Separation of oil in water emulsions using integrated membrane technique

By

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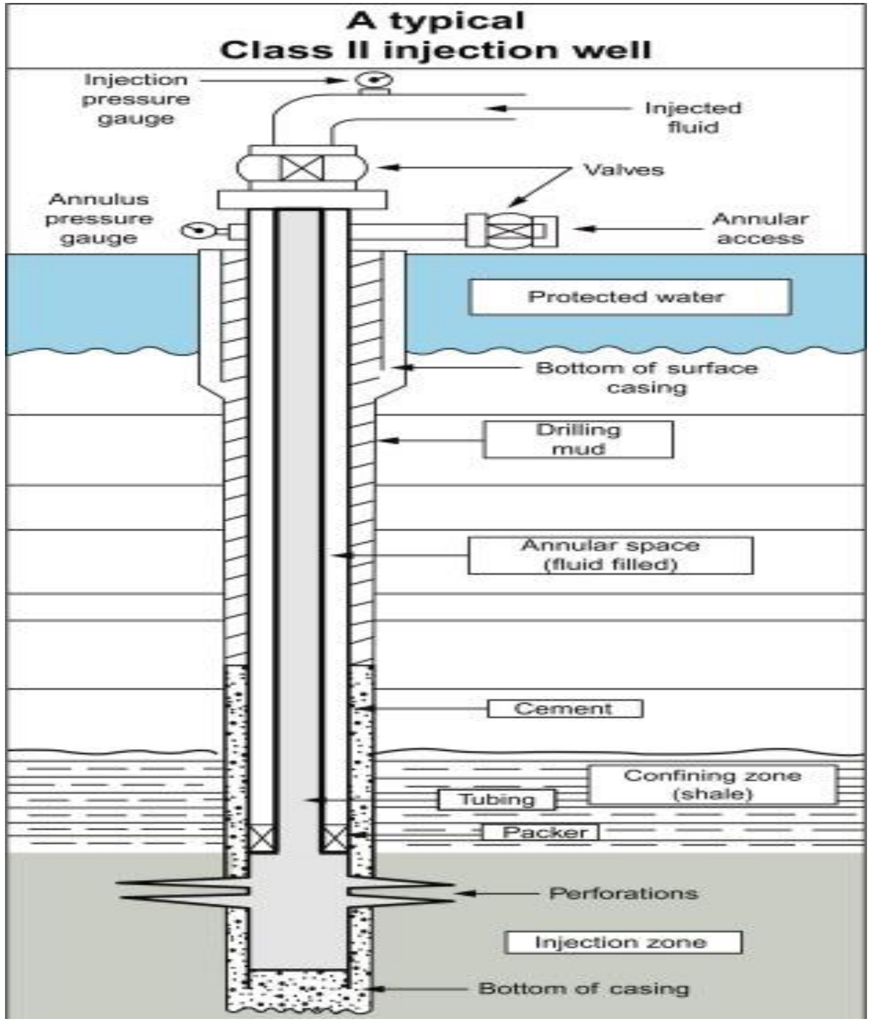
Typical well head with water injection technique



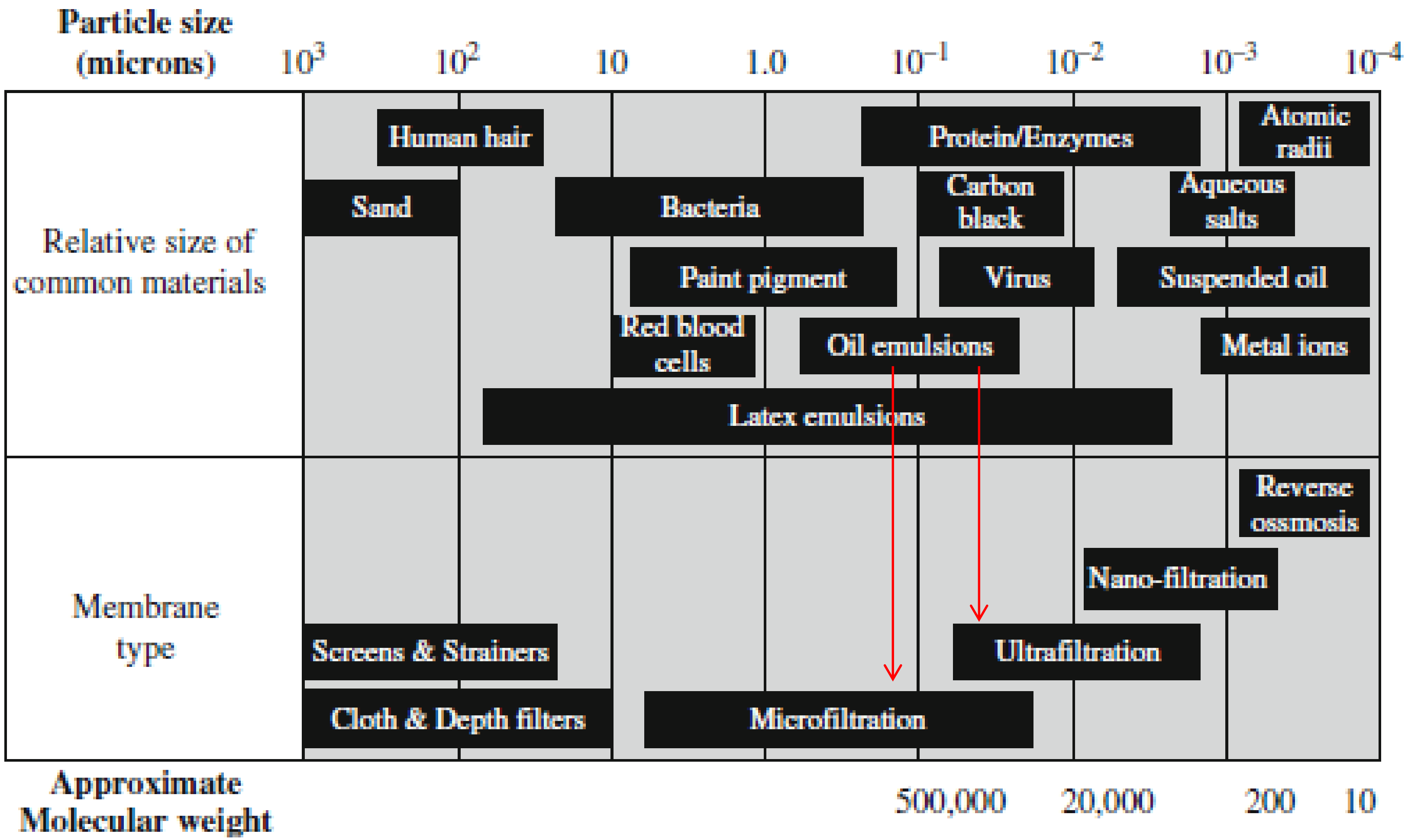
The Problem

- The oil /water separation stage is the most important stage at the oil industry.

- Oily wastewater (more than 15 ppm) is toxic, harmful and has potential risks to the marine environment.

- The high salinity of the produced water , which can’t be reinjected directly to the well head and the sea water.

Membranes Types

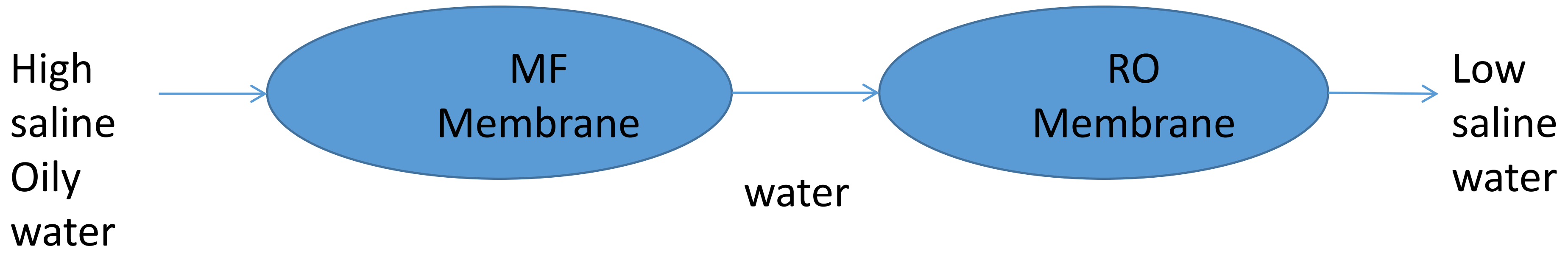


Membrane process selection for various oil droplet size categories

Aim of Work

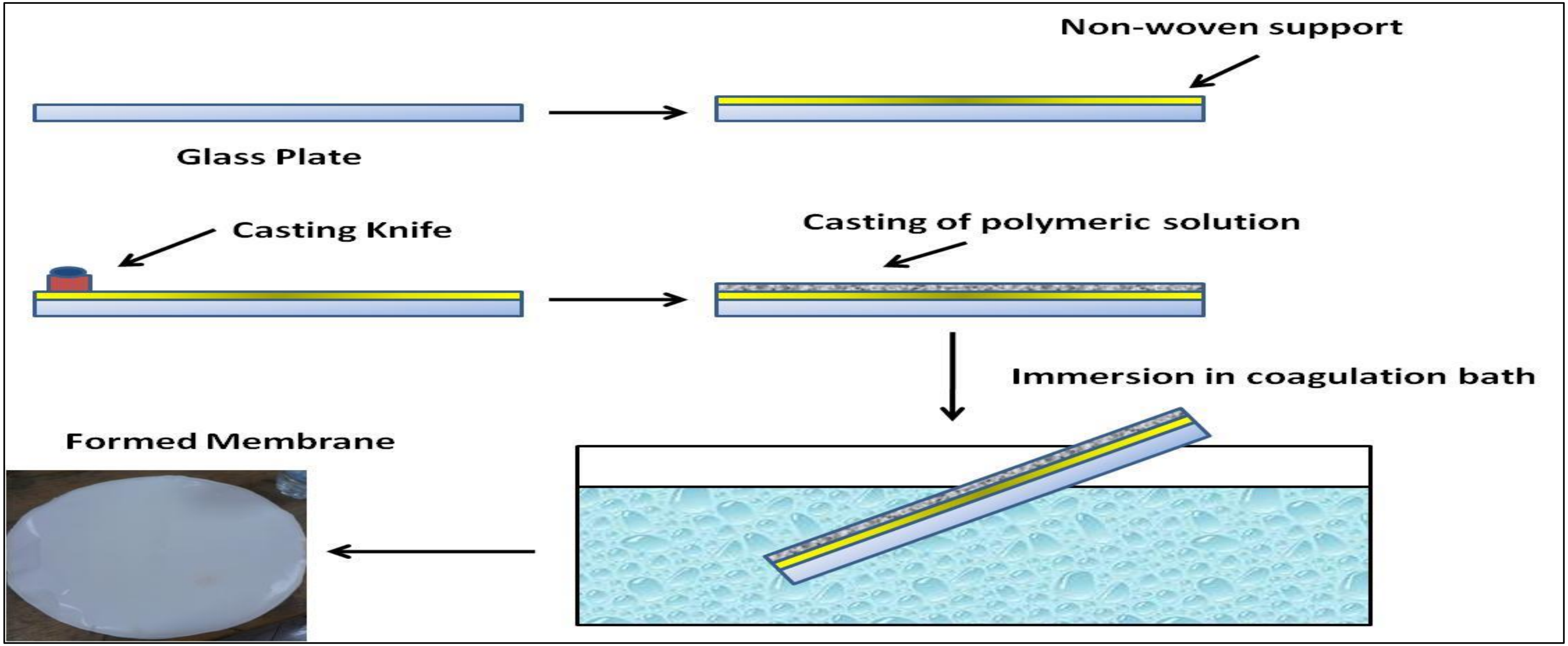
- Preparation of an antifouling and antibacterial blend microfiltration membrane that can be used in oily wastewater treatment in the oil field to improve quality of oil/water separation (max. 15 ppm).

- Prepare self-cleaning Reverse Osmosis membrane to reduce the salinity of the water received from the microfiltration unit to be used and reinjected to the well head.



1. Microfiltration Membranes

- **Membrane preparation**



1. Microfiltration Membranes – Cont'd

- **Analysis :**
- **a. Membrane Performance :**

1. Oil separation % vs. different membrane type.

2. Permeate flux % vs. different membranes types at 2 bar with 0.1 g oil/l .

3. Bacterial removal % vs. different membranes types at 2 bar with 0.3 g oil/l.

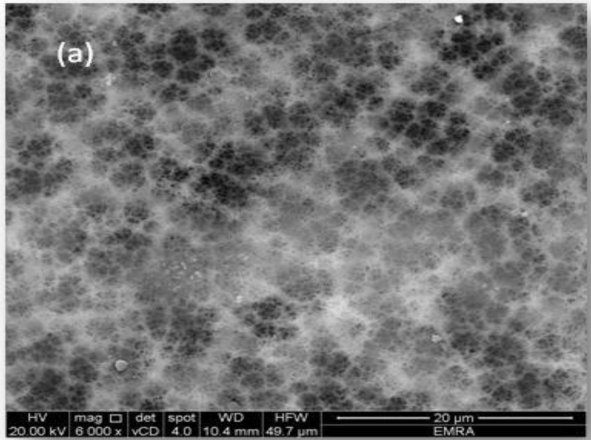
4. Membrane Fouling Testing.

1. Microfiltration Membranes–Cont'd

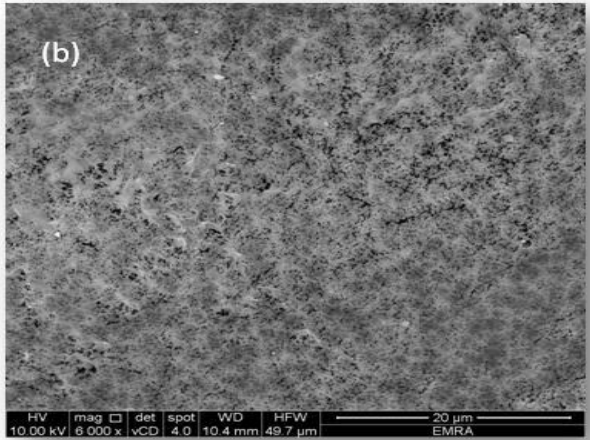
- **Analysis :**
- **b. Membrane Characterization:**

1. Scanning electron microscopy (SEM)
2. Mechanical properties (tensile and elongation)
3. Fourier transform infrared (FTIR)
4. Porosity measurements
5. Membrane contact angle
6. Thermal gravimetric analysis (TGA)

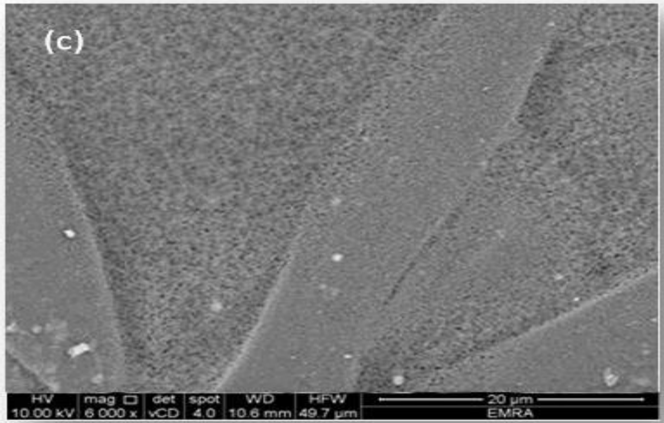
Micro Filtration Membrane
Scanning Electron Microscopy



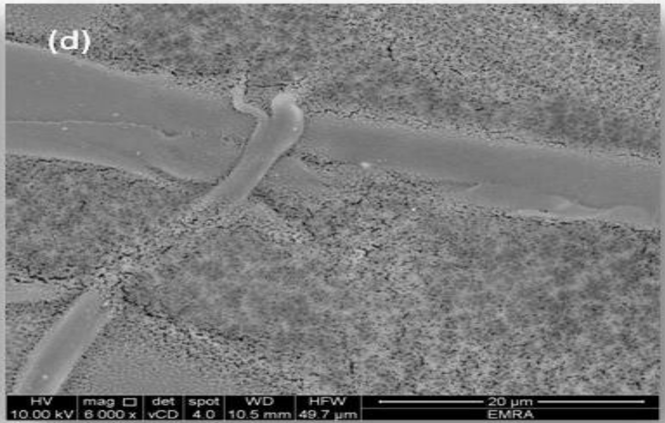
(M1)Bare PVDF



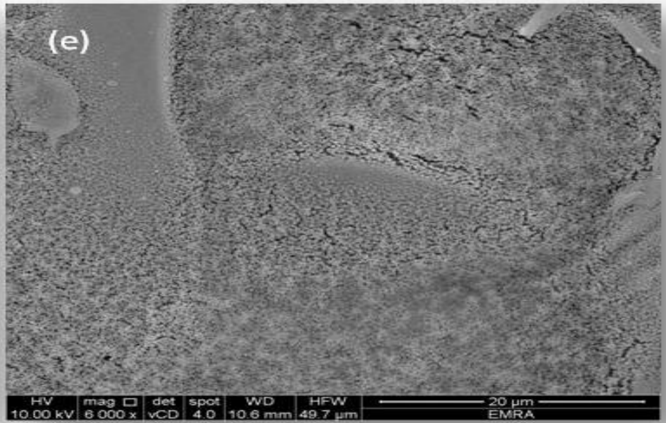
(M2) PVDF/ 0.3% PEI



(M3)PVDF/ 0.5% PEI



(M4)PVDF/ 0.7% PEI



(M5)PVDF/ 0.9% PEI

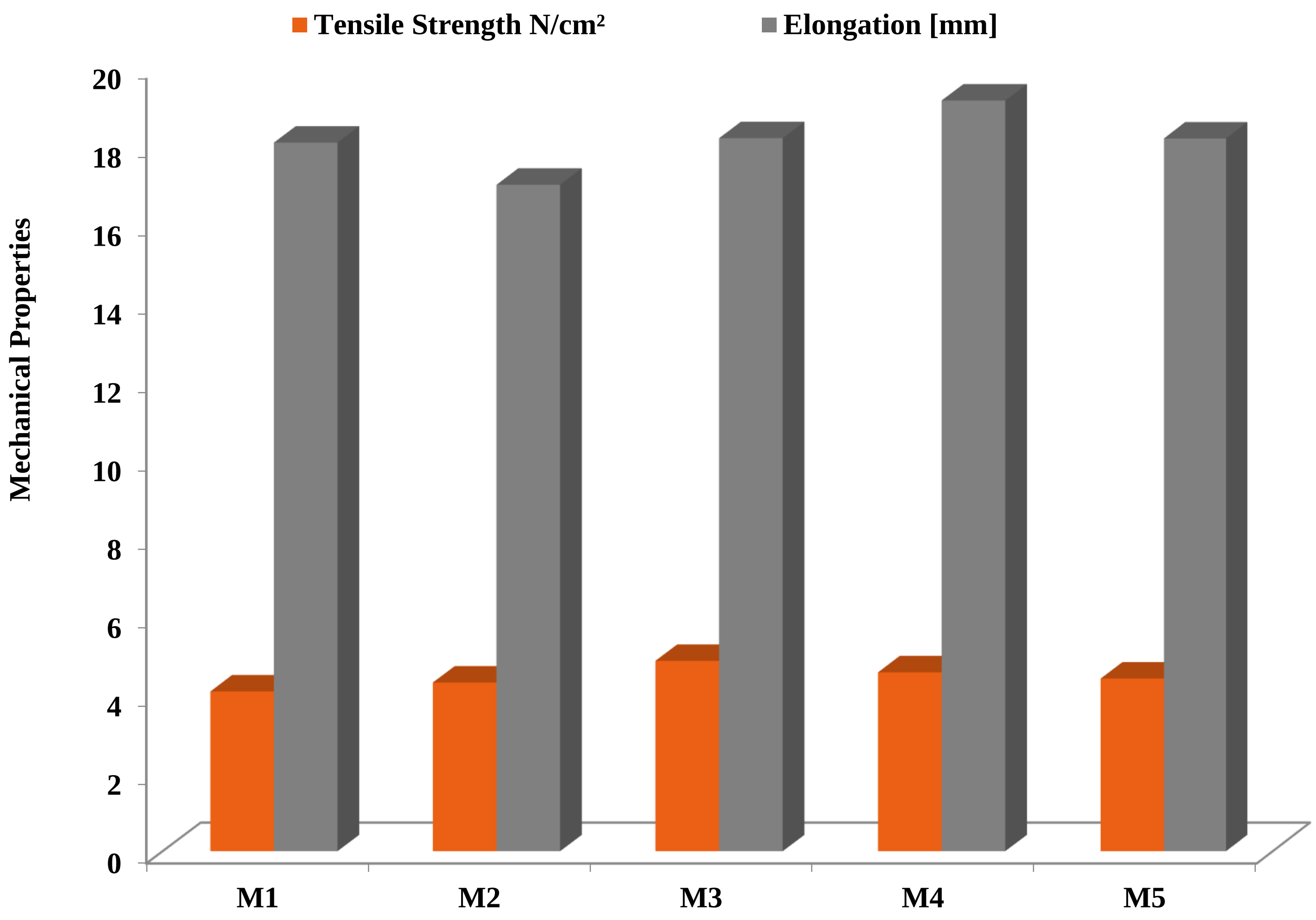
Micro Filtration Membrane Scanning Electron Microscopy-Cont'd

- M1 has largest microvoids due to addition of PEG.
- M2 pore size decreased due to the addition of 0.3 wt% PEI.
- M3 the microvoids seems to be too small due to increasing PEI (O.5 wt %)
- M4 and M5 the pores size increased , although the PEI increased to 0.7 and 0.9 wt% respectively. That is due to increasing the viscosity of polymeric solution, that as a result can make problem in the preparation step which may cause cracking of the membrane top layer.

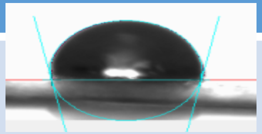
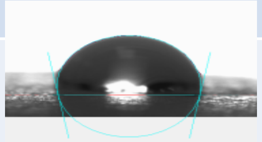
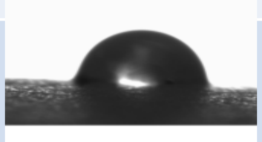
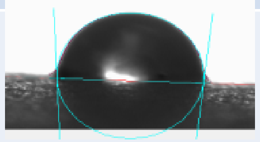
Mechanical properties

- The tensile strength is in the following sequence M3>M4>M5>M2>M1, while the elongation is in the following sequence M4>M3>M5>M1>M2.

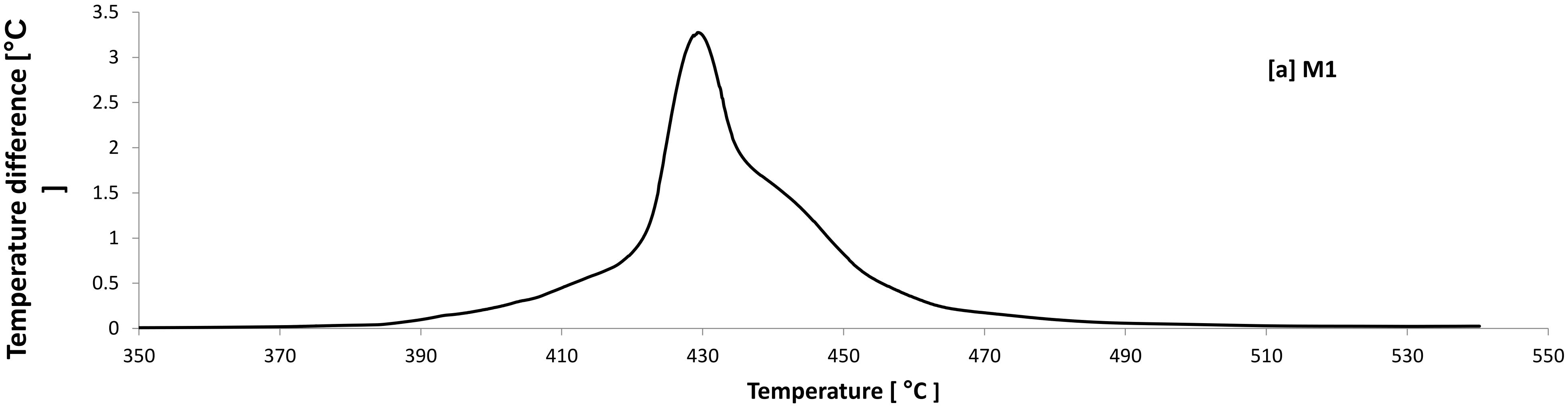
- It is obvious that M1, which was prepared only from PVDF, has the lowest tensile strength and the addition of PEI enhances the tensile strength of the rest membranes.

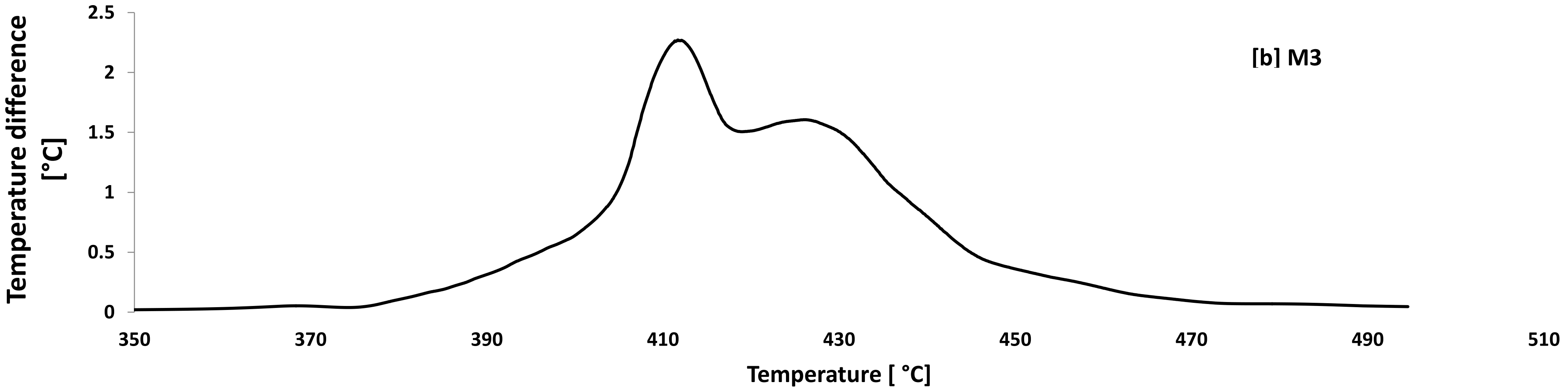


Membrane porosity, air permeability and Contact Angle

Membrane Symbol	PEI %	Porosity %	Air Permeability $cm^3/cm^2.s$	Contact Angle	Membrane wettability photos
M1	0	53.2	1.7	**100.4 º**	
M2	0.3	47.7	1.8	99.8 º	
M3	0.5	**38.2**	0.989	97.6 º	
M4	0.7	45.8	1.295	94.3 º	
M5	0.9	44.35	2.06	**78.3 º**	

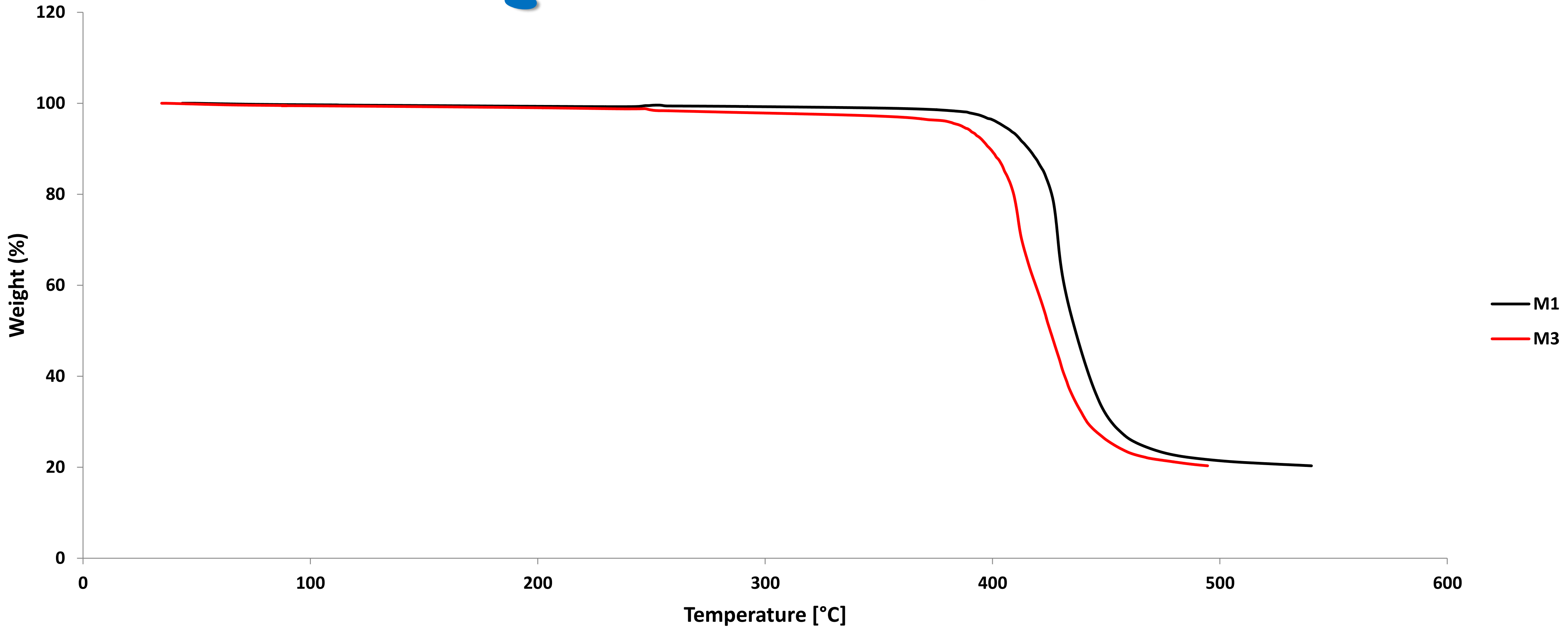
Thermo gravimetric analysis (TGA)





- By adding the PEI , the glass transition temperature of the prepared membranes decreased from 430 to 410 °C.

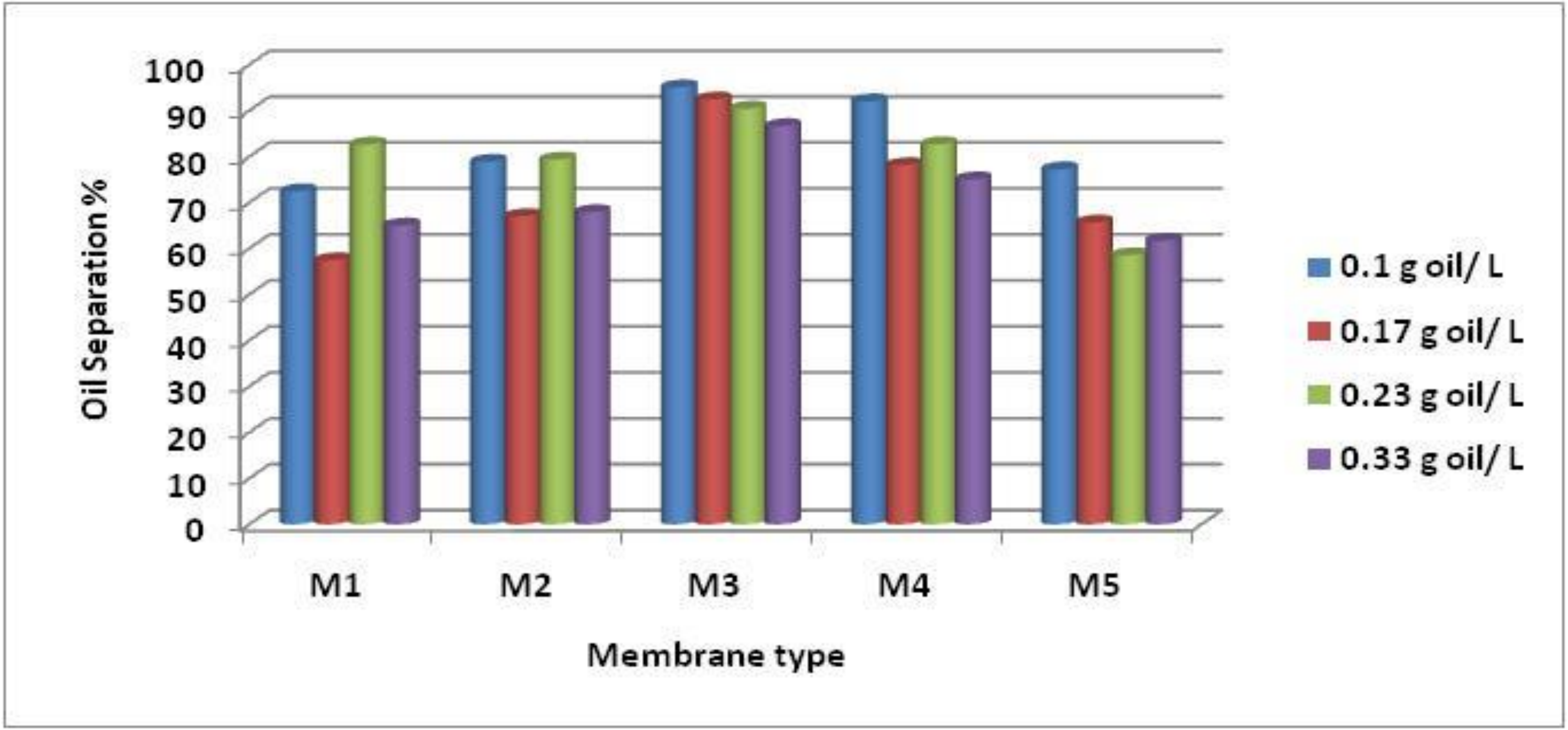
Membrane decomposition Temperature Results



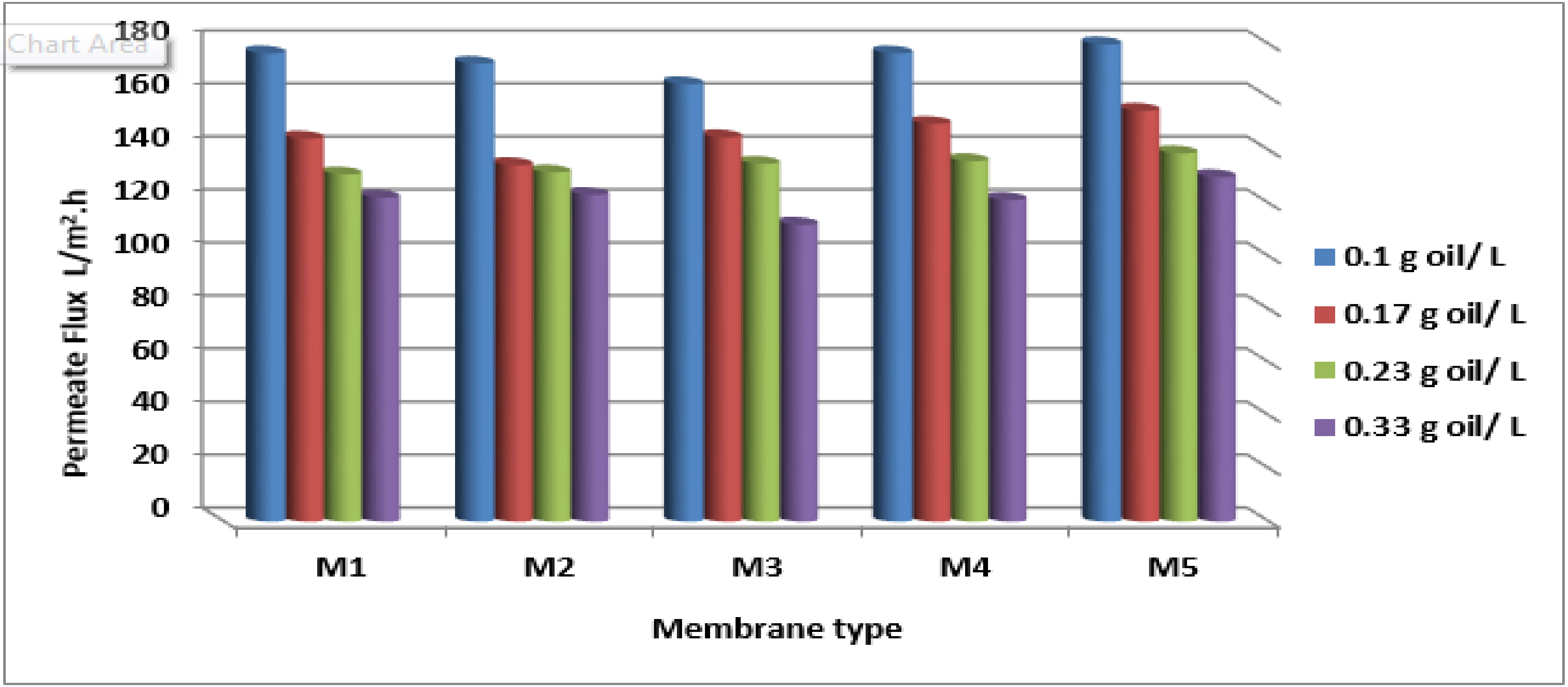
The weight loss of M1 was observed at 384 to 469 ºC to be 80% at 540 ºC.

The first weight loss step was observed at 223 to 379 ºC and the second one ranged from 407 to 463 ºC. The weight loss percent of M3 was 80% at 495 ºC.

Membrane performance
a. Oil Separation vs. membrane types

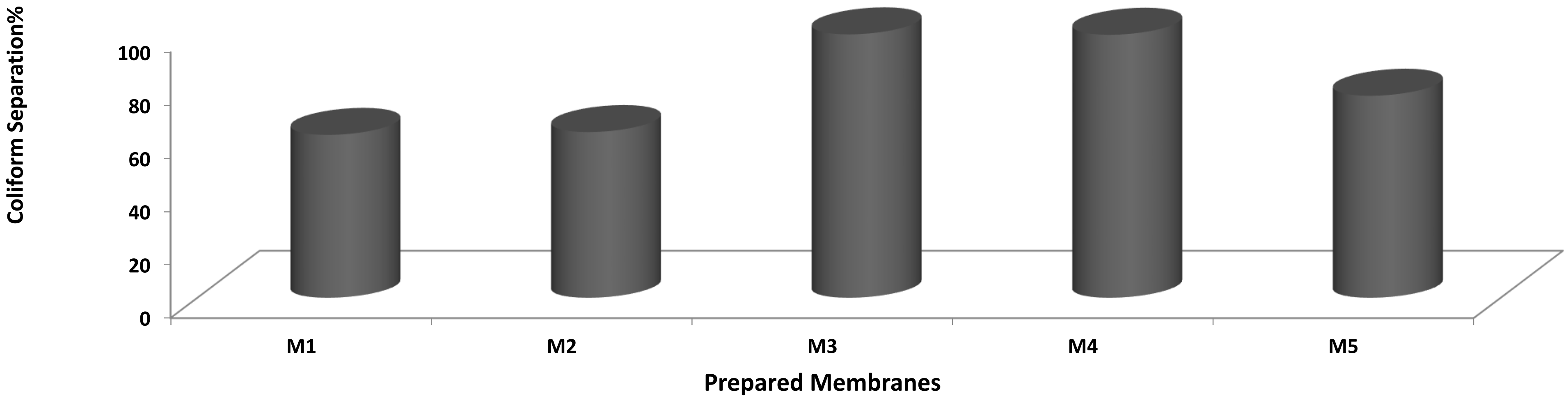


Membrane performance
b. Permeate Flux vs. membrane types



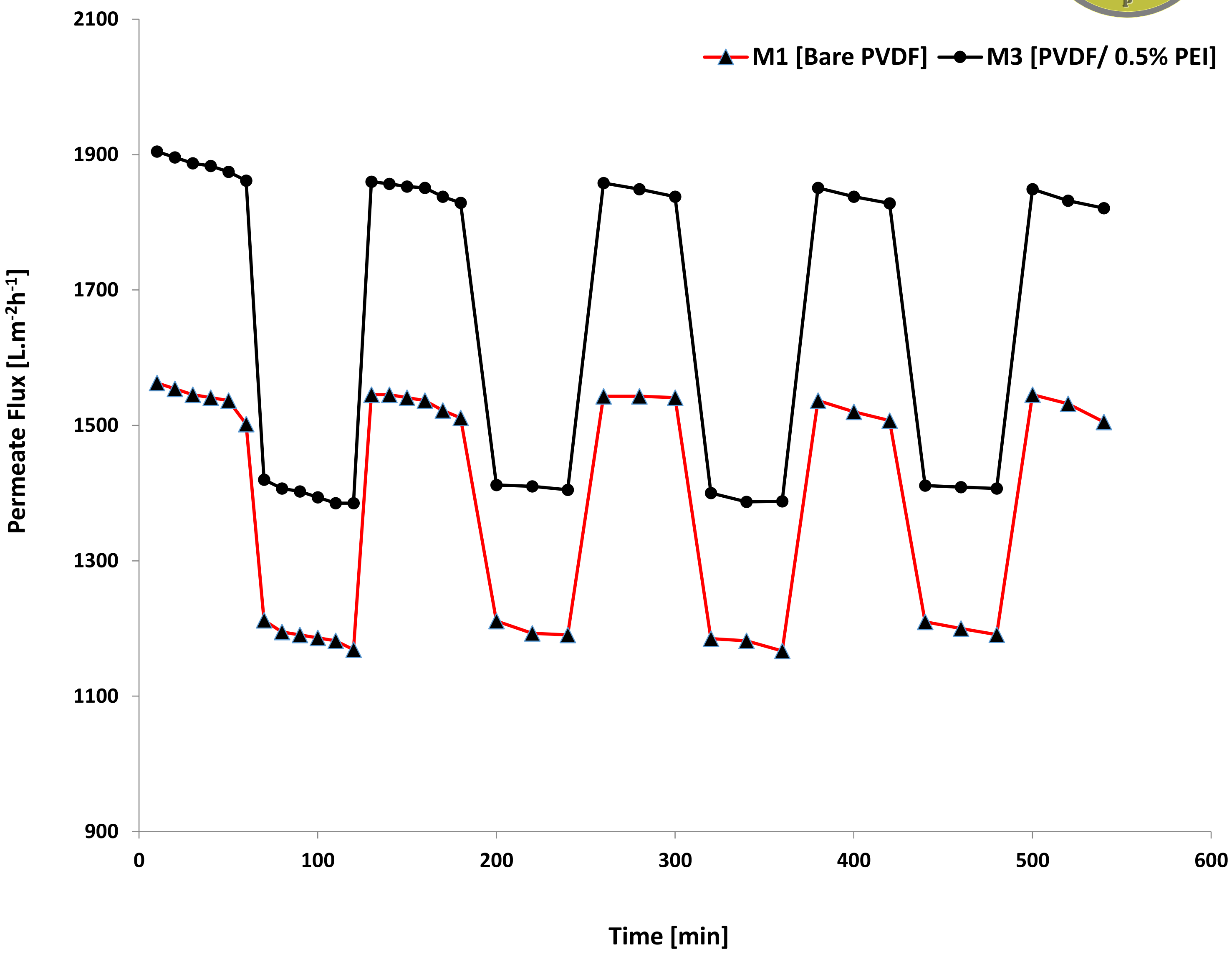
c.Pollution Control and Bacteria Removal Test

Membrane symbol	COD [mg/l]	BOD [mg/l]	Total Coliform Bacteria amount [CFU/100ml]
Feed sample	1110	660	18
M1	430	255	7
M2	420	248	6.5
M3	12	6	**0.16**
M4	16	7	**0.19**
M5	260	158	4.3



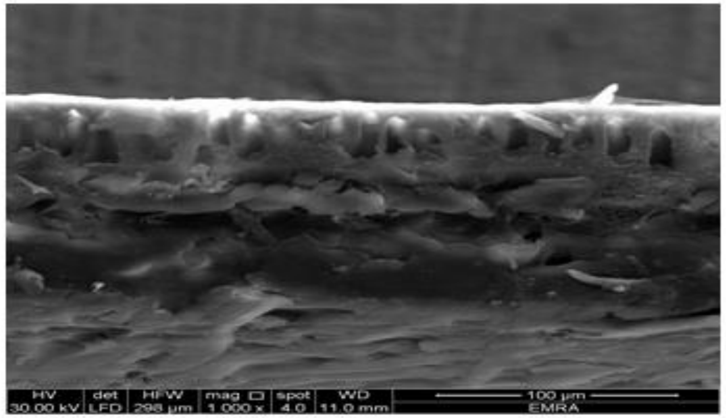
d. Membrane Fouling Testing

- (Reversible fouling ratio)Rr was 23.9% for M1 and 24.6% for M3
- (Irreversible fouling ratio) Rir was 2.2% for M1 and 0.93 % for M3
- (Flux Recovery Ratio) FRR for M1 was 97 % and for M3 was 98%
- The fouling test indicates that the addition of PEI to the polymeric solution leads to formation of antifouling membrane by decreasing irreversible resistance

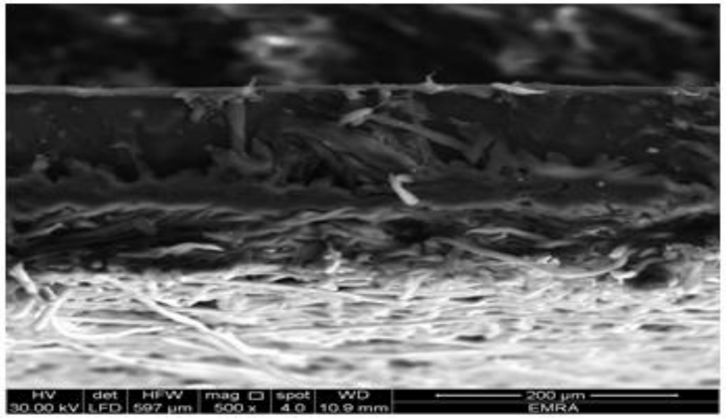


Reverse Osmosis Membrane

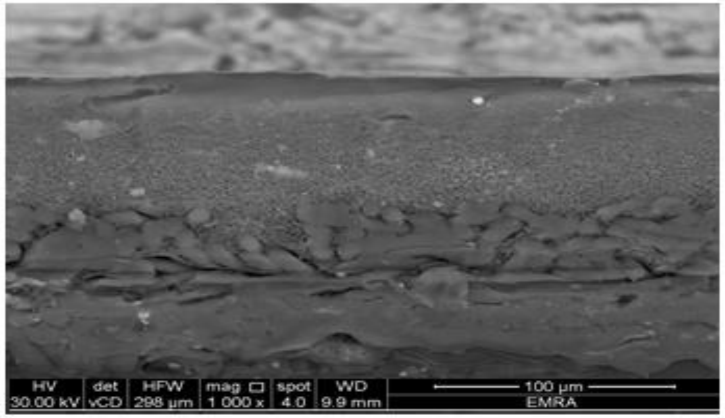
Reverse Osmosis Membranes Scanning Electron Microscopy



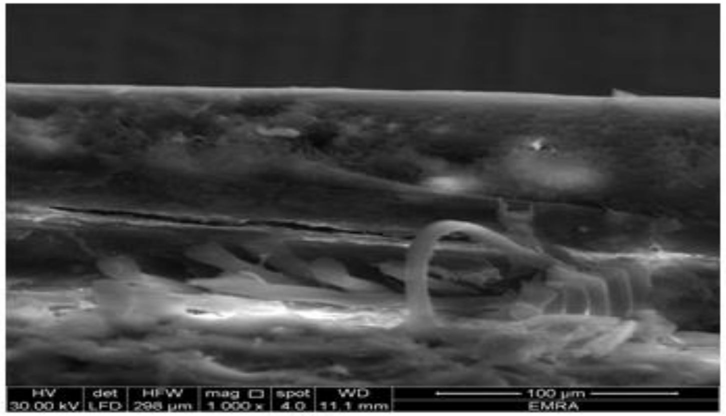
(a) R1



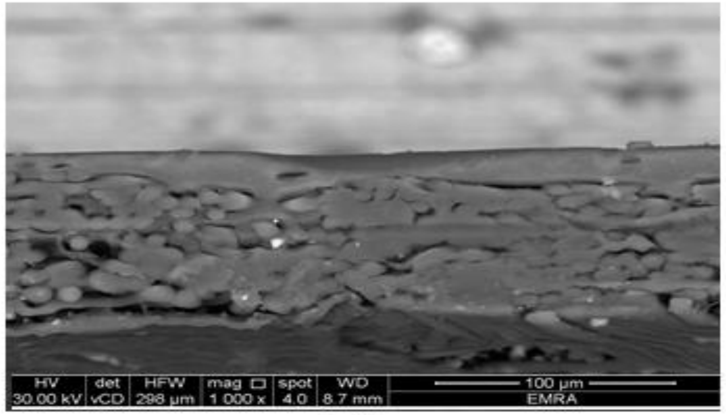
(b) R2



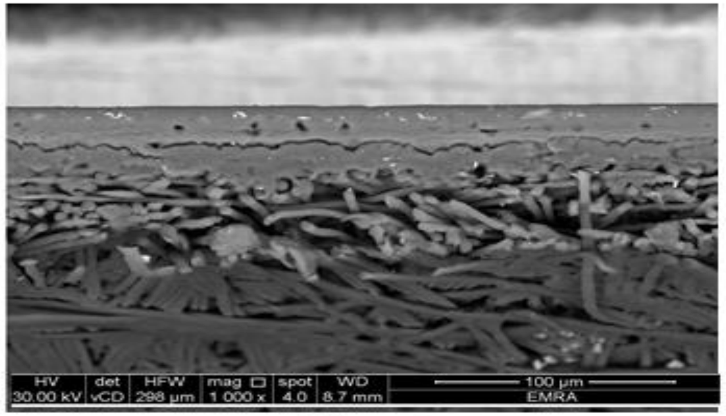
(c) R3



(d) R4



(e) R5



(f) R6

Reverse Osmosis Membranes Scanning Electron Microscopy-Cont'd

- R1 has finger like and porous structure because this membrane was prepared without ZOH or Coating.
- R2 has dense layer due to addition of ZOH solution which leads to decrease in membrane pores size.
- R3 which indicates three layers: porous bottom layer, dense spongy structure in the middle layer and highly dense top layer, due to coating the top layer of membrane by PVA crosslinking layer.

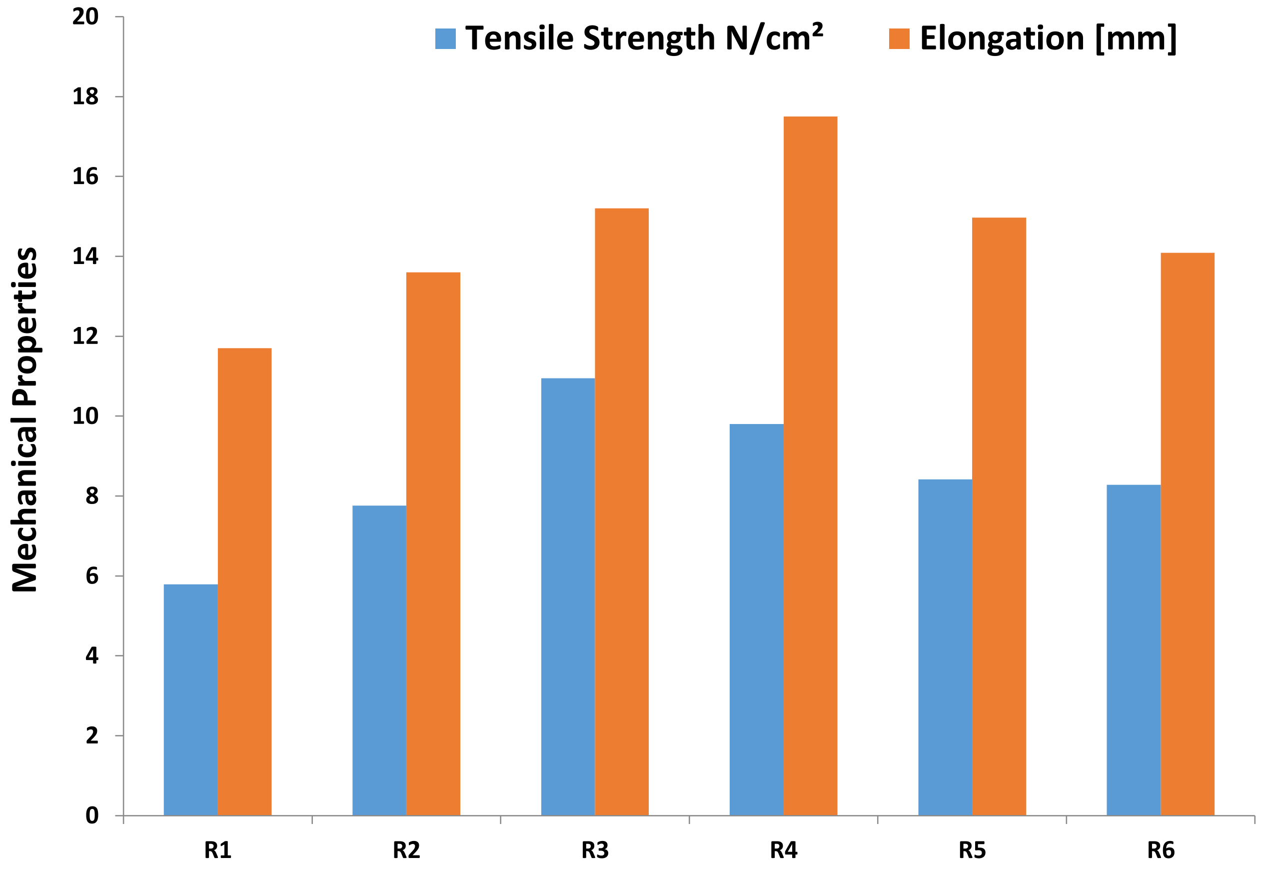
Reverse Osmosis Membranes Scanning Electron Microscopy-Cont'd

- R4 membrane; indicates also three layers porous in the bottom due to using non woven support, dense spongy structure in the middle due to increasing the percentage of ZOH to 1.5% and dense top layer.
- Due to increasing the percentage of ZOH to 2% this indicates high dense top layer for R5.
- Fig(F) indicates high dense top layer for R6 with appearance of finger like in the middle layer may be due to decreasing the ZOH percentage to 0.5%.

Mechanical Properties

- The tensile strength was in the following sequence R3>R4>R5>R6>R2>R1, also the elongation was in the following sequence R4>R3>R5>R6>R2>R1

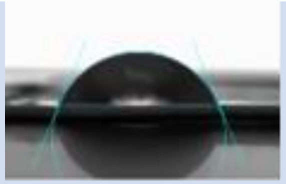
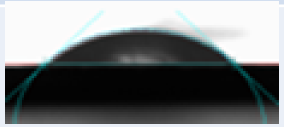
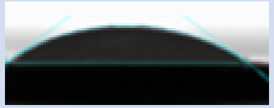
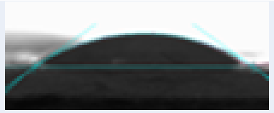
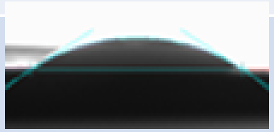
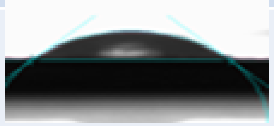
- Best was R3 with 1 wt % ZOH



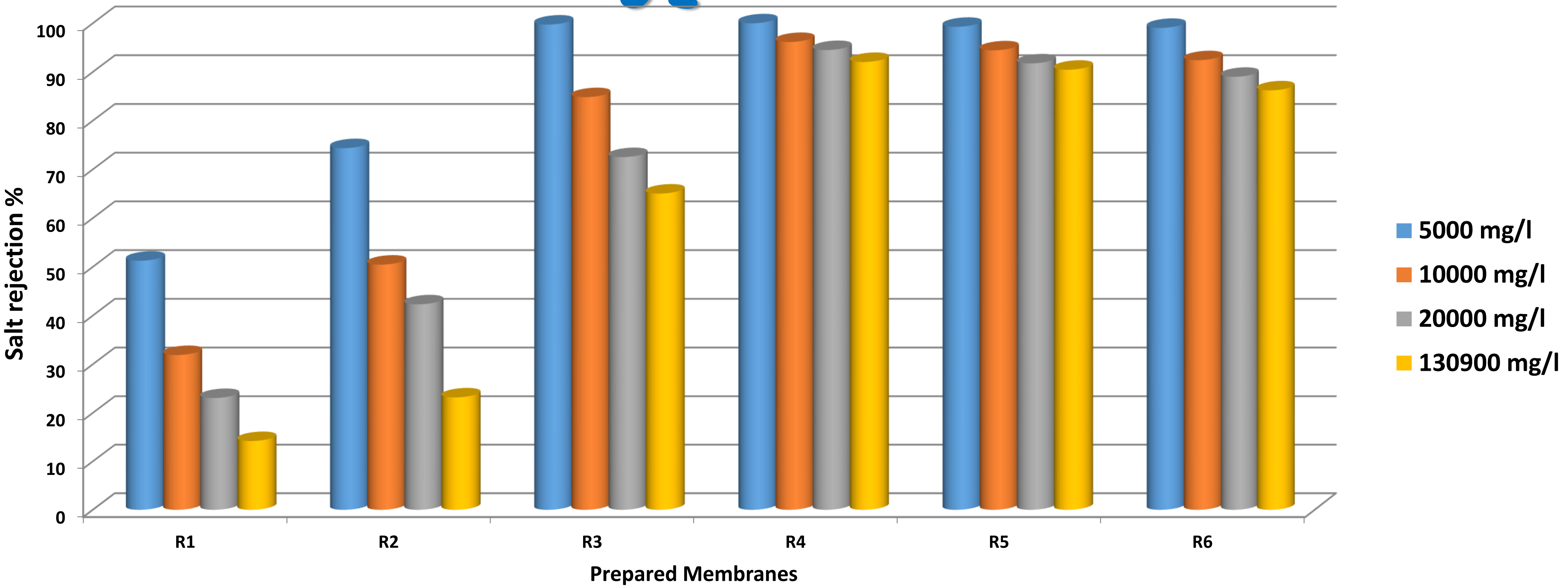
Membrane internal surface area (BET area)

Membrane Type	BET area m^2/g	Total pore volume (cm^3/g)	Mean pore diameter (nm)
R1	1.66	5.3×10^{-3}	15.2
R2	4.33	1.1×10^{-3}	8.66
R3	19.4	3.3×10^{-2}	3.2
R4	15.2	$\mathbf{5.6\times10^{-2}}$	**1.6**
R5	10.4	1.67×10^{-2}	6.6
R6	8.1	1.45×10^{-2}	7.1

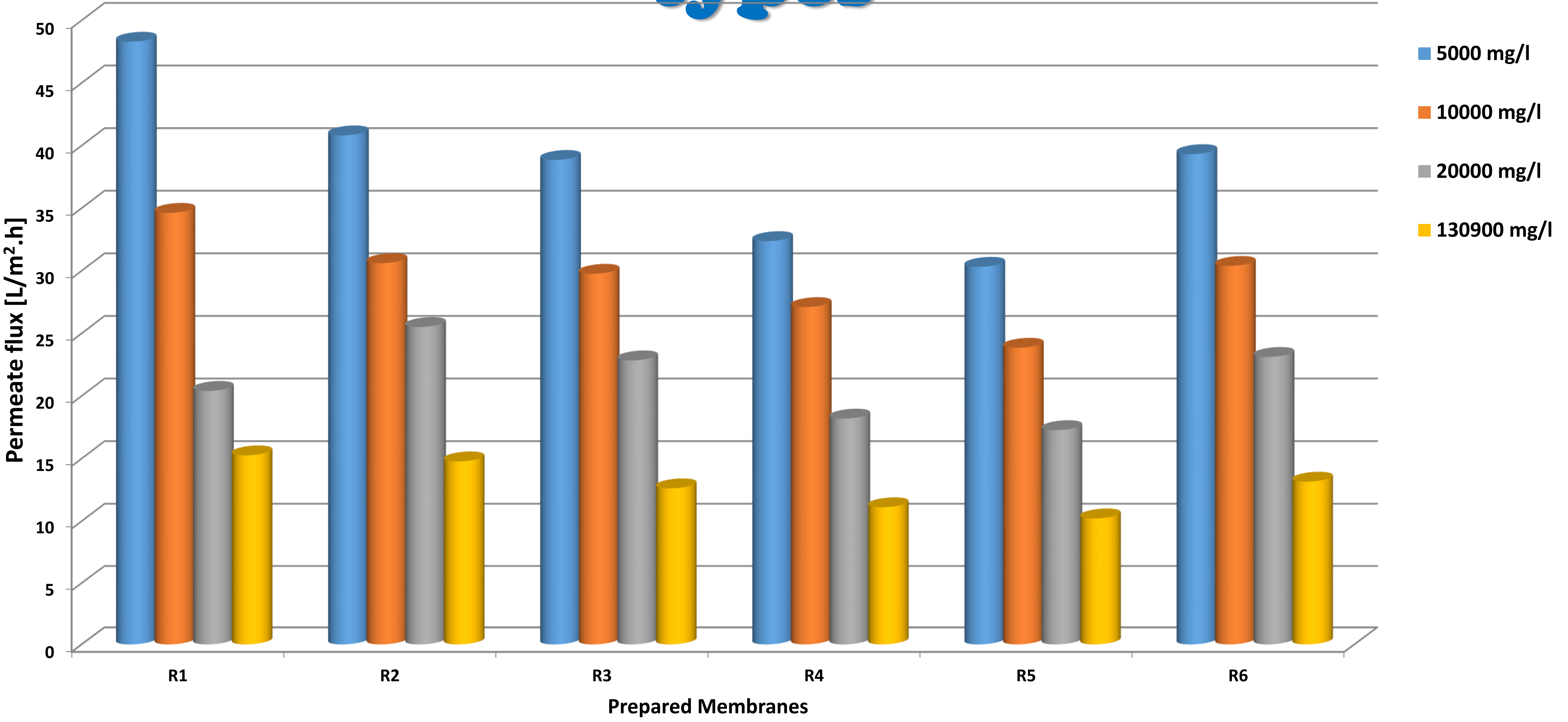
Contact angle measurement

Membrane	ZOH%	Contact angle	Membrane wettability
R1 without coating	0	**67.6°**	
R2 without coating	1.5	48.9	
R3	1	44.2°	
R4	1.5	39.7°	
R5	2	**32.3°**	
R6	0.5	46.4°	

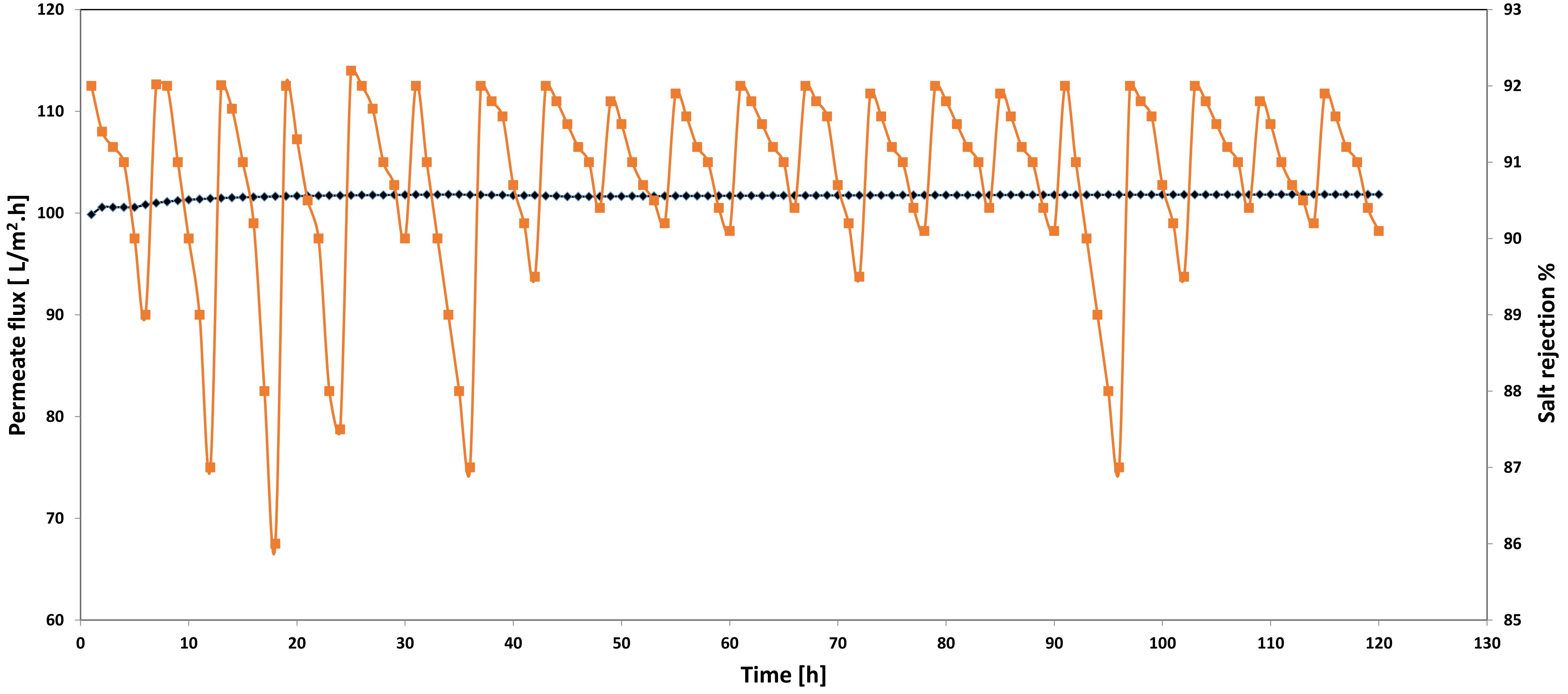
Membrane performance
a. Salt Separation vs. membrane types



Membrane performance
b. Permeate Flux vs. membrane types



Long term membrane testing



Conclusions

MF Membrane Conclusions

- PVDF/PEI blended membranes were successfully prepared via wet phase inversion technique to study the effect of various percentage of PEI on membrane performance and anti bacterial effect. The following conclusions can be drawn from the present work:

- From SEM, addition of PEI (0.5%) reduces the membrane porosity, while high percentage of PEI leads to increasing the microvoids due to increasing the viscosity of the polymeric solution which leads to delay in the phase separation and can cause cracks in the selective layer of membrane.

- The membrane performance test on oil removal indicates that the best membrane was M3, where oil separation percentage reached 95% at 0.1 g oil/ L. While, M5 (using 0.9% of PEI) provides highest permeate flux (180 L/m2.h at 0.1 g oil/ L).

MF Membrane Conclusions –Cont'd

- From the mechanical strength test, M3 membrane provides the highest tensile strength (4.872 N/cm2)with elongation of 18%.

- From contact angle test, M5 (16% PVDF,0.9% PEI) was the highest hydrophilic membrane with 78.3° contact angle while M1, which is a bare PVDF membrane , is the highest hydrophobic membrane with 100.4° contact angle.

- From bacteria removal test, M4 and M3 provides the best results of bacteria removal, due to addition of PEI because it is a microbicidal ingredient that has a variety of formulations ranges.

- Fouling test indicates that the addition of PEI improved the antifouling properties of membrane, where flux recovery reached to 98% using M3 with very low irreversible resistance (0.93%).

RO Membrane Conclusions

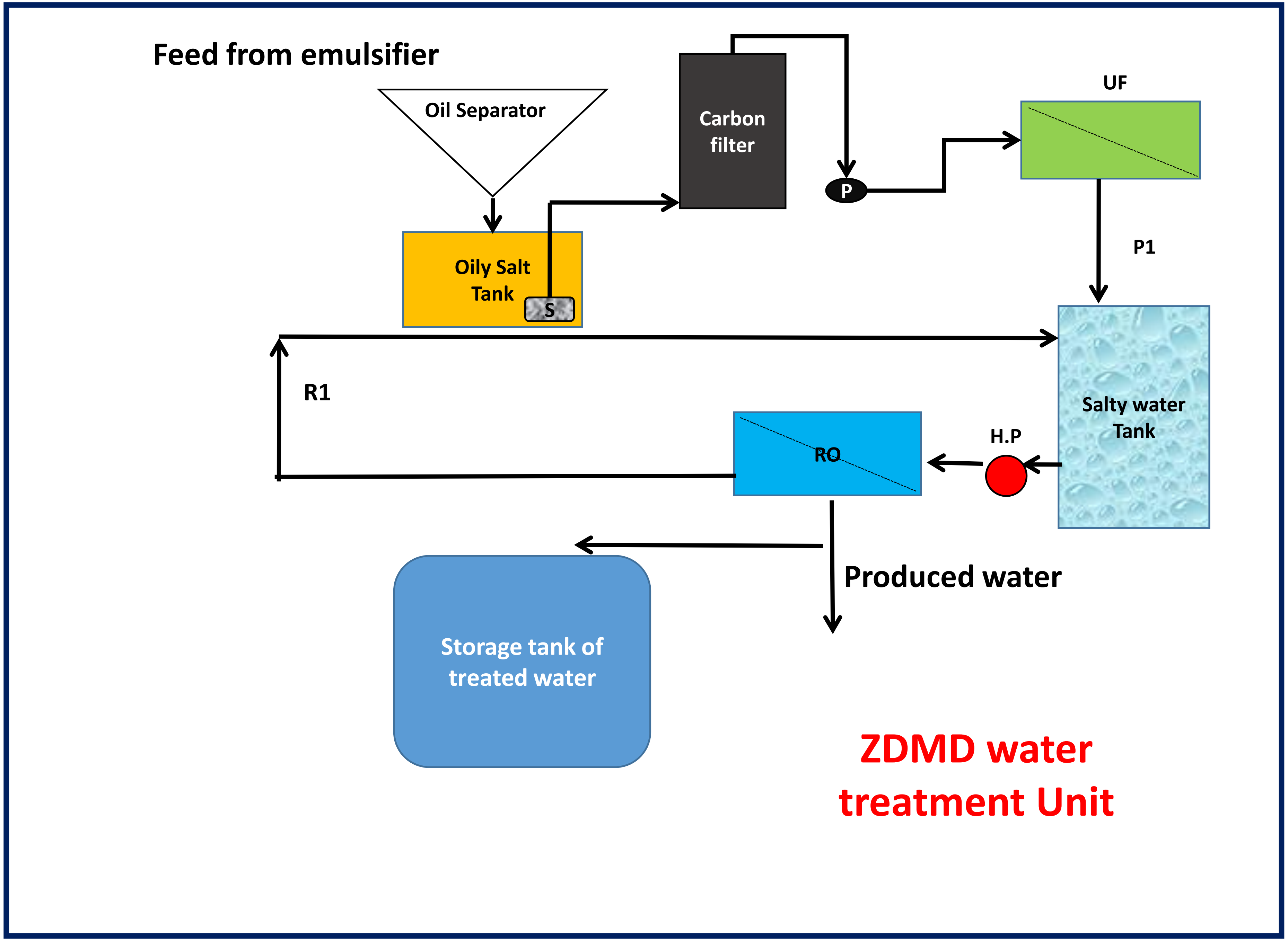
- Using ZOH solution leads to decrease in membrane pore size.

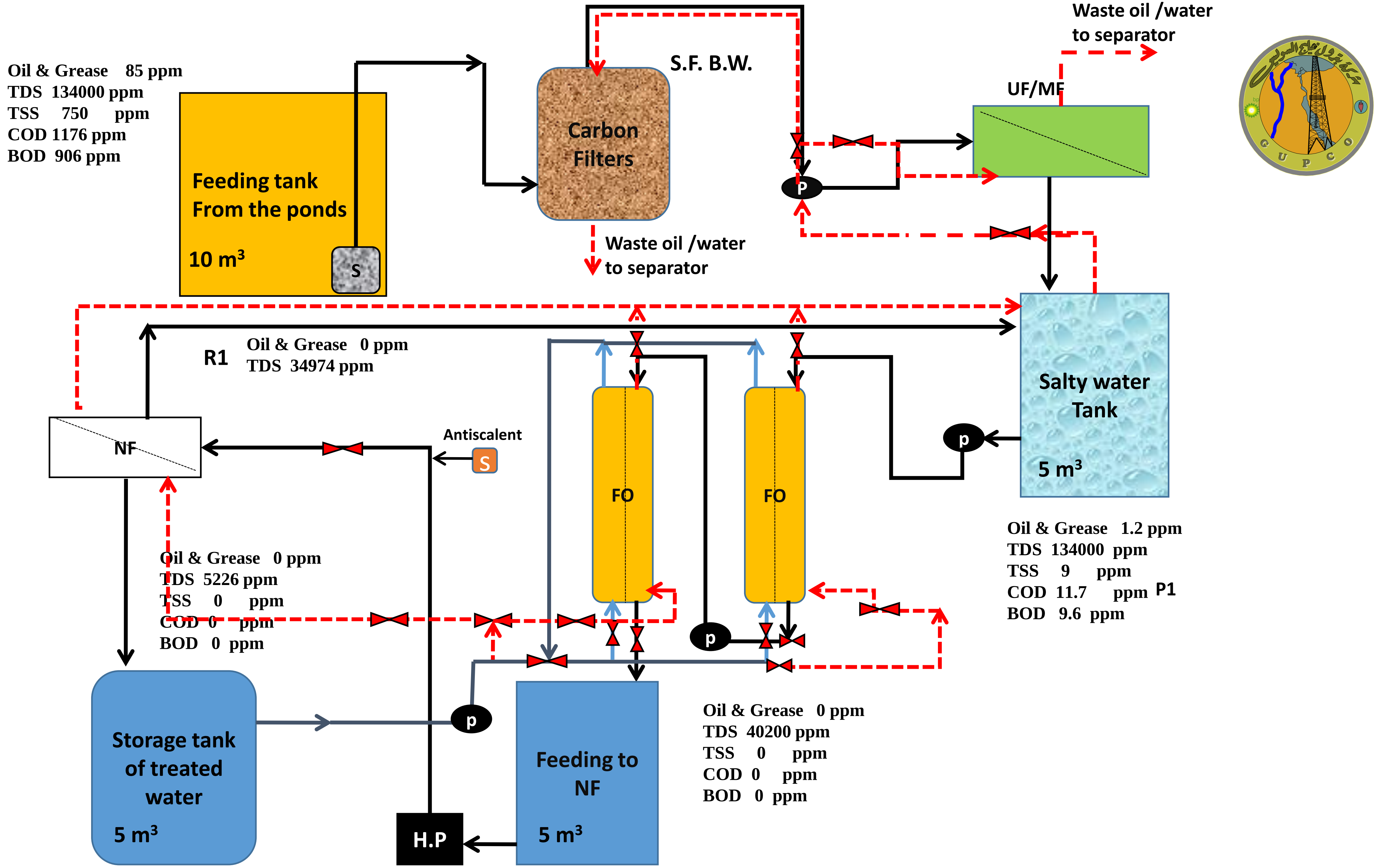
- The coating PVA layer on prepared membrane surface using ZOH during membrane preparation improve the membrane hydrophilicity as shown by reducing the contact angle of the membrane surface.

- R4 exhibits good membrane performance regarding to salt rejection, where, it provides salt rejection 99.9% for salt concentration 5000 mg/l, 96.2% for salt concentration 10000 mg/l, 94.5% for salt concentration 20000 mg/l and 92% for real sample brine sea water (130900 mg/l salts).

- The membrane durability of R4 indicates that this membrane can be considered as self cleaning membranes.

Industrial Applications


Feed from emulsifier
Oil Separator
Oily Salt Tank
S
Carbon filter
P
UF
P1
Salty water Tank
H.P
RO
R1
Produced water
Storage tank of treated water
ZDMD water treatment Unit


Oil & Grease 85 ppm
TDS 134000 ppm
TSS 750 ppm
COD 1176 ppm
BOD 906 ppm
Feeding tank
From the ponds
10 m3
S
Carbon
Filters
S.F. B.W.
Waste oil /water
to separator
Waste oil /water
to separator
UF/MF
P
R1
Oil & Grease 0 ppm
TDS 34974 ppm
NF
Antiscalent
S
FO
FO
Salty water
Tank
5 m3
p
Oil & Grease 1.2 ppm
TDS 134000 ppm
TSS 9 ppm
COD 11.7 ppm
P1
BOD 9.6 ppm
Oil & Grease 0 ppm
TDS 5226 ppm
TSS 0 ppm
COD 0 ppm
BOD 0 ppm
p
p
Storage tank
of treated
water
5 m3
H.P
Feeding to
NF
5 m3
Oil & Grease 0 ppm
TDS 40200 ppm
TSS 0 ppm
COD 0 ppm
BOD 0 ppm

Steps of any petroleum company Treatment Process

1. Carbon Filters :

Sand Filters can remove precipitate in removal of oil and grease from water by adsorption process.

Then the flow will be pumped by a low pressure pump (5-10 bar).

2. Microfiltration/Ultrafiltration membranes:

MF/UF membrane provides the highest permeate flux (130 to 180 $L/m^2.h$) using 0.33 to 0.1 g oil/ L(100 ppm Oil/l).

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) for produced treated water from this membrane was measured and indicated in the following table.

Membrane symbol	COD [mg/l]	BOD [mg/l]	Total Coliform Bacteria amount [CFU/100ml]
Feed sample	1110	660	18
UF	12	6	0.16
MF	16	7	0.19

Steps of GUPCO Treatment Process – Cont’d

3. Reverse Osmosis

Recently reverse osmosis achieved a great progress as a faster and economic technique for desalination of sea and brackish water.

The flow will be pumped to this stage by using the high pressure pump (60-100 bar).

Recommendations

1. To study the cost of these membranes that will be economically used and its reablitiy to be used in an industrial scale.

2. Also, industrial scale experiments should be performed to make sure of its performances.