Study of Wastewater Treatment Plant

S. Al Jilil and M. Sajid

Abstract—The study was carried to evaluate the performance of nanofiltration (NF) and reverse osmosis (RO) technology for reducing the total salt concentration from waste water. The nanofiltration proved very effective in removing the polyvalent cations and anions such as $\text{SO}_4^{2-}$ where the removal efficiency was 97.22%. It is well known that the RO water treatment process removes all the cations and anions from waste water or brine or sea water especially removing the monovalent ions such as $\text{Cl}^-$ where the percentage removing efficiency was 94.4%. The performance efficiency of RO and NF water treatment processes declined significantly during the first 3-years of operation due to fouling and biofouling of the membrane. These significant findings provided concrete clue for the important issue to replace or reject the existing water use methods. The research further highlighted the necessary to replace the NF and RO membranes used in these two water treatment techniques.

Keywords—Membrane bio-reactor (MBR), Nano-filtration (NF), Reverse osmosis (RO), Waste Water Treatment (WWT).

I. INTRODUCTION

WATER uses are manifolds ranging from domestic, agriculture and industries. Among these, chemical industry uses water as a coolant and to generate steam from boilers for use in different industrial processes for the production of different types of products. Depending on its source; water may contain appreciable amount of dissolved calcium and magnesium salts which are a source of hardness in waters. In boilers, water evaporates continuously and the dissolved salts precipitate after reaching saturation stage at equilibrium thus forming a hard scale that deposits on the inner walls of the boiler. There are several disadvantages of these deposits. Among these, the most important is the corrosion which decreases the efficiency of the boiler unit through clogging of pipes, valves and condensers of the unit, decreases the heat transfer rate, causes excessive use of fuel and a danger of explosion. Therefore, wastewater treatment is important for safe operation of boilers. Among the traditional methods of water softening, addition of lime-soda is one process. But this process has some disadvantages i.e. leaves more sodium chloride as residue in the raw water and the need of reaction tanks equipped with mechanical stirrers in addition of course to the main chemicals used by the process and coagulant to facilitate filtration of the formed precipitates.

Presently, among the various techniques for softening high hardness waters, membrane separation is a new approach. The membrane separation processes have the unique advantage of not requiring energy to affect phase changes compared to distillation or crystallization. Hence it is economically attractive alternative in view of the fact that it is carried out at reduced energy costs.

The objective of this work is to investigate the possibility of using reverse osmosis and nanofiltration processes to improve water quality by removing the major cations and anions such as calcium, magnesium and chloride from wastewater. Also to determine the decline in the performance of RO and NF processes due to membrane fouling.

Review of Literature

RO Technology Application: Membrane technology is playing an increasingly important role in the reclamation of municipal wastewater. Due to the increasing demand for good quality water in urban areas, purification of wastewater has become one of the preferred means of augmenting the water resources [1]. In particular, high quality reclaimed wastewater can be used for industrial customers. For example, it is being used for making boiler feed-water and semiconductor process water. Reverse osmosis (RO) membranes have been proven to successfully treat such water and provide water which exceeds reuse quality requirements. Numerous large-scale commercial membrane plants are now being used to reclaim municipal wastewater. These plants include the 50000 m$^3$/day West Basin, CA, Kranji 40000 m$^3$/day in Singapore, and the 32000 m$^3$/day Bedok plant in Singapore [2]. Additionally, even larger plants are planned such as the 270000 m$^3$/day plant in Orange County, California and the 380000 m$^3$/day plant for Sulayabia, Kuwait [3]. The magnitude of these RO-based reclamation plants demonstrates the acceptance that this technology has gained recently.

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A typical process for municipal wastewater consists of primary, secondary and tertiary treatments. The resulting effluent is low in turbidity and can be disinfected for discharge. However, the level of dissolved solids is not reduced by this process and the water is not generally suitable for reuse. When tertiary effluent from a conventional treatment process is supplied to a RO system, it is common to have all forms of fouling - colloidal, biological, scaling and organic fouling. The coatings of foulant will impede water transport through the membranes. Early attempts to treat this water with RO membranes resulted in rapid fouling and required membrane cleaning as frequent as twice per week. This shortened membrane life and greatly increased operating cost.

Since the development of the first practical cellulose acetate membranes in the early 1960’s and the subsequent development of thin-film, composite membranes, the uses of reverse osmosis have expanded to include not only the traditional desalination process but also a wide variety of wastewater treatment applications. Several advantages of the RO process that make it particularly attractive for dilute aqueous wastewater treatment include: (1) RO systems are simple to design and operate, have low maintenance requirements, and are modular in nature, making expansion of the systems easy; (2) both inorganic and organic pollutants can be removed simultaneously by RO membrane processes; (3) RO systems allow recovery/recycle of waste process streams with no effect on the material being recovered; (4) RO membrane systems often require less energy and offer lower capital and operating costs than many conventional treatment systems; and (5) RO processes can considerably reduce the volume of waste streams so that these can be treated more efficiently and cost effectively by other processes such as incineration [4, 5, 6, 7, 8, 9]. In addition, RO systems can replace or be used in conjunction with other treatment processes such as oxidation, adsorption, stripping, or biological treatment (as well as many others) to produce a high quality product water that can be reused or discharged. Applications that have been reported for RO processes include the treatment of organic containing wastewater, wastewater from electroplating and metal finishing, pulp and paper, mining and petrochemical, textile, and food processing industries, radioactive wastewater, municipal wastewater, and contaminated groundwater [4, 8, 9, 10].

**Contaminated Drinking Water**

The ability of RO membranes to remove both inorganic and organic compounds have made these attractive for the treatment of contaminated drinking water supplies [11]. Reverse osmosis processes can simultaneously remove hardness, color, many kinds of bacteria and viruses, and organic contaminants such as agricultural chemicals and trihalomethane precursors. Eisenberg and Middlebrooks [12] reviewed RO treatment of drinking water sources, and they indicated RO could successfully remove a wide variety of contaminants. Chian et al. and Johnston and Lim [13, 14] studied several agricultural chemicals which can contaminate water supplies and found removals were good; however, these adsorbed on the membranes studied. Regunathan et al. [15] reported good removals of the pesticides endrin and methoxychlor as well as trihalomethanes (THMs) with an RO-adsorption system. Nusbaum and Riedinger, Odegaard and Kootattep, and Bhattacharyya and Williams [16, 17, 18] reported that humic and fulvic materials, which are THM precursors, were highly removed by RO membranes. Clair et al. [19] also found excellent removals (>95%) of dissolved organic carbon from natural waters using FT30 membranes. Sorg et al. [20] showed that a RO system could effectively remove radium from contaminated water. Sorg and Love [21] conducted studies with actual groundwater in which only a few of the pollutants being studied were spiked; several different commercial membranes were studied. Most inorganics were highly (>90%) rejected while organic rejection depended upon the organic and membrane studied. Baier et al. [22] studied removal of several agricultural chemicals from groundwater using several different membranes. Rejections ranged from 0% to >94% for the different compounds and membranes studied; pilot plant experiments indicated water fluxes could be maintained over long terms with periodic cleaning. Fronk [23] investigated RO removal of over twenty VOCs and pesticides using several different RO membranes. Average organic removals were 80%. The study indicated that RO could be used to effectively remove both inorganics and organics from drinking water supplies. Taylor et al. [24] found that RO membranes could be used to remove 96% of DOC, 97% of color, 97% of trihalomethane formation potential (THMFP), and 96% of total hardness. Tan and Sudak [25] examined several RO membranes and found all were capable of acceptably removing color from groundwater even over long operating periods.

**Municipal Wastewater**

The application of RO membranes to the treatment of municipal wastewater has also had some success. Reverse osmosis can remove dissolved solids which cannot be removed by biological or other conventional municipal treatment processes. In addition, RO membranes can also lower organics, color, and nitrate levels. However, extensive pretreatment and periodic cleaning are usually needed to maintain acceptable membrane water fluxes. Early studies [26, 27, 28] showed that high removals of TDS and moderate removals of organics could be achieved. Tsuge and Mori [29] showed that tubular membranes (with a substantial pretreatment system) could remove both inorganics and organics from municipal secondary effluent and produce water meeting drinking water standards. Stenstrom et al. [30] studied municipal wastewater treatment over a 3 year period using tubular cellulose acetate membranes. TDS rejections were 81%,
and TOC rejections were >94%, making the permeate suitable for reuse. However, feed pretreatment was necessary to maintain high water flux levels. Richardson and Argo [31], Allen and Elser [32], Argo and Montes [33], Nusbaum and Argo [34], and Reinhard et al.[35] have discussed municipal wastewater treatment at a large scale plant (Water Factory 21, Orange County, California). The feed to the plant consisted of secondary effluent, and the process was composed of a variety of treatment systems, including RO membranes (several different types) with a 5 MGD capacity. The process reduced TDS and organics to levels that allowed the effluent to be injected into groundwater aquifers used for water supplies. Suzuki and Minami [36] reported studies on use of several RO membranes to treat secondary effluent containing various salts and dissolved organic materials. TDS rejections of up to 99% and TOC rejections as high as 90% were found possible, and fecal coliform group rejections were >99.9%. Losses in water flux over time were noted but could be partially restored by periodic cleaning.

Cséfalvay et al. [37] stated that membrane separations are finding greater use in wastewater treatment because of their efficiency. In order to prove the effectiveness of membrane filtration an applicability study is carried out. Nanofiltration and reverse osmosis membranes are tested under quite different conditions to reduce the chemical oxygen demands (COD) of wastewaters to meet the Council Directive 76/464/EEC release limit. Two kinds of real wastewaters were selected for the investigation. The wastewaters represent extreme different circumstances since the difference between their COD is two orders of magnitude. All of the membranes tested can be applied either to the treatment of wastewater of low COD (pharmaceutical wastewater) or wastewater of high COD (dumpsite leachate), since the different conditions do not change the membrane characteristics. The experimental data show that none of the membranes can decrease the COD to the release limit in one step. However, if two-stage filtrations (nanofiltration followed by reverse osmosis) are accomplished for both of the wastewaters, a total COD reduction of 94% can be achieved. With the application of the two-stage filtration the COD of the wastewater of low COD can be decreased below the release limit but in case of wastewater of the high COD further treatment will be required.

**Nanofiltration Applications**
Nanofiltration membranes, which have high water fluxes at low pressures, are a recent development that have made possible new applications in wastewater treatment. Nanofiltration membranes are often charged (usually negatively-charged), and, as a result, ion repulsion is the major factor in determining salt rejection. For example, more highly charged ions such as $SO_4^{2-}$ are rejected by most nanofiltration membranes to a greater extent than monovalent ions such as $Cl^-$. These membranes also reject organic compounds with molecular weights above 200 to 500. These properties have made possible some interesting new applications in wastewater treatment, such as selective separation and recovery of pollutants that have charge differences, separation of hazardous organics from monovalent salt solutions, and membrane softening to reduce hardness and trihalomethane precursors in drinking water sources [8, 38, 39].

**Contaminated Drinking Water Supplies**
Nanofiltration membranes, although a relatively recent development, have attracted a great deal of attention for use in water softening and removal of various contaminants from drinking water sources. Nanofiltration (NF) processes can reduce or remove TDS, hardness, color, agricultural chemicals, and high molecular weight humic and fulvic materials (which can form trihalomethanes when chlorinated). In addition, NF membranes typically have much higher water fluxes at low pressures when compared with traditional RO membranes used for this application. Conlon [40] reported that FilmTec NF50 membranes could effectively remove color (96%) and TOC (84%), reduce hardness and TDS, and lower trihalomethane formation potential (TMFP) to below regulatory levels. Eriksson [38] and Cadotte et al. [39] also indicated that NF membranes (such as FilmTec NF40, NF50, and NF70) could be used to reduce TDS, hardness, color, and organics. Dykes and Conlon [41], Conlon and McClellan [42], Watson and Hornburg [43], and Conlon et al. [44] have also identified NF as an emerging technology for compliance with THM regulations and for control of TDS, TOC, color, and THM precursors. Clifford et al. [45] discussed the use of NF70 membranes for contaminated groundwater treatment. Removals included 91% for radium-226 and 87% for TDS. Taylor et al. [46] reported that NF70 membranes could allow control of THM formation, DOC, and TDS and produce a high quality product water from an organic contaminated groundwater; they indicated costs of a NF process would be competitive with conventional treatment processes which do not control THMFP. Lange et al. [47] also suggested that NF treatment would be a reliable method of meeting existing and future THM limits compared to chemical treatment alternatives. Amy et al. [48] used NF70 membranes to remove dissolved organic matter from both groundwater (recharged from secondary effluent) and surface water in order to reduce THM precursors; they found that the process was effective in reducing the organics as well as conductivity in both water sources. Tan and Amy [49] showed that NF membranes could remove >88% of color, 51% of TOC, 46% of TDS, and 79% of THMFP from a contaminated water supply. Duranceau et al. [50] and Taylor et al. [51] have reported on the use of NF70 membrane separation of several agricultural chemicals spiked in groundwater. Ethylene dibromide and dibromochloropropane removals averaged 0% and 32%, respectively, while the remaining organics (chlordane,
heptachlor, methoxychlor, and alachlor) were 100% removed. Rejections of TDS were 85% and THMFP were 95%. However, it was also indicated that some of the organics adsorbed on the membrane.

**Wastewater** Nanofiltration has also been used to remove both organics and inorganics in various wastewaters. Bindoff et al. [52] reported the use of NF membranes to remove color-causing compounds from effluent containing lignins and high salt concentrations in a wood pulping process. Color removals were >98% at water recoveries up to 95% while the inorganics were poorly rejected, allowing the use of low operating pressures (since Δπ was small). Ikeda et al. [53] indicated NF could give high separations of color-causing compounds such as lignin sulphonates in paper pulping wastewaters. Afonso et al. [54] found NF removal (>95%) of chlorinated organic compounds from alkaline pulp and paper bleaching effluents with high water fluxes. Simpson et al. [55] reported the use of NF membranes to remove hardness and organics in textile mill effluents. Gaeta and Fedele [56] also indicated high water recoveries (up to 90%) from textile dye house effluent could be achieved with NF membranes. Perry and Linder [57] discussed the recovery of low molecular weight dyes from high salt concentration effluent. Ikeda et al. [53] and Cadotte et al. [39] reported the use of NF membranes in the treatment of food processing wastewaters. Some specific uses included the desalting of whey and the reduction of high BOD and nitrate levels in potato processing waters (Anonymous, 1988b). Bhattacharyya et al. [58] used NF40 membranes to selectively separate mixtures of cadmium and nickel. Williams et al. [59] and Bhattacharyya and Williams [18] examined NF40 membranes with and without pretreatment by feed preozonation to study removal of various chlorophenols and chloroethanes. TOC rejections up to 90% were possible with ozonation pretreatment. Rautenbach and Gröschl [60] also discussed the separation results of several organics (ranging from methanol to ethylene glycol) by various NF membranes. Chu et al. [61] detailed the use of NF in a process for treating uranium wastewater; NF40 uranium rejections were 97% to 99.9%. Dyke and Bartels [62] discussed the use of NF membranes to replace activated carbon filters for the removal of organics from off shore produced water containing residual oils. The produced waters contained ~1000 mg/L soluble organics (mostly carboxylic acids) and high inorganic concentrations (~15,000 mg/L Na⁺ and ~25,000 mg/L Cl⁻ as well as other dissolved ions). Organic rejections were suitable to meet discharge standards while inorganic rejections were low (~20%), allowing operation at low pressures.

**Analysis of Wastewater Samples** The water samples were analyzed for pH, cations and anions. Cations and anions such as chloride, sulphate were determined by using Dionex 300 Ion chromatography. The requirements for this analysis are Dionex ion chromatography with column AS-14 (4mm), guard column AS-12, suppressor-ASR-1, fluent mixture of carbonate and bicarbonate, deionized water and nitrogen gas. The results of different Parameters like Cl⁻, SO₄²⁻ were obtained in mg/L. The total dissolved solids (TDS) were estimated by using Oven Heraeus Instruments. The pH was measured by using Hach HQ D40.

**Experimental set-up:** The AWWTU at KACST consists of two units representing two different water treatment technologies such as Reverse Osmosis Unit (RO-Unit) and Nanofiltration (NF).

1. **RO-Unit** The Pre-treated water from biological unit is desalinized by applying RO-technology. Its water production capacity is 0.12 m³/h (Fig 1).

2. **NF- Unit:** The Pre-treated water from biological unit is desalinized by applying NF-technology. Its water production capacity is 0.12 m³/h (Fig 2).

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**Materials and Methods** The experiment was carried at Wastewater Treatment Plant (WTP), National Center for Water technology (NCWT), King Abdulaziz City for Science and Technology (KACST) during 2012-2013.
Results and Discussion  

The results of RO and NF wastewater treatment technologies containing cations and anions are presented in Fig. 3. Only modest rejection was observed for monovalent species as expected with NF. However, rejection/removal of polyvalent cations and anions was strongly observed. On the other hand, strong rejection was observed for monovalent cations and anions by RO [63, 64]. Where the rejection of the species ions (\( \text{REJ}(\%) \)) can be calculated as follows:

\[
\text{REJ}(\%) = \left[ \frac{C_F - C_P}{C_F} \right] \times 100
\]

where  

- \( C_F \) = Concentration of species in the feed and  
- \( C_P \) = Concentration of species in the permeate

Data in Fig. 4 shows the results of advanced treatment RO and NF of waste water containing cations and anions when the experiment was carried out using old RO and NF membranes (worked for 3 years). It was found that the rejection of cations and anions decreased for monovalent species. This behavior is expected with old membranes. Also, modest rejection was observed for polyvalent cations and anions. In another hand, modest rejection was observed for monovalent cations and anions by RO. The reason behind this behavior is that the performance of these membranes were decline due to membrane fouling and biofouling. This reason strongly right, because the waste water has different types of bacteria and pathogens and organic material. The organic material adsorbed on the membrane surface and increase the fouling problem.

Fig 3. Comparison of the performance of new RO and new NF membranes

Fig 4. Comparison of the performance of old RO and old NF membranes

The performance of NF and RO for the rejection of TDS is shown in Fig. 5. In general, the TDS rejection decreases with increase in feed concentration due to an increase in concentration polarization at the membrane solution interface [65]. It was observed that TDS rejection was less by NF than RO. This could be attributed to the monovalent ions such as \( \text{Na}^+ \) which represents the main component in the feed water, therefore, the ability of NF in rejection of the monovalent ions is weak.

Fig 5. Percentage rejection of TDS versus feed concentration for RO and NF membranes

Fig 6 shows the performance of NF and RO in rejection of TDS at the same pH of feed water. The percentage rejection of the \( \text{Na}^+ \) ion by RO membrane was higher than by NF membrane. This could be attributed due to the fact that the rejection of monovalent ions such as \( \text{Na}^+ \) by NF is weak [63, 64]. In addition, the pH did not affect the membrane rejection where the polyamide membrane pH operating ranges between 4-11.
Fig 6. Effect of pH on removing sodium ions using RO and NF membranes

Fig 7 shows the results of RO for waste water treatment containing cations and anions by running the experiment using old RO and new RO membranes. The old membrane was 3 years old. It was found that the percentage rejection decreased for all species ions. For example, the percentage rejection of $Cl^-$ ion was 94.4% and after three years the membrane percentage rejection was 43.9. This means that the membrane performance declined due to fouling and biofouling.

Fig 7. Comparison of the performance of RO membranes during three years operation

Fig 8 shows the results of NF for wastewater treatment containing cations and anions by running the experiment using old NF and new NF membranes. The old membrane worked for 3 years. It was found that, the rejection decreased for polyvalent cations and anions. This behavior was expected with the old membranes. On the other hand, the percent rejection of monovalent cations and anions by NF was not affected. For example, the percentage rejection of $Cl^-$ ion was 11.6% after three years and the membrane rejection was 9.62%. While the rejection of $SO_4^{2-}$ ions was 97.22% after three years and the membrane rejection was 61.43%. A strong rejection was observed for polyvalent cations and anions by NF [64].

Fig 8. Comparison of the performance of NF membranes during three years operation

Fig 9 and Table 1 show the percent performance decline of RO for treatment of waste water containing cations and anions. It is clear that the decline in the performance of RO was high during three years operation. This decline in performance could be attributed to fouling and biofouling on the surface of the membrane. In conclusion, this promising method, based on these results, suggest to replace the old membrane by new product. The percentage decline of performance of membrane ($PDPM_{(\%)}$) can be calculate as follows:

$$PDPM_{(\%)} = \frac{NREJ_{(\%)} - OREJ_{(\%)} \times 100}{NREJ_{(\%)}}$$

Where $NREJ_{(\%)} = $ Rejection of new membrane (%) and $OREJ_{(\%)} = $ rejection of old membrane(%)

Fig 9. Percentage decline of the performance of RO during three years operation

Fig 10 and Table 2 show the percent decline in the performance of NF for treatment of waste water containing cations and anions. It is clear that the decline in the performance of NF is high during three years operation which might be due to fouling and biofouling on the surface of the membrane. The results of this investigation suggest that the old membrane should be replaced with the new product.

Table 1: Percentage decline of the performance of RO

<table>
<thead>
<tr>
<th>Species</th>
<th>$PDPM_{(%)}$ of RO</th>
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<tbody>
<tr>
<td>$Ca^{2+}$</td>
<td>28.38</td>
</tr>
<tr>
<td>$Mg^{2+}$</td>
<td>20.39</td>
</tr>
<tr>
<td>$Na^{+}$</td>
<td>21.98</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>53.45</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>31.73</td>
</tr>
</tbody>
</table>
Fig 10. Percentage decline of the performance of NF during three years operation

Table 2: Percentage decline of the performance of NF

<table>
<thead>
<tr>
<th>Species</th>
<th>PDPM (%) of NF</th>
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</thead>
<tbody>
<tr>
<td>Ca^{2+}</td>
<td>37.67</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>12.72</td>
</tr>
<tr>
<td>Na^{+}</td>
<td>9.37</td>
</tr>
<tr>
<td>Cl^{-}</td>
<td>16.97</td>
</tr>
<tr>
<td>SO_{4}^{2-}</td>
<td>36.81</td>
</tr>
</tbody>
</table>

**Affecting Factors** the decline performance of the membrane such as membrane fouling and biofouling, membrane degradation by oxidation and hydrolysis, mechanical damage, inorganic colloids, adsorbed organics, coagulants, silica scale and other inorganic scale and fouling with waste water. In general, the biofouling and fouling are the major constraints that cause decline in the performance in membranes. In order to find the possible reasons causing decline in membrane performance, membrane autopsy was conducted to collect sheet membrane samples for examination by using energy dispersive x-ray to analyze the fouling deposit. Also, fourier transform infrared spectroscopy was used to identify the components of the deposition that deposit on the membrane. In addition, SEM can be used with the membrane samples to show the advanced fouling on the membrane surface.

**Control Factors** can be used to control fouling on the membrane. These factors are:
1. Efficient pretreatment for the water.
2. Prompt action should be taken in membrane cleaning in the early stages of fouling.
3. Control of bacterial growth by depriving bacteria from nutrition by controlling the organic content in the feed water.
4. Efficient control of membrane fouling by proper sanitization of membrane system by using chlorination or UV.

**Conclusions:** The nanofiltration (NF) is very effective in removing polyvalent cations and anions such as SO_{4}^{2-} (where the percent rejection of SO_{4}^{2-} ions was 97.22%). While the RO membrane is very effective in removing all ions especially monovalent cations and anions such as Cl^{-}, where the percent rejection of Cl^{-} ions was 94.4%. The decline in the performance of RO and NF is significantly high during the first 3-years operation. The main reason behind this is the fouling and biofouling on the surface of the membrane. The suggestion based on these results is to replace the membrane by new one.

**Recommendations and suggestions:**
1. Change the membrane by new one
2. Observe the performance after fixing a new membrane and make backwash at 10% of decline of the performance.
3. Conduct training for the technicians in RO and NF systems maintenance including the backwash and fouling problem.
5. Make a membrane autopsy for the old one to know the exact reason behind the decline of the performance.
6. Use another type of membrane such as ceramic membrane.

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