QATAR UNIVERSITY

COLLEGE OF ENGINEERING

A NOVEL HYBRID ELECTRO-COAGULATION/ FORWARD OSMOSIS MEMBRANE SYSTEM FOR TREATMENT OF PRODUCED WATER

BY

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ABSTRACT

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Title: A Novel Hybrid Electro-Coagulation/ Forward Osmosis Membrane System for Treatment of Produced Water

Supervisor of Thesis: Abdelbaki Benamor.

Large volumes of fresh water are consumed in the process of oil and gas exploration, producing even larger volumes of highly contaminated produced water (PW) which exhibits a major environmental problem.

This work investigates the application of a novel hybrid system by combining electro-coagulation and forward osmosis (FO) for the treatment and reclamation of PW. Electro-coagulation was applied at three different current densities 10, 30 & 60 mA/cm^2 for 10 and 30 minutes. Following that, the treated produced water was further treated by Forward Osmosis (FO) using polymeric membrane. Two orientations of the membranes (active layer facing draw solution and active layer facing feed solution) and three flow rates 0.8, 1.2 and 2 LPM were applied. By applying electro-coagulation, the optimum water quality was obtained after 10 minutes run time, at a current density of 10 mA/cm^2. Electro-coagulation achieved 91 and 97% removal of total organic carbon (TOC) and oil and grease (O&G), respectively. FO used in pressure retarded osmosis (PRO) mode achieved the highest flux at a flow rate of 1.2 LPM and reduced the PW conductivity to 16%. Overall, the hybrid system attained a total of 99% removal of total suspended solids (TSS). The obtained improved water quality suggests a high potential of practicability of the applied hybrid system in the treatment and reclamation of PW.

DEDICATION

I dedicate this thesis to

My parents

and

My partner in life Khalid Aboumaali

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LIST OF ABBREVIATIONS

EC	Electro-Coagulation
AL-DS	Active Layer Facing Draw Solution
AL-FS	Active Layer Facing Feed Solution
API	American Petroleum Institute
CECP	Concentrative External Concentration Polarization
CICP	Concentrative Internal Concentration Polarization
CP	Concentration Polarization
CTA	Cellulose Triacetate
DECP	Dilutive External Concentration Polarization
DI	Deionized
DICP	Dilutive Internal Concentration Polarization
DS	Draw Solution
EC-FO	Electro-Coagulation/Forward Osmosis
ECP	External Concentration Polarization

FO	Forward Osmosis
FO-MD	Forward Osmosis/Membrane Distillation
FS	Feed Solution
GTL	Gas to Liquid
IC	Inorganic Carbon
ICP	Internal Concentration Polarization
LNG	Liquefied Natural Gas
MTA	Million Metric Tons Per Annum
NDIR	Non-Dispersive Infrared
O&G	Oil and Grease
PPW	Process Produced Water
PRO	Pressure Retarded Osmosis
PVDF	Poly (Vinylidene Fluoride)
PW	Produced Water
RO	Reverse Osmosis
SAGD	Steam Assisted Gravity Drainage
SEM	Scanning Electron Microscopy

TC	Total Carbon
TDS	Total Dissolved Solids
TFC	Thin Film Composite
TOC	Total Organic Carbon
TS	Total Solids
TSE	Treated Sewage Effluent
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
UV	Ultra-Violate

CHAPTER 1: INTRODUCTION

1.1 Overview

Water scarcity has become one of the most important global challenges [1]. Currently around two-thirds of the world's population live in water stressed regions; it is expected that this number will continue to increase in the few coming years [2]. The need of fresh water will increase, as the population is increasing and living standards in developing countries are rising [3].

Qatar is a major oil and gas producing country at which oil and gas are the main contributors in the Qatari economy. Production of oil and gas generates an aqueous stream that is highly contaminated with dispersed oils, organics constituents, suspended solids and dissolved salts. This stream is referred to as "produced water". In oil and gas production, enormous produced water is generated where its ratio is estimated to be 4:1 produced water to oil and gas product [4]. The volume of oil and gas produced water is expected to rise further in the years to come [5]. When this oily wastewater is released to the environment, it forms films on water surfaces and deposits on shorelines, this consequently affects ecological resources and functions [6, 7]. It also affects human health and aquatic life [8, 9]. Moreover, oil takes a long time to biodegrade naturally in the ecosystem. In the long term produced water components affect environmental biological functions.

The methods currently available for the treatment of high oil content water are inefficient in the removal of fine emulsified oil droplets that need a relatively long time to separate by gravitational means [10]. Moreover, typical treatment methods only recover 50 to 60% of the contaminated produced water [11]. Once drilling is complete, the produced water is usually injected into deep wells (class II) removing it from the water cycle completely [12]. Hence, there is an urgent need globally to better manage the produced water, in terms of the recycle and reuse, as well as implementing new technologies for produced water treatment [13-15]. Due to the large volumes of water used in oil and gas production and the water stress that the world is going through generally, and lack of fresh water sources of Qatar specifically, new novel technologies must be investigated to find a cost effective, efficient and reliable produced water treatment technology.

In the recent years, electro-coagulation (EC) has gained interest for the treatment of produced water and oily wastewater. Due to several advantages to the process, such as; fewer amount of sludge production, use of simple equipment and short treatment time [16]. Also, forward osmosis (FO) has recently gained attention owing its low and reversible fouling property of the membrane [17]. As well as other advantages like high salt rejection and low energy needs [18-20].

The application of an integrated EC-FO water treatment system for the purpose of reuse of produced water is investigated in this work. The effect of current density and time will first be studied in EC process, followed by, water flux and fouling of membrane according to different flow rates and membrane orientation in FO.

1.2 Tangible Objectives

The purpose of this research is the treatment of produced water from oil and gas production, by using a novel hybrid electrocoagulation/ forward osmosis treatment system (EC-FO).

The impact of different parameters is studied in electrocoagulation (EC):

- Reaction time (10 and 30 minutes).
- The current density (10, 30 and 60 mA/cm^2).
- Consumption of anode.

While in forward osmosis (FO) system, the following parameters are taken into consideration:

- Impact of flow rate on flux.
- Impact of membrane orientation on flux.
- Fouling of the FO membrane.

1.3 Thesis Structure

The first part of this dissertation focuses on demonstrating the challenges of treating produced water from oil and gas production, and presents its characteristics. In the second chapter, a comprehensive review of existing produced water treatment systems is presented along with a summary of the researches conducted in EC and FO systems for the treatment of oily wastewater in recent years. The third chapter in this thesis sheds light on the methods and materials that were used to successfully assemble and test the EC-FO hybrid system. Testing procedures and employed characterization techniques of the raw produced water and the treated sample were also included in this chapter. In chapter 4, the results of each system; EC and FO are explained in depth and relationships are drawn to give a full picture of the water quality obtained. Moreover, the viability of the hybrid EC-FO system is discussed. Lastly, conclusions on the work are presented with recommendations for future work on such system.

CHAPTER 2: LITERATURE REVIEW

2.1 Origin of Produced Water

Qatar is an oil and gas producing country at which oil and gas are the main contributors to its economy. Qatar is a major gas producer producing around 100 Million metric ton per annum (MTA) of liquefied natural gas (LNG) in addition to gas to liquid (GTL) and other petrochemical products. In oil and gas production, enormous amount of produced water is generated where its ratio is estimated to be 4:1 produced water to oil and gas product [4].

Produced water quality differs due to the different origins; some produced water is originally existing in the well whereas some produced water is from the injected water that has been used to enhance the oil recovery from the well, which is very common in oil and gas production wells [21].

2.2 Produced Water Management

Produced water has several components which need to be treated or removed in order to meet the reuse or discharge regulatory standards, these components include; salinity, heavy metals and COD. Plants manage the produced water generated through several techniques, such as; injection of produced water, Discharge of produced water, usage of produced water in processes, usage of produced water in purposes other than the process and no produced water on the surface. Each of these managements methods are discussed below.

Reinjection of produced water: the produced water collected from the separation process on the ground is injected into the same reservoir or into another one and it aims to enhance the oil and gas recovery from the well. This produced water is not injected directly; it gets treated to remove the fouling components from it before the injection to prevent the fouling probabilities.

Discharge of Produced Water: simply, produced water is treated to ensure its quality and to fulfill the regulatory discharge quality demands and then discharged.

Usage of produced water in the process: produced water is treated and then used in the process when it meets the usage quality requirement.

Usage of produced water in purposes other than the process: produced water is treated to meet the local regulatory demands for the reuse of produced water in several purposes such as agriculture and cooling purposes [22].

No produced water on the surface: to prevent produced water from reaching the surface, polymeric gel is injected at which it stops the water from escaping to the surface. The separated produced water would be re-injected in the adequate formation.

2.3 Produced Water Characteristics

The produced water characteristics vary based on the geological location, below are the characteristics according to the National produced water database of U.S. geological survey.

Table 1

Organic and Inorganic Constituent in Conventional Produced Water [23]

Organic Constituents	**Concentration Range (ppm)**	**Inorganic Constituents**	**Concentration Range (ppm)**
TOC	BDL* - 1,700	TDS	100 – 400,000
COD	1,200	Sodium (Na)	150,000
TSS	1.2 – 1,000	Chloride (Cl)	250,000
Total Oil	2 – 565	Barium	850
Volatiles	0.39 – 35	Strontium	6,250
Total Polars	9.7 – 600	Sulfate	15,000
Phenols	0.009 – 23	Bicarbonate	15,000
Volatile Fatty Acids	2 – 4,900	Calcium	74,000

BDL* = Below Detection Limit

2.4 Produced Water Treatment

The demand on fresh water is increasing urging to find suitable effective technologies to treat wastewater (produced water). The different origins of produced water results in the variation of their quality, and the direct use of this water with its variant qualities is biologically hazardous and could damage the environment. Hence, the development of an effective treatment process in order to reuse and recycle the produced water is very important to remove the pollutants which have an adverse effect on the environment. Pollutants are numerous in the produced water whereas organic pollutants consume oxygen from water and the removal of these pollutants is carried out through different stages and processes [24]:

Physical process: uses the physical properties and physical principles without the addition of chemicals or bacteria to remove solid and biomass; filtration and sedimentation are examples of such physical treatment processes.

Chemical process: uses chemicals to separate dissolved particles from the suspended particles. The addition of chemicals adds extra expenses on the treatment process and this would be the chemical process disadvantage. Flocculation and coagulation are typical examples of such chemical treatment processes.

Biological process: uses bacteria to remove biodegradable material through the consumption of the organic content and nutrients within the water body that needs to be treated. The biological processes are either aerobic or anaerobic. The aerobic process is carried out at the presence of oxygen, whereas the anaerobic process is conducted at the absence of oxygen. Activated sludge process is an example of such biological treatment process.

Table 2

Treatment Processes and Treatment Unit Operation [5]

Process	Treatment Unit Operation
Physical	• Floatation • Sedimentation • Filtration • Membrane Separation
Chemical	• Adsorption • Chemical Oxidation • Coagulation / Electro-Coagulation
Biological	• Aerobic Digestion • Anaerobic Digestion

Several Components are meant to be removed from the produced water and among those are oil and grease and they need to be removed in all of their forms from the produced water. The removal of oil and grease should follow United States Environmental Protection Agency (USEPA) standards to verify the usage of the treated produced water in the services of the oil and gas industry. The USEPA standards limits the oil and grease to maximum of 42 mg/L per day and 29 mg/L per month on average. Various technologies used to remove oil and grease of different particle size shown below.

Table 3

Oil and Grease Removal Technologies and The Minimum Particle Size They Can Remove [22]

Technology	**Particle Minimum Size Can Be Removed (Microns)**
API Gravity Separator	150
Corrugated Plate Separator	40
Induced Gas Floatation (Without Flocculants)	25
Hydrocyclone	10 – 15
Mesh Coalescer	5
Media Filter	5
Induced Gas Floatation (With Flocculants)	3 – 5
Centrifuge	2
Membrane Filter	0.01

It is worth mentioning that among those technologies, American Petroleum Institute (API) separator and Hydrocyclone are the most commonly used technologies in oil and grease removal.

API gravity separator uses the gravitational force only to settle down the oil particles that tend to flocculate and coagulate at the suitable operating conditions. Oil particle are left to settle down, and accordingly this process is highly dependent on the retention time and the tank's design. Moreover, the efficiency of the separator varies with different size particles. The disadvantage of the API separator would be its high capital cost, maintenance duration and the dependence of the treated produced water quality on the tank's design [25].

Hydrocyclone technology uses the centrifugal force in a cone structure reactor to separate water from oil by keeping the light oil droplet in the middle and pushing the heavy water particles outwards. The separation process could be enhanced by the addition of gravitational force to the separation process. This technology has a very good removal performance at high organic loading rates, but the system needs to be operated at high pressure which limit the removal process. Moreover, the system experiences blockages at the bottom or on the surface due to the solids accumulation; moreover, the maintenance of hydrocyclone is a cost extensive process [26].

Soluble organics are one of the components that need to be removed from the produced water. Soluble organics are considered as oil and greases contaminants; however, they cannot be removed with the same technologies used for oil and grease removal and this is due to their solubility in water. Aromatic compounds and polar hydrocarbon are types of the soluble organics that can be found in produced water. Aromatic compounds such as benzene, toluene and xylene do not get affected by pH, nevertheless, polar hydrocarbons such as fatty acids are sensitive and they can get affected by pH; thus, resulting in the change of the organics solubility in water. Fatty acids become more soluble in water at high pH as they transfer to an ionic form and become insoluble in water at low pH as they form carboxylic acid.

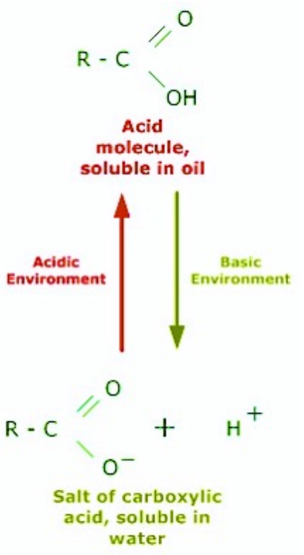

Figure 1: Solubility of Fatty Acids with Different pH [27].

Soluble organics can be treated via some approaches; such as adsorption process at which an adsorption column is used. The column would be filled with adsorbent solids or filtrate, these include among others, clay and activated carbon. The adsorbent of filtrate provides a contact surface area with the water that needs to be treated. The higher the surface area of the adsorption solids, the higher is the removal percentages of these organics from the produced water. The effectiveness of the process is limited by several factors; such as hydraulic retention time and the capacity of the reactor. Other approaches include the oxidation of soluble organics with strong oxidizers, O_3 and OH^-

, which turn organics into carbon dioxide that can be stripped via ultra-violate (UV) air stripper.

Total dissolved solids (TDS) are also components that need to be removed from the produced water and the technology selection to be used for that purpose is highly dependent on the quality of the produced water needs to be treated. The common methods to remove TDS are: electrocoagulation, membrane technology and evaporation and filtration technology.

Treatment of produced water requires the removal of algae and bacteria in order to inhibit the formation of any contaminant after the treatment process. The removal of theses contaminants is done using chemicals such as chlorine and O_3 as conventional methods and UV light as an alternative method [27].

The efficiency of these technologies and the feasibility of their application in the designated treatment purpose has been studied through several researches [28]. Among the technologies those were studied, electrocoagulation showed a great potential in term of operational cost, effectiveness and oil and grease removal efficiency.

2.5 Electrocoagulation

In the 19th century, Michael Faraday discovered the electrocoagulation process, at which the science of electrochemistry is used to flocculate, coagulate and oxidize the particle in wastewater [29]. A chemical reaction results, as electrocoagulation proceeds, from the passage of an electric current between 2 electrodes through an electrolytic solution [30]. The electrocoagulation process is composed of: electro flocculation, electro coagulation and electro oxidation, and it has the ability to remove pollutants and particles from wastewater by creating, disturbing, and neutralizing the repulsive forces between those particles causing them to from larger particles, and hence settle down. Accordingly, electrocoagulation has an advantage among other treatment processes for its ability to treat oily water as the tiny oil droplets would be electro coalesced and then removed [31]. This process, electrocoagulation, destabilizes the oil emulsion in water by turning the oil droplets surface to a negatively charged surface and accordingly a double electrical layer will be formed between these droplets and the positively charged water body. The potential of this double layer decreases when oil droplets moves away creating a repulsive force that pushes oil droplets away and prevents them from colliding resulting in inhibiting the coalescence of oil droplets [32]. The strength of this double layer is referred to as Zeta Potential, and it is the difference in potential between the negatively charged oil droplets and the surrounding water body [33]**.** The zeta potential is a measure for the tendency of the oil droplet emulsion to stabilize as the higher value of zeta potential expresses a higher tendency of this emulsion to stabilize during the process of electrocoagulation [32]. This double layer can be illustrated as Figure 2 is showing below:

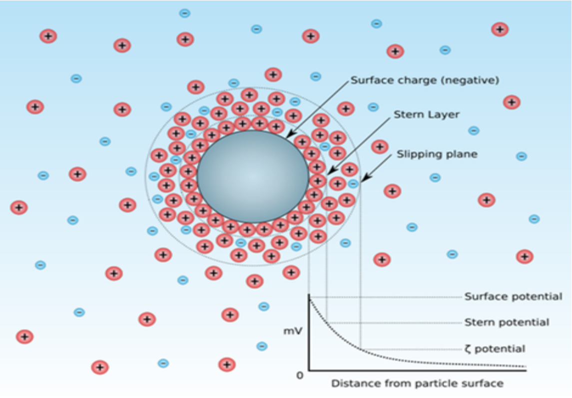

Figure 2: Electric Double Layer Around a Negatively Charged Particle [33].

Weakening this potential is required to allow the emulsion to flocculate or coagulate so that is can be removed from the water body. The potential can be reduced by generating ions at the anode, those would neutralize the charged ions present in water causing the electrostatic repulsion between the oil droplets and water body to reduce, so that oil forms flocs and settle down as a sludge [34]. Another method to reduce the potential could occur at the cathode side at which hydrogen is generated. The formed Hydrogen bubbles are move upwards carrying with them oil droplets, as a result of the adhesion between the bubble and the oil droplets, those would flocculate on the surface [35].

2.6 Membrane Treatment

2.6.1 Reverse Osmosis

Reverse osmosis (RO) is a membrane based separation technology that has been commercialized since the 1970's for saline water desalination. RO produces fresh water and concentrated brine by applying a pressure to saline feedwater through a semipermeable membrane. The pressure is supplied by a high pressure pump; pressure needs to exceed osmotic pressure to allow water passage through the membrane [42]. The RO membranes are selective, where they restrict the passage of anything other than fresh water. The first RO membrane synthesized in the laboratory, using phase inversion technique, was by Sidney Loeb and was made of cellulose acetate [43, 44]. Other polymeric membranes are used in RO, such as polyamides and polyimides; these are currently employed as they possess better salt rejection properties, more durability and require less energy [45]. There are several membrane configurations, two of them are spiral wound and hollow fine fiber [46, 47]. Figure 3 shows a representation of RO process.

The RO process operates at ambient temperature; however, fluctuations of feedwater may occur; RO membranes are able to withstand temperatures up to 35-40 ^{o}C. Fluctuations in the feedwater temperatures affect the membrane performance, due to the difference in water viscosity. At higher temperatures, higher flux is obtained. The operating pressure for seawater desalination ranges between 55 and 68 bar; it is highly dependent on the salinity of feedwater [48].

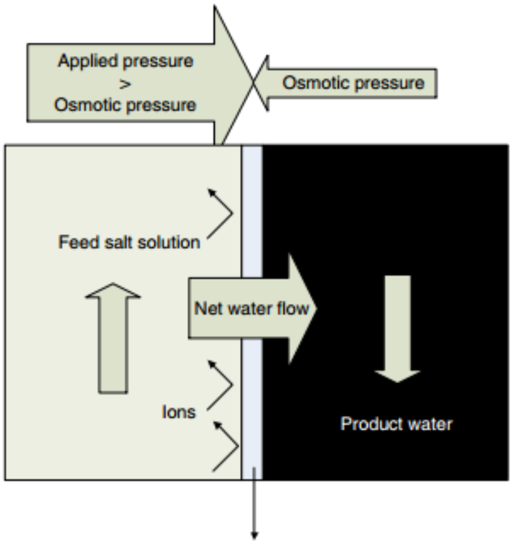

Figure 3: Reverse Osmosis [49].

The energy requirement for RO desalination is a factor of recovery ratio, flux, membrane, temperature, feed water salinity and system orientation [50]. The total energy requirement for RO unit including pre- and post- treatment with no energy recovery is estimated to be around 12 kWh/m^3 [51]. Two methods have been found to reduce the energy requirement of RO, which are synthesizing new membranes and using energy recovery devices [52]. Implementing energy recovery, the total RO energy requirement is reduced to the order of 3-6 kWh/m^3 [53, 54].

2.6.2 Forward Osmosis

Forward osmosis (FO) is one of the promising water treatment technologies; it is driven by osmotic pressure difference across a semi-permeable membrane to produce water and is considered as a clean energy process [18, 55]. The semi-permeable membrane allows only water to pass while ions are withheld. The draw solution (DS) is a highly concentrated salt solution, which has low water chemical potential. The DS is used to draw feed solution (FS) through the semi-permeable membrane, due to its higher osmotic pressure. The diluted DS is then separated by utilizing an energy efficient technique to recover fresh water. FO process, unlike reverse osmosis, does not require the application of hydraulic pressure to recover fresh water from the FS; FO takes advantage of the natural occurring osmotic pressure difference, as shown in Figure 4.

FO separation process includes two steps: firstly, the semi-permeable membrane allows the passage of FS to the DS. Secondly, the DS is recovered to produce fresh water.

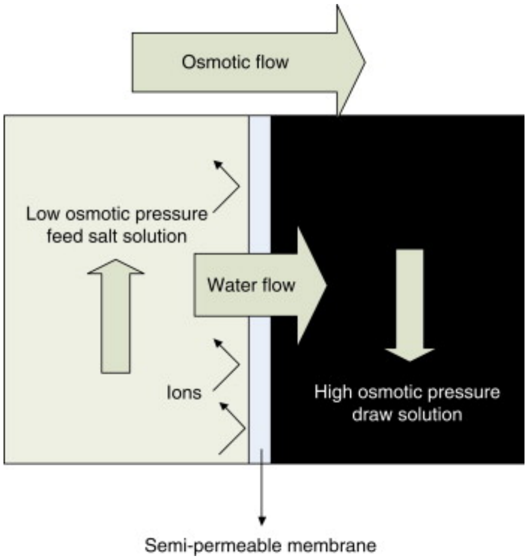

Figure 4: Forward Osmosis [49].

There are several advantages of the FO process, some of these advantages include: relatively low energy consumption when compared to RO, as mentioned previously; this is due to the utilization of the natural occurring osmotic pressure rather than applying hydraulic pressure [56]. Fouling in the membrane of the FO process is very low, and if fouling occurs, it can be easily reversible by backwashing [18, 56, 57]. FS quality rarely affects the FO process as it can withstand highly contaminated feeds [18, 58-61]. FO considerably has high water recoveries in comparison to other desalination methods [55].

2.6.2.1 Concentration Polarization (CP)

FO membranes are asymmetric and have a dense active layer (for salt rejection) on one side and a support porous layer on the other side [18]. There are two possible orientations for FO membranes; Active layer facing draw solution (AL-DS), and active layer facing feed solution (AL-FS) referred to as forward osmosis (FO) and pressure retarded osmosis (PRO) respectively [62].

Concentration polarization (CP) is a phenomenon occurring in the FO membrane, it is associated to the transport across the membrane [18, 63, 64]. The CP phenomena cause lower actual flux than theoretically possible, and this is because of lower osmotic pressure difference occurring across the AL of the membrane when compared to the bulk pressure difference [65-67]. There are two forms of CP; the external concentration polarization (ECP) and the internal concentration polarization, these two phenomena affect and lower the effective osmotic pressure difference in the FO treatment process [68].

2.6.2.2 External Concentration Polarization (ECP)

ECP is the phenomena that take place at the dense active layer of the membrane, and it can be either concentrative external concentration polarization (CECP) or dilutive external concentration polarization (DECP) according to the orientation of the membrane. When the orientation of the membrane is in FO mode (active layer is facing the feed solution) CECP occurs as shown in Figure 5.

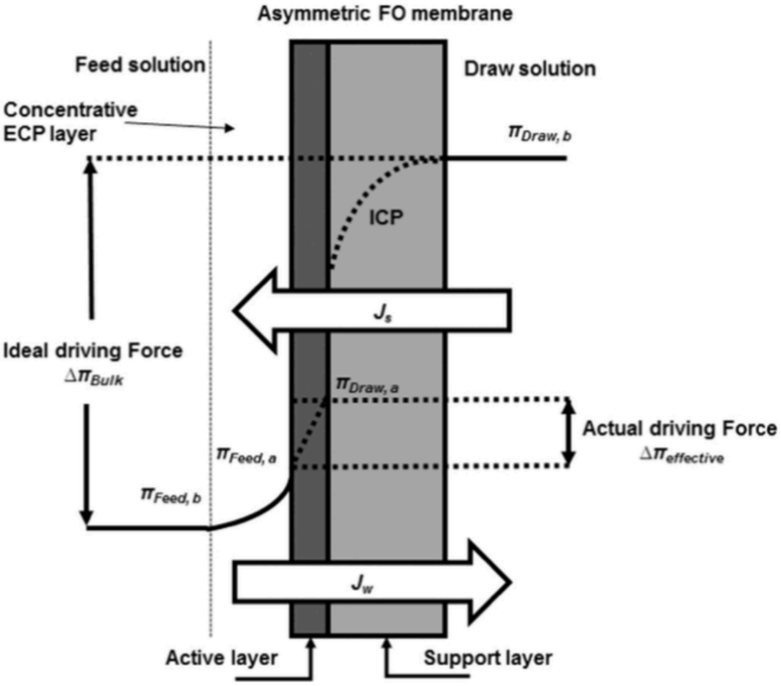

Figure 5: Effective Driving Force for Water Transport in The Presence of Concentration Polarization When Active Layer is Facing Feed Solution (FO) [68].

Alternatively, when on PRO mode (active layer is facing the draw solution) DECP is the dominant phenomena, as shown in Figure 6. In FO mode, CECP build up solutes on the dense active layer of the membrane and hence increases the concentration of the feed solution at the active, as a result of feed solution flow. Consequently, the net deriving force decreases and hence the water flux also decreases. On the other hand, ECP effect can be mitigated by optimizing the flow rate to increase turbulence [18, 63, 65]. Generally, due to the lack of high pressure in the system, solute buildup is not major on the membrane. Hence, ECP effect is minimal on reducing the water flux.

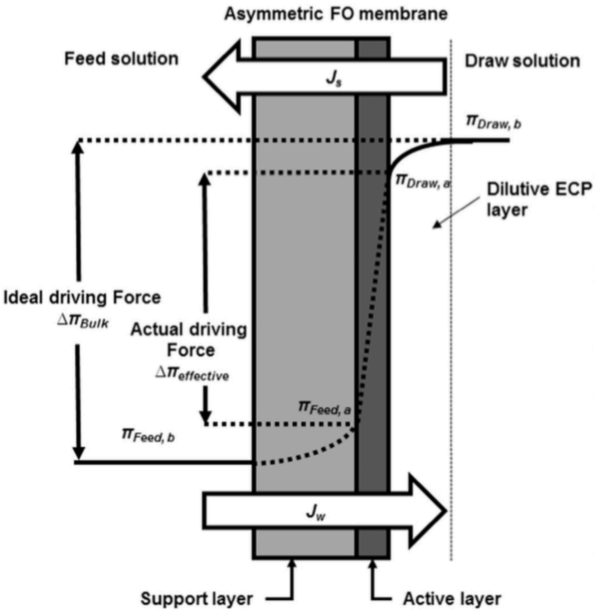

Figure 6: Effective Driving Force for Water Transport in The Presence of Concentration Polarization When Active Layer is Facing Draw Solution (PRO) [68].

2.6.2.3 Internal Concentration Polarization (ICP)

ICP occurs within the asymmetric FO membrane and is the main contributor to the decrease in FO water permeation as it was shown by various researches [66, 67, 69-72]. There are two types of ICP, concentrative internal concentration polarization (CICP) and dilutive internal concentration polarization (DICP). CICP occurs in PRO mode when the active layer is facing the draw solution. It is a result of accumulation of solute inside the porous support layer of the asymmetric FO membrane, the accumulation polarizes the active layer of the membrane. The difference between CICP and CECP is that the former occurs within the pores of the support layer, thus increasing the flow rate cannot mitigate CICP effect [68]. On the other hand, DICP takes place in FO mode when the active layer is facing the feed solution. The transport of water from the feed side to the draw side, reduces the concentration of the solute within the pores of the support layer. This phenomenon, DICP is a major drawback in FO desalination because it can reduce the water permeation rate up to 80% than the theoretical value. Just like CICP, CICP cannot be mitigated by increasing flux and turbulence [65].

2.7 Previous Work Using Electrocoagulation and Forward Osmosis for Oily Water Separation

2.7.1 Previous Electrocoagulation Studies on Oily Wastewater

Electrocoagulation treatment is a process that has been implemented for a long period of time, Table 4 summarizes some of the studies of electrocoagulation used for the purpose of treating oily wastewater.

Xu and Zhu [36], investigated the removal of oil from restaurant wastewater by electrocoagulation. The water generated from restaurants contains a considerate amount of oil and grease which get disposed in the drainage. The presence of oil and grease causes fouling and a foul smell in the sewer system. Xu and Zhu, studied the different operational conditions to get optimal removal of oil. They have found that applying a current density between 10 and 14 A/m^2 for 30 minutes, using iron electrodes with a distance of 10 mm between them, achieves a removal efficiency of oil exceeding 95%.

Table 4

Summary of EC Studies for Oily Wastewater Treatment

Year	Oily Wastewater Source	Electrode	Current Density (A/m^2)	Run Time (Min)	Ref.
2004	Restaurant wastewater	Iron	10 - 14	30	[36]
2006	Slaughterhouse wastewater	iron	150	25	[37]
2008	Oilfield wastewater	Aluminum	18.5	40	[23]
2010	Bilge water	Platinum/Iridium	128	240	[38]
2014	Bilge water	Iron and aluminum	6	75	[39]
2015	Produced water	Aluminum and iron	1343	6.8 L/min	[40]
2017	Automobile garage wastewater	Viz. mild steel and aluminum	60	15	[41]

Kobya et al. [37] examined the treatment of slaughterhouse wastewater. Slaughterhouse wastewater typically contains fat, oil and organic constituents. Kobya et al. achieved high COD removal efficiency by applying a current of 150 A/m^2 for 25 minutes, using iron electrodes. A removal efficiency of oil and grease reached a maximum of 98%.

Bande et al. [23] investigated the removal of oil from oilfield wastewater. The tested samples contained dispersed fine oil emulsified with water. He used perforated aluminum electrodes. He found that oil removal efficiency can be improved by decreasing the salinity of the effluent.

The treatment of bilge water was studied by Körbahti & Artut [38]. The oily water was treated by a batch electrocoagulation process, using platinum/iridium (Pl/Ir) electrodes. The applied current density was 128 A/m^2 for 240 minutes. Which, achieved oil removal efficiency of 93.2%. Körbahti & Artut reported that the reaction temperature plays a role in the removal efficiency of COD. As the temperature increase, mass transport increase and hence COD removal also increase.

Rincón and La Motta [39], also investigated the treatment of oily bilge water, however, their study focused on the removal of oily emulsions and heavy metals like, zinc, copper and nickel. They achieved an oil removal efficiency of more than 99%. Yet still, the removal rate of copper and nickel didn’t exceed 70%.

Esmaeilirad et al. [40] used electrocoagulation to treat oilfield wastewater. The ability to treat oilfield wastewater on site, reduces the added cost of transportation and of providing fresh water for drilling. Esmaeilirad et al. achieved oil removal of 60% by using aluminum and iron electrodes, applying a current density of 1343 A/m^2.

Oil removal from wastewater generated by automobile garages by electro-coagulation was investigated by Manilal et al. [41]. In the study two electrodes were uses; aluminum and iron. Several parameters were examined; salt concentration, current density, pH and time effects of the removal of oil and grease. The results showed that aluminum anode performed better than iron electrode. The aluminum electrode removed 90.8% of oil at a current density of 60 A/m^2 running for 15 minutes.

2.7.2 Previous Work Using Forward Osmosis for Oily Water Separation

Recently, forward osmosis has been deemed as a promising treatment technology for the more complicated and challenging liquid streams. Forward osmosis has been implemented successfully in various treatment processes, such as; seawater desalination, landfill leachate concentration, wastewater treatment and desalination of brackish water [18, 63, 73]. In Table 5 a summary of the available publications on the applications of forward osmosis tested specifically in the treatment of oily water streams is presented.

Table 5

Overview of FO Treatment for Oily Wastewater

Year	Feed Solution	Draw Solution	Membrane	Ref.
2010	Frac water	26% NaCl saltwater	spiral-wound FO membrane	[74]
2013	representative drilling wastewater	26% NaCl	cellulose triacetate (CTA) polymer cast over a fine polyester support mesh	[75]
2013	Frac flowback from the Marcellus shale	NH_3/CO_2 6.0 M (carbon) 12.0 M (nitrogen)	spiral wound FO membrane array	[76]
2014	synthesized oily wastewater	0.58 M, 2M NaCl	Lab-fabricated thin film composite (TFC) membranes based on cellulose triacetate (CTA) hollow fiber supports and poly (vinylidene fluoride) (PVDF) hollow fiber membranes	[77]
2015	Process Produced Water (PPW)	70 g/L NaCl	flat sheet thin film composite membranes	[5]
2016	Produced water	salt solution	semipermeable polyamide thin-film composite (TFC) membrane with embedded polyester screen support	[78]

The treatment of oily waste water using FO process was first investigated by Hutchings et al. [74]. The process success was evaluated by the ability of the system to reduce the demand of freshwater. The membrane used for the process was 8-in. diameter x 40-in.-long spiral wound FO membrane. While, the draw solution to the process was 26% sodium chloride (NaCl).

In the year 2013, Hickenbottom et al. [75] optimized the previous work of Hutchings et al. [4]. The study used CTA membrane that was custom made for the purpose of the study. The draw solution used was also 26% NaCl. The findings of this study confirmed Hutchings results, that forward osmosis process proved to be a valid method for the concentration of oil and grease wastewater that was generated from drilling.

Hancock et al. [76], treated oil and gas wastewater in three steps; pretreatment, FO treatment and polishing of product brine. In the pretreatment step, he used soda ash to generate flocs that have low solubility and precipitate, while in the FO process, he used a new patented draw solution composed of ammonia and carbon dioxide. The feed to the FO system is the pretreated oily water. Then in the final stage, the draw solution was regenerated by heating then condensing the diluted draw solution.

Zhang et al. [77], investigated the use of a hybrid forward osmosis/membrane distillation (FO-MD) system. The oily wastewater which was the draw solution to the FO, was synthesized at the lab by oil in water emulsion, and also, they used fabricated cellulose triacetate (CTA) – based thin film composite (TFC) and polyvinylidene difluoride (PVDF) hollow fiber membranes. He concluded that membrane fouling increased marginally as the concentration of oil increased, water flux affected the extent of fouling due to the presence of oil. Lastly it was noted that when using the membrane in PRO mode, fouling would increase

The reduction of produced/process water (PPW) volume was studied by Minier-Matar et al. [5], in 2015. In the study, he used 70 g/L sodium chloride as a draw solution to simulate brine from thermal desalination or sea water. The forward osmosis process feed solution was varied between treated PPW and untreated PPW, to investigate the effect of pretreatment on the FO performance. The results proved that pretreated feed was superior to the untreated PPW, because it reduced fouling on the FO membrane.

Most recent study was done by Bhinder et al. [78]. He aimed to treat water from bitumen extraction from oil sands. The process used for this extraction is called steam assisted gravity drainage (SAGD). SAGD produced water was used as the feed to the FO treatment system. The draw solution consisted of salt solution. The study found that increasing the temperature of feed water would increase the flux. He also noticed that CP was minimized by increasing the flow rate. TOC rejection of the process was between 85-96%, a water flux as high as 25 LMH was achieved.

CHAPTER 3: EXPERIMENTAL MATERIALS AND METHODS

3.1 Synthesis of Produced Water

Produced water (PW) was prepared by mixing salts, solids and oil content in deionized (DI) water. Selected salts included, Iron(II) sulfate (FeSO4), Calcium chloride ($CaCl_2$), Potassium Chloride (KCl), Magnesium chloride ($MgCl_2$), Sodium chloride (NaCl), Calcium sulfate (Ca_2SO_4), Monosodium Phosphate (NaH_2PO_4), Sodium bicarbonate ($NaHCO_3$) and Boric Acid (H_3BO_3). These salts were all purchased from Sigma-Aldrich. The chemicals were of analytical grade and were used as received without any further treatment. Oil & Grease spiked by commercial oil for engine and gear box and solids contained cellulose material and as stated by the standard method (ASTM D5907).

Salts were first dissolved completely in DI water according to the amounts shown in Table 6 below. Solids were then added to act as suspended solids. Eventually oil and grease content was characterized by their addition in high shear rates mixer for four (4) hours to ensure complete emulsion of oil in water. The synthesized samples were then immediately used in electrocoagulation tests.

Table 6

Charachteristics of Produced Water

Characteristics	
Turbidity (NTU)	915
TSS (ppm)	3116
TOC (mg/L)	1260
Oil and Grease (mg/L)	950
pH-Value	6.3
Conductivity (mS/cm)	96.4
Color	Black
$FeSO_4$ (mg/L)	100
$CaCl_2$ (mg/L)	7000
KCl (mg/L)	2000
$MgCl_2$ (mg/L)	7500
NaCl (mg/L)	55000
Ca_2SO_4 (mg/L)	2000
NaH_2PO_4 (mg/L)	40
$NaHCO_3$ (mg/L)	1000
H_3BO_3 (mg/L)	200

3.2 Electrocoagulation

Electrocoagulation tests were carried out in 1 L volume beaker equipped with a magnetic stirrer to provide uniform mixing throughout the experiment time, the speed of stirring was maintained at 250 rpm throughout the whole experiment time. Two rods of aluminum with surface area of 53.9 cm^2 (9.8 cm x 5.5 cm, 1mm) each and thickness of 1 mm, were used as anode and cathode, show in Figure 7. Three different current intensities were applied by DC amplifier, for 10 and 30 minutes. The electro-coagulation tests took place at room temperature (25.0 ±2 ^{o}C).

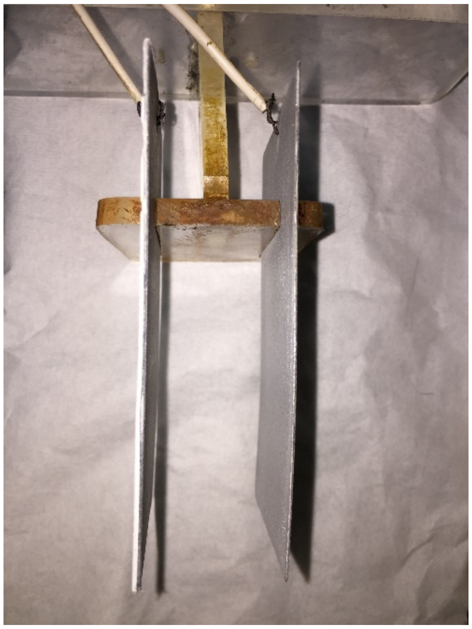

Figure 7: The Aluminum Plates Used as Anode and Cathode on PVC Mount.

A picture of the laboratory setup of the electro-coagulation test is shown in Figure 8, a schematic diagram of the system is illustrated in Figure 9.

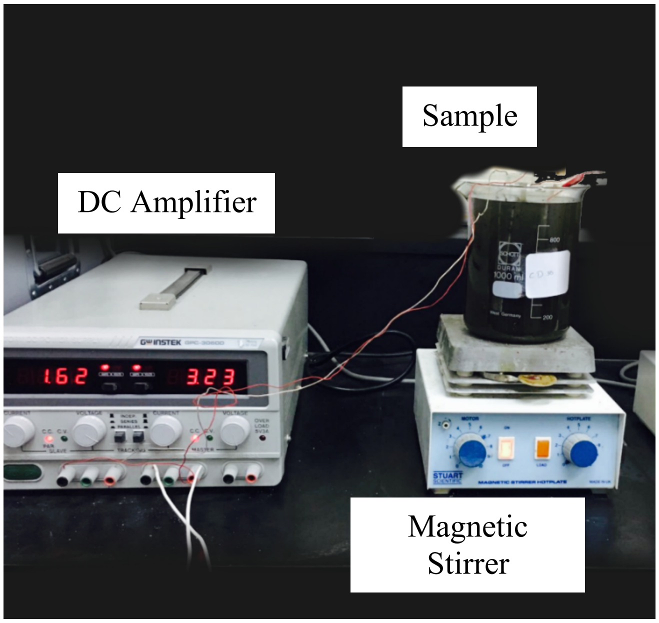

Figure 8: Electro-Coagulation System Laboratory Setup.

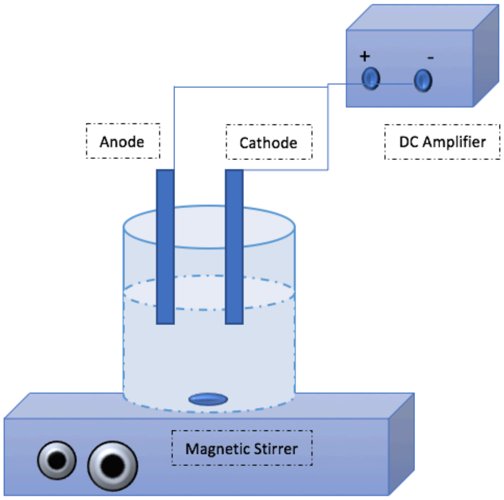

Figure 9: Schematic Diagram of The Electro-Coagulation System.

All the electrocoagulation tests were carried out following the same procedure. The produced water synthesized was used immediately after oil emulsification to prevent the oil separation with time. After each experiment, the treated samples were left for 24 hours to settle the precipitates generated from the electrocoagulation process and then the pure sample was pumped out in to a clean beaker. The conductivity, TSS, pH, turbidity and TOC of produced water were measured prior to the starting of each set of experiments and after collection of pure sample.

The analyzed parameters removal efficiency was calculated by Equation 1:

$$\% \, Removal \; efficiency = \frac{C_i - C_f}{C_i} \times 100, \qquad (1)$$

Where;

C_i: initial concentration

C_f: final concentration

3.3 Forward Osmosis Unit

After the Electro-coagulation tests, the electro-coagulated water (EC), after sedimentation for 24 hours, was transferred to the draw solution (DS) tank of the FO module using treated sewage effluent (TSE) as feed.

- Feed solution used for the FO was secondary treated sewage effluent (TSE) after passing through the clarifier, the TSE was acquired from Doha West Waste Water Treatment Plant.
- Draw solution used for the FO was produced water after the electrocoagulation treatment tests.

FO tests were carried out in Sepa CF042D forward osmosis unit supplied by Sterlitech™ Corporation, presented in Figure 10, using the principle of crossflow between feed and draw solutions. The FO module was made of stainless steel, which gives it the advantage of resisting corrosion and working safely at high flow rates.

Figure 10: Sterlitech™ Forward Osmosis Unit [79].

CTA membrane shown in Figure 11, was used for the separation process. The CTA membrane (11.5x5.57 cm, 0.5 mm) was acquired from Hydration Technology Innovations (Albany, OR), it composed of a cellulose triacetate (CTA) active layer with an embedded woven support mesh and an active area of 0.0042 m^2. Cellulose acetate membrane possesses various positive properties, such as; robustness, affordability, resistance and delivery of acceptable water flux [80]. Various other studies have used this FO membrane, due to its ability to withstanding harsh conditions, like high TSS and TOC and thus they were used in this study [57, 63, 81, 82]. However, these membranes are prone to biological attack, and may undergo hydrolysis. Accordingly, pH of feed and draw solution must be maintained between 4-6, and operation temperate should not exceed 35°C [18].

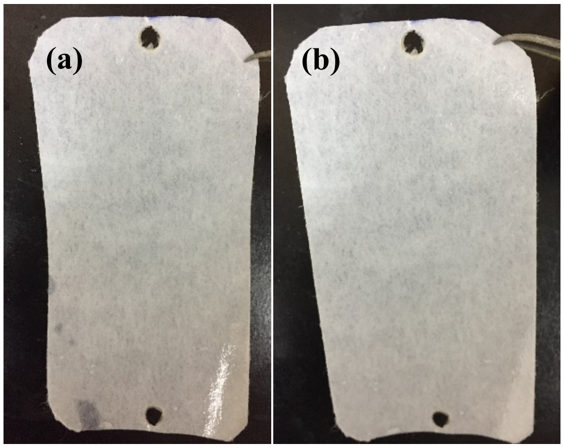

Figure 11: Forward Osmosis Membrane (a) Active Layer, (b) Support Layer.

A polymeric mesh spacer (Sepa CF high fouling spacer, 8x3.5 cm) shown in Figure 12, was used on the support layer side of the membrane. Mesh spacers are known to enhance the flow turbulence and provide membrane support. In this set up, the mesh spacer was used in order to prevent the membrane from breakage.

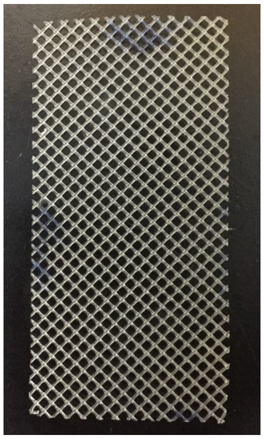

Figure 12: Polymeric Mesh Forward Osmosis Spacer.

A gear pump (75211-15, Cole-Parmer®) was placed on both the feed and draw solution side to circulate and maintain their flow rates. The system used two pressure gauges and two site read panel mount flow meters (Blue-White) at the inlet and outlet of the cell to observe the transmembrane pressure and flow rate of both feed and draw solutions.

A mechanical stirrer was used at the feed tank at constant speed throughout the experiment, and a magnetic stirrer was used at the draw tank to avoid settling of suspended solids.

The feed solution tank was placed on a digital balance (EW-11017-04, Ohaus Ranger™) which has a capacity of 12 kg, to measure the feed solution weight change. The weight difference was recorded on to the PC in 10 minute intervals throughout the total run time of the experiment, to calculate the water flux. Both feed and draw solution tanks initial volume was 4.0 L each. Temperature and pressure were constant throughout the whole experiment time. Figure 13 shows a schematic diagram of the experimental set-up including the FO unit and all the other units and equipment used to monitor and control the system.

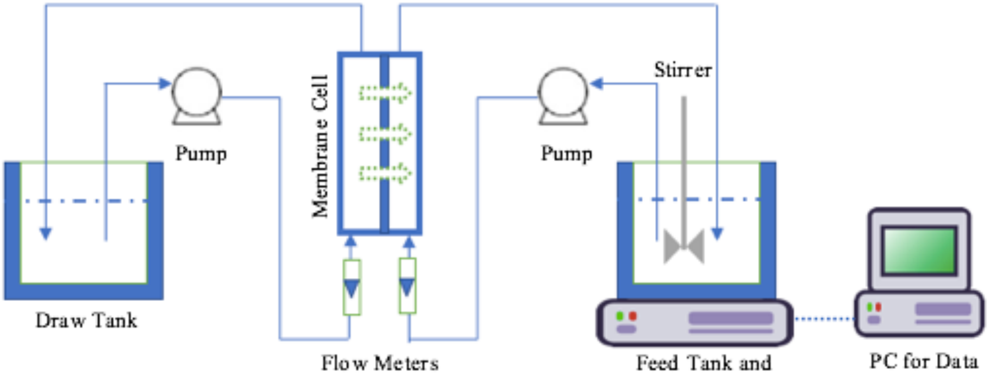

Figure 13: Schematic Diagram of Forward Osmosis Unit.

All the FO experiments were carried out following the below protocol:

The membrane was first soaked in deionized (DI) water for 24 hours prior to its first use, this was done to release any preservatives present on the new membranes. The FO system was then operated for 1 hour with DI water in both feed and draw tanks. After operating the system with DI water, the feed and draw tanks were drained and filled with actual feed and draw solutions. The conductivity, TSS, pH and turbidity of both feed and draw solutions were measured prior to starting each test at a specific flow rate. Once the experiment was completed after 1000 minutes run time, the conductivity, TSS, pH and turbidity were measured for both feed and draw solutions then the system was flushed with DI water.

3.4 Hybrid system

The whole process including Electro-coagulation and FO was named as EC-FO. The produced water first enters the EC system to remove and reduce TSS, TOC, oil & grease and conductivity. Then the effluent of the EC system inters FO membrane system for further treatment and dilution, where the conductivity of water is significantly reduced. The feed to the FO system is treated sewage effluent (TSE). A schematic diagram of the full setup is shown in Figure 14 below.

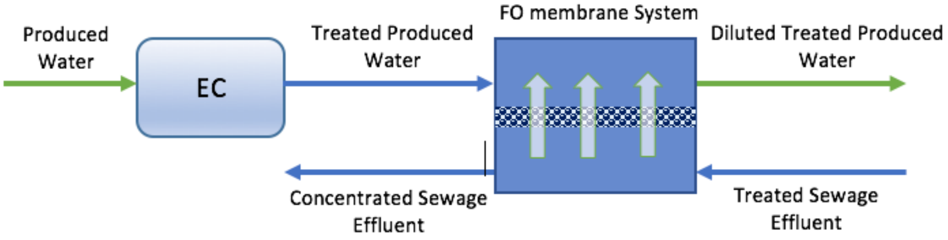

Figure 14: Schematic Diagram for Hybrid EC-FO System.

3.5 Measured parameters

3.5.1 Dissolved, Suspended and Total Solids

Total solids (TS), total dissolved (TDS) and total suspended solids (TSS) measurements were determined according to standard method (ASTM D5907), the measurements were taken for produced water prior and after electro-coagulation and for produced water and treated sewage effluent before and after forward osmosis treatment.

Total suspended solids measurements were done by taking a volume of 50 mL of a well-mixed sample and filtering it through glass fiber filter with pore size of 1.5 μm. The filter paper was then placed in drying oven at a temperature of 105^{o}C until it was completely dry, then the filter paper was weighed using a precision balance (PGW 6002e, aeAdam Company).

The total suspended solids in ppm were calculated using the following equation:

$$Suspended\ Solids\ (ppm) = \frac{(A-B)\times 1000\frac{mg}{g}\times 1000\frac{mL}{L}}{V_s}, \qquad (2)$$

Where;

A: weight of filter paper with the dried residue (g)

B: standard weight of filter paper (g)

V_s: volume of the sample (mL)

Figure 15: Drying Filter Paper Used for Calculating Total Suspended Solids.

The total solids were measured by the following procedure; first the weight of an empty clean evaporation dish was taken on balance (PGW 6002e, aeAdam Company), then it was filled with 50 ml of the well mixed sample. The filled evaporation dish was placed inside the drying oven at a temperature of 105 °C until the sample was completely dry. The evaporation dish was then taken out of the oven and placed in a desiccator to remove the humidity from the sample, then it was measured by the balance and the weight was noted. The total solids (ppm) were measured by the following equation:

$$Total\ solids\ (ppm) = \frac{(A-B)\times 1000\frac{mg}{g}\times 1000\frac{mL}{L}}{V_s}, \qquad (3)$$

Where;

A: weight of dish containing residue (g)

B: weight of dish (g)

V_s: Volume of the sample (mL)

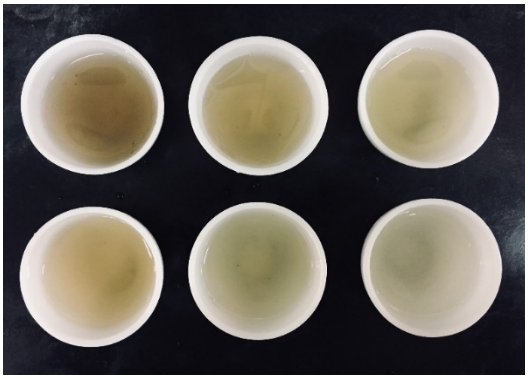

Figure 16: Samples Placed in Evaporation Dishes Before Drying in The Oven for TS measurements.

The total dissolved solids value is the difference between suspended and total solids and it was determined by the subtraction of the total suspended solids from total solids present in the sample.

$$TDS = TS - TSS, \tag{4}$$

3.5.2 Determination of Oil Concentration

Infrared reference method was used for determination of oil concentration following (ASTM D7066-04) standards. The measurement was carried out with S-316 polymeric solvent. The samples pH was adjusted to 2 using hydrochloric acid (HCl). The solvent and prepared sample were then poured into the separating funnel and shook vigorously for 10 minutes. Once the separation of the two layers was observed, the solvent phase (at the bottom) was filtered through filter paper which contained anhydrate sodium sulfate ($NaSO_4$, sigma-aldrich,99%) to remove any moisture present in the extract. The extracted sample was then measured using Horiba oil content analyzer OCMA 350 device. The oil concentration in samples (C_{oil}, ppm) was determined as follows:

$$C_{oil} = \frac{CV_{sol}}{V_{sample}} , \tag{5}$$

Where;

C: concentration of oil read on calibration curve (ppm)

V_{sol}: volume of solvent used for extraction (mL)

V_{sample}: volume of sample (mL)

3.5.3 Total Organic Carbon (TOC) Measurement

Total organic carbon (TOC) of each sample was measured after the electro-coagulation test. The method used for determining TOC was oxidative combustion-infrared analysis using a Shimadzu TOC 680 °C analyzer which adopts the 680 °C combustion catalytic oxidation method, with ASI-L Autosampler. Where; the total carbon (TC) is measured by injecting the sample into a heated combustion tube packed with an oxidation catalyst. The heat vaporizes the water and carbon converts to carbon dioxide (CO_2). A carrier gas carries the CO_2 from the combustion tube into a non-dispersive infrared gas analyzer (NDIR). The NDIR measures the concentration of CO_2. Then, using a calibration curve that was previously prepared using standard solutions, the TC concentration of the samples was obtained. Inorganic carbon (IC) is determined by the injection of sample in phosphoric acid solution chamber. TOC is obtained by the difference between TC and IC as shown in the equation below.

$$TOC = TC - IC, \tag{6}$$

TOC provides an indication of the total organic matter concentration in water.

3.5.4 Anode Consumption

The anode consumption was determined by taking the weight difference of anode before and after electro-coagulation. The anode, composed of aluminum plate was cleaned thoroughly, the cleaning method included submerging the plate in hydrochloric acid (HCL) then sanding the plate with sand paper, this mechanism of cleaning was done to insure the removal of any metal oxide present on the surface of the plate as the its presence may affect the elector-coagulation process. After cleaning, the weight of the plate was noted and then used for electro-coagulation test. Once the test was finished, the plate was removed and washed wish deionized (DI) water and dried for weight measurement on precision balance (PGW 6002e, aeAdam Company).

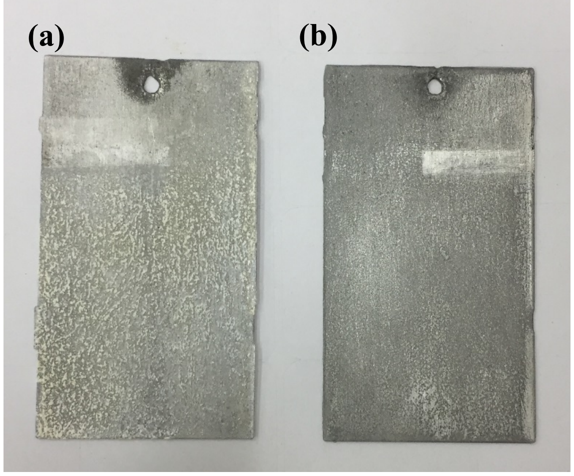

Figure 17: Aluminum Plates After EC Treatment, (a) Cathode, (b) Anode.

The percentage reduction of anode weight was calculated by the following equation:

$$Anod\ reduction\ (\%) = \frac{m_{Ai} - m_{Af}}{m_{Ai}} \times 100, \qquad (7)$$

Where;

m_{Ai}: initial anode weight (g)

m_{Af}: final anode weight (g)

3.5.5 Scanning Electron Microscopy

Microstructure and macrostructure imaging of sample with transmission or reflection modes offer valuable information on metallurgical, biological and geological samples. Scanning electron microscopy (SEM-bench top Jeol) is capable to magnify sample up to 60,000 x. SEM images were taken for the FO CTA membrane before and after the treatment of water. The equipment used to take the SEM images was (Benchtop SEM- JCM 6000).

3.5.6 Water Characterization

Characterization of water samples was done prior and after both electrocoagulation and forward osmosis tests. This characterization included pH, conductivity and turbidity of measurements. A digital pH meter (Digimed DM-2) was used for pH measurements, the conductivity was measured using a conductivity probe (Hach 51800-10, sensION) and turbidity measurements were conducted using a turbidimeter (HACH, 2100P). All samples were measured by taking an adequate well mixed representative sample after each test. Prior to each measurement each respective device was thoroughly cleaned with DI water.

CHAPTER 4: RESULTS & DISCUSSION

This chapter mainly discusses the results obtained in this work. The chapter starts with the electro-coagulation (EC) tests results. Then, discusses the results obtained from forward osmosis tests (FO), and finally discusses the outcome of a hybrid combined water treatment system of electro-coagulation and forward osmosis (EC-OF).

4.1 Electrocoagulation

Three main processes occur during electrocoagulation, they are: electrolytic reactions, formation of coagulants and adsorption and removal of soluble and colloidal pollutants [83]. The electrolytic reactions occur on the surface of the electrode, while the coagulants formation occurs in the aqueous phase. The adsorption and removal of pollutants take place via either sedimentation or floatation [84]. In this work, Aluminum electrodes were used because they have shown an enhanced removal efficiencies of total suspended solids, turbidity and color compared to other steel electrodes [85]. When using Aluminum electrodes, a series of reactions occur in the electrocoagulation process, these reactions take place at the anode and cathode surface, and are as follows [84, 86-88]:

Anode Reactions: $$Al_{(s)} \rightarrow Al^{3+}{}_{(aq.)} + 3e^-, \quad (8)$$

$$Al_{(s)} \rightarrow Al^{2+}{}_{(aq.)} + 2e^-, \quad (9)$$

Cathode reaction: $$H_2O + 2e^- \rightarrow H_{2\,(g)} + 2OH^-, \quad (10)$$

Solution/Electrolyte: $Al^{3+}{}_{(aq.)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$, (11)

The removal process of the pollutant involves the dissolution of metal ions. The metallic hydroxide, Aluminum Hydroxide, formed by electrolytic oxidation in the aqueous solution destabilizes the emulsified oil droplets those are negatively charged so they get neutralized by the positively charged aluminum ions present in the solution [86].

When the anode's potential is high, direct oxidation of the chlorine ions and the organic compounds present in wastewater might occur as secondary reactions and produce the very strong oxidant chlorine. This produced chlorine can promote the electrode reactions and oxidize the organic compounds [86].

Chlorine oxidation: $2Cl^- \rightarrow Cl_2 + 2e^-$, (12)

All in all, the electrical energy would generate these oxidants that will oxidize the organic compounds and remove them either via floatation or sedimentation [86].

4.1.1 Effect of Current Density

Current density is defined as the current loaded per unit area. Current density can be varied externally and has a direct effect on the movement of particles, oxidation of electrode, release of hydrogen, pollutant removal and operating cost of the process [84, 89, 90]. In the current study, the effect of three current densities 10, 30 and 60 mA/cm^2 was investigated to determine its effect on the electro-coagulation process performance. The samples investigated were given abbreviations; CD10, CD30 and CD60 for current densities of 10, 30 and 60 mA/cm^2 respectively. Four parameters were investigated;

total suspended solids (TSS), turbidity, oil and grease (O&G) content and total organic carbon (TOC) to assess the performance of electro-coagulation process.

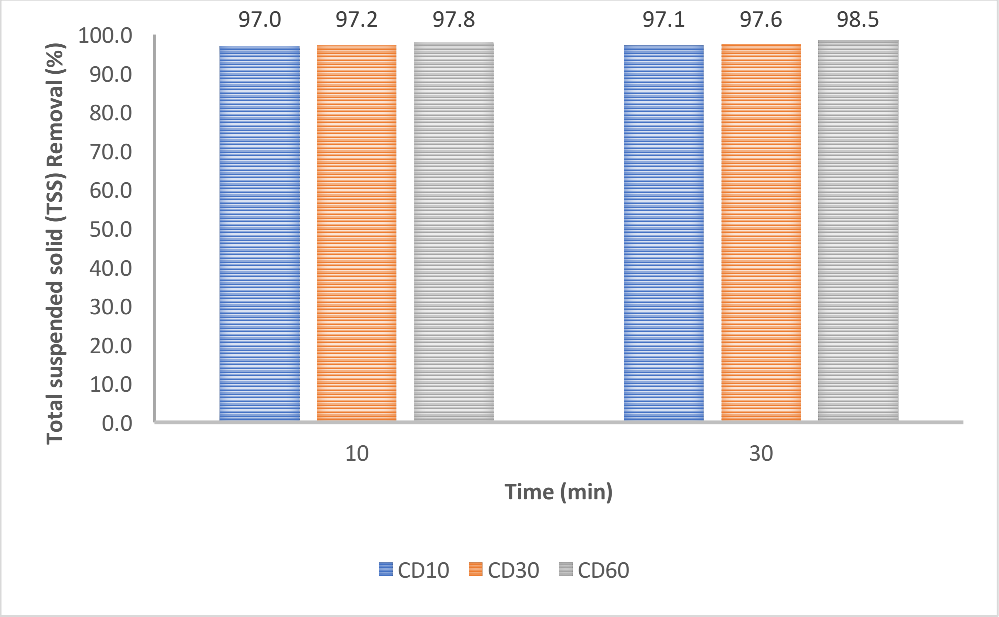

Figure 18: Total Suspended Solids (TSS) Removal for Different Current Densities at Different Times.

Figure 18, shows the total suspended solids removal rate for the different runs performed. The highest TSS removal rate of 98.5% was achieved at current density 30 mA/cm^2 and 30 minutes run time. All the runs had very close removal rates. The highest enhancement was achieved at 60 mA/cm^2. The TSS removal rate at CD60 was enhanced by 0.82% and 1.44% at run time 10 and 30 minutes, respectively. An increasing trend can be seen between the different current densities that shows as the charge increase the TSS removal rate increase. All the TSS removal values are at the high range as all the samples achieved a removal rate higher than 97%. This shows that a plateau was reached, where at a certain current density the increase in removal rate will be limited due to the increasing amount of coagulant that will precipitate at the bottom of the beaker [88, 91, 92], this is shown in the following equation:

$$Al^{3+}{}_{(aq.)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+, \qquad (13)$$

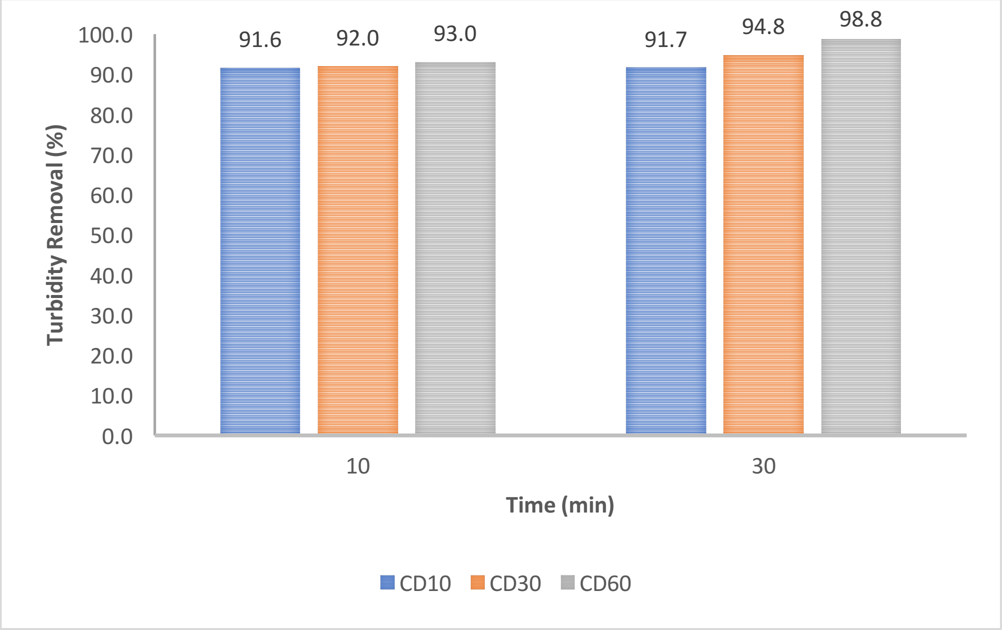

Figure 19: Turbidity Removal for Different Current Densities at Different Times.

Figure 19, shows the turbidity removal at various current densities. At 10 minutes run time, CD10 showed the lowest turbidity removal rate of 91.6%. As the current density increase the removal rate of turbidity also increase and at CD60 the removal rate reaches 93%, an enhancement in the turbidity removal of only 1.53% between the highest and lowest values at this run time. At a longer run time, the effect of current density can be seen more clearly. The removal rate was increased by 7.74% when the current density increased from 10 to 60 mA/cm^2. An overall increasing trend can be noticed when increasing the current density and that is primarily due to the abundancy of charge present in the solution to completely destabilize it [92]. These findings of TSS and turbidity removal agree with previous findings and can be explained; as the current density increase for a fixed detention time, the amount of aluminum cations (Al^{3+}) released by the anode will also increase and thus the amount of coagulant ($Al(OH)_3$) will increase and therefore, the coagulant produced destabilize the colloidal particles and form precipitates which settle down easily, following the reaction equation that was previously stated in this chapter [88, 91, 92].

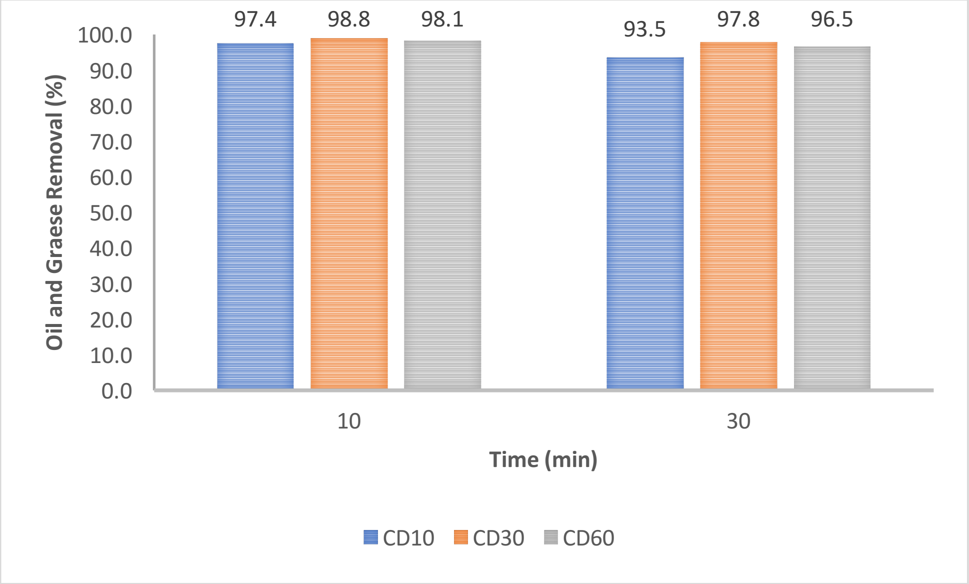

Figure 20: Oil and Grease Removal for Different Current Densities at Different Times.

The current density has a direct relation with the percent of oil and grease removed, as the current density increase the oil and grease removal increase [41, 93]. This is because, the higher the current density the more efficient becomes the anode and cathode, this increase in efficiency results in the increase of flock production, which leads to higher removal rates of O&G [94]. The results in Figure 20 shows that the oil and grease at both run times 10 and 30 minutes, are following the same pattern. The removal of oil increases with increasing current density and then decreases slightly at higher current density of 60 mA/cm^2. The slight decrease in the oil and grease removal was reported to occur at higher current densities and this is attributed to the presence of excess aluminum ions (Al^{3+}). The oil droplets are negatively charged, the surplus of the aluminum cations reverses the charge of the oil droplets and results in the decrease of oil removal [83, 95, 96].

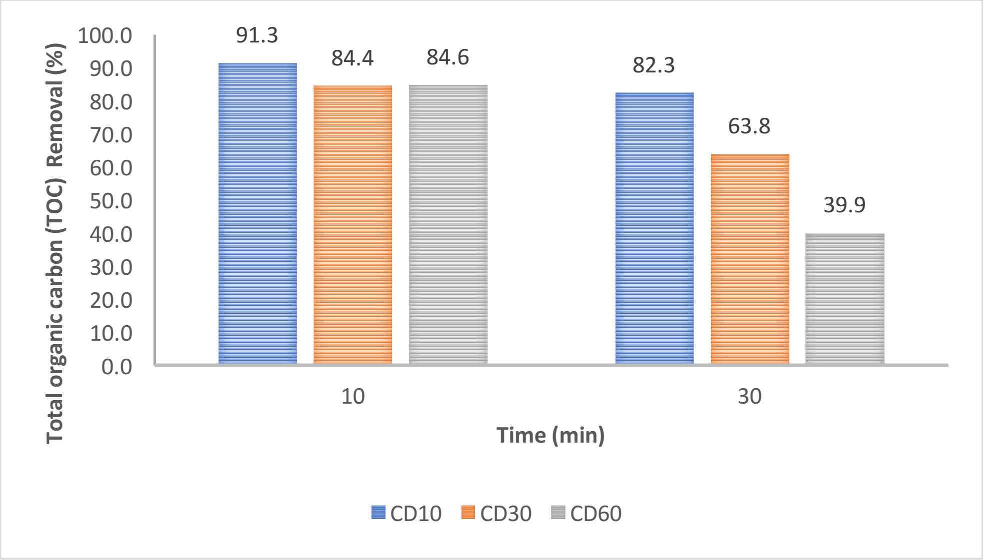

Figure 21: Total Organic Carbon (TOC) Removal for Different Current Densities at Different Times.

The highest total organic carbon (TOC) removal rate of 91.3% was obtained at run time of 10 minutes and current density of 10 mA/cm^2. The results show that an increase in the current density causes a decrease in the removal efficiency and this might be attributed to the same reason the oil and grease removal decrease at higher current densities. At high current density, excess Aluminum cations (Al^{2+}) are produced and this excess can affect the removal of TOC. This effect can be even more obvious at a longer reaction time as shown in Figure 21.

4.1.2 Effect of Contact Time

Effect of contact time in the electro-coagulation tests was investigated for two different durations, 10 and 30 minutes because the electrolysis time is an important factor in the electrocoagulation process [97]. This was performed to evaluate the effect of process time on the removals of total suspended solids, turbidity, oil and grease and total organic carbon.

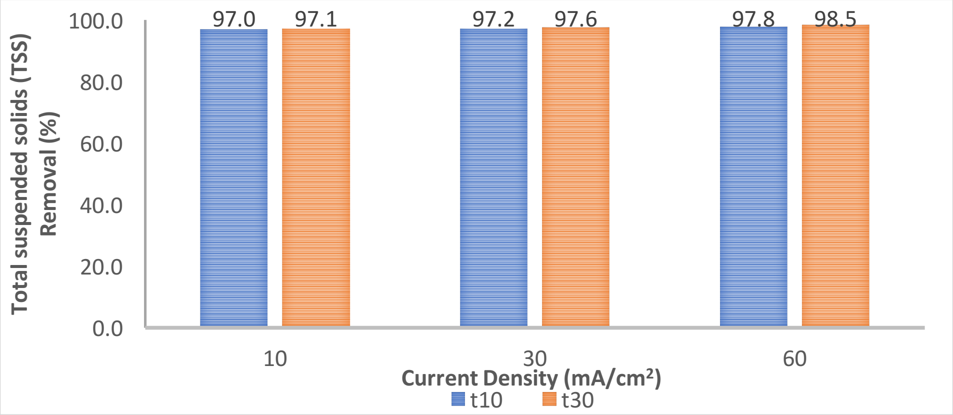

Figure 22: Total Suspended Solids (TSS) Removal Rate of Samples at Two Different Times.

From Figure 22, it can be seen that only a slight difference in the removal of suspended solids took place. Overall, after running the experiment for 30 minutes, the TSS removal was enhanced by 0.1, 0.4 and 1.7% for current densities 10, 30 and 60 mA/cm^2 respectively. Increasing the run time only slightly increased the removal rate. This is because the removal achieved at the lowest density and shortest time already achieved high removal, and therefore minor enhancement was observed.

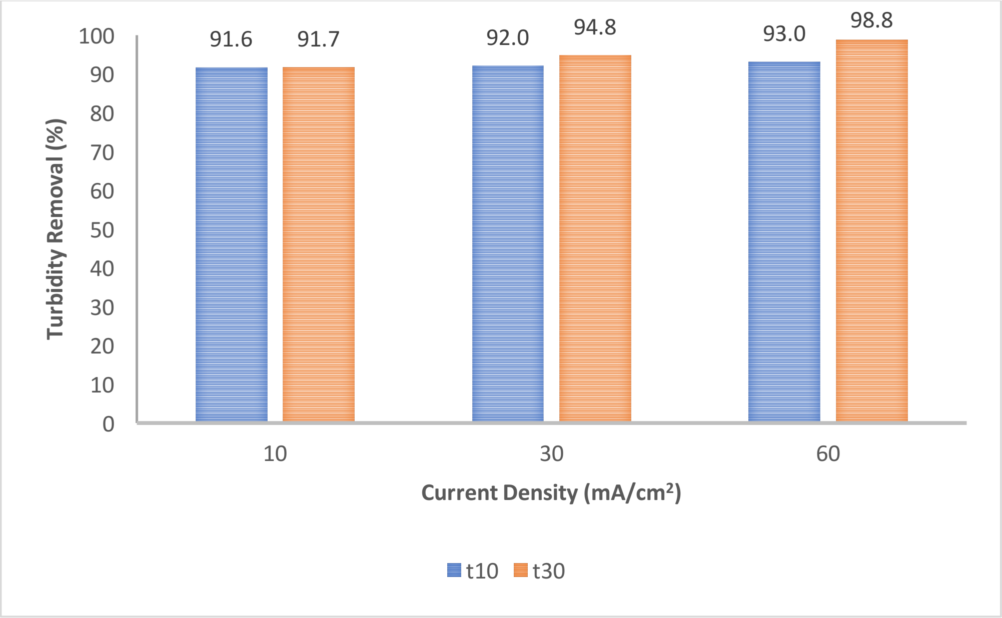

Figure 23: Turbidity Removal Rate of Samples at Two Different Times.

Figure 23, shows the removal of turbidity. The turbidity removal rate at 10 minutes run time was 91.6%, and the removal rate was almost the same at 30 minutes. However, when the current density increased to 30 mA/cm^2, the effect of reaction time was more evident as removal rate increased from 92% to 94.8%. Also, at current density of 60 mA/cm^2 an increase of removal between the two times was noticed and it was calculated to be 6.24%. This increase in the efficiency of removal is higher than the one obtained at the other two current densities studied. The highest turbidity removal rate obtained in the study was at 30 minutes run time for the current density of 60 mA/cm^2. It can be observed that the increase of electrolysis time resulted in better turbidity removal rate, and this finding can be supported by various previous research [36, 92, 94].

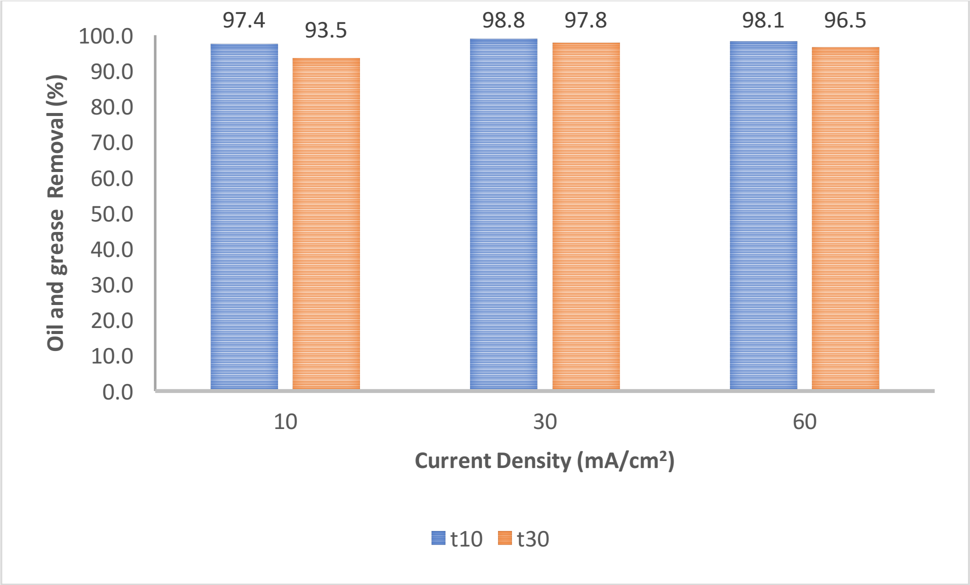

Figure 24: Oil and Grease Removal Rate of Samples at Two Different Times.

Oil and grease removal rate is shown in Figure 24. The increase of the contact time did not show an enhancement in the removal of oil and grease. It is noticed from the figure that the 10 minutes run time exhibited a slightly higher removal rates than the longer contact time of 30 minutes. The removal rate of oil and grease decreasing slightly when the time is increased, is attributed to the production of excess Aluminum cations (Al^{3+}). The oil droplets in the produced water samples are negatively charged, the surplus of the aluminum cations reverses the charge of the oil droplets and results in the decrease of oil removal [83, 95, 96]. This phenomenon resulted in obtaining an optimum point for the removal of oil and grease. This optimum point of removal was attained at 10 minutes run time when applying a current density of 30 mA/cm^2.

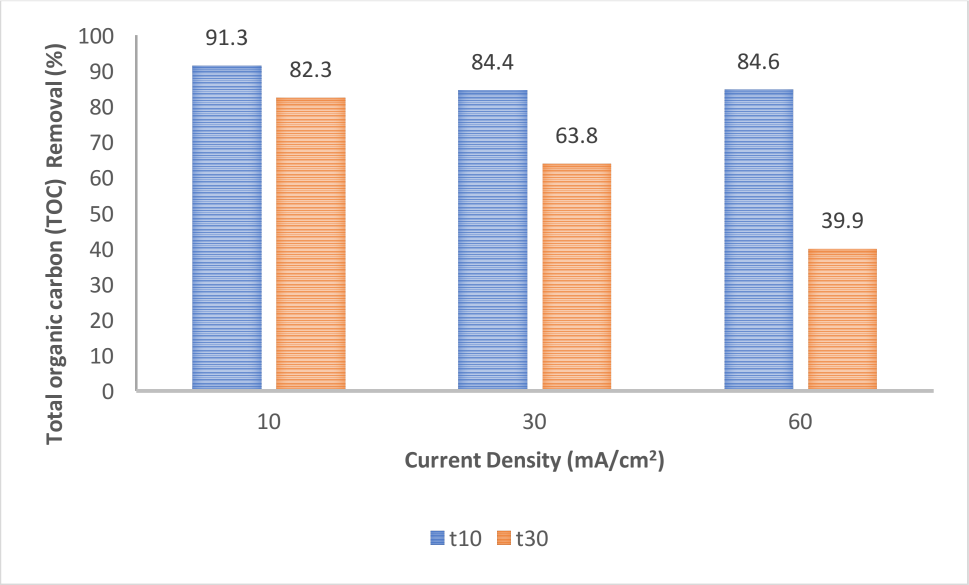

Figure 25: Total Organic Carbon (TOC) Removal Rate of Samples at Two Different Times.

In Figure 25, the total organic carbon removal trend is shown. The highest removal achieved was at run time 10 minutes with an applied current density of 10 mA/cm^2. The removal of TOC is then affected by increasing time, and the lowest removal is observed at run time 30 minutes and 60 mA/cm^2. Just like the removal of oil and grease, excess cations prevent the removal of TOC. The decrease in the TOC removal capacity when time progresses reflects the formation of excess flocs [83]. The effect here on the other had is more evident than in oil and grease tests.

4.2 Other Factors in Electrocoagulation

4.2.1 Electrode Consumption

Figure 26, shows the amount of aluminum electrode consumed in the electrochemical cell as the current density increase at two times of 10 and 30 minutes. The highest electrode consumption was at the highest current density and longest run time, 60 mA/cm^2 and 30 min respectively. Similarly, the least amount of anode consumed was attained at the lowest current density of 10 mA/cm^2 and shortest run time of 10 minutes. The current density and aluminum electrode consumption is proportional. Moreover, as the time of the test increase, the consumption of the electrode also increases. These results support the previous findings; at higher current density and longer run time more aluminum cations are produced, due to the consumption of the electrode. The aluminum cations produced affect the process of the removal of constituents present in the produced water during the electro-coagulation process. Accordingly, the results suggest the importance of residence time to the process performance. Also, the importance of anode consumption because, it has a direct effect to the feasibility of the treatment economically.

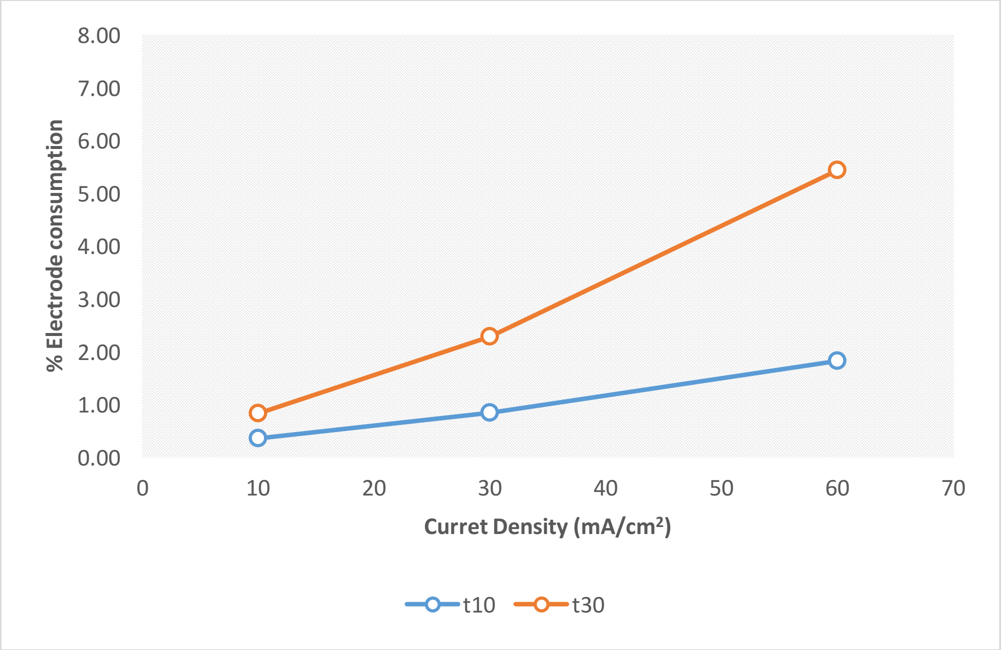

Figure 26: Current Density Vs. Electrode Consumption for Samples at Different Test Times.

4.2.2 Conductivity and Time Relationship

In Figure 27, the change of conductivity of the sample with applying different current densities is shown for two run time 10 and 30 minutes. The initial conductivity of the untreated PW sample was 96.4 mS/cm, after treatment the conductivity decreased slightly. The conductivity of the six different samples fluctuated between 92.6 and 90.5 mS/cm. hence, the change in conductivity can be said to be random and not significant. The EC system only slightly affected the conductivity of PW. To be able to get satisfactory results for the reuse of PW, conductivity must be further reduced and this could be achieved by using the FO system. FO system is further discussed in section 4.3.

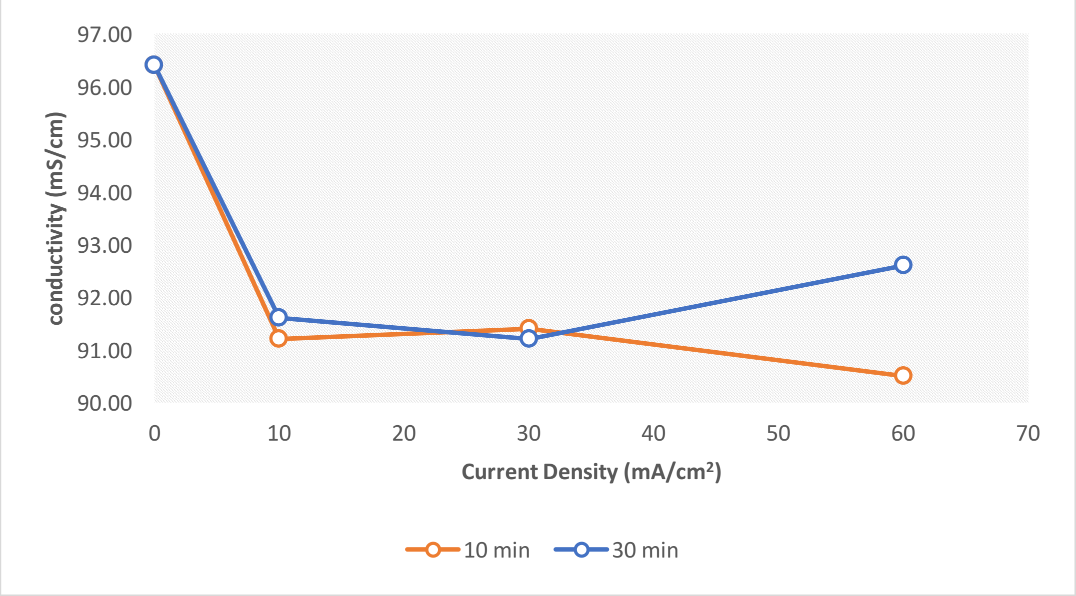

Figure 27: Conductivity Change with Current Density for Samples at Different Times.

4.2.3 pH and Time Relationship

The relationship of pH with the current density is shown if Figure 28. Three samples were tested at each time 10 and 30 minutes. The starting pH of the produced water was 5.9 pH. The pH fluctuated between 6.9 and 6 pH. It is evident form the results that the electrocoagulation process did not either increase nor decrease the pH of the PW drastically. The pH can be said to be almost constant throughout the different runs. Chen et al. reported that this could occur as a result of the complex chemical reactions that take place in the PW, also due to the high initial conductivity of the solution [98]. The initial conductivity of the PW treated was around 96 mS/cm.

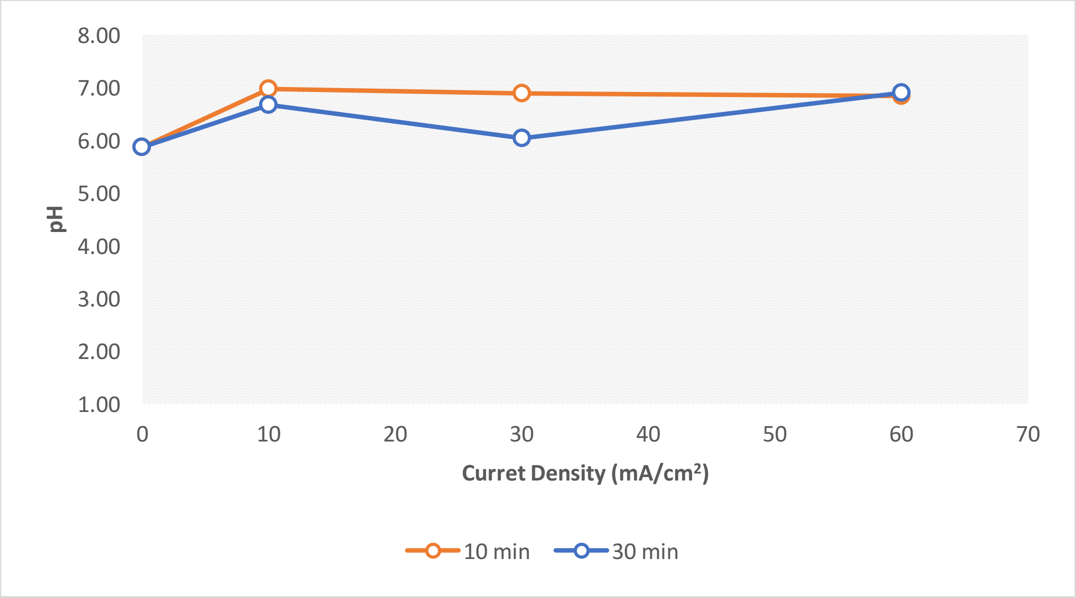

Figure 28: pH Change with Current Density for Samples at Different Times.

4.3 Filtration Studies (Forward Osmosis)

The feed solution to the process was treated sewage effluent (TSE) and the draw solution used was the electro-coagulation treated produced water. Two orientations of the membrane were tested; Active layer facing draw solution (AL-DS), and active layer facing feed solution (AL-FS) referred to as forward osmosis (FO) and pressure retarded osmosis (PRO) respectively in this study. The flow rates of feed and draw solutions were equal at all times, to prevent any pressure effect. Three flow rates at each orientation were tested; 0.8, 1.2 and 2 LPM. In both orientations, a spacer was used and placed on the support layer of the membrane. The draw solution was stirred throughout the experiment, to prevent settling of suspended matter. All tests were conducted at room temperature for 1000 minutes.

The Flux (J_w, L/m^2.h) was determined by observing the change of weight through time, using the following equation:

$$J_w = \frac{W_2 - W_1}{t_2 - t_1} \,/\, A_e, \tag{14}$$

Where;

W_1, W_2: weight recorded at interval 1 and 2 (g)

t_1, t_2: time recorded at interval 1 and 2 (h)

A_e : effective area of the membrane (m^2)

Recovery rate (% Ret) and flux reduction (%) where also calculated

$$\%Ret = \left(\frac{W(t) - W(t=0)}{W\,(t=0)}\right) \times 100\ , \tag{15}$$

Where;

W(t=0): initial weight at the beginning of the experiment (g)

W(t): final weight after 1000 minutes of run time (g)

$$Flux\ reduction = \left(\frac{J_w(t=0) - J_w(t)}{J_w(t=0)}\right) \times 100, \tag{16}$$

Where;

$J_w(t=0)$: initial flux calculated at the beginning of the experiment (L/m^2.h)

$J_w(t)$: final flux calculated after 1000 minutes of run time (L/m^2.h)

4.3.1 *Effect of Flow Rate on Membrane Flux*

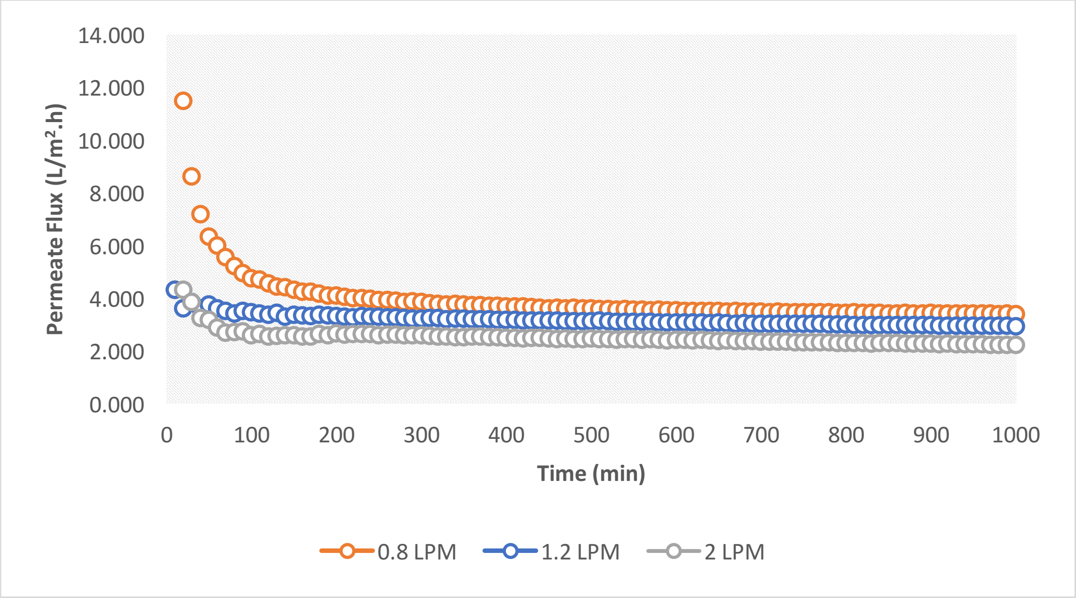

Figure 29: Permeate Flux Change with Time (FO Mode) for Three Different Flow Rates 0.8, 1.2 and 2 LPM.

In Figure 29, it can be seen that the highest flux was achieved at 0.8 LPM, starting at 11.5 L/m^2.h and then settling into an average of 3.5 L/m^2.h. The flow rate of 1.2 LPM achieved an average flux of 2.9 L/m^2.h, while the lowest average flux of 2.3 L/m^2.h was acquired at a flow rate of 2 LPM.

All runs showed a decrease in the flux at the beginning of the experiments then became constant as the time started to progress and this is due to the decrease in the osmotic pressure difference on the membrane sides. Also, the accumulation of foulants on the membrane surface which is due to permeation drag that reduces the flux [78]. The slight deviation of the flux from linearity may be attributed to the salt present in the porous support layer that is being diluted by the water coming from the feed side, this phenomenon is known as the dilutive concentration polarization (DCP) phenomenon, and occurs in highly concentrated draw solutions like the one in this study [99, 100]. As the flow rate increases, the presence of suspended solids and dissolved organic cause fouling to the membrane and hence low osmotic pressure lowering the flux of water [101, 102]. The highest flux was noticed at flow rate of 0.8 LPM. This can be explained by the increased fouling of the membrane as the flow rate increases. Increased fouling can be due to the presence of the spacer on the support layer, where the colloidal particles get trapped between the spacer and the membrane surface. These results are more visible by SEM images of the membrane that will be later discussed in section 4.3.3.

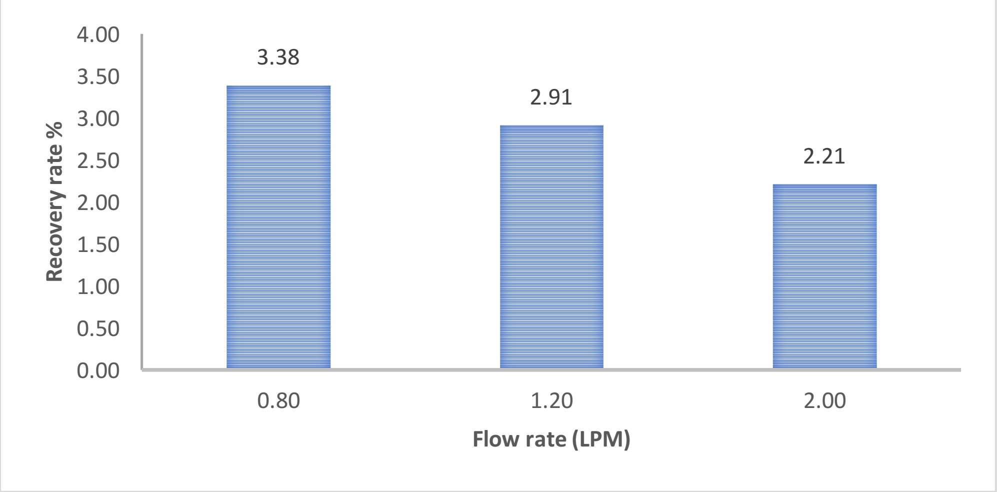

Figure 30: Recovery Rate Under Three Different Flow Rates for FO Mode Membrane Orientation.

The highest recovery rate was obtained at flow rate of 0.8 LPM as it can be seen in Figure 30. The recovery rate kept decreasing as the flow rate increased. This is consistent with Figure 29 observation, where the flux decreased as the flow rate was increasing. This is mainly attributed to the use of spacer in the draw side which led to the entrapment of colloidal particles between the spacer and the rough support layer, leading to severe flux reduction as the flow rate increased. These results are evident in the SEM images that will be later discussed in this chapter, in section 4.3.3.

4.3.2 Effect of Membrane Orientation on Membrane Flux

Figure 30, shows the trend of flux with time, between the three different flow rates tested in PRO mode, the highest average flux of 5.5 $L/m^2.h$ was attained at a flow rate of 1.2 LPM. At the flow rate of 2 LPM, an average flux of 5.3 LPM. At the flow rate of 0.8 LPM, the initial flux was the highest. At the star of the experiment the starting flux was 12.9 $L/m^2.h$, however the flux sharply declined with the progress of time until the average flux reached the lowest value among all the other average fluxes attained for the other flow rates.

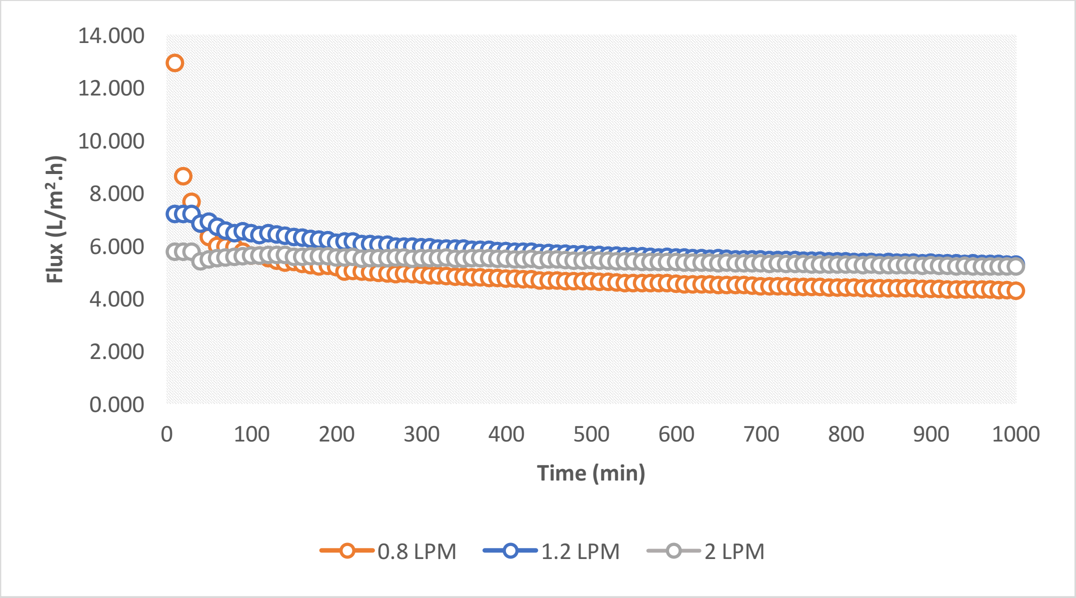

Figure 31: Flux Change with Time (PRO Mode) for Three Different Flow Rates 0.8, 1.2 and 2 LPM.

Figure 31, shows that the flux starts off very high at the flow rate of 0.8 LPM and then reduces significantly, this is due to the hydraulic resistance created on the membrane surface due to the membrane surface fouling. On the other hand, flow rate of 0.8 LPM exhibited lower flux than 1.2 and 2 LPM flow rates after 1000 minutes. This can be attributed to the decrease of CP on the membrane, this trend is explained by previous researches [103]. As the flow rate increases the ECP is decreased due to the reduction of the concentration boundary layer, this consequently improves the mass transfer between the boundaries.

The highest membrane flux after 1000 minutes of run time was found at flow rate of 1.2 LPM, as Figure 31 shows. The presence of the spacer in the feed solution side reduced the accumulation of particles on the membrane surface due to the increase solution turbulence this cause CICP mitigation [104].

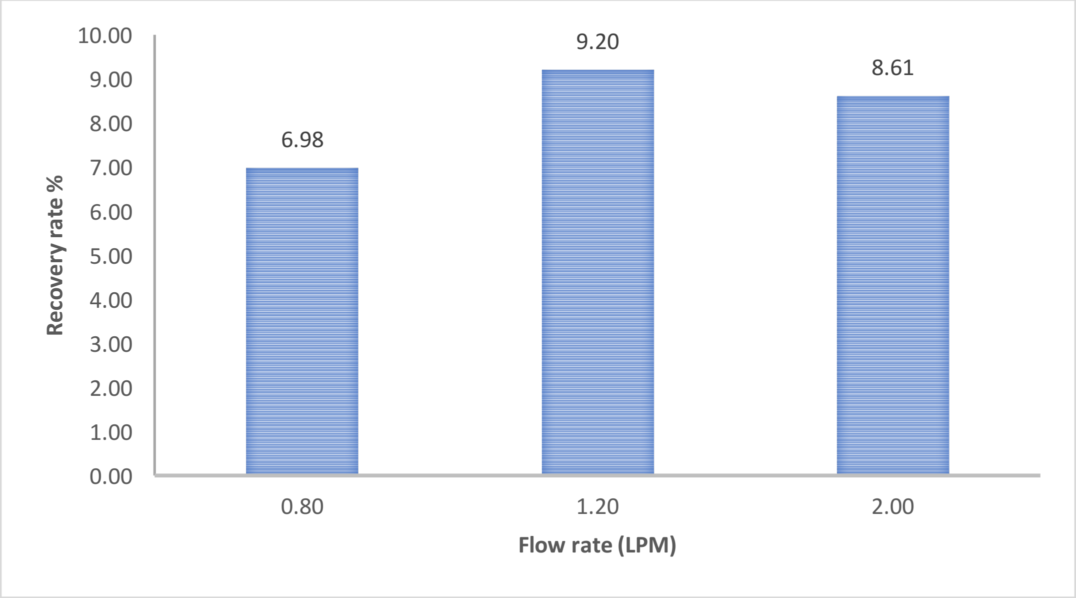

Figure 32: Recovery Rate Under Three Different Flow Rates for PRO Mode Membrane Orientation.

From Figure 32, it could be indicated that the highest recovery rate was obtained at the flow rate of 1.2 LPM, where it possessed a 9.2% removal as the flow rates of 0.8 and 2 LPM only recovered 6.98 and 8.61% respectively. It could be concluded that with the increasing flow rate the PRO mode recovery rate will increase until reaching an optimum value. This can be attributed to the increase of colloidal particles entrapped between the spacer and the membrane.

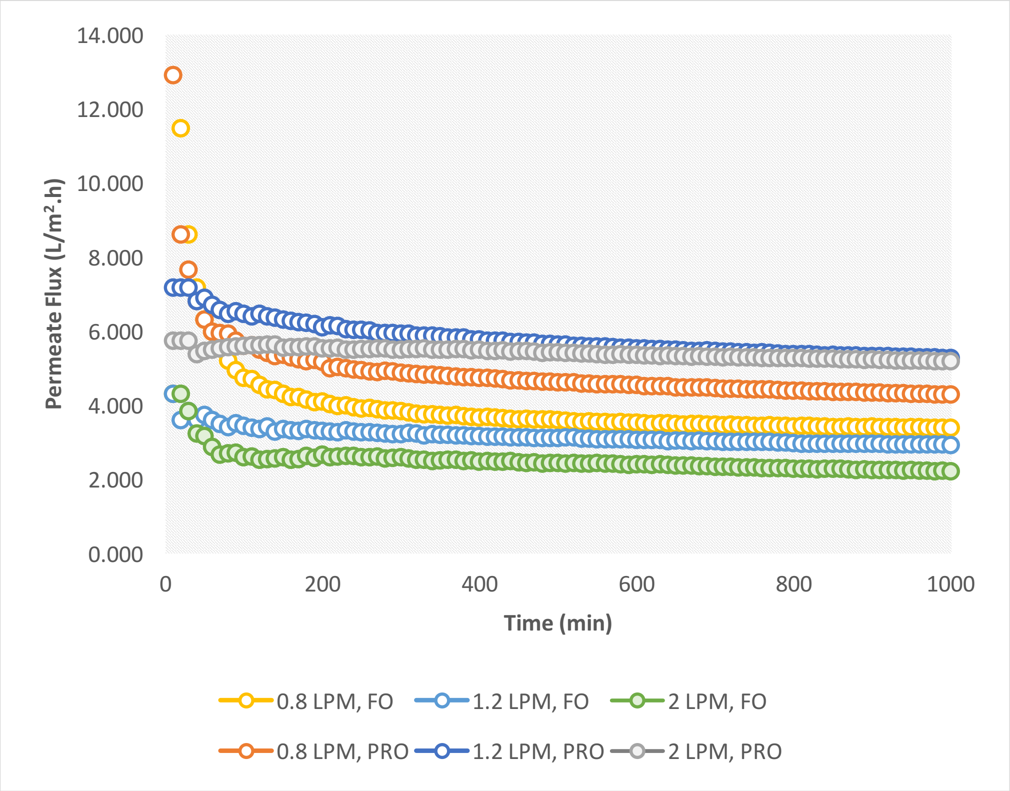

Figure 33: Comparison Between FO and PRO Modes Flux Change with Time for Three Different Flow Rates 0.8, 1.2 and 2 LPM.

It can be noted from Figure 33, that the PRO mode provided higher fluxes than FO mode at the same operating flow rates. This can be explained by the reduced effect of dilutive concentration polarization at the draw solution side when the orientation on the active layer is facing towards draw solution side. This is attributed to the smooth and dense surface characteristics of the active layer, which helps in reducing the shear stress of the fluid on the surface of the membrane. This in turn reduces both ECP and ICP because it reduces the accumulation and diffusion of salts on the membrane [105-107]. Also, since the concentration of the draw solution was significantly higher than that of the feed, the CICP of PRO mode was less than DICP in FO mode, which contributed to the higher flux at the PRO mode.

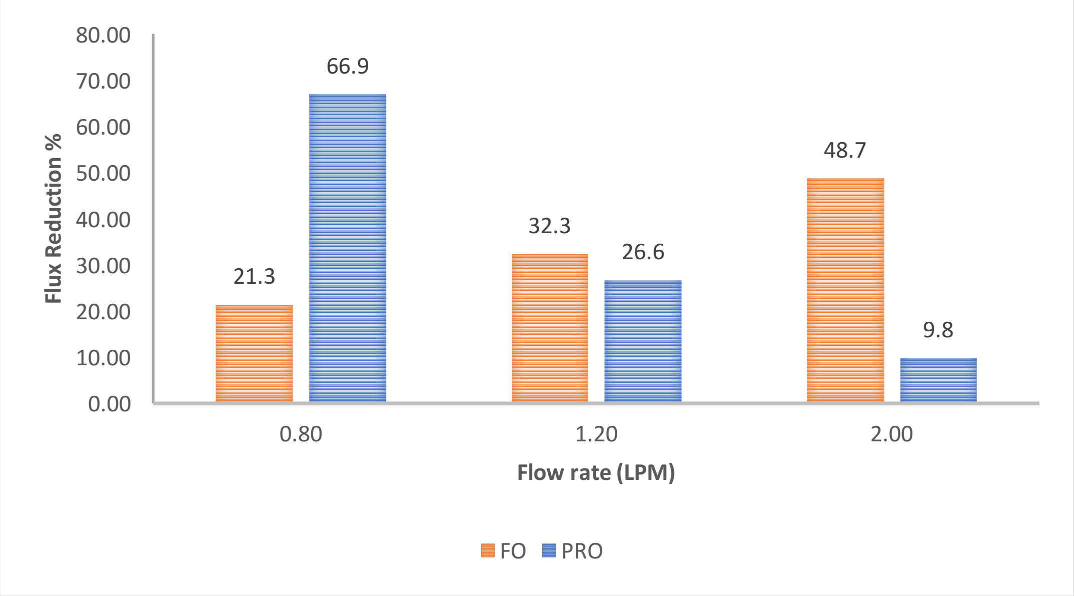

Figure 34: Water Flux Reduction Under Three Different Flow Rates for FO & PRO Orientations.

At the flow rate of 0.8 LPM the flux reduction is 21.3 and 66.9 % for PRO and FO mode respectively, in PRO mode the flux reduction is much greater than that of FO, this is consistent with previous studies [108]. At flow rate of 1.2 LPM the flux reduction of both the FO and PRO modes are close to each other. While at the flow rate of 2 LPM the flux reduction of PRO mode was only 9.8% compared to the 48.7% in the FO, this result is consistent with Figure 34, where it could be seen that the initial flux in FO mode was reduced from 4.3 to 2.2 L/m^2.h, while at the same flow rate in PRO mode only a minor change in the flux was seen where the initial flux was 5.7 L/m^2.h and the final flux was 5.2 L/m^2.h.

4.3.3 Membrane Fouling

SEM images revealed the formation of organic fouling on the membrane surface. The irregular structure that appeared on the membrane in Figure 35, represents organic foulants. The foulants caused fouling to the FO membrane because they blocked the pores of the membrane. The presence of the spacer on the support layer side also contributed greatly to the increased fouling where the foulants were entrapped in between. This result is in agreement with the hypothesis made by Li et al. [109]. Li et al. suggested that the membrane surface roughness has a direct relationship with the number of colloidal particles attaching to it. The rougher the membrane surface, the more particles will adhere to it. The support layer is the porous side of the membrane and is rougher than the active side which is the dense side of the membrane and is relatively smoother. Foulants will attach to the rough support side. During PRO orientation, the active dense layer will foul at a slower pace when compared to the porous support layer, the SEM images of PRO mode are shown in Figure 36. This explains the higher flux attained during the PRO mode when compared to the FO mode.

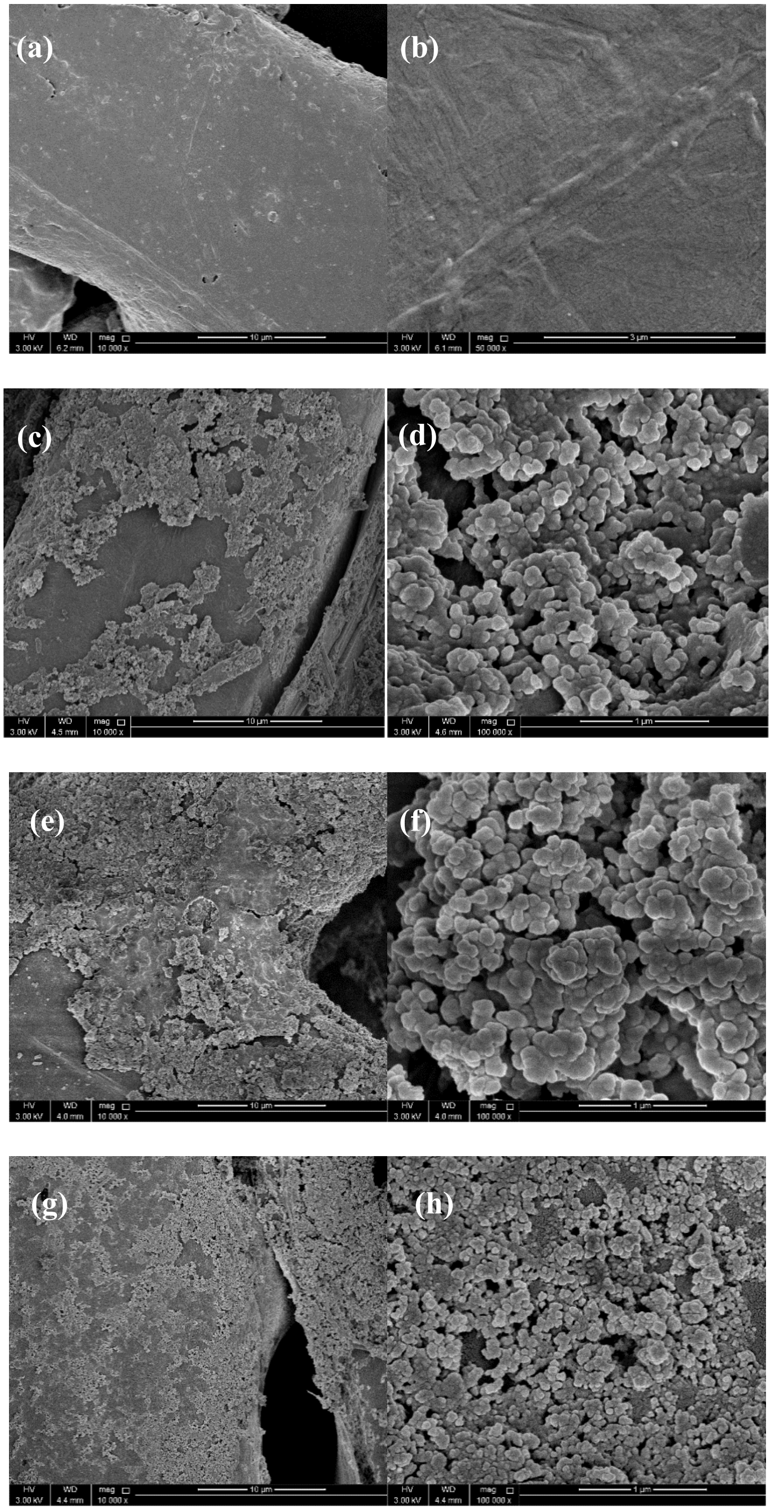

Figure 35: SEM Images of Membrane (in FO Mode) Support Layer (a)(b) Blank, (c)(d) 0.8 LPM, (e)(f) 1.2 LPM, (g)(h) 2 LPM.

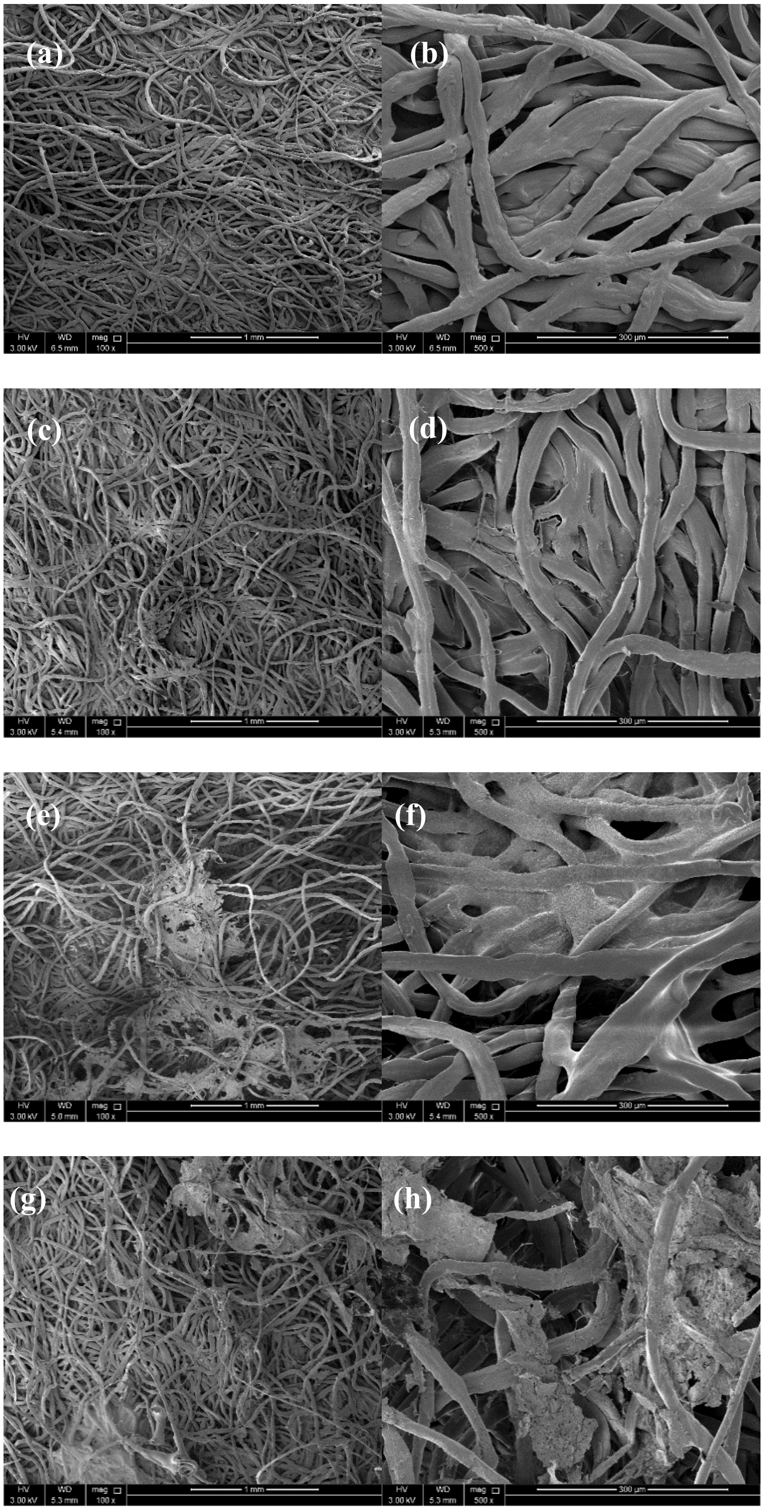

Figure 36: SEM Images of FO Membrane (in PRO Mode) Support Layer (a)(b) 0.8 LPM, (c)(d) 1.2 LPM, (e)(f) 2 LPM.

Figure 37, shows the support layer of both FO and PRO membrane orientations. The PRO support layer side showed a loose organic layer formed at the surface, whereas the FO support layer showed a denser layer formation. This was anticipated because of the high organic loading in the draw solution which would increase the ECP, that hence led to sever fouling and reduced flux.

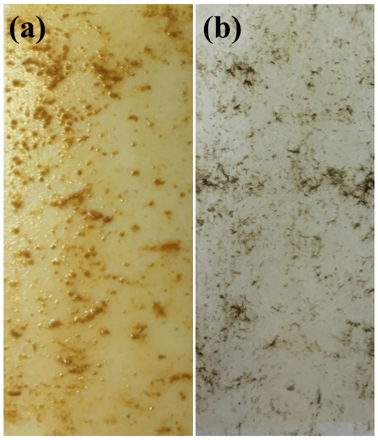

Figure 37: Fouling on FO Membrane Support Layer After Water Treatment Using a Flow Rate of 2 LPM, (a) FO mode, (b) PRO mode.

4.4 Performance of The Combined Electro-Coagulation/Forward Osmosis System

Table 7, presents the removal efficiencies of EC and combined EC-FO processes. The EC and FO running conditions were as follows; current density of 10 mA/cm^2 was applied to the EC system for 10 minutes, as for the FO system the membrane was facing the DS side and the flow rates of FS and DS were maintained at 1.2 LPM.

Table 7

Removal Efficiency of EC and EC-FO Processes

Parameter	**EC (%)**	**EC-FO (%)**
TSS	97.0	99.0
Turbidity	91.6	98.2
Conductivity	5.4	16.3

The removal of TSS was significantly increased, changing from 97.1% with EC treatment alone to 99% with EC-FO hybrid system. When comparing the two treatment systems, the highest difference can be seen in the conductivity reduction (5.4% using EC and 16.3% using EC-OF) and turbidity removal (91.6% for EC and 98.2% for EC-FO). The hybrid system enhanced the quality of the treated water and achieved the purpose of decreasing the high conductivity of the PW. It is possible to further reduce the conductivity by extending the experiment run time of the FO system, in this case the PW can be further diluted and the concentration of minerals will be lowered. The combined hybrid EC-FO system showed improvement in all measured parameters; TSS, turbidity and conductivity removal, and shows promising possibility for PW treatment.

CONCLUSIONS & RECOMMENDATIONS

In this study, the viability of using a novel hybrid electrocoagulation/forward osmosis (EC-FO) system for the treatment of oil and gas produced water was investigated. The performance of EC on its own was first studied, then the performance of FO system, followed by the overall combined system of EC-FO.

In EC treatment process, the total suspended solids, turbidity, oil and grease and TOC removal efficiencies were studied. Electrode consumption, pH and conductivity were also monitored throughout the experiments. Electro-coagulation was applied at three different current densities 10, 30 and 60 mA/cm^2 for 10 and 30 minutes. Effective removal of oil and grease, TSS, turbidity and TOC from the produced water was observed and assessed during the study. Removal efficiencies were above 97%, 91% and 93% for TSS, turbidity and oil and grease respectively. The optimum water quality was obtained after 10 minutes run time, at a current density of 10 mA/cm^2. The maximum removal efficiency of TOC achieved at the optimum conditions was 91.3%. EC was not effective in the removal of conductivity.

Following EC process, the treated produced water was further treated through Forward Osmosis (FO) using two orientations of the membranes (active layer facing draw solution and active layer facing feed solution), and three flow rates 0.8, 1.2 and 2 LPM. Several parameters where investigated, the effects of different flow rates and membrane orientation on the flux. Also, fouling of the membrane was investigated and SEM images of the membrane at different flow rates and different orientations were taken and analyzed. It was found that when FO was operating in (AL-DS) mode, the membrane flux decreased with the increase of flow rate of feed, due to colloidal particles between the spacer and the rough support layer. The highest flux was obtained at a flow rate of 0.8 LPM. The flux started at 11.4 L/m^2.h and dropped to 3.4 L/m^2.h after 1000 minutes, with a recovery rate of 3.4%. (AL-FS) operation mode, yielded better results than (AL-DS). The maximum flux achieved was at a flow rate of 1.2 LPM. The flux started at 7 L/m^2.h and dropped to 5.3 L/m^2.h at the end of run time, the recovery rate obtained was 9.2%. Hence, FO operating in (AL-FS) mode at a flow rate of 1.2 LPM was the optimum condition and reduced the PW conductivity to 16%.

Overall, the hybrid system efficiently removed a total of 99, 98 and 16% TSS, turbidity and conductivity respectively. The obtained improved water quality suggests a high potential of practicability of the applied hybrid system in the treatment and reclamation of PW.

For further work, it is recommended to further investigate the EC-FO system using the following operating conditions for each EC and FO treatments; EC system operates for 10 minutes using a current density of 10 mA/cm^2, these conditions insure optimal removal of oil and grease and TOC at lower operational costs. The FO system operates in (AL-FS) mode, using a spacer on the DS side, with a flow rate of 1.2 LPM to obtain the highest permeate flux and recovery rate. It is also recommended for further investigation that the EC operates using a variety of applied current such as AC, DC and pulsation mode. Also, to experiment using lower current densities, for several running times. Moreover, coagulants can be used in the EC treatment, to examine its effect on the quality of water treated. In the FO system, it could be useful to identify the possible interactions between the dense polyamide active layer with the feed and draw solutions, in order to assess the integrity of the active layer, applying different types of polymeric membrane and compare them to the one presently used, is another option that may also be considered.

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