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Performance investigation of surface modified ceramic microfiltration membranes and the effects of ionic strength

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PERFORMANCE INVESTIGATION OF SURFACE MODIFIED CERAMIC

MICROFILTRATION MEMBRANES AND THE EFFECTS OF IONIC STRENGTH

by

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ABSTRACT

The performance of ceramic membranes surface coated with cysteic acid to improve efficiency and reduce fouling rate was studied under two transmembrane pressure (TMP) and constant crossflow velocity (CFV). The filtration process was done in crossflow mode to allow for extended operation of the membranes. the performance of the membranes were determined in terms of the measured fluxes and on content rejection. Cleaning-in-place (CIP) was done on the membranes to ensure flux recovery after each run. The results showed significant improvement on the performance of the membranes with respect to high permeate fluxes and high oil content rejection ($> 99.5\%$). When compared to other coating materials such TiO_2 and graphene, cysteic acid presented exhibited better performance. Also, the effects of ionic strength on membrane performance was tested. Using 1000ppm oil in various ionic concentration solutions, results showed that ionic strength has a significant impact on membrane performance. Droplets sizes were impacted by ionic strength whereby as the ionic strength increased droplets size also increased as well as the permeate fluxes. These observations were explained in terms of viscous, electroviscous and solvation effects and pore size distribution.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

The demand for high living standards continues to drive industrialization and this is not without consequences on health, safety and the environment. The waste generated from industrialization greatly impacts negatively on the environment bringing about severe and toxic pollution problems. Effluents of industrialization such as greenhouse gases and oil in water etc., have continued to raise issues of global concern and these issues are garnering global attention to mitigate against the impacts of industrialization and if possible, eliminate the concerns.

Industries such as the oil and gas, pharmaceuticals, heavy metals, power etc., produce effluents in order of higher magnitudes. For instance, the oil and gas industry produce oil in water effluents (produced water) alongside extraction of oil and/or gas. According to Neff et al [1], produced water represents the largest volume waste stream in oil and gas production operations with an estimated 0.8 billion cubic meters of produced water released to the oceans from offshore platforms globally in 2003. This release has the potential to cause extended and prolong degradation of the ocean environment. It is therefore imperative to treat effluents before discharge or disposal to the environment.

Produced water which is an oil in water effluent requires treatment to remove the oil and other hazardous constituents before either discharge to the environment and/or reinjection into the reservoir to enhance hydrocarbons recovery or for underground storage. In an effort to protect the environment, the discharge and/or re-use of oil in water effluents is governed by various regulations set by government agencies in different regions. These agencies set the maximum allowable limits for effluent discharge to the environment. The U.S. Environmental Protection Agency (USEPA) has a maximum daily

allowable limit of 45 ppm or less oil in water regulation and any violation may results in severe sanctions and heavy fines.

In order to avoid sanctions and heavy fines, producers of effluents employ several existing treatment technologies to manage their effluents in order to meet the required standards. These existing technologies are selected by producers of effluents based on several criteria especially the type and concentration of the waste stream, cost of technology, and energy requirements. Some technologies that exist for the treatment of oil in water effluent include gravity separation, gas/air floatation, filtration (sand, membrane, etc.), absorption and adsorption, chemical oxidation, biological treatment etc.

1.1. CERAMIC MEMBRANE FILTRATION

The works reported herein emphasize the application of intensified ceramic microfiltration membranes for the treatment of stable oil-in-water emulsion, and also to examine the effects of salt solution environment on membrane performance. Ceramic membranes are made from oxides of metals such as aluminum, titanium, silicon, zirconium, etc. Also, membranes made from polymers (polymeric membranes) exist for such application and are widely used for wastewater treatment because of their relatively cheap cost. But ceramic membranes are becoming more popular because they possess high mechanical, chemical, and thermal stability and the ability for extended usage for long periods compared to polymeric membranes.

The ceramic membranes adopted for the studies herein, are made out of alpha aluminum oxide with mean pore size of 0.22µm putting them in the microfiltration range. The ceramic membranes are intensified meaning that their surface are modified with

another compound to improve their characteristics. For example, Cysteic acid, an organic compound is used to modify the surface of the membranes and this surface modification technology has been patented by Barron et al. [2]. It has been shown that surface modification of ceramic membranes employed for filtration purposes with other suitable compounds enhances either the hydrophilic or hydrophobic properties of the membranes depending on the purpose of application. For the purpose of our application, this surface modification is intended to increase the hydrophilic characteristics of the membranes making them super-hydrophilic. Studies have shown that surface modification of filtration membranes enhances the performance of the membranes with respect to higher permeate fluxes, high separation efficiency and reduced membrane fouling.

Barron et al [2] patented the technology in which they coated the surface of ceramic microfiltration membranes with cysteic acid (an organic compound) to enhance the performance of the membranes in terms of higher fluxes and rejection efficiency when challenged with produced water. These membranes exhibited increased performance with reduced fouling rate. The organic acid molecules have a carboxylic functional group that chemically reacts with the ceramic of the membrane body to create an organo-metallic covalent bond between the acid and the ceramic membrane and it is this covalent bonding that makes the ceramic membranes organophobic.

Chang et al [3] coated the surface of aluminum ceramic microfiltration membrane with nano-titanium oxide particles to increase the membrane hydrophilicity. The membranes performed better compared to non-modified membranes in the treatment of hydraulic oil-in-water emulsion. Zhou et al [4] used nano-sized zirconium oxide to modify the surface of aluminum oxide membranes for stable oil-in-water emulsion

treatment. Hu et al [5] used graphene oxide to modify aluminum oxide microfiltration membranes for application in oil/water separation. Maguire-Boyle et al [6] functionalized aluminum microfiltration membranes using cysteic acid making them super-hydrophilic for the separation of hydrocarbons from frac and produced water.

Also, nanotechnologies are being used to design filtration membranes with high performance. Although this technology has not been widely explored, the technology presents a promising future for membrane filtration [7]. Zhu and co-workers [7] produced ultrathin single-walled carbon nanotube network films for ultrafast separation of emulsified oil/water mixture. Nanotubes, nanowires and nanofibers made from nanomaterials such as carbon and manganese oxide are used in constructing fibrous films and their small diameter make their effective pore size and separation layer tunable on the nanometer scale.

1.2.   OBJECTIVES

The objective of this work is to assess the performance of ceramic microfiltration membranes intensified by cysteic acid coating [2] on oil-in-water separation with and without the presence of salts. The specific objectives with respect to the reports herein are:

1: Investigate the performance of surface functionalized ceramic microfiltration membranes with cysteic acid in the treatment of emulsified oil water with respect to rejection efficiency and flux.

2: Investigate the effects of ionic/salt strength on the performance of intensified ceramic microfiltration membranes in the treatment of emulsified oil/water.

Given that the membranes adopted for these studies were obtained from Molecular Filtration Inc., with modification in situ, the bases for results comparison was done with similar work done in the literature using similar ceramic membrane configuration without any surface modifications and modifications with other compounds other than cysteic acid.

PAPER

I.   PERFORMANCE STUDY OF SURFACE FUNCTIONALIZED CERAMIC MEMBRANE IN THE MICROFILTRATION OF OIL-WATER EMULSION

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ABSTRACT

Stable oil-in-water emulsion was treated using surface modified ceramic microfiltration membranes in crossflow mode. The ceramic membranes were surface treated with cysteic acid ($HO_3SCH_2CH(NH_2)CO_2H$) in order to improve their performance evaluated by flux monitoring and oil rejection efficiency. The cysteic acid is not intended to create a separation layer on the membrane surface but to enhance the hydrophilic feature of the membrane. The ceramic membranes showed high hydrophilicity by attaining a high steady sustained flux in a short time. The flux was monitored under constant pressure operation and results showed that the membrane performance was improved significantly. The membrane efficiency was found to be greater than 99.5% with permeate quality of less 5mg/L oil concentration. The cysteic

acid coating when compared to other coating materials like nano-TiO_2 and nano-ZrO_2, and graphene, exhibited a superior capability in improving membrane performance.

1.   INTRODUCTION

Oil in water as an industrial effluent has significant repercussions on business in terms of sanctions and fines when there are discharge oversights by the business. And on the environment when the effluents cause a degradation of the environment. There are certain environmental standards that require producers of effluents to comply with regulations of reducing their effluent contents to maximum threshold limits before reuse, disposal or discharge to the environment. The oil and gas industry is one such industry that produces oil-in-water effluents in very large quantities. Produced water, which is a form of oil-in-water effluent represents the largest volume waste stream in oil and gas production operations [1] (Figure 1 shows the volume quantity of produced water both onshore and offshore). Produced water is water from underground formations that is brought up to the surface during oil and gas production which contains some of the chemical features of the formations and the hydrocarbons [2]. The challenge of managing produced water has triggered research in finding efficient ways to treat and handle produced water for reuse and/or discharge at levels that are environmentally friendly and at low cost [3]. The characteristics of produced water vary from field to field due to the geological makeup of the reservoirs. Produced water comprises a complex potpourri of dissolved and particulate organic and inorganic chemicals in water [1] and these chemical compounds must be removed either to the barest minimum or completely before disposal because of their environmental footprint.

There are several forms in which oil can be present in water. Either free, dispersed or dissolved oil. Free oil is large oil droplets that float on the surface of water. Oil in dispersed form is present in the form of small droplets suspended in water, while oil in dissolved form is present in a soluble form [4].
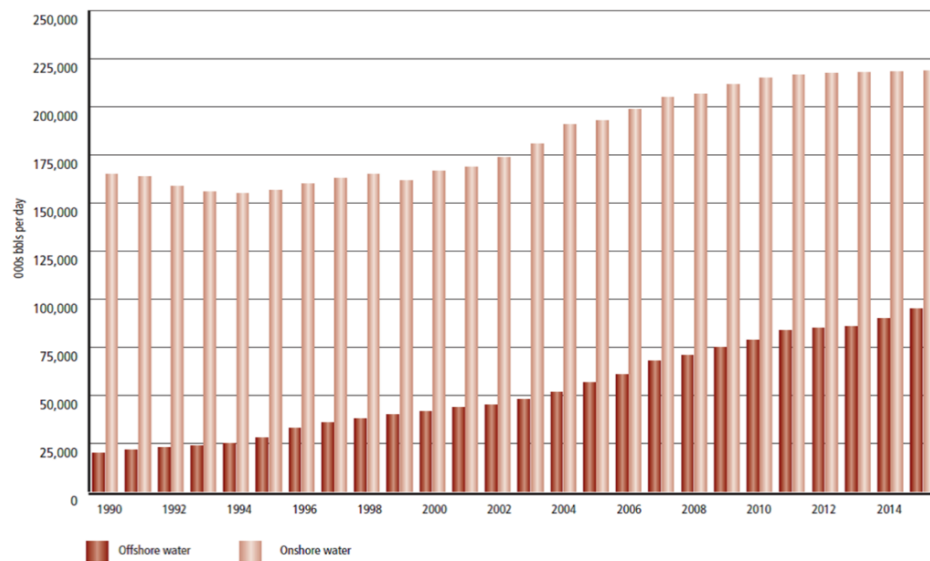
Figure 1. Overview of world produced water production [5]

Several methods exist in treating and handling produced water. The method or technology adopted to treat produced water depends on the makeup of the produced water. However, because of the multi-complexity of produced water (PW), more than one technique is applied for the treatment of produced water (Figure 2 shows an overview of the different technologies).

Application of membrane technology – especially ceramic membranes – for the treatment of produced water (PW) is gaining wide acceptance in oil and gas industry as well as other industries that deal with effluents. Two main types of membrane based on

the material of make are available for industrial applications; (1) polymeric membranes and (2) ceramic membranes. Over the years, polymeric membranes had dominance in application because of their low-cost value. But this class of membranes, though cheap, have their shortcomings with regards to longevity, thermal resistance, mechanical resistance and fouling rate.
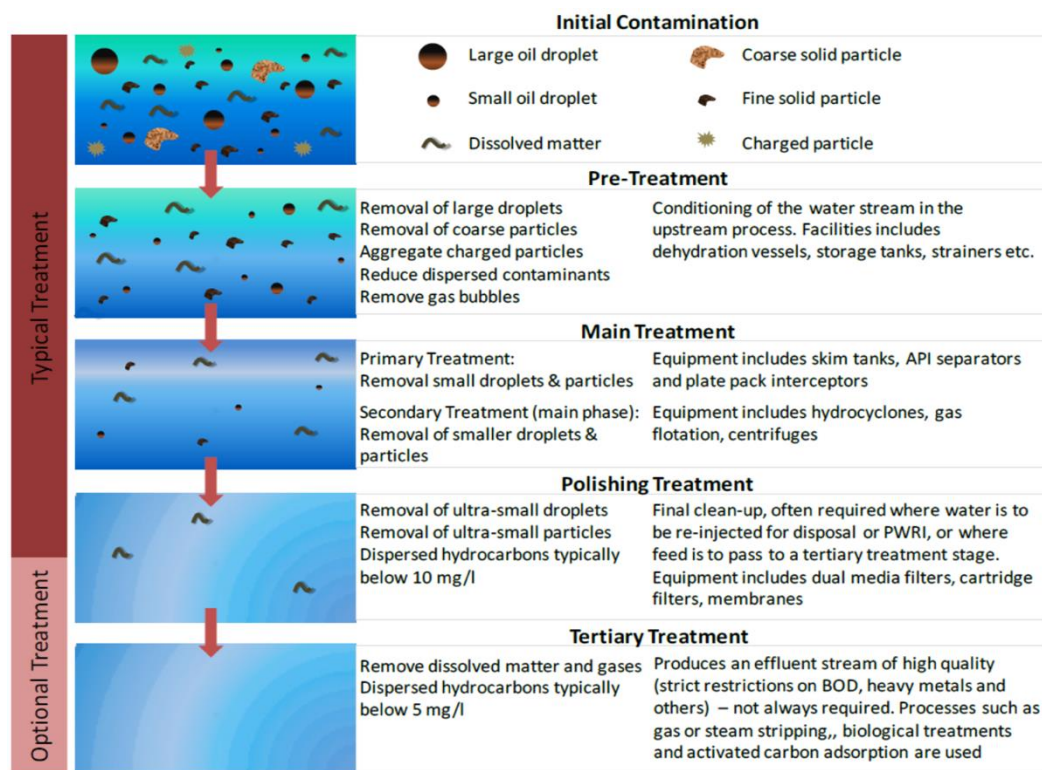
Figure 2. Typical oil-in-water treatment process [6]

These shortcomings continue to hamper on the application of polymeric membranes. On the other hand, ceramic membranes are receiving more attention in recent years because of their great benefits. Despite the high cost of ceramic membranes,

their advantages compensate for their high cost. Table 2 shows a general overview of the advantages, disadvantages and applications of ceramic membranes.

Membrane technology offers a feasible solution to the challenge of micron sized oily wastewaters [7]. Table 1 shows typical types of ceramic membrane separation processes with respect to their pore size. One major setback in the application of ceramic membrane filtration technology in treating effluents is membrane fouling which can occur either by cake/gel formation which is the forming of layers on the membrane surface by solutes adhering to the surface of the membrane.

Table 1. Layer structure of composite ceramic membranes

Separation process	Number of layers	Average pore size
Microfiltration (MF)	1	5 µm
	2	0.25 µm
Ultrafiltration (UF)	3	100 nm
Nanofiltration (NF)	4	2 nm
Reverse osmosis (RO), gas separation, pervaporation, vapour permeation	5	10 Å

Source: After Bonekamp [8].

In order to improve the performance of ceramic-based membranes, studies have shown that treating the surface of membranes with other compounds significantly increase membrane antifouling characteristics and increasing the rejection efficiency thereby improving the performance of the membrane. One such way by which membrane performance is improved, is through surface modification. Surface modification by either chemical reaction or physical absorption has become an efficient approach towards

overcoming membrane surface fouling by increasing the hydrophilicity of the membrane surfaces [9].

Hu et al [10] created a novel membrane by modifying the surface of aluminum oxide microfiltration membrane with graphene oxide and observed a superior permeate flux and high oil rejection when compare to unmodified membranes. Howarter et al [11] used perfluorinated end-capped polyethylene glycol surfactants which possesses amphiphile to covalently graft glass membranes to improve oil-in-water separation efficiency. Their work reported high resistance to fouling and high rejection efficiency. Rovens et al. [12] used solvent based surface modification to functionalize titanium oxide microfiltration membranes using an organophosphonic acid to enhance oil/water filtration. The membranes showed great improvement in oil rejection with low fouling.

Lee et al [13] performed a facile surface modification of pristine aluminum ceramic membranes using binary titanium oxide and silicon oxide for achieving greater fouling resistance and higher flux performance in the treatment of oil effluents. Zhou et al [14] used nano-sized zirconium oxide to modify the surface of aluminum microfiltration membrane to treat stable oil-water emulsion. The modified membranes exhibited high performance. Maguire-Boyle et al [15] created a functionalization strategy for oil-water separation membranes by using cysteic acid to coat the surface of aluminum microfiltration membranes in order to enhance performance and reduce fouling rate. Results show tremendous improvement in performance and low fouling rate in oil-water separation.

This work reports the study done on the application of ceramic membranes made from alumina (Al_2O_3), and surface treated with cysteic acid ($HO_3SCH_2CH(NH_2)CO_2H$)

in treating oily wastewater, to investigate the efficiency of the modified membranes. Crossflow microfiltration mode was chosen for the study and the flux was monitored in a constant pressure operation.

The study aimed to compare the efficiency of surface modified ceramic membranes with cysteic acid to other surface modified ceramic membranes with different materials such as nano-TiO_2, nano-sized ZrO_2 and graphene oxide.

2. MATERIALS AND EXPERIMENTAL

2.1. MATERIALS

The microfiltration ceramic membranes were supplied by Molecular Filtration Inc. (MFI) and all chemicals used were purchased from Sigma-Aldrich and were used without any further purification. The filtration prototype rig utilized was made available by Molecular Filtration Inc. (MFI)

2.2. MEMBRANE CHARACTERISTICS

The membranes used for this investigation are tubular in shape with an average pore size of 0.22µm enclosed in a stainless-steel housing.

The membranes were prepared by extrusion and sintering. Table 3 list the characteristics and specifications of the ceramic membranes used.

Table 2. Advantages, disadvantages and current applications of ceramic membrane*[16]

Advantages	Disadvantages	Current status	Applications
Thermal stability ($>200\,^{\circ}C$)	Low hydrothermal stability of composite membranes with a silica top layer. Complicated sealing at high temperatures	Surface modification to improve hydrothermal stability	Reactions at high temperature, pervaporation, gas separation
Resistance to organic solvents	Expensive source materials, complex processing; relatively high capital installation costs		Separation of organic liquids and oils, waste-water treatment
Chemical stability over a wide pH range	Difficult sealing and module construction		Chemical cleaning, separation at extreme pH, recovery of acids/bases
Long-time operational stability, no ageing, potentially lower life cycle cost	Low packing density		Small-scale application
Mechanical stability under large pressure gradients	Brittleness incurs special configurations and sup- porting systems		Operation at high flux (up to 500 l/(m^2 h)), backwashing at high flux
High structural integrity	Relatively high installation and modification costs in case of defects	Depends on the separation process	
Uniform pore size distribution	Difficulty to achieve high selectivity on a large scale		Precise size-based separations in pharma and bio applications
(Electro)catalytic and electrochemical activity easily realizable	Low permeability of high-selectivity (dense) membranes at medium temperatures		Solid oxide and other dense electrolyte fuel cells

*The advantages of ceramic membranes depend largely on the type of ceramics used in their preparation.

Table 3. Characteristics of ceramic membranes used

Property		Value
Product code		MFI-CRM301940
Number of channels		19
Dimension	Outer diameter	30 mm
	Channel diameter	4 mm
	Unit surface area	0.24 m^2
Parameters	Porosity	~41 %
	Mean pore size	0.22 µm
Support material		99% α-Al$_2$O$_3$
Membrane material		Al$_2$O$_3$/ZrO$_2$
Suitable temperature		< 150°C (< 302°F)
pH value		1 - 14
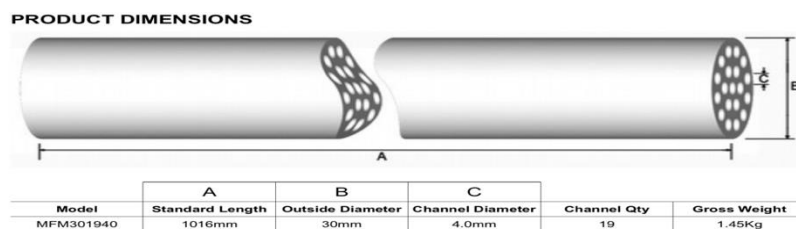
Figure 3. Ceramic membrane configuration

2.3.   MEMBRANE FUNCTIONALIZATION USING CYSTEIC ACID

In order to enhance the membranes, the surface of the membranes were modified with cysteic acid. The coating of the membranes was done in place i.e. while the membranes were fixed in the membrane housing connected to the filtration rig. 1M cysteic acid solution was prepared using distilled water in the feed tank and preheated to 65°C. The filtration rig was then run with the permeate side open for 12 hours at a temperature of 85°C. Conductivity measurements from the permeate side were taken and when four approximately equal conductivities were obtained, the process was considered

complete. Once the functionalization was complete, the solution was removed, and distilled water was used to rinse the membranes. The filtration rig was run with distilled water for about 40 minutes and the membranes were left to dry.

2.4.   SYNTHESIS OF THE PROCESS FEED

In testing the performance of the functionalized membranes, synthetic produced water (PW) was synthesized in the lab using heavy mineral oil with density 0.862g/mL. 20 liters feed water containing 1000ppm oil in water was synthesized. 20g of heavy mineral oil was added to 1liter water and 10wt% span 80 surfactant was added to the oil-water mixture to enhance the stability of the emulsion. An IKA RW 20 digital lab mixer was used to mix the oil-water-surfactant mixture for 30 minutes at 600rpm. In order to create a homogeneous mixture of the oil-in-water emulsion, the filtration rig was run at a very high speed with the permeate outlet closed for 30 minutes creating a jet mixing effect resulting in a turbulent mixing of the feed which resulted to a homogeneous mixture. The emulsion created was highly stable because when left to stand for 6 hours, no visible phase separation was observed. In determining the oil droplet size in the emulsion feed, a laser diffraction particle size analyzer, model Litesizer 500 manufactured by Anton Paar Austria was used. The figure below shows the droplet size distribution of oil in the feed with an average droplet size of 0.58 µm.
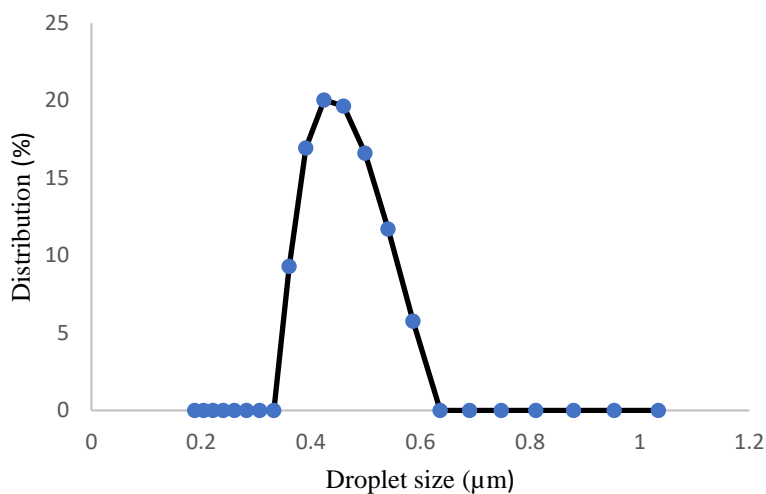
Figure. 4. Droplet size distribution of oil droplets in the synthetic feed

2.5.   MEMBRANE CLEANING

In order to ensure that the membranes maintain adequate flux and separation

efficiency, the membranes were cleaned according to the procedure outlined in Table 4

below.

2.6.   EXPERIMENTAL SET-UP AND OPERATION

The set up for the experiment is represented by the flow diagram illustrated in

Figure 5. The set up consist of a feed tank of 50 liters capacity. The system was run in

cross flow mode and both the retentate and the permeate were recycled back to the feed

tank in order to keep the feed concentration relatively constant. Operating the system in

crossflow mode instead of the dead-end mode, allows for extended filtration cycles since

the shear acting on the membrane as the retentate flows across the membrane serves to

suppress membrane fouling [17]. Two membranes of the same configuration

Table 4. Cleaning-in-place procedure

Reagent (20 L)	Recirculation time and temperature
1. Water flushing	30 minutes @ 25°C
2. 2M NaOH	30 minutes @ 60°C
3. Water rinsing	30 minutes @ 25°C
4. 1M Oxalic acid	30 minutes @ 60°C
5. Water rinsing	30 minutes @ 25°C

were enclosed in two different housings and arranged in series as can be seen in the Figure 5. This setup allows for a greater separation efficiency. A feed of 20 liters was charged into the feed tank and circulated through the system with the aid of a circulation pump. The permeate side was open to the atmosphere and the permeate flowrate (L/h) was read via a flow meter on the permeate line. The experiment was run at ambient temperature (25°C ± 5°C). Operating pressure as well as cross flow velocity were adjusted using the control valves on the system.

2.7. ANALYTICAL METHODS

2.7.1. Permeate Flux (L/m2 h). Permeate fluxes (J_p) were estimated as a function of time under the specified operating conditions using the following equation:

$$J_p = \frac{Q_p}{A\Delta t} \tag{1}$$

where Q_p is the volume of the permeate (L), A is the effective membrane surface area (m^2) and Δt is the sampling time (h).

2.7.2. Membrane Separation Efficiency. The oil removal efficiency was evaluated by the following equation:

$$R\% = 1 - \frac{C_p}{C_f} \tag{2}$$

where C_p and C_f are the concentrations of oil in the permeate at sustained flux and in feed (mg/L), respectively. The UV-spectrophotometer was used to determine the concentrations of oil in the feed and permeate.

3.   RESULTS AND DISCUSSION

3.1. EFFECT OF CYSTEIC ACID ON CERAMIC MEMBRANE

Coating the surface of the ceramic membranes with cysteic acid increases the hydrophilicity of the membranes i.e., it increases membrane performance. The performance of cysteic acid can be explained with respect to the hydrogen bonding of amine and sulfonyl portion, on functionalized cysteic acid and its zwitterionic form (Figure 6a). The amine and sulfonyl parts can form several hydrogen bonds with the solvent, thereby making the surface of the membrane hydrophilic [18]. The cysteic acid covalently bonds with the ceramic of the membrane body rendering the membranes organophobic. Figure 7 shows the SEM images of the cross-section of the functionalized (a) and unfunctionalized (b) membrane with cysteic acid.

The cysteic acid coating does not form a new separation layer but alters the surface features by chemically adsorbing onto the surface and into the pores of the membrane, and this does not change the pore structures/size.

Figures 6b and 6c show the effect of cysteic acid on the wettability of the membrane surface. Wettability is generally influenced by surface roughness and chemical composition of the membrane.
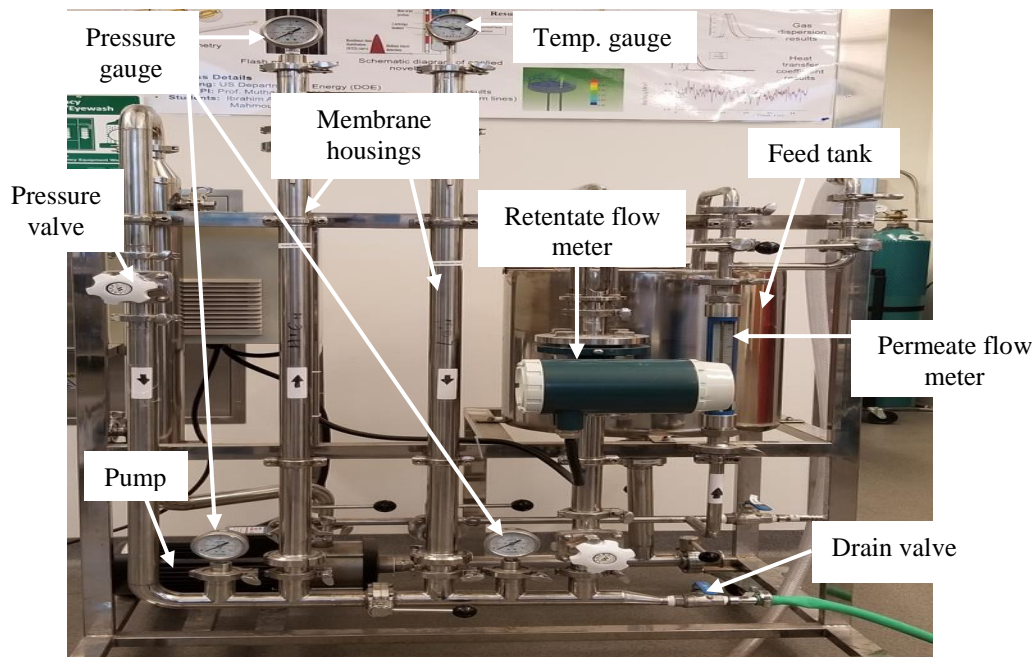
Figure 5. Picture of membrane filtration unit

Because cysteic acid increases the hydrophilic properties of the membrane, this tends to make the surface of the membrane have more affinity for water. We observe how a water droplet spreads on the surface of the functionalized membrane; it spreads easily on the surface (Figure 5c) with a contact angle of 5° demonstrating the increased hydrophilicity of the membrane compared to the unfunctionalized membrane surface (Figure 5b) which has a contact angle of 38°.

The wettability feature of the functionalized ceramic membrane makes it suitable for application in oil/water emulsions separation. The hydrophilic membrane surface contributes to repel oil droplets from adhering to membrane surfaces, thereby, weakening the effect of membrane fouling.

(a)
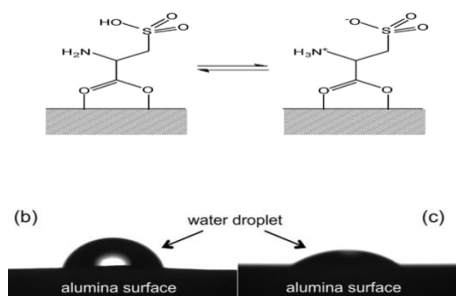
Figure 6. (a) Bonding sequence of cysteic acid on alumina surface. Photographic image of a water droplet on (b) unfunctionalized and (c) functionalized alumina surface
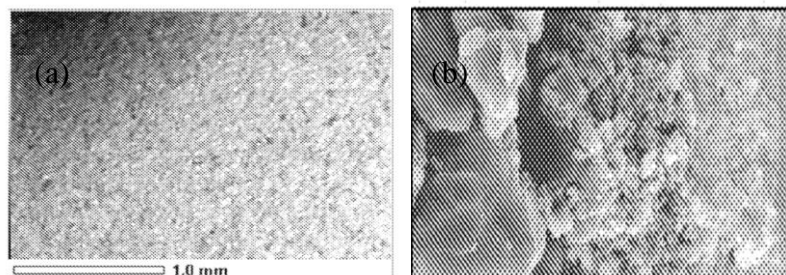
Figure 7. SEM image of (a) functionalized and (b) unfunctionalized ceramic membrane

3.2.   OIL/WATER EMULSION TREATMENT

Stable oil-in-water emulsions can be difficult to deal with because of the fineness of the oil droplets dispersed in water and the oil droplets do not coalesce. The driving force in the application of ceramic membranes for the separation of impurities (such as oil) from water is the change in pressure (ΔP) across the membrane, and the separation efficiency is dependent on the molecular weight cut-off (MWCO) of the membrane which also depends on the purpose and mode of treatment (MF, UF, NF, RO). In microfiltration (MF), when the oil droplet size is larger, a high rejection efficiency is observed but this is followed by a considerable decline in permeate flux due to the

deposition of oil droplets on the surface of the membrane which creates a resistive layer to flow. But the smaller the droplet size, a less rejection efficiency is obtained because the droplets can easily pass (by way of deformation) through the membrane pores.

In order to reduce the effects of fouling and low rejection efficiency, surface functionalized membranes are used. surface functionalized membranes are made to be oil repellent and water 'loving'. These membranes stop oil droplets from passing through the pores of the membranes and also prevent the droplets from adsorbing onto the surface of the membranes because their surface has become organophobic.

Figure 8 presents visual images of the stable oil-surfactant-water emulsion (left) and the permeate/filtrate (right). Permeate obtained had a permeate quality of $< 5mg/L$ with a rejection efficiency of $> 99.5\%$. This result is promising as the permeate obtained is from a single pass without any pretreatment.

3.3.   FLUX MONITORING

In membrane microfiltration, maintaining a consistent high enough flux is very important. This is indicative of the membrane performance as applied to any function. Parameters such as transmembrane pressure (TMP), crossflow velocity (CFV), temperature, feed composition/concentration, membrane morphology (pore size and surface characteristics) etc., have considerable effect on membrane performance and these effects are observable in the flux. The flux is also an indicator of the fouling rate of the membrane.

Figure 8. Image of process feed (left) and Permeate (right)

The flux and the fouling rate are usually inversely related while the flux and parameters such as TMP, CFV, and temperature are proportionally related. There are two modes in which a membrane module can be operated either operated in constant flux or constant pressure mode. Operation in constant flux mode, the flux through the membrane remains constant, but the TMP rises as the operation proceeds. Conversely, operation in the in constant pressure mode, the pressure remains constant, but the flux decreases [16].

In monitoring the flux of our system, the membrane module was operated in the constant pressure mode and we used two different transmembrane pressures (0.13 MPa and 0.20 MPa) to observe the behavior of the flux. The reason why we focused on the TMP is because the general driving force for membrane filtration is a pressure differential. Figure 9 illustrates the behavior of the system flux with respect to the transmembrane pressure with time. From the Fig. 8, it is observed that the permeate flux is greatest at higher TMP and vice versa. The flux at the beginning of the run at a TMP of 0.20 MPa was 875 L/m^2 h. After 20mins, a stable permeate flux was observed.
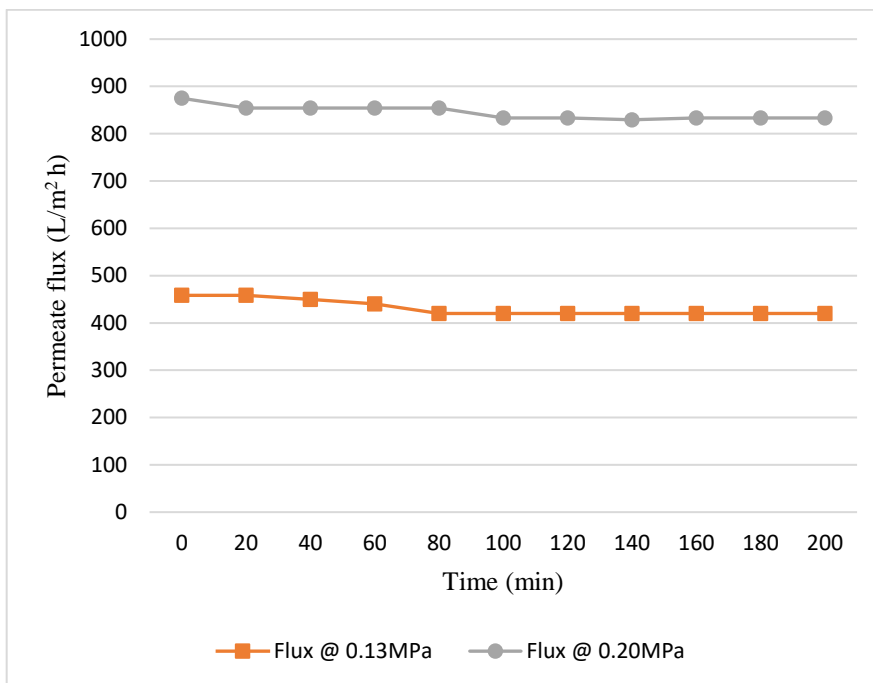
Figure 9. Permeate flux behavior with time at two different TMPs

Despite the flux fluctuation observed at t = 100 mins and t = 140 mins, the system always returned to a stable flux. These fluctuations can be explained by reason of a pressure differential across the membrane. At t = 160 mins, a sustainable flux of 833 L/m^2 h was observed and the oil concentration at the end of the run at a TMP of 0.20MPa was found to be <5 mg/L with an efficiency >99.5%. The sustained flux obtained maintains 95% of the original flux and this shows that fouling of the membranes is minimized. A similar trend is also observed for the run performed at a TMP of 0.13 MPa. The flux at the start of the run was 458 L/m^2 h and a sustained flux of 420 L/m^2 h was achieved at t = 80mins. The sustained flux was 92% of the original flux, again showing that the performance of the membranes is superior. The permeate quality at the end of the run exhibited the same quality as the permeate quality obtained from the run at 0.20MPa.

The high sustained flux observed for both runs can be attributed to the fact that the membrane surface coating (with cysteic acid) allows the membranes to repel the hydrophobic oil droplets preventing the membrane pores from obstructions/blockage to flow. In other words, the oil droplets do not create a resistance to flow, thereby maintaining a sustained flux. When our results were compared to similar work [10, 18] (Table 5), the comparison showed that cysteic acid has more potential in enhancing ceramic membrane's hydrophilic properties.

Studies [10, 14, 17, 18, 19, 20] have shown that unfunctionalized membranes exhibit rapid flux declines due to fouling. Flux declines in unfunctionalized membranes have been observed to drop up to 70% of the initial flux in a short time. Unfunctionalized membranes do not possess the feature that allows them repel oil droplets and oil is easily absorbed unto the surface of the membrane constricting the pores of the membrane thereby resisting flow and increasing fouling rate.

Table 5. Results comparison with similar work

	Modified Membrane			Unmodified Membrane
	Cysteic acid	Nano-TiO2	Graphene oxide (GO)	
Stable flux (L/m2 h)	833	350	667	210/522
Permeate quality (mg/L)	< 5	9	12.8	12/18.8
Reference	This work	[18]	[10]	[10, 18]

4. CONCLUSION

This study has shown that treating the surface of commercial Al_2O_3 ceramic microfiltration membrane with cysteic acid improves the performance of the membranes. the membranes were subjected to a 1000 mg/L oil-in-water emulsion in order to observe the effects of cysteic acid coating on the performance of the membranes. When compared to other coating materials such as nano-TiO2 and graphene oxide, cysteic acid displayed greater improvement of membrane performance with high rejection efficiency and extended steady sustained flux. In order to understand thoroughly the transport phenomena of mass transfer on the surface of the membranes, it is recommended that molecular dynamics simulation studies be done to explain on a microscale the performance of the modified membranes.

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II. INVESTIGATIVE STUDY OF IONIC STRENGTH EFFECTS ON THE PERFROMANCE OF SURFACE FUNCTIONALIZED CERAMIC MEMBRANE MICROFILTRATION OF EMULSIFIED OIL/WATER TREATMENT

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ABSTRACT

Ionic effects on membrane performance is evaluated with respect to droplet size and membrane flux. Two alpha-alumina microfiltration membranes operated in crossflow mode were challenged with feed water containing 1000 ppm oil in various ionic concentration solutions. The membranes have a mean pore size of 0.2 µm and are tubular in shape. The results of the study showed the significant impact of ionic solution environment on both membrane performance and oil droplet size. With respect to oil droplet size, analysis showed that the oil droplet sizes increased as the ionic strength of the solution environment increased. This effect on oil droplet size was interpreted in terms of reduction in droplet surface charge which weakens the repulsive forces between particles causing them to merge/floc. Also, permeate fluxes were greatly affected by ionic strength. Permeate fluxes decreased significantly from the feed without salt to the feed with 0.1 M salt concentration and then increased with increasing ionic strength even

though some studies showed otherwise. The effect on permeate fluxes was attributed to a more permeable gel layer formation that poses less resistance to flow at high ionic strengths compared to the dense gel layer formed at lower ionic strength.

1.   INTRODUCTION

The physico-chemical properties of ceramic membranes make them suitable for application in the filtration treatment of various types of industrial effluents ranging from oil and gas industry, pharmaceutical industry, heavy metal industry, and treatment of water for potable use etc. Their mechanical and thermal stability make ceramic membranes suitable for long term effluent treatment. In addition, their ability to withstand harsh chemical and temperature environments widen their applications further. Ceramic membranes are synthesized from oxides of metals such as aluminum, titanium, silicon, zirconia, etc.

Ceramic membranes have garnered attention in recent years because of their advantages and potential applications. Numerous studies have been performed to either understand membrane performance or to improve performance through different combinations of physicochemical conditions. Huisman et al. [1] studied viscous and electroviscous effects of water permeability in ultrafiltration and ceramic microfiltration membranes. They observed that when they increased the ionic strength of the solution environment from 30 μM to 0.1 M, water fluxes increased simultaneously by 2% to 8% for both ultrafiltration and microfiltration membranes. They attributed the increase in permeability to electroviscous effects explaining that increasing salt concentrations lowered the zeta-potentials, thinning the double-layers thereby resulting in less resistance

to flow of water. They also highlighted that measuring water fluxes at various ionic concentrations are a simplistic way of studying the zeta-potentials of membranes.

Zhao et al. [2] performed experiments on the effects of inorganic salts at different concentrations on ceramic membrane microfiltration of titanium oxide suspension to observe filtration behaviors with respect to the variation in solution environment based on the measurement of particle size distribution, zeta-potentials of both ceramic membranes and TiO_2. Their results showed that ionic solution environment affected the dispersity of TiO_2 particles making them floc at higher ionic strengths. Flocs formation produces a more permeable cake layer which exhibits less resistance to flow thus increasing permeate flux. They also showed that the particle sizes of TiO_2 were significantly influenced by the ionic environment whereby as the ionic strength increased, particle size also increased which enabled the formation of flocs. They also observed that there was a decline in permeate flux when the TiO_2 particles had high zeta-potential. This caused an increased particle dispersion under high charge density producing a cake layer with high resistance consisting of fine particles. Kwon and Vigneswaran [3] observed while using membranes with 0.2 µm mean pore size that ionic strength greatly influenced critical flux compared to particle size while studying how particle size and surface charge can affect the critical flux of crossflow microfiltration. They observed that large particle sizes of 11.9 µm did not show any significant resistance to flow despite heavy deposition of particles on the membrane surface. But as the ionic strength was varied, a drop in critical flux was observed at lower ionic strength and as the ionic strength was increased, there was significant increase in the critical flux which could be due to the agglomeration of

particles. On the contrary, Hua et al. [4] reported that higher steady fluxes were observed at lower salt concentrations and vice versa.

Also, Elzo et al. [5] made similar observations to Hua while they were studying the performance of inorganic membrane in a crossflow microfiltration with respect to charge effects. They reported high permeate fluxes at high pH and low salt concentrations and outlined dependency of permeate flux as a function of both particle and membrane surface charges. Macroscopic flow properties of the feed rely on particle-particle interactions arising from interparticle forces, Brownian diffusion and solvent-induced hydrodynamic interactions [6]. Huisman et al. [7] highlighted that the implication of salt concentration is explained by pointing out that decreasing salt concentration translates to an increase in the Debye length. This effect causes significant interparticle repulsion amounting to larger interparticle distances which results in less deposition and more permeable cake layers. In their work - particle transport in crossflow microfiltration, effects of particle-particle interactions – they proposed a model that showed that shear-induced diffusion tends to be the main transport mechanism governing the flux in the microfiltration of suspensions of micron-sized particles, and that charge effects can increase fluxes significantly.

Nazzal and Wiesner [8] studied the effects of pH and ionic strength on the performance of ceramic membranes in water filtration using three different feeds: particle-free electrolyte solutions, silica suspensions and solutions of humic acid. Higher fluxes were measured at lower ionic strength for both the particle-free electrolyte solutions and silica suspensions. Permeation rates were insensitive to pH and ionic strength in the presence of humic material but a significant decline in flux was observed

and this was attributed to that fact humic material adsorbs onto the surface of the membrane pores which impedes the flow of permeate.

Studies suggest that ionic strength effects may alter the stability and conformation of suspensions in the feed water with implications for membrane-foulant interactions. Ionic strength and pH influence the propensity of organic matter to sorb, the permeability of cake or gel layers and the potential for aggregation of suspensions [8].

In this work, the effects of ionic strength on the performance of ceramic microfiltration membranes that have been surface modified with cysteic acid were studied when applied for the treatment of oil/water emulsion. The filtration process was performed in crossflow mode and the observations were made in terms of the permeation flux at various ionic concentrations in the feed. The results were interpreted with respect to oil droplet size, viscous and electroviscous effects and solvation effects.

2.   METHODOLOGY

Two α-Al_2O_3 microfiltration ceramic membranes, coated with cysteic acid and arranged in a series configuration were employed for this study. The ceramic membranes supplied by Molecular Filtration Inc. company were tubular in shape with 19 channels each. The membranes were encased in a stainless-steel casing and operated in crossflow mode. Table 1 and Figure 1 summarizes and shows the characteristics and specifications of the ceramic membranes.
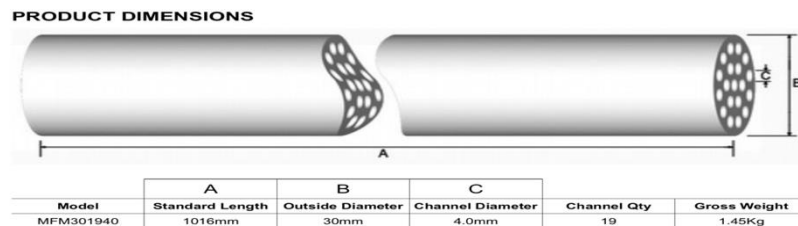
Figure 1. Ceramic membrane configuration

Table 1. Characteristics of ceramic membranes

Property		Value
Product code		MFI-CRM301940
Number of channels		19
Dimension	Outer diameter	30 mm
	Channel diameter	4 mm
	Unit surface area	0.24 m^2
Parameters	Porosity	~41 %
	Mean pore size	0.22 μm
Support material		99% α-Al$_2$O$_3$
Membrane material		Al$_2$O$_3$/ZrO$_2$
Suitable temperature		< 150ºC (< 302ºF)
pH value		1 - 14

2.1. CHEMICALS

All chemical compounds used were of analytical grade and purchased from sigma-Aldrich. Chemicals were used without any further purification.

2.2. MEMBRANE COATING

The coating of the membranes was done in place i.e. while the membranes were fixed in the membrane housing connected to the filtration rig (Figure 2). 1 M cysteic acid solution was prepared using distilled water in the feed tank and preheated to 65ºC. The filtration rig was then run with the permeate side open for 12 hours at a temperature of

85ºC. Conductivity measurements from the permeate side were taken and when four

approximately equal conductivities were obtained, the process was considered complete.

Once the reaction was complete, the reaction solution was removed, and distilled water

was used to rinse the membranes. The filtration rig was run with distilled water for about

40 minutes and the membranes were left to dry.

2.3. PROCESS FEED

To investigate the effects of ionic strength on ceramic membrane microfiltration

of stable oil/water emulsion (synthetic oily wastewater) coated with cysteic acid, oil-in-

water emulsions with 1000 ppm oil were prepared in three different ionic solution

environments. Sodium chloride (NaCl) solutions at ionic strengths of 0.1 M, 0.3 M, and

0.5 M were prepared and used to provide the ionic effects required for the study. The feed

volume used was 10L. Each ionic solution was prepared by dissolving 58.44g, 120g, and

292.2 g NaCl in 10 liters deionized water to obtain 0.1 M, 0.3 M, and 0.5 M solutions of

NaCl, respectively. 10 g of heavy mineral oil in the presence of a span 80 surfactant was

mixed in each of the ionic solution environment to produce the feed stock. An IKA RW

20 digital lab mixer was used to mix each mixture at 600 rpm for 30 minutes creating

stable emulsions. The stability of the emulsions was determined by allowing the

emulsions to stand for roughly 6 hours and no visible phase separation was observed. The

oil droplet size for each feed stock was analyzed using a laser diffraction particle size

analyzer, model Litesizer 500 manufactured by Anton Paar Austria. The conductivity and

pH of the feeds were measured using YSI 3200 conductivity instrument (YSI

incorporated Yellow Springs Ohio) and an OAKTON pH ecotestr, respectively.

2.4.   EXPERIMENTAL PROCEDURE

The experiments were performed in a prototype industrial scale filtration equipment (filtration rig) supplied by Molecular filtration Inc. company (Austin, Texas). The rig comprised of a mounted pump that was used for feed circulation, a 60 liters capacity feed tank, two stainless-steel casings that housed the microfiltration ceramic membranes, retentate and permeate lines with the ability to redirect both flows either out of the system or back into the feed tank. The rig consisted a temperature gauge for temperature monitoring/measurement, three pressure gauges; one located at the inlet of the first membrane, one at the outlet of the first membrane serving as the inlet to the second membrane and one at the outlet of the second membrane. The gauges aided the reading and setting of the transmembrane pressure of the system. All runs were carried out at a constant transmembrane pressure of 0.20 MPa and at a temperature of $25^{\circ}C \pm 5^{\circ}C$. The pump speed was adjusted to 45 Hz and was used for all runs. The system was operated in crossflow mode and the retentate and the permeate were fed back into the feed tank to maintain consistent feed concentration. Each feed stock was charged into the feed tank and circulated with the installed pump at the conditions mentioned earlier. Each run lasted for 3 hours and 30 minutes. The flux used for the study is the permeate flux and readings of permeate flux were recorded in 20 minutes intervals.

Prior to performing filtration test of each feed, the microfiltration membranes were cleaned in place with 2 M NaOH solution circulated for 30 minutes after which deionized water was used for rinsing for 30 minutes, this was followed by a 1 M oxalic solution cleaning for another 30 minutes then rinsed with deionized water for 30 minutes.

Clean water test was performed after each cleaning and pure water flux was recorded. After performing a clean water test, a 0.5 M NaCl solution test without oil was conducted and the flux measured. This was done to ascertain the cleanliness of the membrane by comparing the fluxes before and after each run and also to ensure reproducibility of the test.
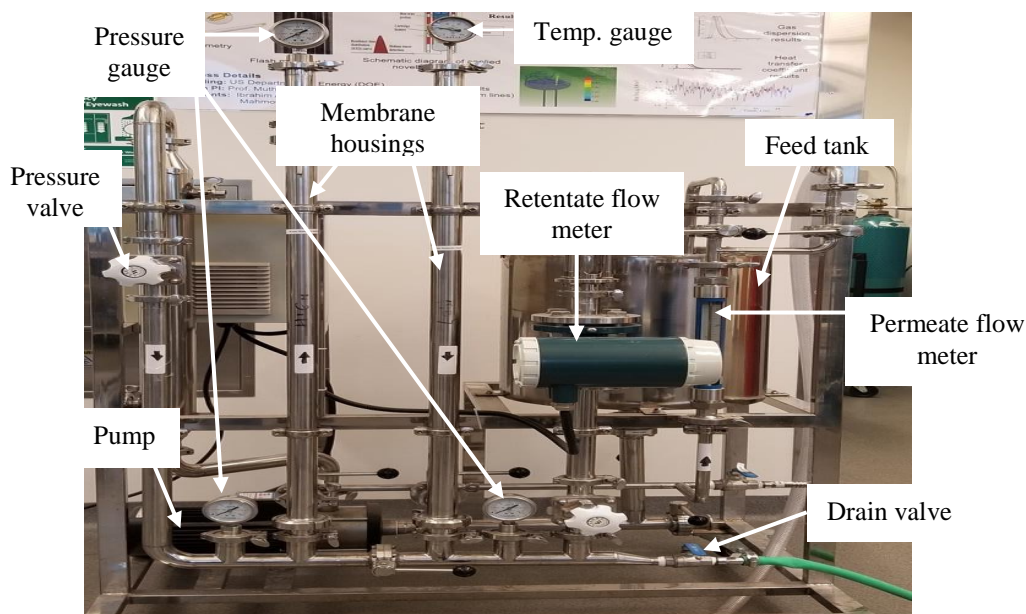
Figure 2. Picture of experimental setup

3.   RESULTS AND DISCUSSION

3.1.   EFFECTS OF IONIC STRENGTH ON OIL DROPLET SIZE

Droplet size analysis of the feed at different ionic concentrations was performed to determine if solution environment affected or influenced oil droplet size. The results obtained showed that ionic solution environment has a significant impact on the oil droplet size. It was observed that droplet size increased with increasing ionic strength (i.e.

the higher the ionic strength the greater the feed droplet size). And this indicates that the

performance of the surface coated ceramic microfiltration membrane will be impacted by

this observation. Figure 3 illustrates our observation graphically. It shows how feed

droplet size progressively increased with increase in ionic strength. For the feed with zero

ionic strength, the oil droplet size was 0.5µm and when the ionic strength went from 0.1

M, 0.3 M, and 0.5 M, oil droplet sizes of 4 µm, 9.1 µm, and 15.8 µm respectively were

obtained. This clearly tells us that there is significant interaction between the oil droplets

and the ionic solution environment. Similar observations from other works have been

made on change of particle size as a function of ionic strength. Zhao et al. [2], in their
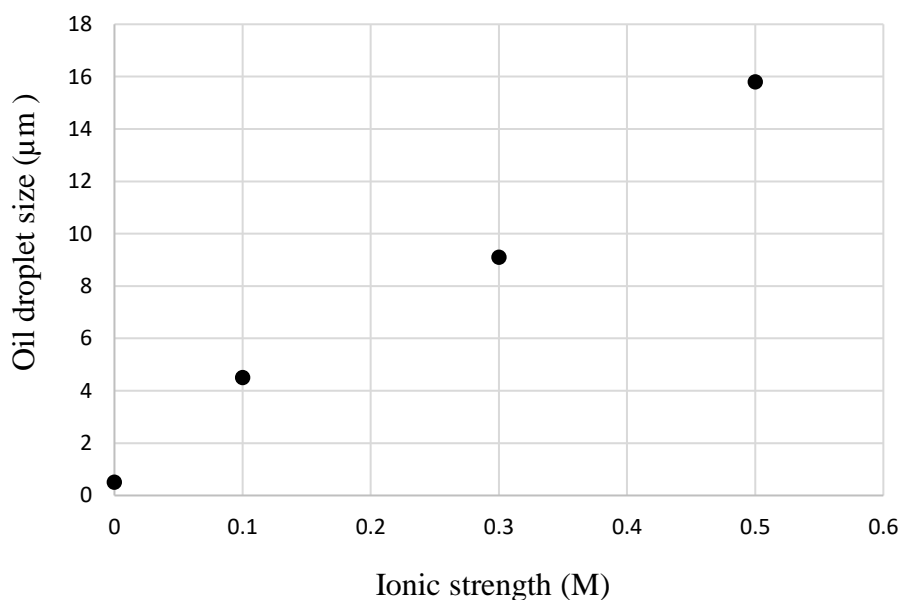

Figure 3. Change in oil droplet size as a function of ionic strength

work while studying the influence of ionic strength on ceramic microfiltration of TiO_2 suspensions reported that TiO_2 particles in suspension increased in size as the ionic strength of the solution environment also increased.

This change was attributed to increase in flocculation of TiO_2 particles in suspension with increasing ionic strength.

Zhang et al. [9] also reported that the particle size of polyacrylamide particles increased with increasing ionic concentration in their study of effects of polyacrylamide and inorganic salts on the ceramic membrane treatment of produced water. As the particle size increased, the pore blocking severity of the membrane pores increased and this created greater resistance to flow thereby reducing flux due to membrane fouling. These observations, including in this work explains that the presence of a salt in an emulsion/suspension weakens the surface charge of the oil droplets hence, reducing their repulsive forces. As a result of this reduced repulsive forces, the particles tend to floc thereby increasing in size.

3.2. EFFECTS OF IONIC STRENGTH ON MEMBRANE FLUX

A significant decline in membrane performance was observed when the ionic concentration of the feed was varied. The performance of the membrane is observed in terms of the membrane flux. The results obtained showed that the permeate flux decreased rapidly within a short time with varying ionic concentrations. Figure 4 illustrate these observations graphically.

Even though the decline in flux for the feed with 0.5 M ionic strength was less drastic compared to when the feed was at 0.1 M and 0.3 M ionic strength, the reduction in

flux appeared to be very significant. The permeate flux at all ionic strengths drastically decayed within the first 20 minutes and reached a steady state shortly afterwards. It appeared that the surface coating of the ceramic microfiltration membranes with cysteic acid did not have any greater significance on the performance of the membranes. For the feed with ionic strength of 0.1 M, the initial permeate flux was 68.4% of the original flux while for feeds with ionic strength of 0.3 M and 0.5 M, their initial permeate fluxes were 76.1% and 84% of the original flux respectively. These fluxes, when compared to the initial flux of feed with zero ionic strength (95%), indicates how significantly ionic solution environment impacts on membrane performance. In explaining these observations, we considered first the role of particle size. It has been established that ionic environment influences particle size and this consequently impacts on membrane performance with respect to flux. We observed that membrane flux depreciates as ionic strength weakens despite that particle sizes are smaller at lower ionic strength. The interaction between oil molecules and the ionic solution environment increased adsorptivity of oil molecules onto the surface of the membrane forming a permeable gel layer. It is logical to explain that this permeable gel layer created a resistance to flow and this resistance increased with smaller particle sizes hence the rapid, progressive decline in flux. At lower ionic strength, pore blocking severity due to the reason that small particles are absorbed onto the pores. This outcome was also observed by Zhang et al. [9]. At higher ionic strength, the gel layer formed was less dense than that at lower ionic strength as evidenced by the fluxes. The large particles of the feed at 0.5M ionic strength could not be easily absorbed onto the pore surfaces thereby reducing the severity of pore blocking and because the particles are only adsorbed onto the membrane surface, they

experience hydrodynamic lifting with greater diffusion coefficient caused by shear eroding particles from membrane surface thereby creating a thinner gel layer consequently increasing flux [10].

Contrary to popular demand [7, 8], the salt effects on permeation can be explained/described in terms of the Debye length. The Debye length between molecules increases with decreasing ionic strength and this is supposed to either reduce the apparent viscosity thereby raising permeate flux or cause greater interparticle repulsion creating more distances between particles resulting in less deposition and more permeable cake layers. Our results contradicted this conception probably because there was some interaction between the cysteic acid, oil molecules and the ionic solution environment (more work is required). Even though a more permeable layer was observed, but this was at high ionic strength.

Another phenomenon that can be applied in explaining the decline in flux is solvation effects. The action of solvation within the pores of the membrane may decrease permeate flux. Water that is structured may be 2 to 3 molecules wide at a water-solid interface and the hydrogen bonding with groups that are functional on the membrane may enlarge to a number of molecular monolayers the configured water layer [11, 12]. This effect induces a drag force on the water passing through the membrane pores.

The induced drag force on water molecules increases its apparent viscosity, thereby decreasing permeate flux. And in our study, this effect tends to increase with decreasing ionic strength. And in our study, this effect tends to increase with decreasing ionic strength. Membrane charge can be modified by surface complexation of ionic species.
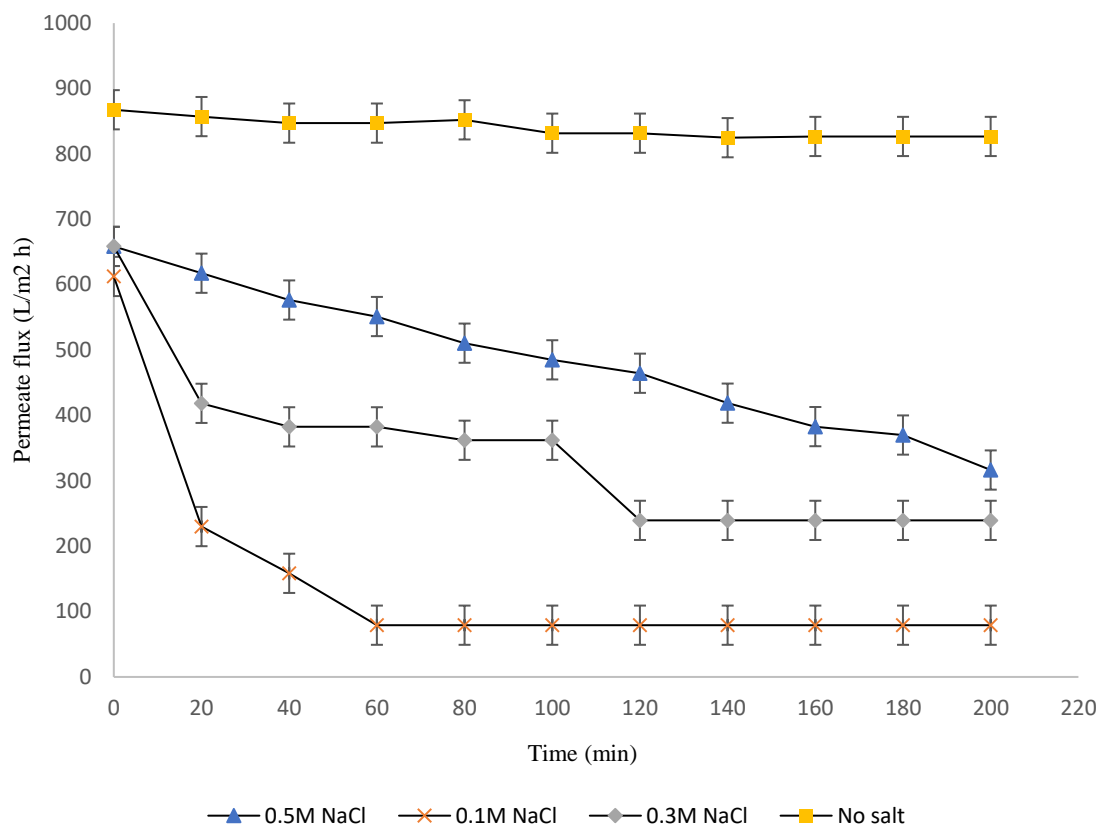
Figure 4. Permeate flux at various ionic strength

The distribution of ionic species together with their surface charges near the surface of the membrane pores may have observable effects with respect to performance on membrane permeability and fouling.

Figure 5 is the reason for the drastic decline in flux as observed during the experiment. The decline in flux drove our curiosity towards knowing what exactly forms on the surface of the ceramic membrane and how it affects the flux of the membranes. A small portion of the feed was agitated with a mixer for the time period of one run of experiment (200 minutes). During agitation, white droplets where observed to form in the mixture and this particles formation progressed with time.

Figure 5. Gel/cake formation

It was observed that the droplets began to floc together and getting bigger till the point where the droplets formed into a gel. The permeability of the gel/cake formed was observed to increase with increasing ionic strength.

4.   CONCLUSION

The difference in permeate fluxes observed between feed at zero ionic strength and feeds at various concentrations of ionic strength is evident that ionic solution environment affects the performance of ceramic membranes used in microfiltration. In the presence of NaCl solution, feed particle sizes become larger with increasing salt concentration and this in turn impacted on flux. The observation of higher fluxes at higher ionic concentrations indicate viscous, electroviscous, electrokinetic, and solvation effects may play a role in the interaction between the feed contents, membrane surface and the ionic solution environment and these effects can be used to describe the

interactions. Also, in order to have a full picture of the interactions, it is recommended that a molecular dynamic simulation study be performed in order to make an all-conclusive statement on which phenomena is most dominant in the interactions.

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SECTION

2.   CONCLUSION AND RECOMMENDATION

2.1   CONCLUSION

Ceramic membrane performance is impacted by various factors as evidenced in these studies. Membrane fouling is mitigated by coating the surface of the membrane with an organic compound (cysteic acid) and this led to increased steady flux rates for extended time periods. Other studies have shown that other materials can be used to coat membrane surfaces in order to improve their performance but comparing results obtained with cysteic acid coating to results of similar studies performed with other materials such as nano-TiO_2 and graphene oxide, the results showed that cysteic acid coating improved membrane performance better.

In the presence of ionic solutions, ceramic membrane performance greatly declined. It can be said that ionic solution environment enhances the formation of gel or cake layer on the surface of the membrane impacting on its performance regardless of the surface coating. At higher ionic strengths though, flux rate improved. Ionic solution environment also impacts on particle size as particles sizes increased with increasing ionic strength. The impact of ionic strength on membrane performance can be explained in terms of viscous, electroviscous and solvation effects.

2.2   RECOMMENDATION

The significance of the interaction of the different component factors affecting membrane performance can be better understood at the molecular level. Therefore, it is

recommended that a molecular dynamic simulation study be performed in order to make an all-conclusive statement on the specific phenomenon that contributes mainly to these interactions and also to understand the interaction process.

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