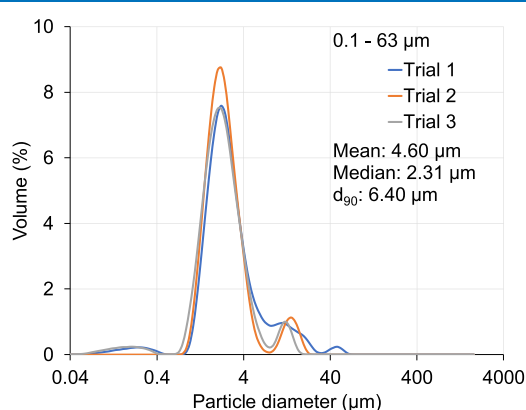
Figure 6. Particle size distribution of synthetic PW (crude oil)..

size distribution for a synthetic PW solution prepared using crude oil as the hydrocarbon source and evaluated in triplicate. All three trials exhibited consistent results confirming the homogeneity of the solution and repeatability of the results. The oil droplet sizes range between 0.1 and 63 μm with an average particle size of 4.60 μm, just within the dissolved oil range (<5 μm). d90 is 6.40 μm, that is, 90% of the droplets are below 6.40 μm, indicating that the solution contains both emulsified and dispersed oil droplets in addition to dissolved oil. Based on this distribution, there is no free oil in the solution (i.e., no oil droplets >150 μm); in fact, that was intentionally avoided because of the nonhomogeneity that results from free oil being in the sample. Microscope images were taken for the synthetic PW and the brine solutions and are shown in Figure 7A,B, respectively. No scaling or precipitation is observed in the brine

sample (Figure 7B), which also appears to be clear under this 40× magnification. The brine sample even showed a "no distribution" when tested through the particle size instrument confirming that all solids are dissolved in the brine. Figure 7A shows a uniform homogenous oil−water emulsion where this picture was taken after examining several samples from the synthetic PW. The stability of this oil-in water emulsion was also evaluated by monitoring the change in the particle size distribution over the course of 20 days, which was observed to be a 9% decrease for the mean and median values and only 1% decrease of d_{90}. The distribution also showed similar trends to the initial analyses represented in Figure 6, which confirms that the emulsion remained stable and homogenous over this period.

On the other hand, a particle size distribution analysis of the synthetic PW sample prepared using motor oil showed no conclusive results as random distributions were observed after analyzing multiple trials with no meaningful statistical data extractable (Figure 8). This confirms the presence of chemical additives that interfere with the particle size measurement.
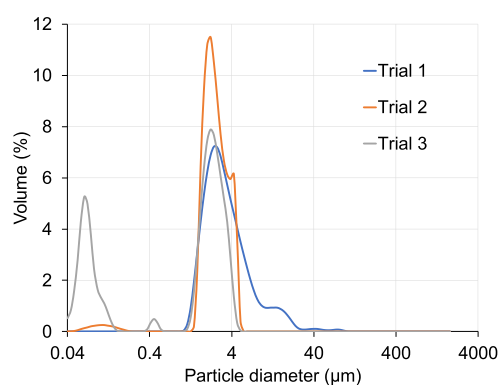
Figure 8. Particle size distribution of synthetic PW (motor oil).

3.4.3. Variation of Solution Properties over Time. The ability to store and use synthetic oil-in-water solutions over a certain period is usually limited because of the instability and loss of organic content as the solution is stored. Typical experimental protocols recommend using the prepared solution directly or within 24 h. This may be impractical in some cases when large volumes of water are required for testing. Hence, the stability of the synthetic PW was evaluated and optimized to maintain reasonable solution characteristics over a maximum period of time without adding too many surfactants that could form difficult-to-break emulsions. Figure 9 below shows the variation in TOC of the synthetic PW over a period of approximately 80 days using both crude and motor oil as the hydrocarbon source in the recipe. During this time, the sample
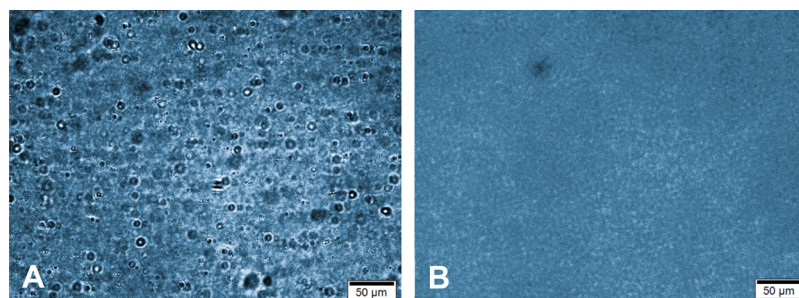
Figure 7. Microscope images under 40× magnification of: (A) synthetic PW solution using crude oil, (B) low-salinity brine.
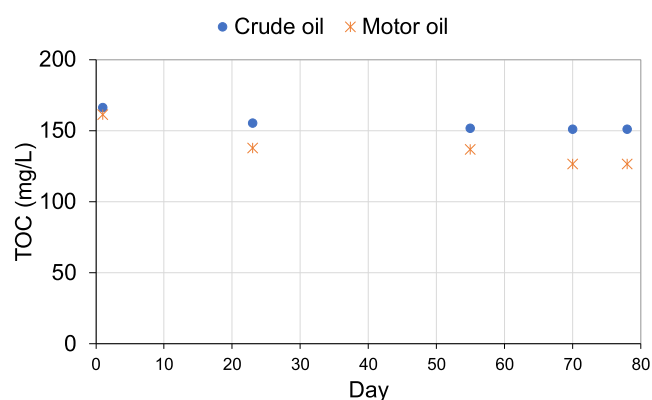
Figure 9. Synthetic PW-variation of TOC over time.

Table 9. Recipe Validation-Analytical Properties of Feed Solutions

parameter	actual PW	synthetic PW (crude oil)	synthetic PW (motor oil)
conductivity (μS/cm)	40,500	41,500	41,040
TOC (mg/L)	56	90	90
turbidity (NTU)	53	59	56
O&G (mg/L)	72	76	56

was stored in a glass bottle under refrigerated conditions (4 °C). The crude oil-synthetic PW maintained an average TOC of 150 mg/L with only a 9% decrease while the motor oil-synthetic PW TOC decreased by 21% down to 127 mg/L. This analysis indicates that the synthetic solution prepared using crude oil may be prepared and used within a period of up to 80 days without concerns of losing the organic content or homogeneity of solution while that of the motor oil showed significant changes in TOC. Other solution properties were also monitored over the same period and the results are summarized in Table 8 below. No major variations were observed in most of the measurements that were all within 4% change for both crude and motor oil PW solutions.

3.5. Validation and Comparison Testing.
To validate the proposed recipe, the behavior of the synthetic PW solutions prepared using either crude or motor oil was compared to actual PW in an oil–water separation bench scale evaluation. Specifically, in MF membrane separation testing using a 0.2 μm PES commercial membrane.

3.5.1. Feed Solutions. Three feed solutions were used in the comparison testing including a real PW sample (intermediate salinity sample in Table 4) and two synthetic PW solutions. The synthetic solutions were prepared based on the protocol presented in Section 3.1 using either crude or motor oil. Table 9 below shows a summary of the analytical properties of these feed solutions.

Table 9 confirms that both the salinity and organic content of all feed solutions are comparable and provide a common baseline for the comparison test. Considering the background TOC of SDS to be 28 mg/L that brings the TOC resulting from oil in both synthetic solutions to 62 mg/L, which is comparable to that of the actual PW. This is validated through the matching O&G content of the actual PW and synthetic PW (crude oil) solutions. It is noted that the O&G of the synthetic PW (motor oil) is lower compared to that of the actual PW indicating that salinity interferences are greater in recipes prepared with motor

oil compared to crude oil and that other additives contribute to the TOC.

Figure 10A−C shows flux comparison and fouling trends of MF PES membranes when subjected to actual PW, synthetic PW (crude oil), and synthetic PW (motor oil), respectively. Two trials were carried out for each test using different membrane coupons to assure reproducibility of the results. The specific water flux in L/m²·h·bar (LMH/bar) is plotted for each stage of the experiment in the order explained in Section 2.3.2 starting with the clean membrane flux, then the actual or synthetic PW, a baseline after the fouling step, and a final baseline after chemical cleaning to measure the total flux loss associated with the experiment. The trends and flux values for all these steps are identical and repeatable in both the actual PW and synthetic PW (crude oil) tests as shown in Figure 10A,B. In addition, the total flux loss is within 2% difference between the actual and synthetic PW (crude oil) tests at 79 and 77%, respectively. In contrast, no significant flux decline (only 12%) is observed for the synthetic solution prepared using motor oil (Figure 10C).

3.5.2. Membrane Filtration. In all three evaluations, the O&G rejection of the membrane was approximately 100% and the TOC rejection was 90−100% (not including SDS). These results confirm that using crude oil following the proposed protocol mimics both the characteristics and behavior of actual PW for membrane testing. While a solution prepared in a similar manner but using motor oil as the model organic phase does not resemble the behavior of actual PW nor contain representative organics of those present in actual PW. In fact, one may argue that high percentage rejection results and low flux loss from the synthetic water would give misleading results when evaluating different membrane materials.

Figure 11 shows the pictures of the membranes taken before and after the experiment to provide a visual comparison between the different tests. This qualitative examination of the membranes reveals informative visual indications when applied together with the quantitative results of flux measurements can shed light on the fouling extent in each experiment. Both the actual and synthetic PW (crude oil) solutions showed a similar looking yellowish/brownish tint on the membrane surface of the organics (oil) accumulating on during the filtration testing. On the other hand, filtration of the synthetic PW (motor oil) showed no change in the appearance of the membrane at all.

Table 8. Variation of Solution Properties Over Time

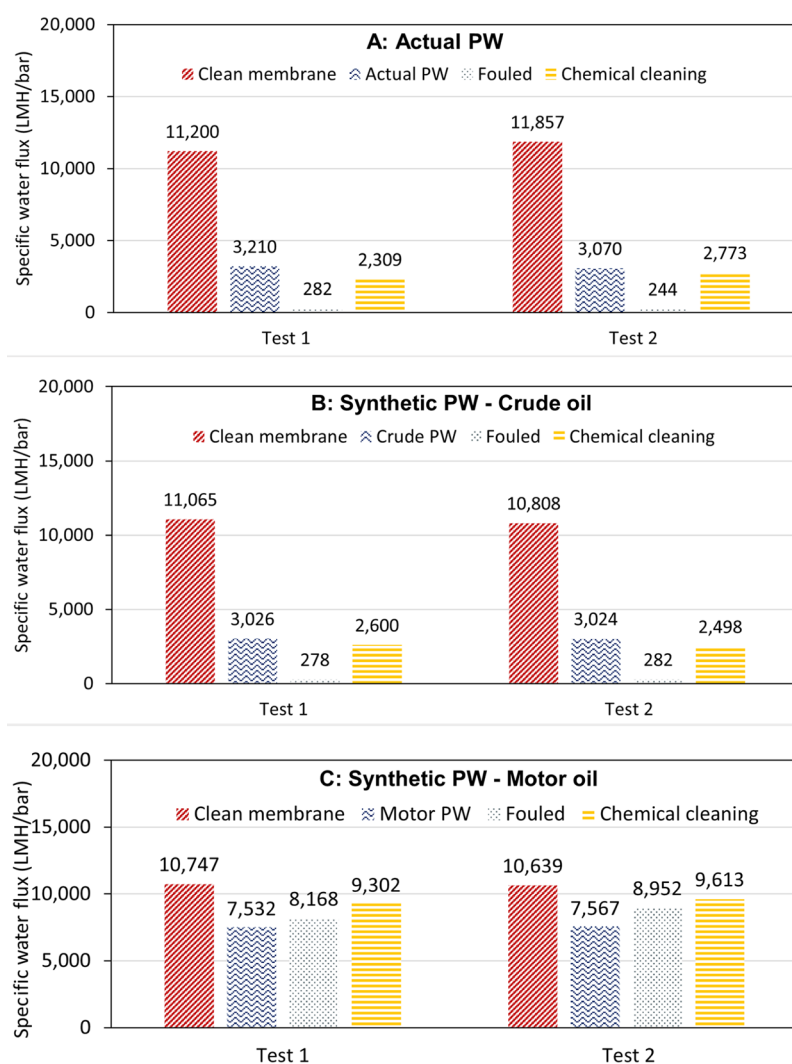| parameter	crude oil			motor oil		
	initial	final	% change	initial	final	% change
pH	8.13	8.03	−1%	8.15	7.93	−3%
conductivity (μS/cm)	7084	6840	−4%	7031	6830	−3%
TOC (mg/L)	166	151	−9%	161	127	−21%
UV254	1.88	1.92	2%	1.04	1.05	1%

Figure 10. Bench scale validation tests (0.2 μm PES membrane flux).
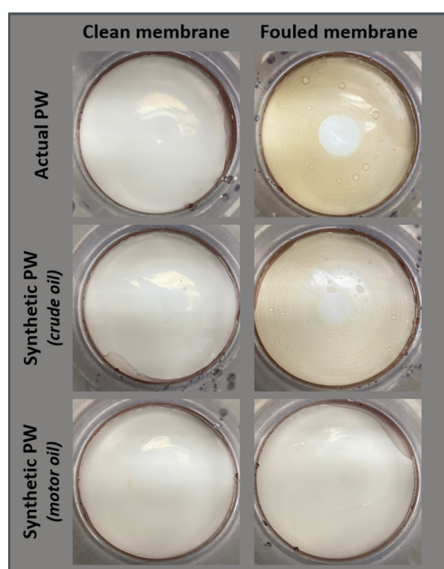

Figure 11. Representative images of the clean and fouled membrane before and after each experiment.

4. CONCLUSIONS AND RECOMMENDATIONS

This study developed a protocol for preparing synthetic solutions with characteristics and behavior representative of actual PW. This recipe provides a baseline for synthetic solutions that can be used in comparative evaluations of physical oil–water separation technologies, specifically membrane materials proposed for the O&G industry. Key outcomes of the study include:

- A representative hydrocarbon source must be used for preparing a synthetic PW solution. This can be crude oil from O&G companies. Commercial oils (e.g., motor oil) should be avoided because they contain chemical additives, which were proven to exhibit analytical properties that are unrepresentative of the organics present in real PW.
- PW typically contains different salts in varying concentrations. Thus, the aqueous phase of a synthetic PW solution should be a representative brine and not just deionized or tap water, which behaves differently when mixed with oil, affecting many properties such as the partition of organics into the aqueous phase.
- A stabilizer must be added to the mixture to form a homogenous oil-in-water emulsion. The use of surfactants provides homogeneity to the solution, enhances blending

and dispersion of the oil-in-water, and stabilizes oil−water emulsions. On the other hand, simple mechanical mixing was found to produce nonhomogenous solutions and a generally unstable formulation.

The synthetic PW solution was proven to be representative of actual PW through extensive analytical characterization. The recipe was also found to be reproduceable, homogeneous, and stable. Chemical additives present in motor oil showed interferences with multiple analytical characterization methods for the measurement of organic contents while consistent results were observed when analyzing the crude oil-synthetic solution.

The recipe was also validated through behavioral comparison with actual PW in MF bench scale evaluations using commercial PES membranes. The flux values and fouling trends were identical and repeatable in both the actual PW and synthetic PW (crude oil) tests. While the comparison test using synthetic PW (motor oil) as the feed solution showed no significant flux loss and unrepresentative trends when compared to actual PW.

Future work involves evaluating other physical oil−water separation technologies and assessing the applicability of using lab-grade crude oil from chemical vendors as the hydrocarbon source in the synthetic solution.

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Notes

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