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Research Article

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Treatment of Oil Wastewater Containing High Salinity with Ultrafıltratıon (UF) and Reverse Osmosıs (RO)

Delia Teresa Sponza

Dokuz Eylül University, Engineering Faculty, Environmental Engineering Department, Buca-İzmir Turkey

***Corresponding author**
Delia Teresa Sponza, Dokuz Eylül University, Engineering Faculty, Environmental Engineering Department, Buca-İzmir Turkey.

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Abstract
The high salinity oil wastewaters contained high salt, chloride, total hydrocarbon concentrations with COD and TSS . In order to treat this wastewater a sequential UF and RO ractor system was used. Before membrane treatment the oil was floated with an API oil separator. The effects of increasing fluxes (12 L/h, 30 L/h and 50 l /h) and pressures (4 bar , 8 bar and 16 bar) on the removals of pollutant parametres were studied in the UF. The influence of the main operating parameters suh as operating pressure (15, 35 and 50 bar), temperature (25, 40 and 55 °C) and feed flowrate (7, 14, 28 L/min, were studied in RO. The maximum salt , chloride, total hydrocarbon, COD,dis-COD, and TSS yields were 90%, 91%, 89%, 89%, 89% and 90%, respectively, at a flux of 60 L/m2.h and at a pressure of 16 bar in UF, respectively. The maximum RO yields in the permeate were around 99% for the pollutant parameters given above at afed flowrate of 28 L/min at 24 bar pressure.

Keywords: Ultrafiltration (UF) Reverse Osmosis (RO), oil

Introduction

A large volume of wastewater in the form of either oil-in-water (o/w) or water-in-oil (w/o) emulsions is generated from various process industries such as metallurgical, petrochemical industries as well as petroleum refineries. In these wastewater oil concentration varied between 500 and 1000 mg/Lwhile suspanded solid concentration werea round 350 mg/L Environmental regulations require that maximum total oil and grease concentrations in the discharge of the environment should be between 10 ana 15 mg/L [1]. The three oil categories in the oil industryl wastewater. Free-floating oil or unstable oil/water emulsions can be readily removed by using conventional separation processes However, for removing stable oil/water emulsion, the conventional processes (biological,-photo-phenton, MBR) are not found to be so effective. Because the emulsion droplets, which are of micron and submicron size, require a very long residence time to rise onto the top for enabling gravity separation and even addition of chemicals cannot break the emulsions effectively[2]. To solve problems the utilization of membranes offers a potential solution to the problem of micron sized oily wastewater. The porous membrane matrix can promote coalescence of micron and submicron oil droplets into larger ones that can be easily separated by gravity [3].

Some of the most promising methods based on membrane separation processes are ultrafiltration ana reverse osmosis membrane processes. The advantages of membrane process such as lower capital cost, the non-requirement of any chemical addition and the capability of generating permeate of acceptable quality are well known. Among all these processes, ultrafiltration (UF) is considered to be a versatile separation process. This pressure-driven process is widely used for separation, purification and concentration of water-soluble solutes or water dispersible materials.According to the literature reports, most studies have focused on the use of ultrafiltration membranes in oily water treatment where oil droplets are completely retained and the continuous phase is permeated. However, because the oil droplets are deformable, depending on the applied pressure, they can be squeezed through the pores and contaminate the permeate. Some recent studies showed that found that emulsion rejection could be maximized if transmembrane pressures were below a critical pressure.

It was reported the effects of emulsion drop size, stirring velocity during permeation experiment, volume fraction of the oil phase and surfactant concentration in the feed on oil permeation flux using a microporous polytetrafluoroethylene (PTFE) flat sheet membrane treatment [4].It was reported that the effects of feed flow rate, operating pressure, membrane pore size and porosity on the separation of dilute oil-in-water mixtures using flat sheet hydrophobic PVDF membranes [5]. The effects of crossflow velocity and transmembrane pressure on permeate flux during separation of oil-in-water emulsion using four organic and inorganic membranes were reported[6].Oily water with emulsion droplets of size higher than 50 µm is in unstable state and less than 10 µm is considered to be highly stable and so is very difficult to separate particularly when oil concentration is in lower range [7].Therefore, oil content in water collected from the effluent treatment plants of most of the industries is quite high and above the allowable discharge standard of 10 mg/L.

In this study, the effects of increasing fluxes (12 L/h, 30 L/h ana 50 l /h) and pressures (4 bar , 8 bar and 16 bar) on the removals of pollutant parametres were studied in the UF. The influence of the main operating parameters suh as operating pressure (15, 35 and 50 bar), temperature (25, 40 and 55 °C) and feed flowrate (7, 14, 28 L/min, were studied in FO.The effects of temperature, (27OC, 35 OC ana 50 oC) increasing TMP (8, 15 and 20 bar) and CVF (0,5,1,0 and 1,5 m/s)) on the treatment eficiency of RO was studied.

Method

A Flat sheet Polymer membrane with a volüme of 670 ml was used to carry out the unstirred semi-batch experiments in UF membrane reactor. The membrane diameter was 6 × 10−2 m and effective membrane area was 9,86 × 10−4 m2. The permeate was withdrawn with a pumpwhile the retentate was taken from the upper part of the reactor system. Ultrafiltration experiments were carried out at a constant concentration of oil (200 mg/L) and at four transmembrane pressures of 10, 15, 20 and 25 bar to detect the effect of transmembrane pressures on the permeate flux and percent oil rejection. TFC polyamide membrane was used as RO membrane. All the pollutant parameteres (oil, COD, BOD5, CODdis, TSS, VSS, TN and TP) were measured using Standard Methods (2012)

Results

Characterisation of oil wastewater

The characterisation of oil wastewater is given in Table 1.

Table 1: Oil wastewater characterisation

Parameter	Value
Oil (mg/L)	100
pH	6,0
Density (g/mL)	0,998
Viscosity (kg/m s)	1,34 x 10^{-3}
COD (mg/L)	3750
TSS (mg/L)	1230
VSS (mg/L)	960
TN (mg/L)	32
TP (mg/L)	18
TSS (mg/L)	1230
Salt(mg/L)	4350
Chloride(mg/L)	2760
Total hydrocarbon(mg/L)	890
VSS (mg/L)	960

Effect of pressures on permeation flux for oil wastewater in UF

Figure 1 shows the permeate flux (Jp/Jw) as a function of time (t). A variation of permeate flux with time at all the pressures is found. The flux not be declined rapidly with time it is increased with time. Possible reason of this is due to not a significant pore blocking from the oil containing high salinity . This can be attributed to to the existence of size distribution of membrane pores and oil droplets and concentration polarization due to an increase in the retentate concentration was not observed However, at the initial stage of the experiment, since the retentate concentration is not very high, the concentration polarization effect will be negligible[8]. In that case, pore blocking by oil droplets could be the major factor for initial flux declination.

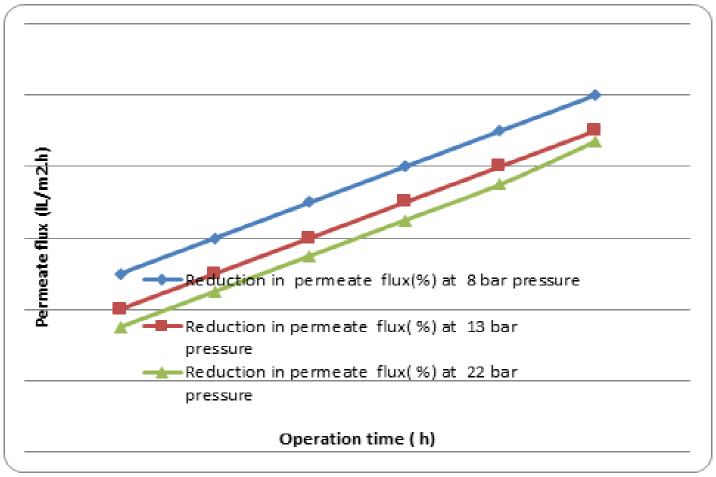

Figure 1: Variation of permeate flux with time at 3 different pressures different membranes. (Initial oil concentration 100 mg/L; pH: 6.1) .

The permeate flux was calculated as a function of transmembrane pressure after 150 min continous operation. The permeate flux continue to increase with increase in pressure. The increase in flux with pressure is due to increase in driving force across the membrane. However, the increase in flux with pressure is not seen to be exactly linear which indicates the existence of additional resistance. The pressure affects the rate of flux decline. Higher the pressure, greater is the rate of flux decline. The increase in flux declination with higher pressure may be connected with the build-up of the concentration polarization layer and with pore blocking mechanisms. Increase in pressure increases the number of collisions between the emulsion droplets, which in turn break the film between the oil and water causing the oil droplets to coalesce and form large droplets.

Reductions in Permeate fluxes in UF

Figure 2 shows the FD (%) of different membranes calculated at increasing time during experiments were started at a transmembrane pressure of 8 bar. The membrane resistance consists of two parts, viz. resistance due to pore blocking and resistance due to concentration polarization. In the first hour, most of the oil droplets participate in the blocking phenomenon by pore sealing causing flux declination at a higher rate. As time passes, pore blocking process is gradually stopped and the oil layer, which is formed by settling of oil droplets on membrane surface, begins to dominate the total membrane resistance. As pore blocking is a very fast process, flux declination also takes place at a faster rate. On the other hand, concentration polarization is a slow process, so corresponding flux declination rate is reduced at the later stage.

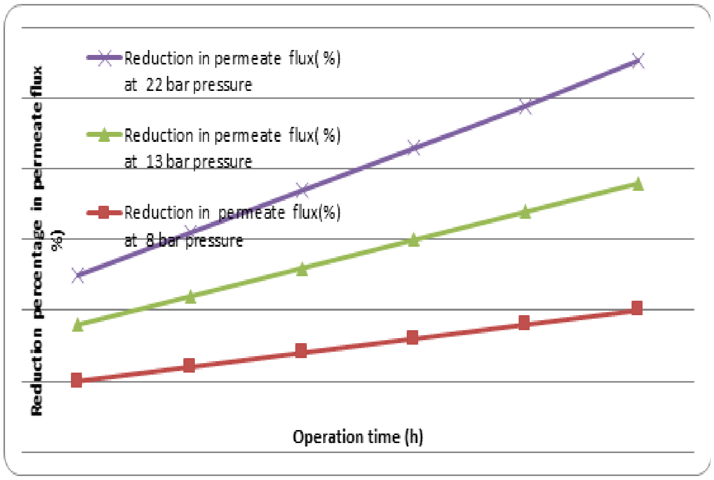

Figure 2: Effect of premeate pressure on the reduction percentages in permeate fluxes in UF

Effect of transmembrane pressure on oil rejection

In this study it was found that the rejection percengaes were sligthly low at lower pressures compared to the high pressures. The rejection percentage showed a slıgtly decreasing trend as the transmembrane pressure was increased from 4 bar to 8 and 16 bar(Figure 3). This can be expalined as follows: at higher pressure slıgtly decrease across the the membrane growth slhglty the wetting and coalescence of the oil droplets by increasing slıgtly the convection. This cause to pass of oil dropletts to the membrane pores in the permeate during operation of ultrafiltration of membrane. As the transmembrane pressure increases, the appliedtransmembrane pressure did slİgtly overcomes the capillary pressure. As a result thus prevents the oil from entering the membrane pores. The optimum oil rejection percentage was found as 89 % at a trans membrane pressure of 4 bar.

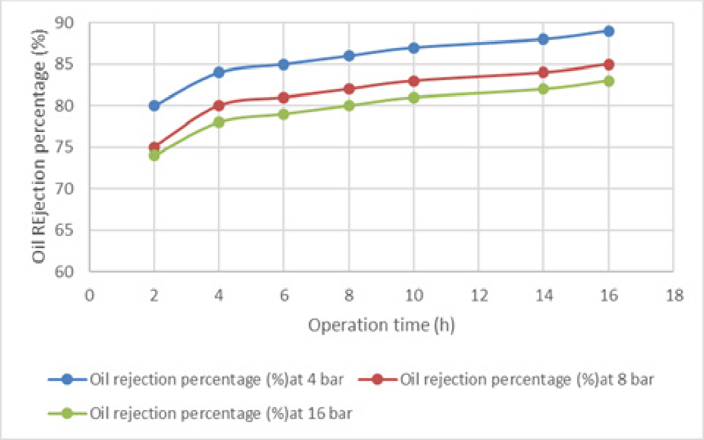

Figure 3: Effect of transmembrane pressure on oil rejection versus operation time

Oil content in the retentates and permeates at different prsssures in UF

Tabe 2 presents the oil concentrations in permeate and retentates of the ultrafiltration membrane reacto at three transmembrane pressure. pressure range. The OİL concentration in the permeate was found to be low at 8 bar transmembrane pressure. The oil concentration also was high at this transmembrane pressure. The ultrafiltration membrane also has low pore size resulting in good separation performance. IT is important to note that at all transmembrane pressures the membrane separation and rejection percentages were found to be above 87%.

Table 2: Effect of transmembrane pressure on oil concentration n retentate

	Transmembrane pressure = 4 bar		**Transmembrane pressure = 8 bar**		**Transmembrane pressure = 16 bar**	
Oil concentration in raw wastewater	Oil concentration in permeate (mg/l)	Oil concentration in retentate (mg/l)	Oil concentration in permeate (mg/l)	Oil concentration in retentate (mg/l)	Oil concentration in permeate (mg/l)	Oil concentration in retentate (mg/l)
100	18	670	5	890	7	800
160	24	670	4,8	900	5	810

Effect of pH on transmembrane flux in UF

Figure 4 shows the time dependence of permeate flux for all the four selected membranes with varying pH of feed. The effect of pH on permeate flux is found to be complex as the trend of flux variation is different with different membranes. The emulsion stability is assumed to be not significantly affected by the decrease of the pH of the feed from its original value of 6.0 or increase of the pH to 8 as the droplet size distributions for both the cases are found to be almost similar. From Figure 4, it is seen that the steady permeate flux is highly dependent on the pH of the feed solution. It is known that the permeate flux is highly dependent on the amount of oil particles adsorbed onto the membrane surface and into the pores of the membrane and the extent of adsorption depends on the type of interactions taking place between the emulsion droplets and the membrane material such as hydrophobic/hydrophilic interactions, hydrogen bonding, Van der Waals interaction and electrostatic effects. Here with the variation of pH, the natural surfactants present in the crude oil possibly play an important role. It is reported that surfactants may either decrease or enhance permeate flux because of their adsorptive interactions with the membrane surface due to electrostatic forces or hydrophobic effects. Because of the different composition of the membranes, the interaction between the membrane surface and the oil particles with surrounding surfactant film also varies with variation of pH; this probably has resulted in different trend of flux variation with different membranes for different values of pH.

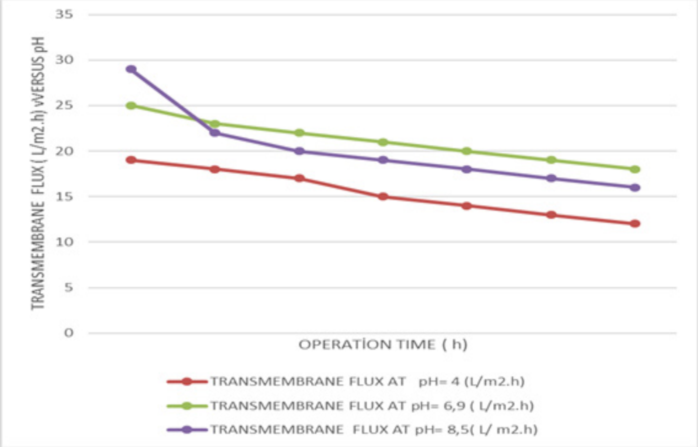

Figure 4: Time dependence of permeate flux (PF) for different pH of feed.

Removal of pollutants in the effluent of UF

The pollutants removals were found to be high as high as 90% (Table 3)in UF

Table 3: Removal of pollutant in UF

Parameter	**Removal efficiency %**
Oil (mg/L)	91
pH	-
Density (g/mL)	-
Viscosity (kg/m s)	-
COD (mg/L)	90
TSS (mg/L)	90
VSS (mg/L)	90
TN (mg/L)	89
TP (mg/L)	89
Salt(mg/L)	90
Chloride(mg/L)	90
Total hydrocarbon(mg/L)	91

Effect of TMP on RO flux and TDS rejecton at increasing temperatures in RO

Effect of TMP Increasing TMP increased permeation flux, but higher TMPs caused the cake layer formed on membrane surface to compress. This accelerates membrane fouling [9]. Thus, at optimum TMP, permeation flux is high and tendency to cake layer formation is low. To study the effect of TMP on permeation flux and rejection, some experiments where carried out within TMP range of 3–25 bar. The results shown in Figure 5 show that permeation flux is linearly increased as TMP increases. The permeation flux for oily wastewater effluent feed increased almost linearly from 20-31 (L/m2 h) at 8 bar to 50-70 (L/m2 h) at 25 bar. According to Darcy’s Law, as TMP increases, while other operating parameters remain constant, permeation flux increases [10]. The Figure 6 shows the effect of TMP on TDS rejection. The results indicate that the rejection was decreased slightly with increased the TMP(Figure 6). This can also be due to the passage of small amount of solute through the membrane at high TMP.

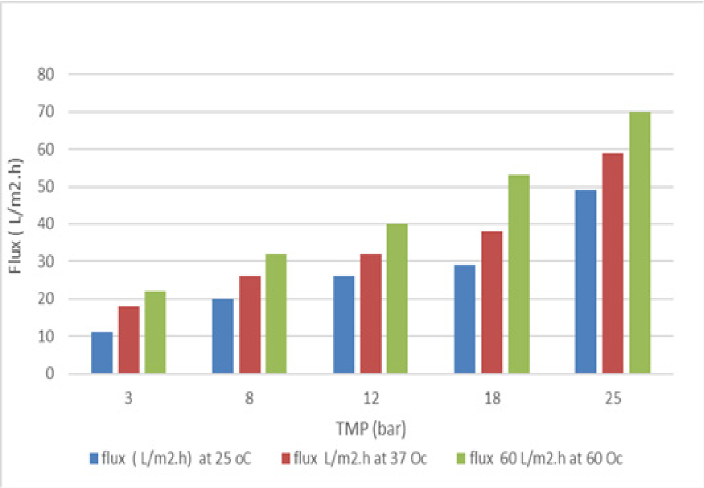

Figure 5: Effect TMP on flux at ncreasing temperatures

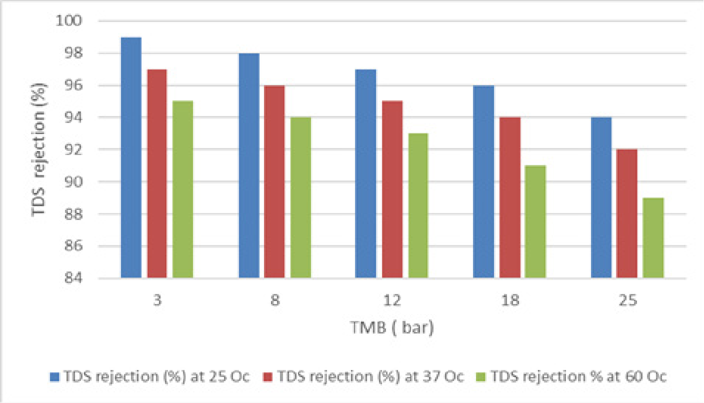

Figure 6: Effect of TMP on TDS rejection yield at increasing temperatures

Effect of CFV on flux and TDS rejection in RO at increasing temperatures in RO

It is well know that increasing CFV increased both the mass transfer coefficient across the concentration polarization boundary layer and the degree of mixing near the membrane surface, there by reducing both the accumulation of a gel layer on the membrane surface, and the fouled membrane.With increase in pressure across the membrane, the flux increases and the relation between the flux and pressure is not exactly linear indicating the existence of an additional resistance besides the membrane resistance (Figure 7). For a constant pressure, the permeate flux is found to be more with more porous membranes though the extent of fouling for different membranes can also be a key factor for altering the final flux values. The flux declination is found to be more while the oil rejection is in decreasing trend with increase in pressure. The transmembrane pressure at which the flux and rejection are optimal is found at a pressure of 3 bar. With increase in concentration, flux decreases and rejection increases due to formation of oil layer on membrane surface leading to increase in total resistance(Figure 8). The pH effects on the flux and rejection fluctuate with membrane composition. However, increasing acidity or alkalinity of the feed solution has caused lower rejection for all the four selected membranes.

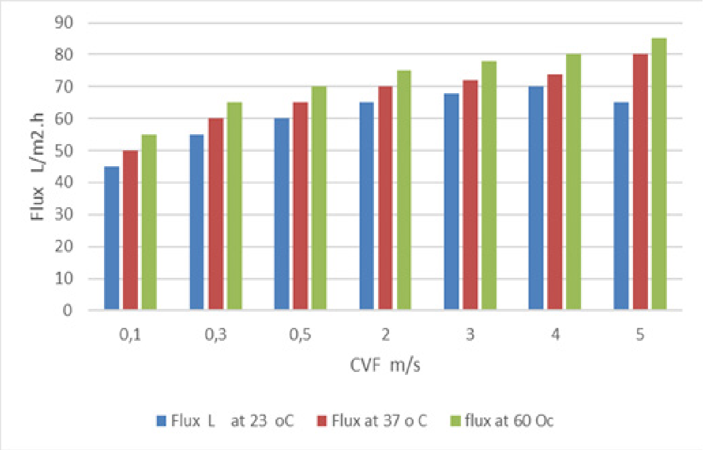

Figure 7: Effect of CVF on the flux at increasing temperatures

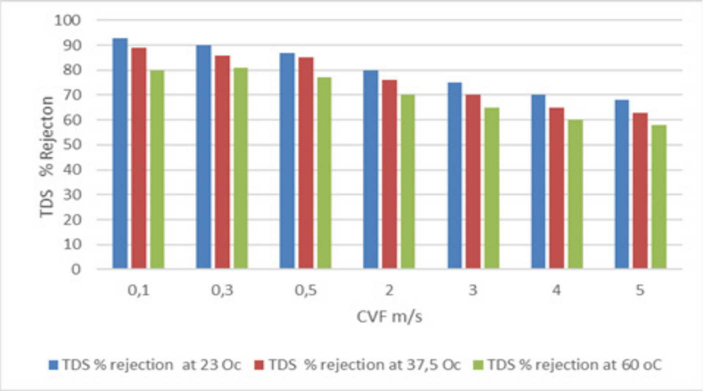

Figure 8: Effect of CVF on the TDS % rejections at increasing temperatures

Effect of temperature on TMP in RO

Effect of temperature Temperature has also a serious effect on permeation flux and this can be represented by Arhenius equation [7]. Also, according to Darcy's Law, increasing temperature increases permeation flux. To study the effect temperature on permeation flux and rejection, some experiments were carried out within a CFV range of 25–50 o C. The results shown in Figure 9 show that permeation flux is almost linearly increased as temperature increases. It is because viscosity decreases and diffusivity increases at elevated temperatures. In Figure 10 the effect of temperature on TDS rejection is shown. According to these results, increasing temperature decreased the rejection. This can also be due to that viscosity reduction that increased solutes permeability.

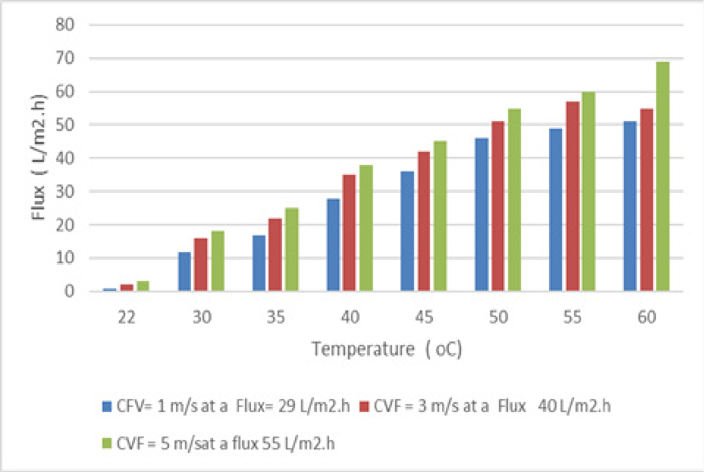

Figure 9: Effect of increasing temperature on flux at increasing temperatures in RO

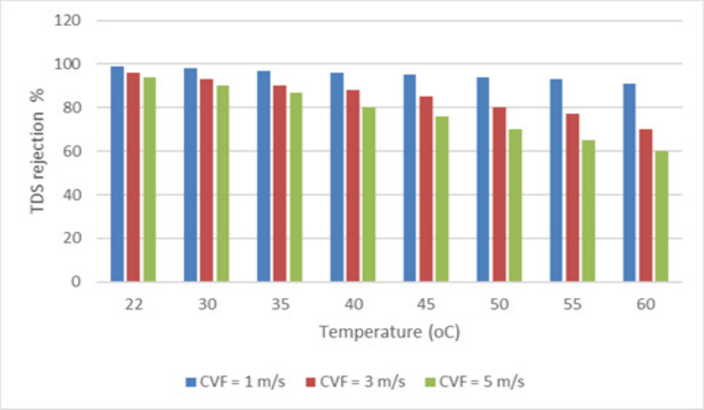

Figure 10: Effect of increasinf temperature on TDS rejecton in RO

Removals of pollutant in RO

The removals were high in the RO as high as 99%(Table 4).

Table 4: Removal of pollutants in the effluent of RO

Parameter	Removal efficiency %
Oil (mg/L)	99
pH	-
Density (g/mL)	-
Viscosity (kg/m s)	-
COD (mg/L)	99
TSS (mg/L)	99
VSS (mg/L)	99
TN (mg/L)	99
TP (mg/L)	98
TSS (mg/L)	99
VSS (mg/L)	99
Salt(mg/L)	99
Chloride(mg/L)	99
Total hydrocarbon(mg/L)	99

Conclusions

The results of this study showed that a sequential UF/RO membranr system effectively treat the pollutants with a yield of 99%. TMP, CVF and feed flow affect the operation of UF and RO membran reactors.

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