REMOVAL OF WASTE OIL/WATER EMULSION BY REVERSE OSMOSIS MEMBRANE

by:

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13617

Dissertation submitted in partial fulfilment of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2014

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Chemical Engineering Programme

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Approved by,

____

(Azry bin Borhan)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(MUHAMAD HAFIZ BIN MUSLEH)

ABSTRACT

Oily waste water that discharges from variety of industries could lead into environmental problem. The oily waste water which discharges into the river or sea could turn into an emulsion by weathering process. This emulsion can have critical impacts on coastal activities by creating hazardous conditions and inconvenience on the shore. Heating, centrifugation, fiber beds, ultra filtration and reverse osmosis are some of the physical methods to break the emulsion. Reverse osmosis membrane method is effective in removal of particles, dispersed and emulsified oil.

Reverse osmosis membrane is a separation process that uses pressure to force a solution through a membrane that retain the solute on one side and allows the pure solvents to pass to the other side. The oil-water emulsion that had been prepared will undergo the reverse osmosis membrane under variety of parameters such as pressure, oil-water concentration and feed pH. The quality of water at the output stream is determined based on the total dissolved solid (TDS).

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful.

Alhamdulillah, all praise to Allah for the strengths and His blessing in completing this thesis. Special appreciation goes to my supervisor, Mr Azry bin Borhan, for his supervision and constant support. His constructive comments and suggestions throughout the experimental thesis works have contribute to the success of this research. I would like to thanks to lab technician for their co-operation and guidance that helps me to conduct my experiment especially Mr Fairis. Sincere thanks to all my friends for their kindness and moral support during my study. Last but not least, my deepest gratitude to my beloved parents for their endless love, prayers and encouragement.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

A wastewater containing emulsion of oil in water mostly generated from industry such as petrochemical, petroleum production, oil refinery factories, metal, cosmetic and food industries (Kong & Li, 1999). The untreated wastewater that discharge directly to marine could harm the aquatic life, increase the turbidity of water and affect the chemical oxygen demand(COD) and biochemical oxygen demand(BOD). Reverse osmosis process is one of the most advance techniques for wastewater treatment and reuse to produce potable water from brackish water and seawater to reclaim contaminated water sources and to reduce water salinity for industrial application (Asano, 1998).

The osmosis system was first discovered by French scientist, Jean Antoine Nollet in 1748 when he found that pig gallbladder can permeate water. Reverse osmosis is purification of water through membrane process which removes most of the total dissolved solids (TDS) in water by reversing the natural process of osmosis (REVERSE OSMOSIS, 2012). Since waste oil/water emulsion from the wastewater could harm the environment therefore the best method to remove it need to be carry out which is reverse osmosis membrane method. Instead of that, the water from the process also can recycle for other purpose. Sample of emulsion and non-emulsion liquid also will be used in the experiment to determine the capability of reverse osmosis membrane. Alumina powder will also used in the experiment to reduce the fouling of the membrane. The parameters that need to be monitor throughout the experiment are concentration of emulsion, feed water pH, feed velocity and feed water pressure.

1.2 PROBLEM STATEMENTS

A large amount of oily waste in the form of oil-in-water emulsion form produce by the process industries such as petroleum, cosmetic, pharmaceutical, agriculture, food, polymer, textile, paper, polish and leather . The used emulsion that discharge directly to sanitary sewers or public waterways without treatment in the past time lead into environmental pollution and loss of oil (Laherie & Goodboy, 1993). The removals of oil in water emulsion thus become an important treatment in the industries. There are several methods of separation of emulsion that can be used such as evaporators, dissolved air floatation (DAF) and membrane separation. From the literature study, membrane separation technology is found to have a great potential in producing clear permeate by removing the oil-water emulsion.

1.3 OBJECTIVES AND SCOPE OF STUDY

- The main objective of this project is to remove waste oil/water emulsion by using reverse osmosis membrane method.
- This project will also study the effect of the pressure, concentration of oil-water emulsion and pH of the feed on the performance of oil/water separation.
- Determine the effectiveness of reverse osmosis membrane based on oil-water Total Dissolved Solid (TDS) at the output stream.
- Study the effectiveness of alumina powder in the process.

1.4 RELEVANCY OF THE PROJECT

This project is important as it deals with current issue in industry which is the wastewater treatment in oil and gas industry. Reverse osmosis membrane is believed to be one of the effective ways to remove waste oil/water emulsion. Hence, this project is relevant as separation of oil-water emulsion by reverse osmosis membrane can benefits the industries.

1.5 FEASIBILITY OF THE PROJECT

This project is feasible as it deals with narrowed scope of experiment whereby only 3 parameters are tested. It is within capability to be executed with helps and guidance from the supervisor and the coordinator. It is positive that this project can be completed within the time allocated with the acquiring of equipment and materials needed

CHAPTER 2

LITERATURE REVIEW

2.1. Reverse Osmosis membrane

Reverse osmosis is the process by which an applied pressure is exerted on the compartment that has the high-concentration solution and the pressure which greater than osmotic pressure forces water to pass through membrane in the direction reverse to that of osmosis (Kucera, 2010). Reverse osmosis membranes are usually made from cellulose acetate, polysulfonate and polyamide. The pore size range of reverse osmosis is between 0.0001μm to 0.001μm which is the finest separation material available in industry. Reverse osmosis is effective in treating water for both large and small flow application such as pharmaceutical, boiler feed water, petrochemical and food and beverage. The performance of reverse osmosis membrane is determined based on the permeate flux and salt retention. These factors are influenced by the pressure, temperature, recovery and salt concentration of feed water.

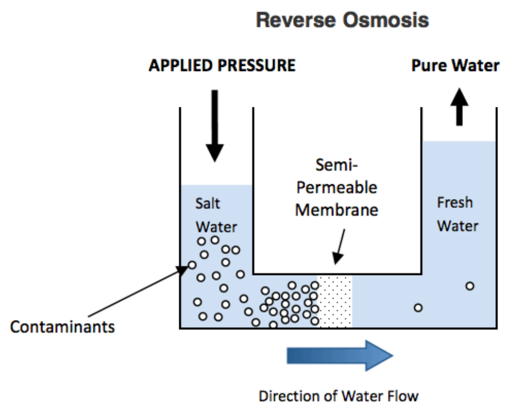


Figure 1: Reverse Osmosis Concept

2.2. Emulsion

An emulsion is a colloidal dispersion of one liquid (disperse phase) in another liquid (continuous phase). Emulsion can be classified into two types based on the nature of disperse phase. Emulsion that present oil as the dispersed phase and water as the dispersion medium is called an oil in water emulsion while emulsion that present water as the dispersed phase and oil act as the dispersion medium is called water in oil emulsion. Multiple or complex emulsion consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase (Oil emulsion, 2013). The emulsion can be characterized by analysis of their stability, droplet size, rheological properties and temperature. According to (Ajay, Abhijit, Achinta, & Keka, 2010), stirring speed and time play an important role in the stability of emulsion.

2.3. Membrane

The finest separation material that available in industry is reverse osmosis membrane which has range of pore size of reverse osmosis is 0.0001 to 0.001 µm. There are four main types of membrane module which are plate-and frame, tubular, spiral wound and hollow fiber. Spiral wound module (Figure 3) is commonly used in reverse osmosis membrane. According to (Gedam, Patil, Srimanth, Sirsam, & Labhasetwar, 2012), the temperature of feed water, pressure and pH could affect the efficiency of RO membrane. These parameter will affect the total dissolve solid (TDS), percentage of recovery, percentage of salt rejection, flux and fluoride concentration. Some of the results on the effect of these parameters that had been studied by Gedam et al is shown in Diagram 2.

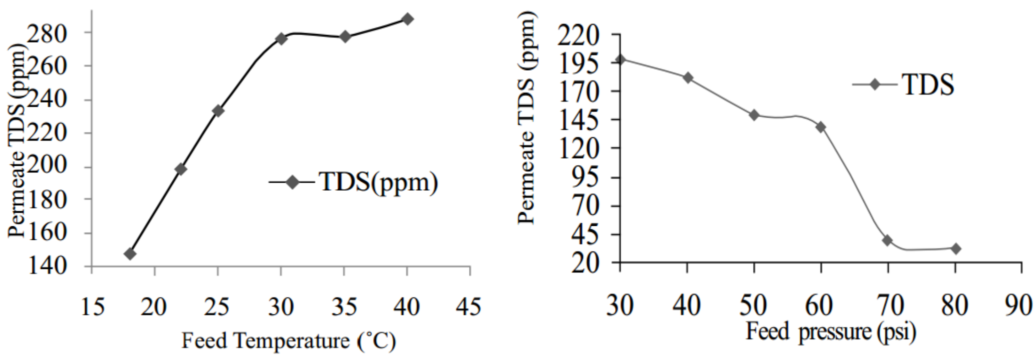


Figure 2: Effect of feed temperature and pressure on Total Dissolve Solid

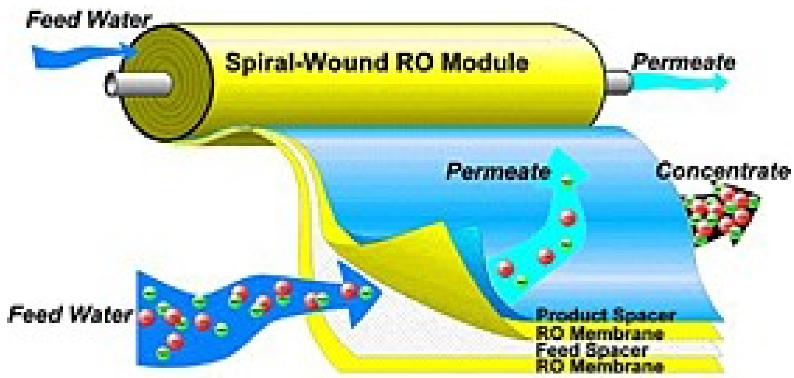


Figure 3: Spiral-wound RO module

2.4. Concentration polarization

Concentration polarization is an accumulation of retained feed solid at the surface of a membrane due to the rate of back diffusion away from the membrane and the balance convective transport toward the membrane (Cheryan, 1998). It affects on the performance of a reverse osmosis membrane because it reduces the throughput of the membrane in three important ways. First, it acts as a hydraulic resistance to water flow through the membrane. Second, the buildup of solutes increases the osmotic pressure within the boundary layer, effectively reducing the driving force for water through the membrane. Lastly, the higher concentration of solutes on the membrane surface than in the bulk solution, leads to higher passage of solutes that would be predicted by the feed water concentration (Kucera, 2010).

2.5. Fouling

Membrane fouling typically occurred on the feed of reverse osmosis membrane. Membrane fouling is a result of deposition of suspended solids, organics or microbes on the surface of the membrane (Kucera, 2010). Biofouling, scaling, organic and colloidal are the main types of fouling in reverse osmosis. The hydraulic permeability of reverse osmosis membrane will be reducing because of the organic fouling and biofouling. Therefore the capital and operational cost for full-scale system will be increase while the productivity decreases (Haiou Huanga, 2011). Pretreatment in reverse osmosis is essential to reduce the membrane fouling. The operations that involve in the pretreatment are coagulation of colloidal matter and chemical treatment to prevent biological growth. Fouling rate can be calculate based on the permeate flow (Q) as shown in the formula below.

$$Q = k_t k_T K A \Delta P_{avg}$$

Where:

K_t = Fouling factor

K_T = Membrane temperature correction factor

K = Clean permeate flow coefficient at standard temperature (105°F)

A = Membrane area, sq ft

ΔP_{avg}=Average transmembrane pressure drop

2.6. Performance of Reverse Osmosis Membrane

Quality of permeate water closely depend on several factors such as feed water temperature, feed water velocity, feed water pressure, feed water pH and concentration of emulsion. Temperature is one of the important parameter that affects the performance of reverse osmosis membrane. According to (Gedam et al, 2012), increasing in feed water temperature could increase total dissolve solid, permeate flux and percentage of recovery. However, increase in pressure decrease the total dissolve solid but permeate flux, percentage of salt rejection and percentage of recovery keep increasing. Besides that, pH value of sample also plays important roles to the performance of reverse osmosis membrane. The hydration and absorption capacity of solution on membrane depends on the pH value of the sample.

2.7. Flux

The volumetric flow rate of a fluid through a given area which is the membrane is called flux. In term of reverse osmosis, flux is expressed as gallons of water per square foot of membrane area per day.

$$J = \frac{\varepsilon \Delta P r^2}{8\tau\mu\delta}$$

Where:

J = permeate flux

ε=membrane porosity

ΔP=pressure drop across the membrane

r=pore radius

μ= fluid viscosity

τ=tortuosity of membrane pores

δ=membrane thickness

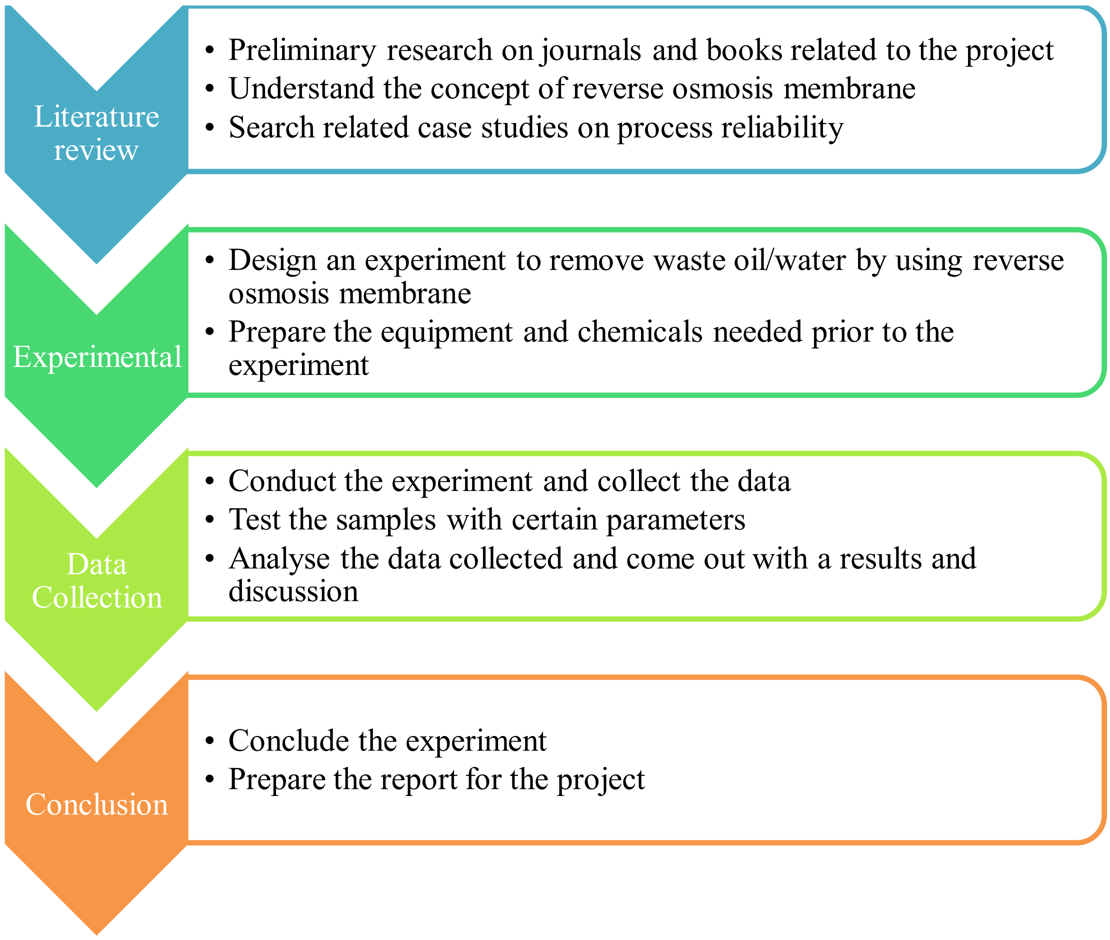
2.8. Scaling

Scaling is the deposition of precipitation of saturated salts onto the surface of the membrane. This problem could increase the energy use and shorter life span of the membrane. The life span of the membrane depends on the contaminant level of water, the maintenance of the system and the amount of water use.

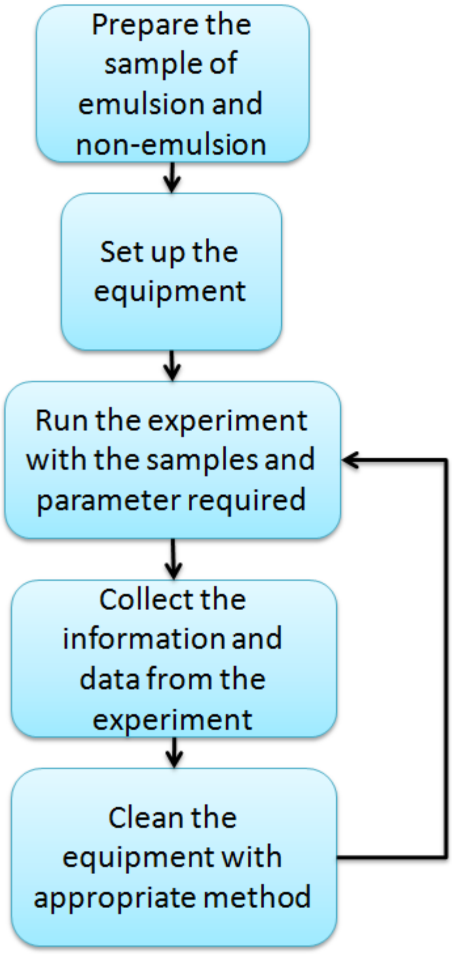
CHAPTER 3

METHODOLOGY

3.1. PROJECT FLOW CHART



3.2. EXPERIMENTAL METHODOLOGY



3.3. Waste oil/water emulsion preparation(Droplet size)

1. Pour 100mL of palm oil into 100mL of water at room temperature.
2. Agitate the mixture about 1000rpm for 15 minutes.
3. Collect a few drops of mixture and pour onto glass plate and observe the size of mixture droplets under an optical microscope fitted with high performance computer controlled digital camera.
4. Add about 10ml of emulsifying agent(Tween 40) into the remaining mixture and agitate about 1000rpm for 15 minutes.
5. Collect a few drops of mixture and put onto the glass plate to observe the droplet size of the mixture.

3.4. Experimental Procedure

1. Prepare three concentration of emulsions(0.50%, 0.10% and 0.15%) with about 1000rpm for 15 minutes.
2. For each of the concentration, adjust the pH value for 5, 7 and 12 with sodium hydroxide(NaOH) and hydrochloric acid(HCl).
3. Ensure that all valves are set according to the table below:

Table 1: Valve operation

Open	Closed
V1	DV1
V2	DV4
V4	V3
V5	
NV1-Open 20%	
NV2-Open 20%	

4. The emulsion mixture is poured into the feed tank and the pressure of the pump is adjusted into 30.4psi. The pressure variables are 30.4psi, 40psi and 50pis.
5. The total dissolve solid of permeate is measured for 10 minutes with two minutes interval.
6. The experiment was repeated with different pH, pressure and concentration of emulsion.

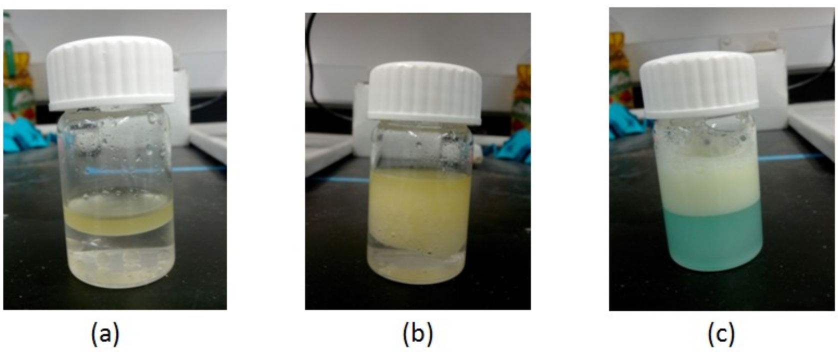


Figure 4:a)Oil-water mixture without agitation b)Oil-water mixture with agitation c)Oil-water mixture with emulsifying agent

3.5. Substance and chemical

List of chemicals needed for this experiment are:

Tween40(Polyoxyethylene sorbitan monopalmitate), hydrochloric acid(HCl), sodium chloride(NaOH), alumina powder(Al_2O_3), and palm oil.

3.6. Experimental Setup

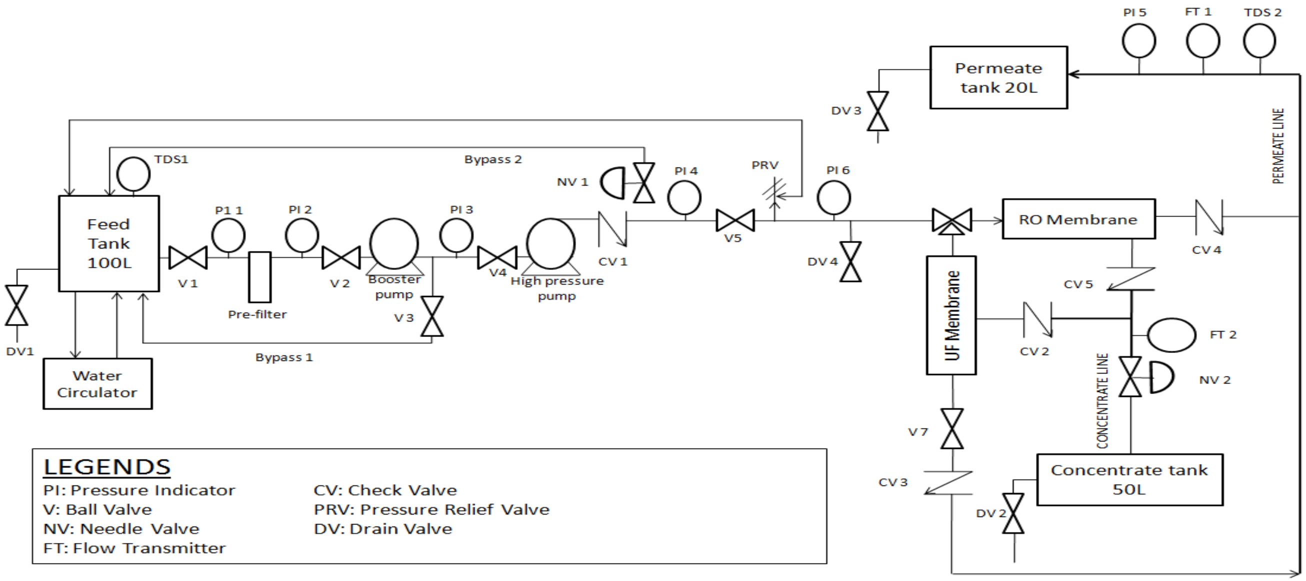


Figure 5: Reverse Osmosis Pilot System

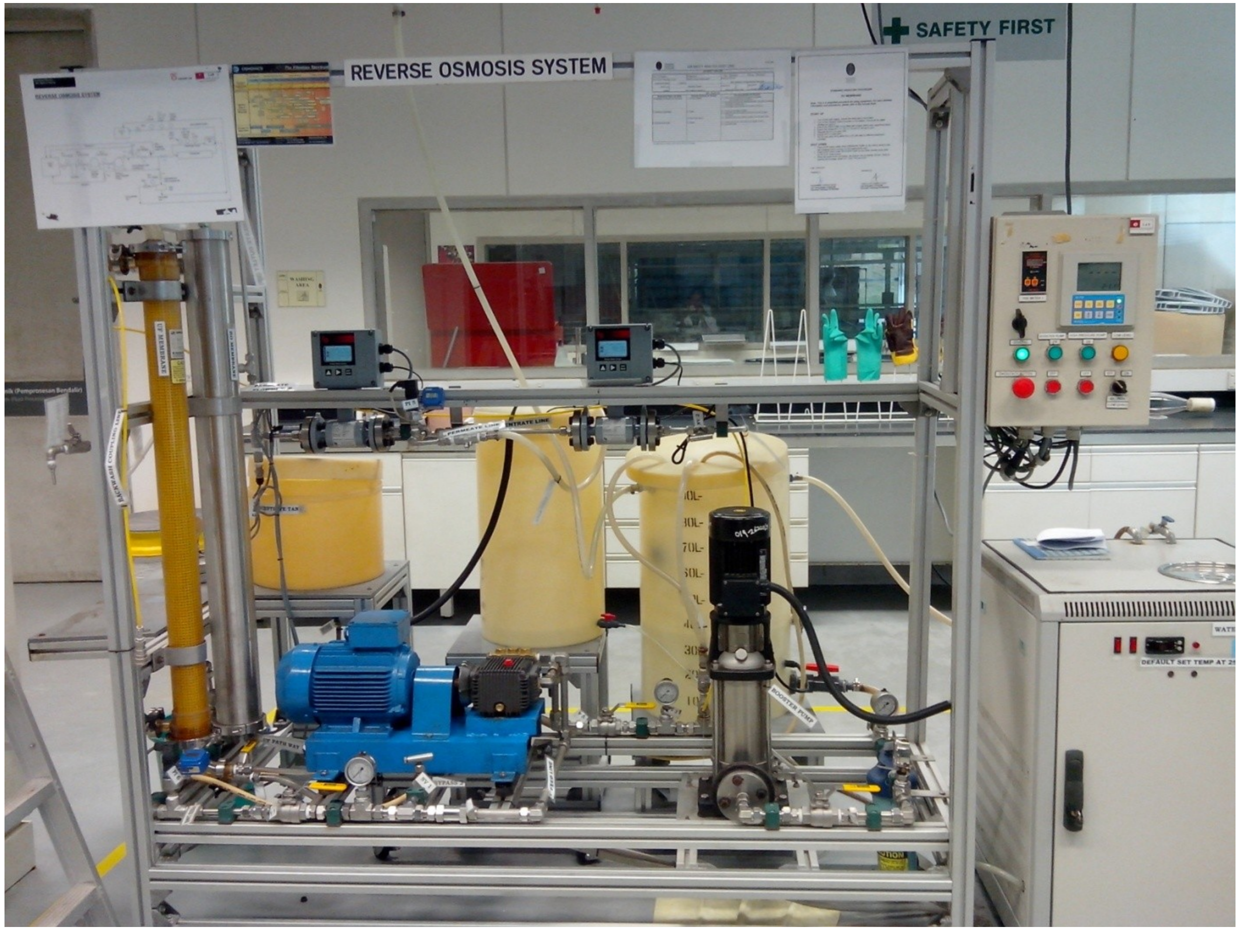


Figure 6: Reverse osmosis membrane system at block 4

The experimental apparatus for oil/water removal is shown schematically in Diagram 5. It consist of a feed tank(100L), ball valves, pressure indicator, booster pump, high pressure pump, check valve, RO membrane, flow transmitter and permeate tank(20L). A pH meter is used to measure the pH value of the sample prior to the membrane. The total dissolved solid is measured in the permeate tank by TDS meter.

3.7. Range of variables

Sample of an emulsion of oil in water being tested with different parameters as shown in Table 2.

Table 2: Parameter test in the experiment

Operating pressure(psi)	pH	Concentration of emulsion(vol%)
30.0	5	0.05
40.0	7	0.10
50.0	10	0.15

3.8. Project Milestone / Gantt Chart

Activities	Week														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Continuation of experiment															
Submission of progress report															
Continuation of experiment															
Pre-EDX															
Submission of draft report															
Submission of dissertation (soft bound)															
Submission of technical paper															
Oral presentation															
Submission of dissertation (hard bound)															

CHAPTER 4

RESULTS AND DISCUSSION

4.1 EXPERIMENT RESULTS

4.1.1 Droplet size of emulsion under microscope

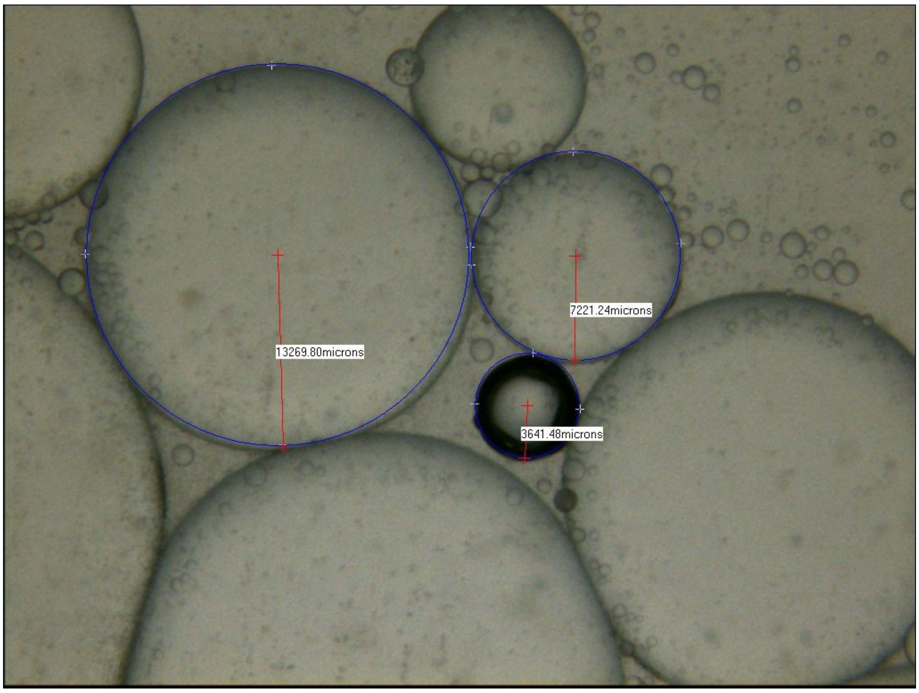


Figure 7: Mixture of oil in water without emulsifier

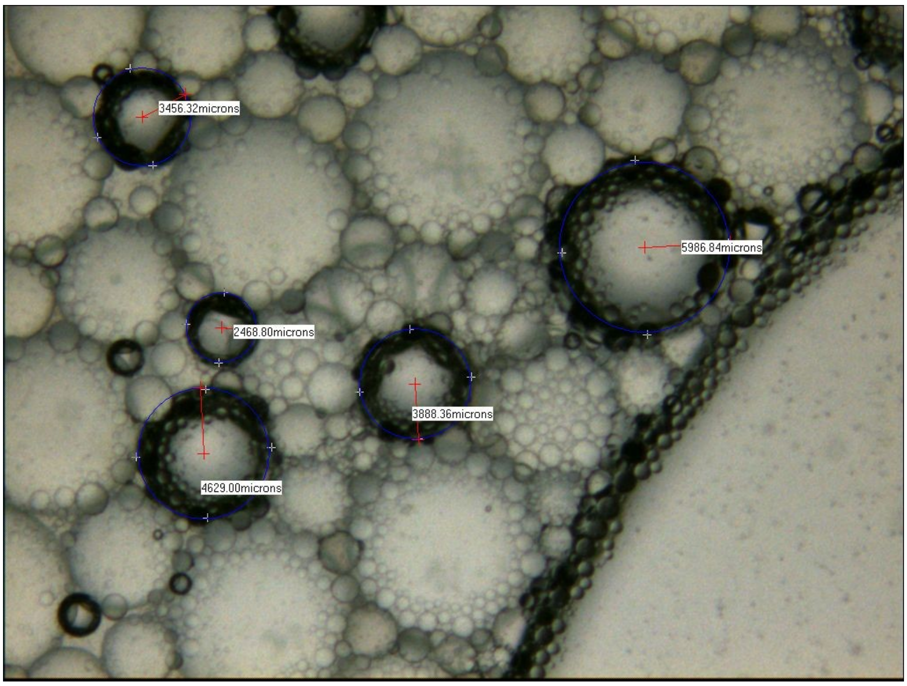


Figure 8: Mixture of oil in water with emulsifier

4.1.2 Emulsion concentration 0.05%

Table 3: TDS of permeate at pH5 in 0.05% emulsion concentration

	Time(min)	pH		
Oil/water concentration		5		
		Pressure(psi)		
		30	40	50
0.05	0	13	13	12
	2	11	9	6
	4	11	4	4
	6	11	4	3
	8	6	4	3
	10	5	4	3

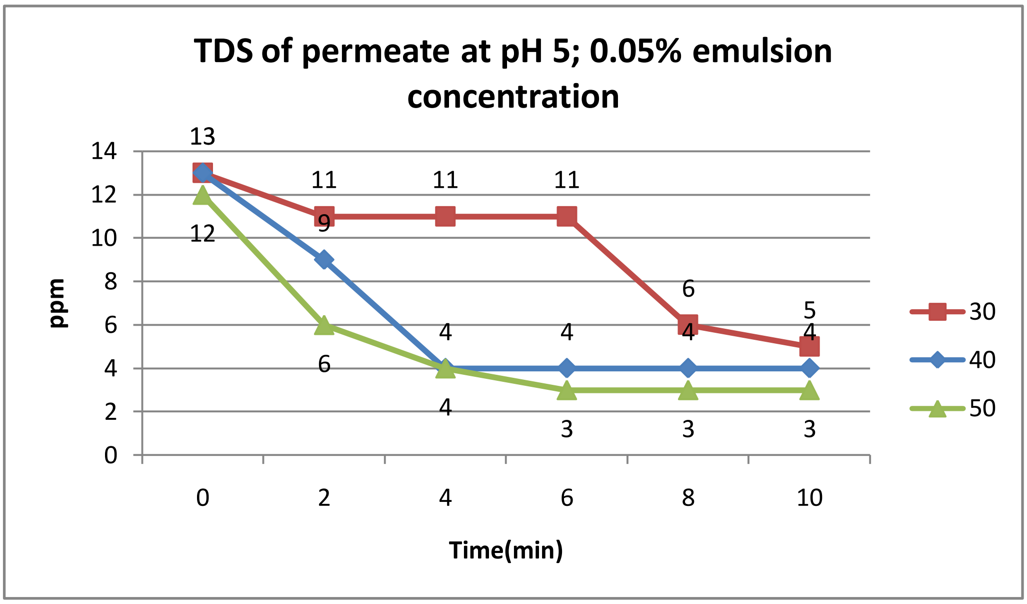


Figure 9:TDS of permeate at pH 5 in 0.05% emulsion concentration with different pressure

Table 4: TDS of permeate at pH7 in 0.05% emulsion concentration

	Time(min)	pH		
Oil/water concentration		7		
		Pressure(psi)		
		30	40	50
0.05	0	57	5	4
	2	36	5	4
	4	7	9	11
	6	6	5	9
	8	5	5	10
	10	5	11	7

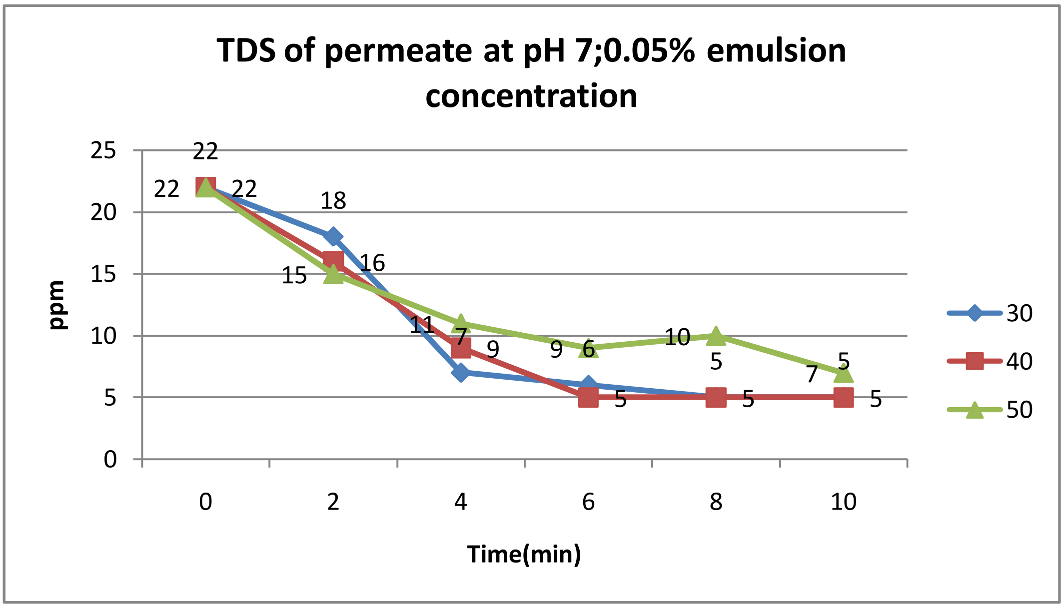


Figure 10:TDS of permeate at pH 7 in 0.05% emulsion concentration with different pressure

Table 5: TDS of permeate at pH10 in 0.05% emulsion concentration

	Time(min)	pH		
Oil/water concentration		10		
0.05		Pressure(psi)		
		30	40	50
	0	18	14	13
	2	15	5	4
	4	13	5	4
	6	5	4	5
	8	5	4	5
	10	5	4	5

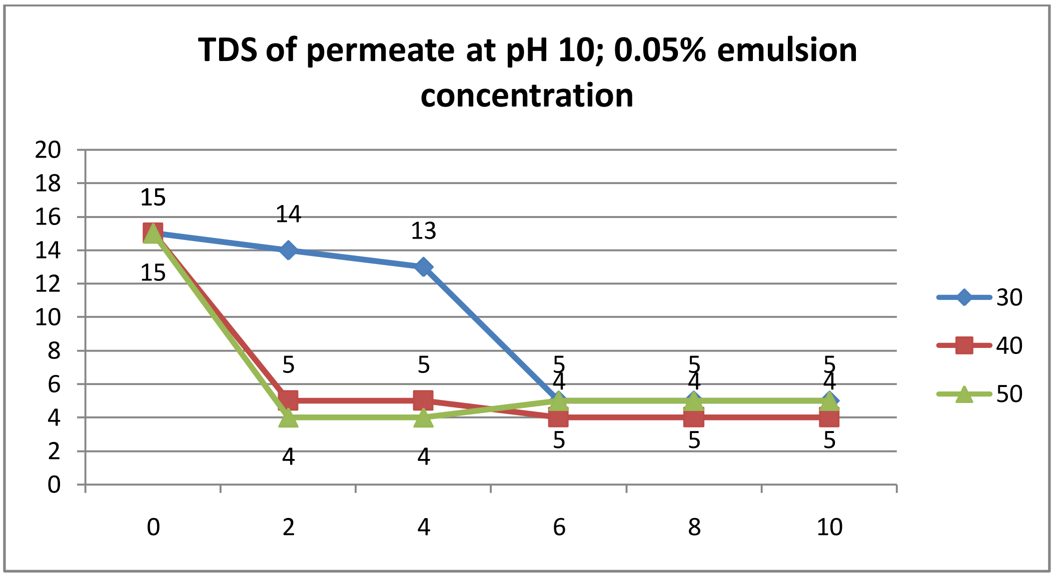


Figure 11:TDS of permeate at pH 10 in 0.05% emulsion concentration with different pressure

4.1.3 Emulsion concentration 0.10%

Table 6: TDS of permeate at pH5 in 0.10% emulsion concentration

	Time(min)	pH		
Oil/water concentration		5		
0.1		Pressure(psi)		
		30	40	50
	0	40	17	14
	2	30	11	11
	4	25	10	6
	6	23	9	6
	8	23	8	5
	10	23	7	5

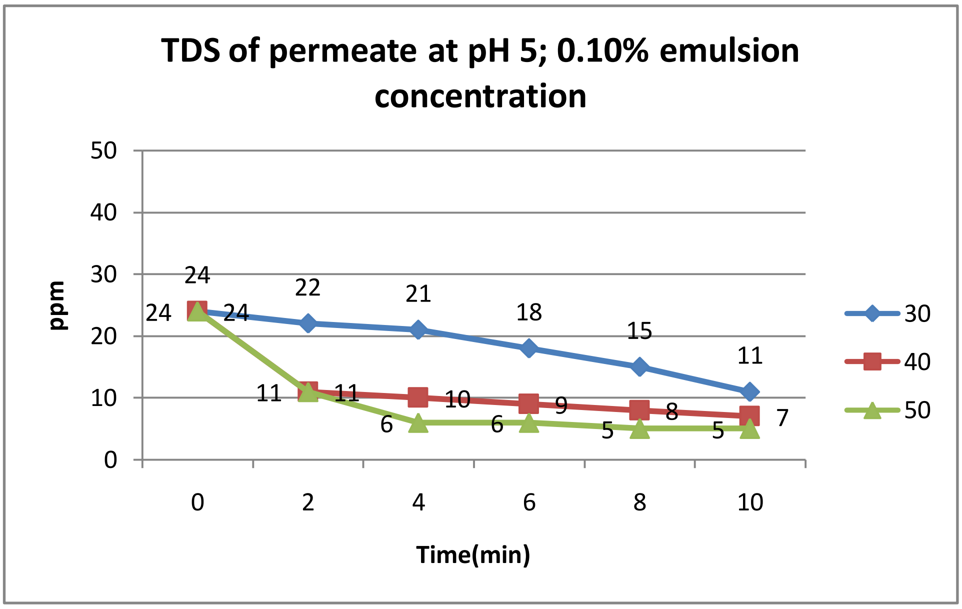


Figure 12:TDS of permeate at pH 5 in 0.10% emulsion concentration with different pressure

Table 7: TDS of permeate at pH7 in 0.10% emulsion concentration

	Time(min)	pH		
Oil/water concentration		7		
0.1		Pressure(psi)		
		30	40	50
	0	133	23	26
	2	113	24	28
	4	88	24	26
	6	59	35	25
	8	23	27	25
	10	23	24	25

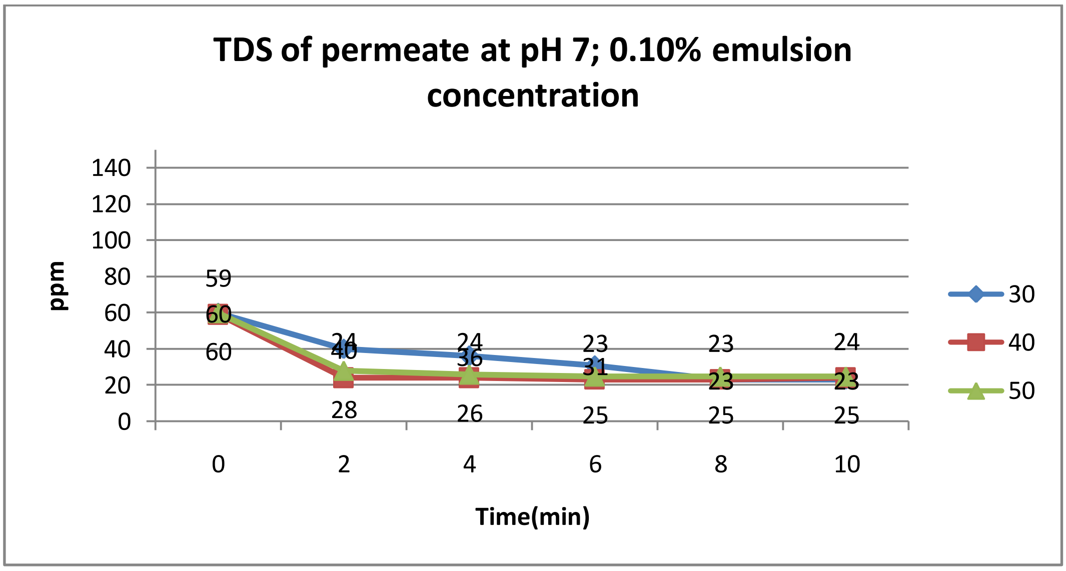


Figure 13:TDS of permeate at pH 7 in 0.10% emulsion concentration with different pressure

Table 8: TDS of permeate at pH10 in 0.10% emulsion concentration

	Time(min)	pH		
Oil/water concentration		10		
0.1		Pressure(psi)		
		30	40	50
	0	38	25	36
	2	32	25	28
	4	28	26	27
	6	24	26	26
	8	24	26	26
	10	24	27	26

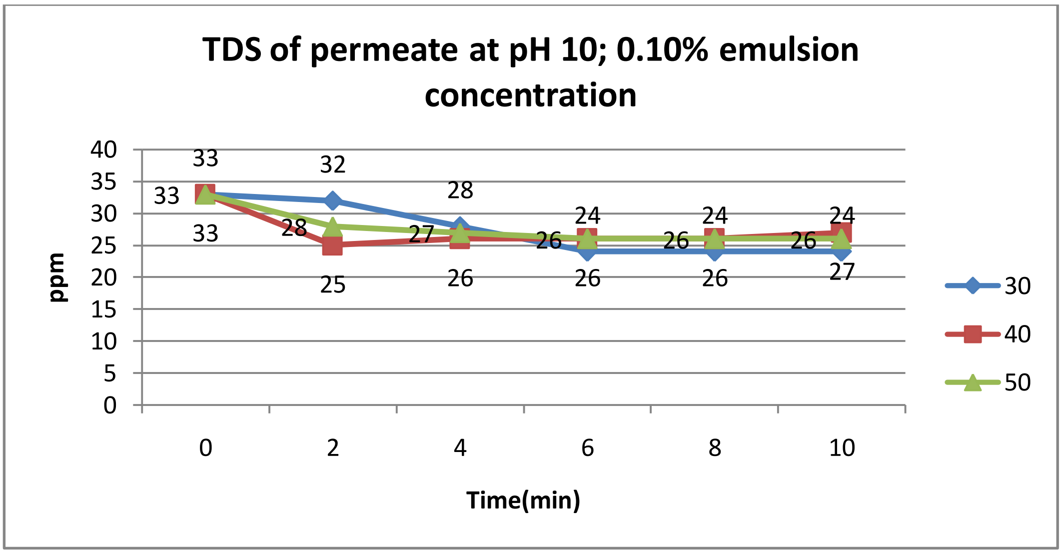


Figure 14:TDS of permeate at pH 10 in 0.10% emulsion concentration with different pressure

4.1.4 Emulsion concentration 0.15%

Table 9: TDS of permeate at pH5 in 0.15% emulsion concentration

	Time(min)	pH		
Oil/water concentration		5		
0.15		Pressure(psi)		
		30	40	50
	0	42	24	30
	2	30	24	24
	4	25	21	22
	6	24	21	18
	8	23	21	17
	10	23	20	16

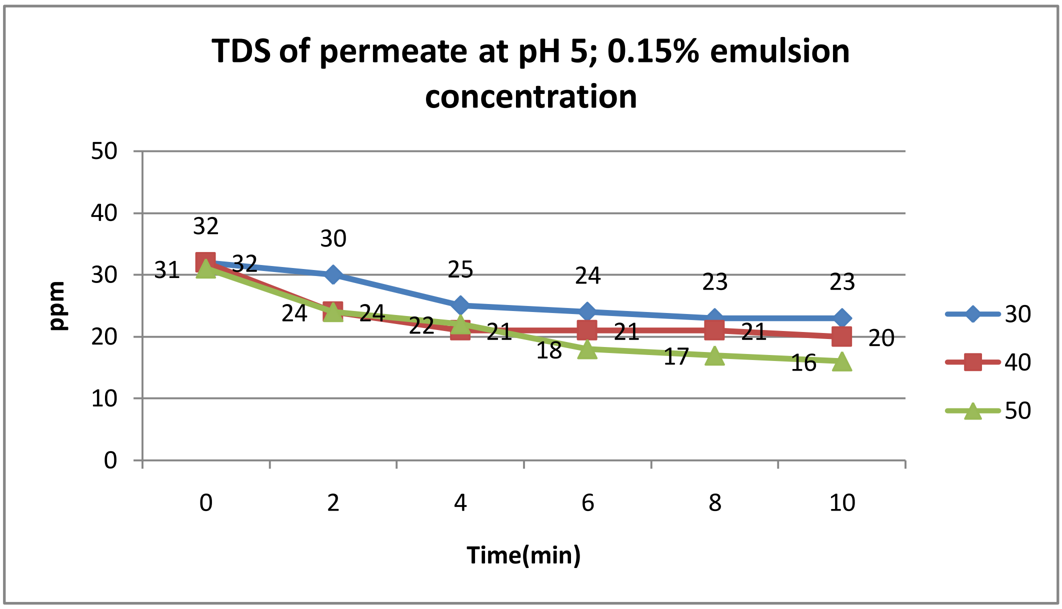


Figure 15:TDS of permeate at pH 5 in 0.15% emulsion concentration with different pressure

Table 10: TDS of permeate at pH7 in 0.15% emulsion concentration

	Time(min)	pH		
Oil/water concentration		7		
0.15		Pressure(psi)		
		30	40	50
	0	37	23	16
	2	25	18	12
	4	20	14	8
	6	17	12	8
	8	15	11	7
	10	14	10	7

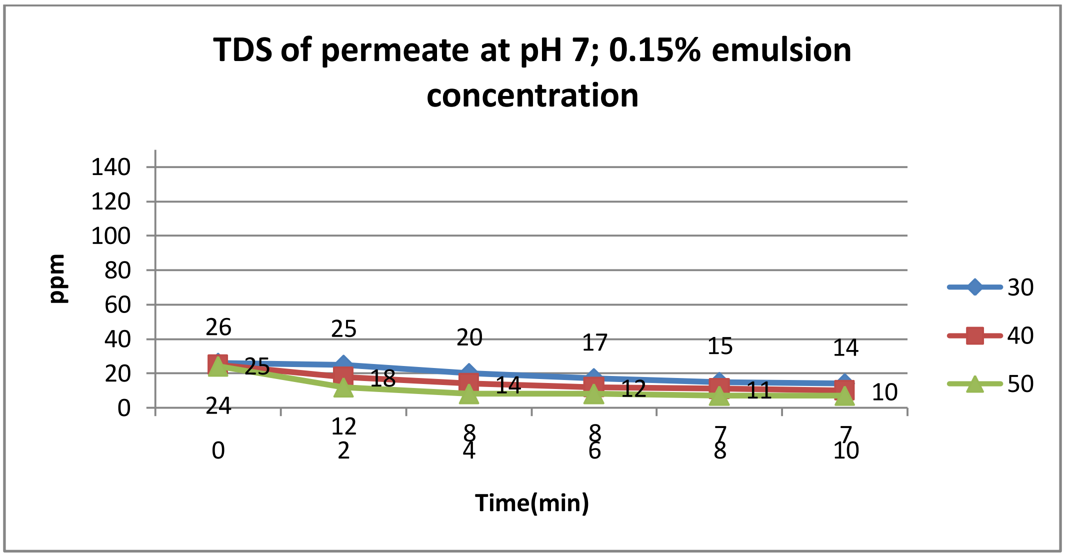


Figure 16:TDS of permeate at pH 7 in 0.15% emulsion concentration with different pressure

Table 11: TDS of permeate at pH10 in 0.15% emulsion concentration

	Time(min)	pH		
Oil/water concentration		10		
0.15		Pressure(psi)		
		30	40	50
	0	47	43	36
	2	34	34	27
	4	27	28	24
	6	27	28	23
	8	27	27	23
	10	27	26	22

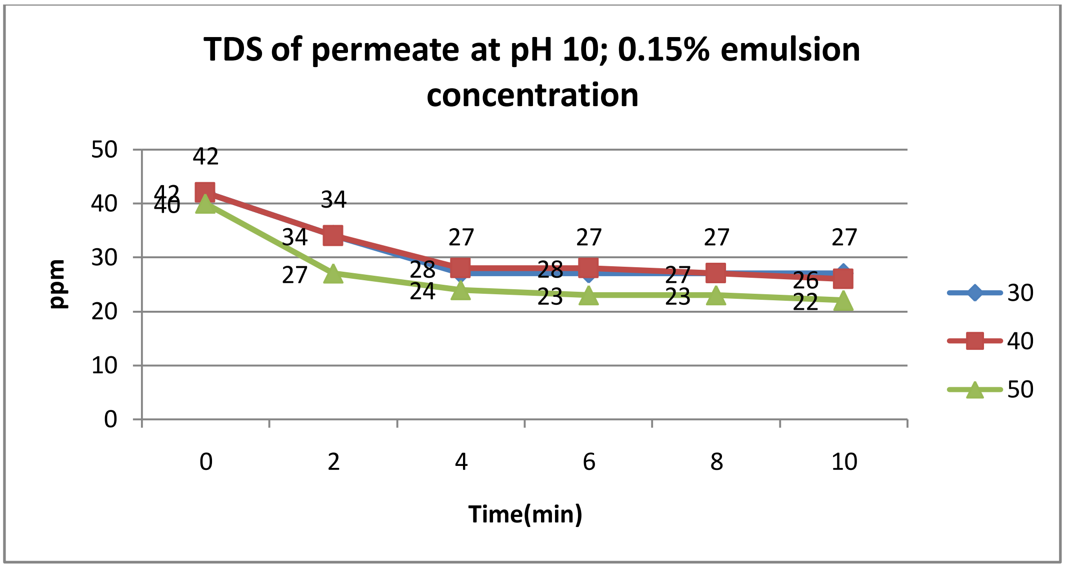


Figure 17:TDS of permeate at pH 10 in 0.15% emulsion concentration with different pressure

4.2 DISCUSSION

4.2.1 Droplet size of emulsion under microscope

From the Diagram 8, the droplet size of mixture is large and there are lot of space between the droplets. The measured droplet size of emulsion without emulsifier under optical mircoscope is 13269 micron. The droplet size of mixture with emulsifier in the Diagram 9 is small and the gap between the droplets is very close.

4.2.2 Effect of pressure

From the tabulated data, it shows that the TDS value is initially found to decline rapidly with time and finally become almost constant with time. The possible reason of the trend is pore blocking due to the existance of oil droplets and concentration polarization because of increase in retentate concentration. The lowest TDS value can be achieve by RO membrane is 3ppm where the pressure is 50psi compare to 30psi and 40psi where the TDS value is 4ppm and 5ppm respectively. The high TDS value indicate that the quality of permeate water is low. Therefore, it shows that the increase of pressure can increase the efficiency of removal waste oil-water emulsion.

4.2.3 Effect of pH value

The pH value of feed had shown variety trend of oil/water removal. For 0.05% oil/water concentration, the pH value of 5 could reduce the TDS value until 3ppm compared to pH 7 and 10. However, for 0.1% oil/water concentration the lowest TDS can be achieved is 5ppm with 5pH value. As the concentration increase, the optimum pH for low TDS value also increase whereby 7 is the optimum value. Collectively, the pH does not significantly affect the removal of oil-water emulsion since the trends are vary for each concentration.

4.2.4 Effect of oil/water concentration

The effect of oil/water concentration indicates that as the concentration increase the TDS value increase. The smallest TDS can be achieve by 0.05% oil/water concentration with 3ppm but as the concentration increase, the TDS also increase which shows that the removal of emulsion is not efficient. This may relate to the increase in resistance to permeate flow due to formation of thicker oil layer on the membrane surface with oil/water of higher concentration.

4.2.5 Effect of alumina powder

The presence of alumina powder also helps in producing good permeate water. This can be seen in the Figure 15 where the total dissolve solid on permeate decreasing.

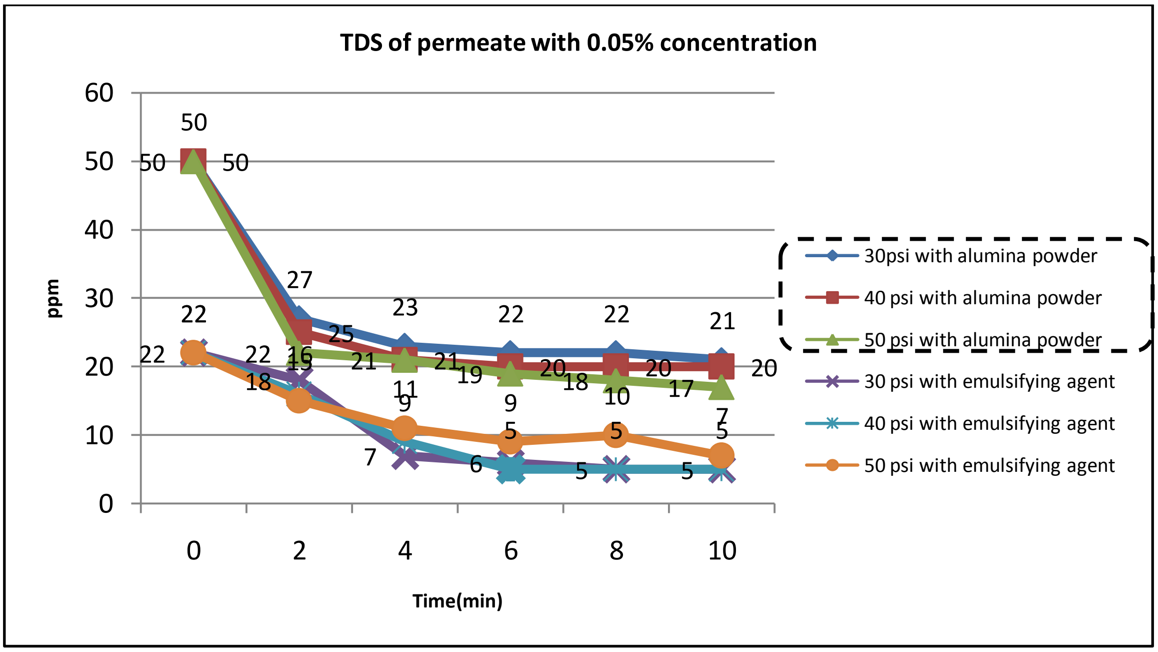


Figure 18: TDS of permeate with 0.05% emulsion concentration with alumina powder and emulsifying agent

4.3 PROBLEM ENCOUNTERED

There are several problems encountered in conducting the experiment. These problems might affect the accuracy of experimental results.

a. **Availability of Reverse Osmosis Membrane equipment**

   The equipment had technical problem which are leaking and pump malfunction. These problem had delay the experiment thus affect the timeline of the project.

b. **Ratio estimation of concentration of emulsion**

   The large feed tank required a large amout of emulsion but due to the distance of emulsion preparation and RO membrane equipment is quite far and the agitator can handle only small amount of volume of emulsion, it is suggest to use ratio estimation.

CHAPTER 5

CONCLUSION

In conclusion, this project is believed to have great contribution on industry especially refinery industry. Reverse osmosis membrane technology has a great potential in removal of oily emulsion as compared to other conventional method.

Based on the results, the low total dissolve solid of permeate prove that the oil in water emulsion can be remove effectively by reverse osmosis membrane. Pressure and oil/water concentration play an important role in the efficiency of reverse osmosis membrane. However, pH value does not really have significant effect of the separation process. The oil layer on the membrane surface could decrease the performance of the membrane.

As a recommendation, the research could be continued by using different type of membrane with different method of emulsion preparation. Besides that, the microscopic view of emulsion from different pH also can be studied to identify either pH value could affect the property of emulsion.

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