



COMPARATIVE STUDY OF NANO AND RO MEMBRANE FOR SODIUM SULPHATE RECOVERY FROM INDUSTRIAL WASTE WATER

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ABSTRACT

A large amount of non-biodegradable inorganic salts having low to high potential of hazards is discharged every year in water bodies by various industrial activities. The salts hazardous depend on nature and their concentration in water. Sodium sulfate is one of them. Although the sulfate's health effect is relatively short-term, it is acute (diarrhea) and a substantial decrease of sulfate content in drinking water is recommendable. It is mainly discharged in to water bodies via commodity product like detergent or via industrial activity manufacturing kraft paper, glass, sodium salts, ceramic glazes, pharmaceuticals, processing textile fibers dyes, Aluminium silicate, rayon etc. These industries requires substantially large amount of process water. This could be met by reusing water as for as possible. Evaporation and crystallization are the most preferred techniques for separation of sodium sulphate but becomes uneconomical when salts concentration is low especially in industrial waste water. In the present work performance of two commercial CSM membranes model NE-1812-70 (nano membrane) and model RE 1812-50 (reverse osmosis membrane) were evaluated for concentrating the waste water stream to recover water and sodium sulphate for reuse. The results show that NE-1812-70 membrane gives higher water recovery compared to RE 1812-50 at same conditions. Also it was found that by using NE-1812-70 membrane waste aqueous stream could be concentrated up to 14.1% compared to 9.29% by RE 1812-50 at pressure of 25bar.

Keywords: waste water, sodium sulphate, nanofiltration, membrane separation, aluminium silicate.

INTRODUCTION

A large amount of inorganic salts having low to high potential of hazards is discharged every year in water bodies by various industrial activities. These salts are non-biodegradable and some times hazardous in nature. Out of these salts sodium sulphate is among them. It is most dangerous in structure conservation. When it grows in the pores of stones it can create high levels of pressure resulting in cracks within structures. It affects on human health is of relatively short-term and it is acute (diarrhea), hence a substantial decrease of sulfate content in drinking water is recommendable (K. Kosutic, *et al.*, 2004). It is mainly discharged in to water bodies via commodity product like detergent or via industrial activity manufacturing Kraft paper, sodium salts, pharmaceuticals, processing textile fibers dyes, Aluminium silicate, rayon etc. These industries demand substantially large amount of process water. This demand could be met by reusing water as for as possible. Having understood the fresh water shortage, various water regulatory agencies are insisting on treating the wastewaters to reuse it in the process itself and achieve 'zero discharge'. The conventional process like evaporation and crystallization are most preferred technique for sodium sulphate separation from aqueous streams but becomes uneconomic at low concentration. At low concentration Membrane based separation processes have gradually proved an attractive alternative to the conventional separation processes for treatment of wastewater. The application of membrane filtration not only enables high removal efficiencies, but also allows reuse of water. Membrane separation potentially offer the advantages of highly selective separation, separation without any chemical additives, ambient temperature operation, usually no phase changes, continuous and

automatic operation, economical operation also in small units, modular construction and simple integration in existing production processes, as well as relatively low capital and running costs (Marcucci, 2002; Bowen and F. Jenner, 1995). Membrane technology has been given special focus in water treatment processes because of its capability in removing physical and chemical matters at a higher-degree of purification.

Nanofiltration is an innovative membrane water treatment technique that find its applications in wastewater and industrial water treatments (e.g. water softening, removal of colorants and organic matter) (Szoke *et al.*, 2002). The NF membranes have separation characteristics in the intermediate range between reverse osmosis (RO) and ultra filtration (UF). Compared to reverse osmosis membranes Nanofiltration membranes have a loose structure, resulting in higher permeate fluxes and lower operating pressures. As most of the nanofiltration membrane have fixed negative surface charges, their separation capacity separation is influenced by the steric effect (due to small pore diameter) and the charge on surface of the pore (Donnan exclusion phenomena) (Seidel *et al.*, 2001). This explains why these membranes exhibit ion-selectivity. At low concentration of ionic solute, the multivalent negative ions are separated by the NF membrane to a higher degree than monovalent ions, as the latter can pass more freely through the pore of the membrane (Orecki *et al.*, 2004). Generally speaking, nanofiltration membranes repulse divalent ions having the same charge as those at the surface of the pore. Because of lower operating pressure, the capital investment for needed for NF membranes systems is generally less compared to reverse osmosis system; this is due to the fact that the pressure-vessel housing the NF membrane



elements can be built with less expensive material like plastics, the pump and the rest of the hardware of the system should cost much less in comparison with high pressure RO membrane system. Because of lower operating pressure, NF membrane systems consume much less energy. Therefore NF membrane systems should be considered first for treatment of water and waste water.

The sulphate salts rejection has been studied by many researchers (Wang *et al.*, 2005; Dai *et al.*, 2002; Zhang *et al.*, 2005; Krieg *et al.*, 2004). Wang *et al.*, (2005) studied ESNA-1 membrane to separate different salts and found that the rejection to most salts decreased with the growth of the concentration and the sequence of rejection to anions was $R(\text{SO}_4^{2-}) > R(\text{Cl}^-) > R(\text{NO}_3^-)$ at the same concentration ranging from 10 mol/m³ to 100 mol/m³. Schaep *et al.*, (2001) had reported that Na₂SO₄ rejection using NF40 and UTC20 membranes was about 95% at 10 bars. Gestel, (2002) have reported that sulphate salt rejection largely depends on charge on membrane surface and this charge could be varied by solution pH. He found that Na₂SO₄ rejection was lower at pH 5 for concentration range 10⁻³- 10⁻²M Na₂SO₄. Another researcher have synthesized N, O-carboxymethyl chitosan (NOCC) composite nanofiltration membranes and they found that the rejection and permeate fluxes to Na₂SO₄ (1000 mg L⁻¹) were 92.7% and 3.0 kgm⁻² h⁻¹, respectively (Miao *et al.*, 2006). Dai *et al.*, (2002) have reported that their SPPEK/PSF10000 composite membranes were able to reject 91% of Na₂SO₄ at room temperature and 0.25MPa pressure for feed of 1000ppm.

In the present work two commercial CSM membranes model NE-1812-70 (nano membrane) and model RE 1812-50 (reverse osmosis membrane) were evaluated for separation of sodium sulphate from synthetic aluminium silicate industry waste. Synthetic aluminium silicate is synthesized by hydrothermal treatment of sodium silicate and aluminium sulphate resulting dilute sodium sulphate as waste stream. Concentration of sodium sulphate in aluminium silicate industries waste is in the range of 1000 mg L⁻¹ to 5000 mg L⁻¹. The aim of the work was simultaneous recovery of by-product sodium sulphate and recycling the membrane permeates to process plant so that fresh water consumption could be reduced.

MATERIALS AND METHODS

Membranes

In the present study two thin-film composite, spiral-wound commercial membranes of CSM, Korea make models no. NE 1812-70 and RE 1812-50 were procured from local dealer. Both membrane details are given in Table-1. Before any experiment membrane were kept immersed in ultra pure water for 24 hours.

Chemicals

Laboratory grade anhydrous Sodium Sulphate anhydrous was procured from Thermo Fisher Scientific India Pvt. Ltd. Ultra pure water was used through in this study.

Table-1. Properties of membrane used.

S. No.	Particulars	Model: NE 1812-70	Model: RE 1812-50
1	Membrane material	PA (Polyamide)	PA (Polyamide)
2	Membrane surface charge	Negative	Negative
3	Permeate flow rate*	379 L/day	189 L/day
4	Operating pH range	3.0 ~ 10.0	3.0 ~ 10.0
5	Operating temperature	45°C, Max.	45°C, Max.

* Feed 250 mg/L NaCl solution at 60 psig applied pressure, 15% recovery, 25°C and pH 6.5~7.0.

Analysis

HANNA make conductivity meter model HI933300 was used to determine the sodium sulphate concentration in permeate at 25°C.

Experimental setup

The experimental setup used in this study is given in Figure-1. The predetermined quantity of sodium sulphate was dissolved in feed tank-1 to prepare solution and this solution was passed through micron filter to remove all micron size particulate and solution was collected in feed tank-2. The temperature of feed tank-2 was maintained by circulating water from temperature

controlled water bath. This constant temperature feed solution was pumped to membrane module via feed tank-3. Permeate and reject was recollected in feed tank-2 to keep solution concentration constant. Air with controlled pressure was fed to tank-3 to avoid fluctuations in the feed to membrane module. The feed solution concentration was varied from 0.308 to 30.878 mg L⁻¹ Na₂SO₄. Pressure was varied from 1-25 bar via adjusting feed control valve No.8 and reject control valves No. 9. After each pressure adjustment the setup was left to stabilize for pressure and permeate conductivity then permeate sample were collected and analyzed for sodium sulphate concentration.



The concentration in reject stream was determined by mass balance using Equation 1.

$$C_R = \frac{V_F C_F - V_P C_P}{10V_R} \tag{1}$$

Where C_R is the % sodium sulphate concentration (wt/vol) in the Reject stream, C_p and C_F are sodium sulphate concentration (g/L) in permeate and the feed streams,

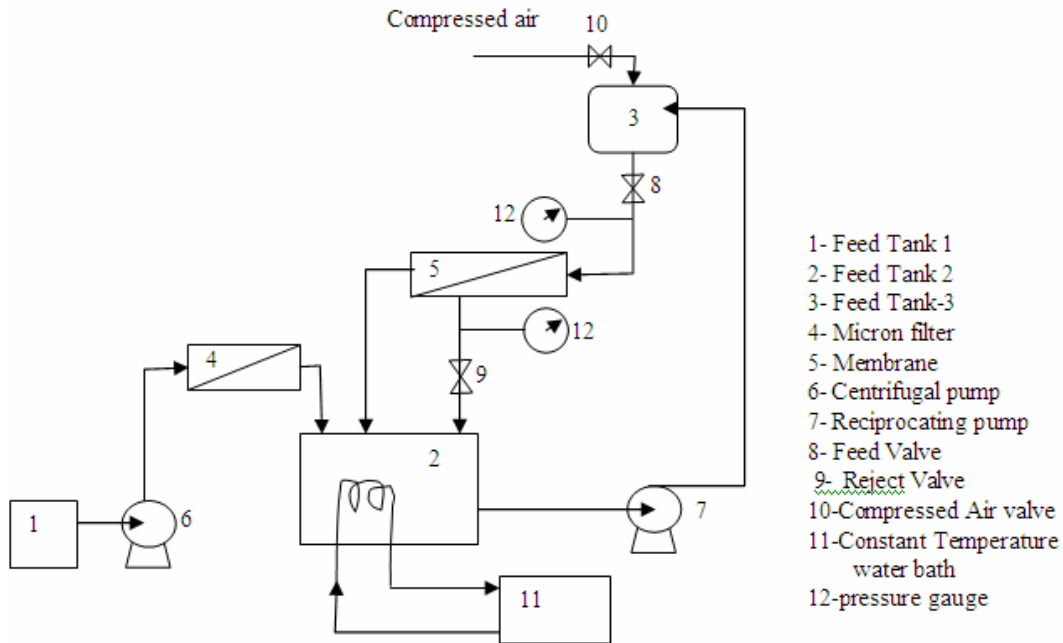


Figure-1. Experimental setup.

respectively and V_R , V_p and V_F are the sodium sulphate volumetric flow rates (L/min) of Reject, permeate and the feed streams, respectively. Permeate flux was calculated as the following equation:

$$J_p = \frac{V_p}{A} \tag{2}$$

where J_p is the permeate flux (L/min m^2), A is the effective area of the membrane. Sodium sulphate rejection was calculated as follows:

$$Na_2SO_4 \text{ Rejection} = \left(1 - \frac{C_p}{C_F}\right) \times 100 \tag{3}$$

Performance of the membranes was checked by determination of clean water flux before and after experimental study. In this study, the data presented were the averages of three measurements conducted with a standard deviation of 5%. All experiments were carried out at 25°C.

RESULTS AND DISCUSSIONS

Pure water permeability

Pure water permeability was determined to characterize the membranes for operating pressure range of 1 to 10 bars before use for experimental run. The results are shown in Figure-2. It was found that pure water flux increases linearly with the operating pressure for both

membranes and pure water permeability were obtained at 0.4769 $Lmin^{-1}m^{-2}bar^{-1}$ and 0.1407 $Lmin^{-1}m^{-2}bar^{-1}$ for NE-1812-70 and RE-1812-50 membranes, respectively. This linear behaviour could be explained by Spiegler-Kedem model according to which in absence of solute, the osmotic pressure effect becomes zero and pure water flux becomes proportional to operating pressure difference across the membrane (Xu *et al.*, 1999).

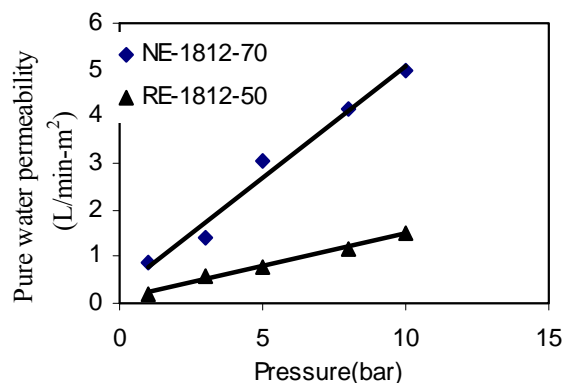


Figure 2: Variation of Pure water membrane permeability with pressure

Effect of operating pressure on sodium sulphate rejection

The Effect of operating pressure on sodium sulphate rejection was studied at feed concentration of 0.308 to 30.878 gm/L is shown in Figure-3 and Figure-4



for NE 1812-70 and RE 1812-50 membranes, respectively. It can be seen from figures that for both types of membranes sodium sulphate rejection increases with increase in pressure range studied and decrease with increase in sodium sulphate concentration in feed. Also from figures it is evident that at low feed concentration the percent rejection is above 94% for NE 1812-70 (Figure-3) and above 97% for RE 1812-50 (Figure-4).

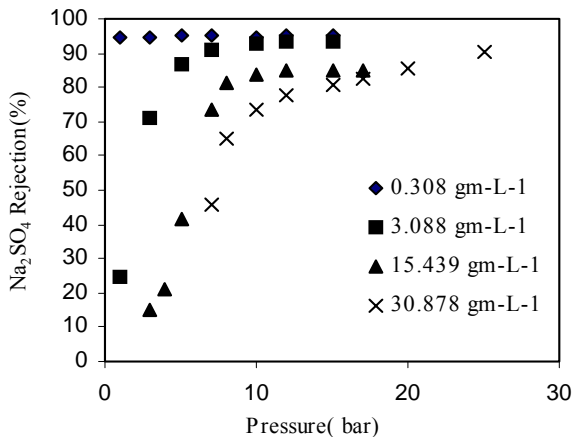


Figure 3: Effect of pressure on Na_2SO_4 rejection for NE-1812-70 at various feed concentration

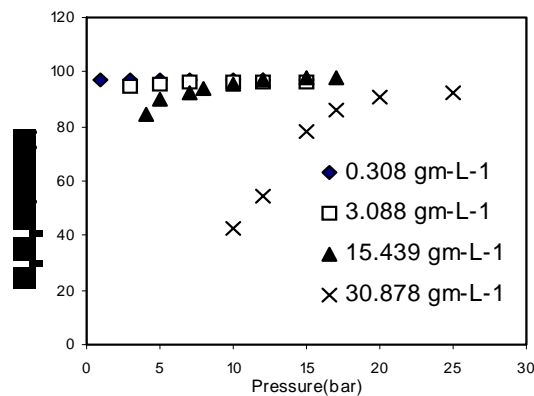


Figure 4: Effect of pressure on Na_2SO_4 rejection for RE-1812-50 at various feed concentration

At higher feed concentration the percent rejection is low for both membrane and varies from 15.29 to 90% for NE 1812-70 (Figure-3) and from 42.4 to 96.3% for RE 1812-50 (Figure-4) depending on feed concentration and operating pressure. This could be explained by the Donnan exclusion theory. The rejection to sodium sulphate mainly resulted from the repulsion between the membrane active layer and sulphate anions because the active layer of the composite membranes contains negative charge. In addition, the rejection increased with membrane charge density regardless of permeation volume flux, as fewer cations can enter the membrane pores (Fievet, *et al.*, 2002). Also with increase of feed concentration the cation shield effect on the membrane negatively charged groups became

stronger resulting in decrease of the membrane charge density and repulsion forces on the anions (Afonso, *et al.*, 2000).

Effect of feed concentration on permeate flux

For design of membrane filtration system permeate flux is an important parameter. It gives the necessary information to determine the membrane area at particular feed concentration. Figure-5 and Figure-6 show the effect of feed concentration on the permeate flux for both NE 1812-70 and RE 1812-50 membranes, respectively at pressure 10 to 15 bar. Figure-5 and Figure-6 show that for both membranes permeate flux decreases with increase in feed concentration and increased with the increase of the operating pressure. Data shows that when feed concentration increased from of 0.308 to 30.878 gm/L, flux decreased from 5.03 to 0.20, 6.22 to 0.29 and 8.17 to 0.58 L/min m^2 at pressure of 10, 12 and 15 bar, respectively for NE 1812-70 membrane while it decreased from 1.31 to 0.01, 1.59 to 0.07 and 1.96 to 0.16 L/min m^2 at pressure of 10, 12 and 15 bar, respectively.

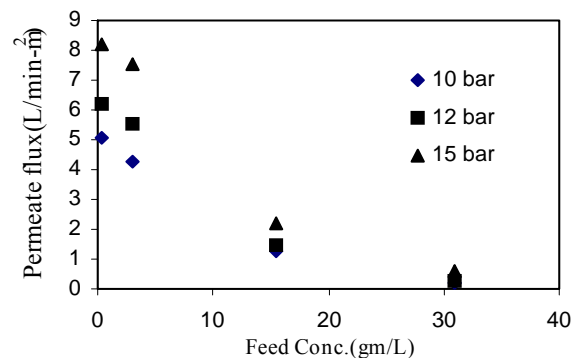


Figure 5: Effect of feed conc. on permeate flux for NE 1812-70 membrane

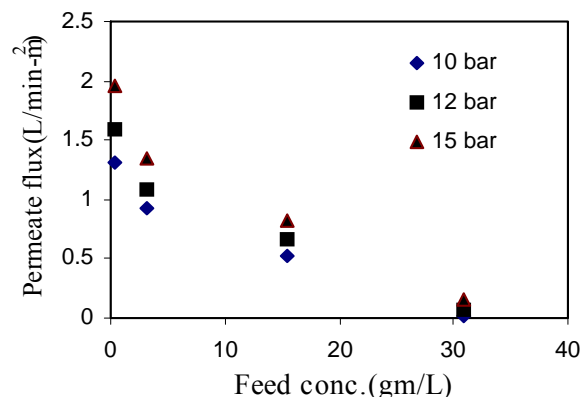


Figure 6: Effect of feed conc. on permeate flux for RE-1812-50 membrane

The change in permeate flux may be explained by Spiegler-Kedem model according to which permeate flux is proportional to pressure difference across the membrane. Also due to increase in feed concentration



osmotic pressure of the solution increases hence more pressure is required for same flux. Hence permeate flux decreases with increase in feed concentration. It was also found that permeate flux was higher for NE 1812-70 membrane compared to RE 1812-50 membrane. This may be due to larger pore opening resulting in larger fraction of area of membrane open for flow.

Effect of feed conc. and pressure on reject concentration

Membrane reject stream concentration (C_R) is an important parameter for design of down stream process equipments. Thus, for both membranes, the effect of feed concentration on reject stream concentration was studied at constant operating pressure of 10 bars and effect of operating pressure on reject stream concentration was studied at constant feed concentration of 30.878 gm/L. The reject stream concentration was calculate in terms of gm of sodium sulphate per 100 ml of solution and expressed as percent concentration (wt/vol.). The results are shown in Figure-7 and Figure-8.

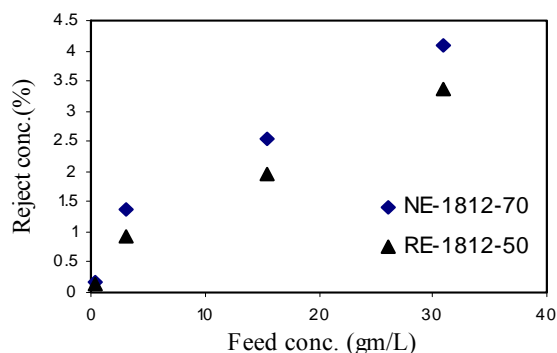


Figure 7 : Effect of feed conc. on reject conc. at 10 bar

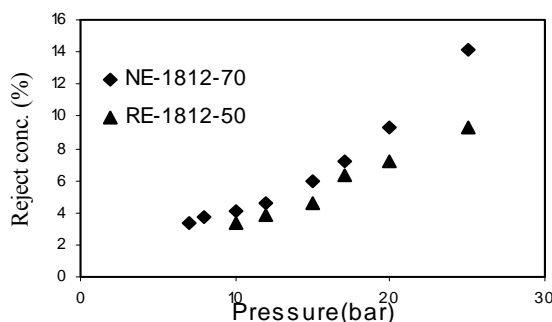


Figure 8 : Effect of pressure on reject conc. at 30.878gm-L⁻¹ feed concentration

From Figure-7 it is evident that for both membrane reject stream concentration increased with increase in feed concentration. This may be due to higher rejection at higher feed concentration. Figure-8 shows that for both membranes the reject stream concentration increased with the increase of the operating pressure. The data shows that reject stream concentration of 14.08%

(wt/vol) was achieved by NE1812-70 membrane compared to 92.9% (wt/vol.) for RE1812-50 membrane. This could be due to two effects. First, the salt flux is a function of salt concentration on both sides of membrane and has no direct relation to the operating pressure. Second, the operating pressure increases, the water flux increases correspondingly but salt flux remains constant. Hence there is an increase of salt concentration in reject stream.

CONCLUSIONS

In this study two CSM membrane were compared for recovery of sodium sulphate from waste water reuse. From the study it was found that out membrane performance largely affected by feed concentration and operating pressure. It is possible to concentrate waste water containing sodium sulphate stream up to 14.1% by use of nano membrane. The membrane NE 1812-70 was found to be more suitable for sodium sulphate recovery at high feed concentration of 30.878gm/L compared to RE 1812-50.

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