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Chemical cleaning of membrane to Enhance Flux in Nanofiltration

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Abstract— Membrane separations are one of the latest techniques widely used in industries in recent years. Its efficiency, low requirement of energy and possibility of hybrid processes makes it better than the conventional processes. The major problems in the membrane processes are flux decline, fouling and concentration polarization due to deposition of solids on the membrane surface. In present work, ethylene glycol-water solution of PCP chemicals Pvt. Ltd. containing large amount of sodium sulphates was treated with HPA-150 nanofiltration membrane on flat sheet module pilot plant. Due to high salt concentration, fouling occurs and the membrane was clogged. Thus solution was diluted and then treated and the effect of dilution was studied. It results in increase in flux and decrease in concentration polarization and thus fouling. The effect of different pressure on the flux and rejection were studied. The flux increases with increase in pressure. Effect of dilution is also studied. The flux increases with the dilution factor and the rejection decreases with dilution factor. Cleaning of the membrane can be done by chemical methods using 2% (w/v) citric acid and 2% (w/v) EDTA solution. The effect of cleaning with both the chemicals was studied and flux recovery was calculated. The flux increases as compared to that with ethylene glycol-water solution, but does not recover completely due to irreversible fouling. The flux recovery after cleaning with 2% (w/v) citric acid solution is around 56% and after cleaning with 2% (w/v) EDTA is around 70%.

Keywords— Flux enhancement, Nanofiltration, Membrane cleaning, Concentration polarization, Effect of dilution

I. INTRODUCTION

A During the last two decades rising in industrialization is also increased in waste water[1]. The quality of natural surface water often does not meet World Health Organization (WHO) standards [2]. Water resources are also contaminated by new types of contaminants such as low molecular organics, heavy metals etc. with human activities. Conventional water treatment techniques often do little to remove these ingredients from water [3]. Conventional water treatment techniques involve appropriate proportioning of added coagulant sand determination of pH of flocculation. Automation of the technological process should solve this problem; yet overdosing of reagents cannot be totally avoided [4]. In consequence, the quality of produced water does not always meet the required standards. In recent years, stringent regulations have stimulated interest in the use of membrane processes. Membrane processes seem to offer the greatest potential and advantages [5]. Membrane processes may be helpful in solving the problems of traditional techniques of water treatment. Among the existing membrane processes, nanofiltration (NF) constitutes the preferred choice for the removal of inorganic and organic pollutants from surface water and groundwater [6]. Reverse osmosis (RO) can successfully desalinate seawater and brackish water but it is not usually selected for the treatment of low salinity water [6]. Energy consumption for RO is higher than for NF due to the higher pressure required to produce water [7]. Due to these advantages, NF is increasingly being used worldwide for waste water treatment. However, like all other pressure driven membrane processes nanofiltration too suffers from the disadvantage of concentration polarization, which results in gradual decrees in permeate flux [8]. This is one of the major problems of nanofiltration which has not yet been addressed sufficiently. Therefore in present work a strategy (chemical cleaning) for flux enhancement has been explored.

II. MATERIALS AND METHODS

2.1. Chemicals

The feed solution for the present study was of ethylene glycol-water solution containing sodium sulphate impurities, which provided by *PCP Chemicals Pvt. Ltd*. Ethylene glycol (ethane-1, 2-diol) is a useful industrial compound found in many consumer products, including automotive antifreeze, hydraulic brake fluids, some stamp pad inks, ballpoint pens, solvents, paints, plastics, films, and cosmetics; it also is used as a pharmaceutical vehicle. For membrane cleaning, fouled membrane was treated by 2% (w/v) EDTA and 2% citric acid.

2.2. Membranes

HPA 150 membrane of thickness 125 micron and MWCO 150 used, with support cloth was used in the study. The membrane was supplied by Permionics Membrane Pvt. Ltd, Baroda, India. It is a thin-film composite membrane element consisting of a non-woven polyeste substrate on which a polyamine layer is coated. The membrane was prepared by solution casting and phase inversion gelling. The effective membrane area was 0.016 m^2.

III. EXPERIMENTAL SETUP

Set-up for nanofiltration with HPA-150 polyamide membrane is shown in the above fig. 1; a total reflux method is used for the treatment. The permeate stream is collected from a separate pipe and the reject is recycled into the feed storage tank. The plunger pump is used to pump the feed into the test cell. The experimental system Perma pilot plant was supplied by Permionics membrane pvt. Ltd. Vadodara, Gujarat. Feed solution from the feed tank was pressurised by high pressure plunger pump (50-400 psi) and introduced into the test cell (dimension: 225 × 150 × 50 mm). The flat sheet membrane HPA-150 is placed in the test cell. The top half of the cell the flow distribution chamber and the bottom half used as membrane support. The upper half of test cell contained a groove for the arrangement of HDPE 'O' ring to prevent leakage at high pressure operations. The permeate sample were collected and analysed for TDS, the flow rate of permeate and reject stream were recycled to the feed tank.

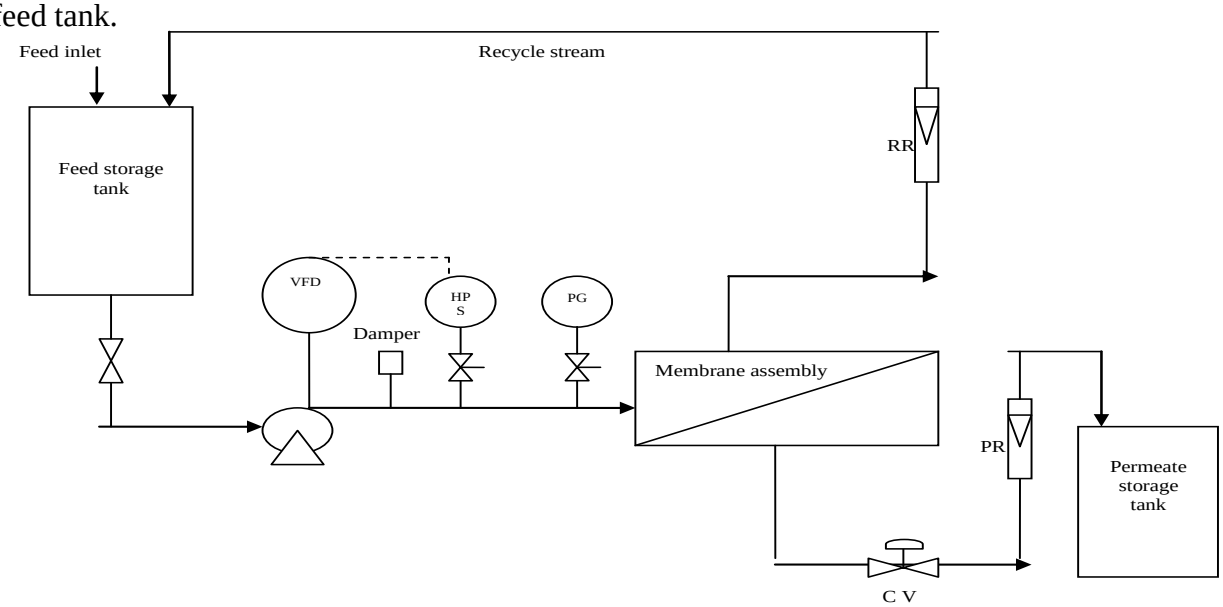

Fig. 1: Schematic of experimental setup for nanofiltration

IV. EXPERIMENTAL PROCEDURE

4.1 Compaction of membrane

Before using a fresh membrane, it was compacted at a pressure of 980 kPa for 3 h using distilled water. During compaction of the membrane, water flux was measured continuously until a constant

flux was achieved. During operation of NF systems, membrane material is exposed to high pressure of the feed water. Exposure of membranes to high pressure may result in an increase in the density of membrane material (called compaction), which will decreases the rate of diffusion of water and dissolved constituents through the membrane. As a result of compaction, higher pressure has to be applied to maintained the design permeate flow. In parallel, a lower rate of salt diffusion will result in lower permeate salinity. The effect of compaction is more significant in asymmetric cellulose membranes than in composite polyamide membranes. In seawater RO, where the feed pressure is much higher than in brackish applications, the compaction process will be more significant. Higher feed water temperature will also result in a higher compaction rate. Usually membrane compaction results in few percent flux decline, and has strongest effect during the initial operating period.

4.2 Dilution of feed

To reduce the salt content of EG-water solution, initial TDS being 30,000 ppm, it is passed through nanofiltration pilot plant. Due to very high TDS membrane was getting clogged. To prevent clogging of the membrane feed was diluted 5 and 10 times and then passed through the membrane. Dilution reduces the deposition of salts on the membrane surface and clogging is prevented. For 5 times dilution 20 litres water was added to 5 litres ethylene glycol solution. This solution was fed into the feed tank. During the two hours run taken, this feed solution goes into the test cell through the plunger pump. The test cell houses HPA-150 membrane. Permeate was collected and various parameters were measured. The reject stream was recycled into the feed tank. For 10 times dilution, 22.5 litres of water was added to 2.5 litres of ethylene glycol solution. Then the same process as above was repeated.

4.3 Effect of pressure on flux and rejection coefficient

Since pressure difference is the driving force for NF process, flux will increase with increase in pressure. The wastewater was treated at different pressures and its effect on flux and rejection coefficient was studied.

The permeate flux is calculated based on the following formula:

$$permeate\ flux = \frac{volumetric\ flow\ rate}{membrane\ area}$$

And the volumetric flow rate is given by:

$$volumetric\ flow\ rate = \frac{volume\ collected}{time}$$

$$J_w = \frac{V}{S \times t} \qquad \ldots\ldots 1$$

Where, J_w = water flux, V = volume, S = membrane area, t = time

Where, volume is in m^3, time in seconds and area of HPA-150 flat sheet membrane is 0.016 m^2.

The salt rejection for the given membrane was calculated based on the formula:

$$R = 1 - \frac{C_p}{C_b} \qquad \ldots\ldots 2$$

Where, R is the rejection, C_p is the permeate concentration and C_b is the bulk concentration.

4.4 Chemical cleaning

Permeability of the HPA-150 membrane was determined with demineralized water. Membrane was treated with 30,000 ppm Ethylene glycol-water industrial waste solution. Then the fouled membrane

was treated by an acid solution of 2% citric acid and 2% EDTA without pressure to observe its cleaning effect on fouled membrane for 1 hour.
Flux recovery of the acid cleaned membrane was determined by passing demineralized water through the membrane.
Flux recovery is calculated by following equation:

$$F_r = \frac{J_{w1}}{J_w} \times 100 \qquad \ldots\ldots 3$$

Where, F_r = flux recovery, J_{w1} = flux after cleaning, J_w = initial flux before cleaning.

4.5 Measurement of Total Dissolved Solids (TDS)
Total Dissolved Solids (TDS) are the solids which are dissolved in the water. Total dissolved solids may be present in the water due to different salt of NaCl, etc. The high content of TDS leads to change in aesthetic as well as quality of water for different purpose. Also high TDS leads to affecting the water transparency which will affect to the aquatic life and also decreases the sunlight transparency. Also, high TDS value will increases the conductivity of water and hardness. The conductivities and total dissolved solids (TDS) of all the streams were measured by an auto-ranging conductivity TDS meter.

4.6 Estimation of membrane permeability
Membrane permeability was measured by conducting experiments using pure distilled water. Flux values at various operating pressures were measured and the slope of the permeate flux versus pressure gave the membrane permeability. Once a set of runs were over membrane was thoroughly washed by distilled water for 15 mins applying maximum pressure of 980 kPa. It was followed by soaking the membrane sheet in 1% surfactant (Sodium dodecyl sulphate) solution for about an hour. After that it was washed again with distilled water to remove the traces of adhered surfactants. Membrane permeability was once again measured with distilled water. It was observed that the membrane permeability remained almost constant between successive runs.

4.7 Estimation of permeate flux and membrane rejection coefficient
Permeate flux (J_w) of the membrane was determined using following relation

$$J_w = \frac{Q_p}{A} \qquad \ldots\ldots 4$$

Where Q_p is the permeate flow per h and 'A' is the active surface area of the membrane (m^2).

Membrane rejection coefficient was estimated by

$$R = (1 - \frac{C_p}{C_b}) \times 100 \qquad \ldots\ldots 5$$

Where C_p is the concentration of permeate and C_b is the bulk concentration.
The effect of pH was found to be marginal for the feed, permeate and reject concentration in the present study. Therefore, pH variation was not considered in the parametric study of nanofiltration.

V. RESULT AND DISCUSSION

5.1 Effect of transmembrane pressure on flux

Since NF is a pressure driven membrane, the flux will increase with increase in pressure. The waste-water was treated in the NF pilot plant at 5 kg/cm^2 and 8 kg/cm^2. The flux is more at higher pressure. The rejection of solutes is almost the same for both the cases. At 5 kg/cm^2 the rejection is 91.66% and at 8 kg/cm^2 the rejection is 91%. The increase in pressure increases the flux but does not have significant effect on the rejection of the membrane. The comparison of flux at different pressure is shown in the graph.

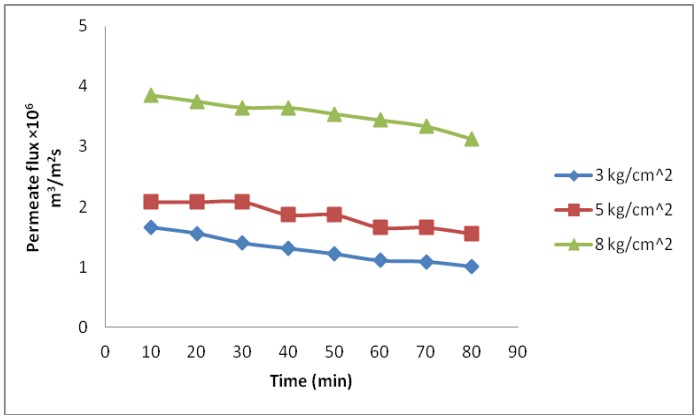

Fig.2: Permeate flux v/s time at different pressure

For both the pressures, the flux decline trend is the same, but as show in graph at higher pressure we can get higher permeates flux.

The permeate flux at different pressures (3, 5, and 8 kg/cm^2) is studied for the EG feed solution. It is observed that the permeate flux increases as the pressure increases. Since NF membrane is a pressure driven membrane, the solvent flux will increase with the increase in pressure. As seen from the experiments, permeate flux increases proportionally with increase in the transmembrane pressure drop. We can say that the operation is pressure controlled. With increase in operating pressure, at a fixed feed concentration, the driving force across the membrane increases, resulting in enhancement of the permeate flux. At a pressure of 3 kg/cm^2, the flux is 1.295 m^3/m^{2}s. At a pressure of 5 kg/cm^2 the flux increases to 1.8575 m^3/m^{2}s and at a higher pressure of 8 kg/cm^2 the flux increases to a value of 3.5415 m^3/m^{2}s.

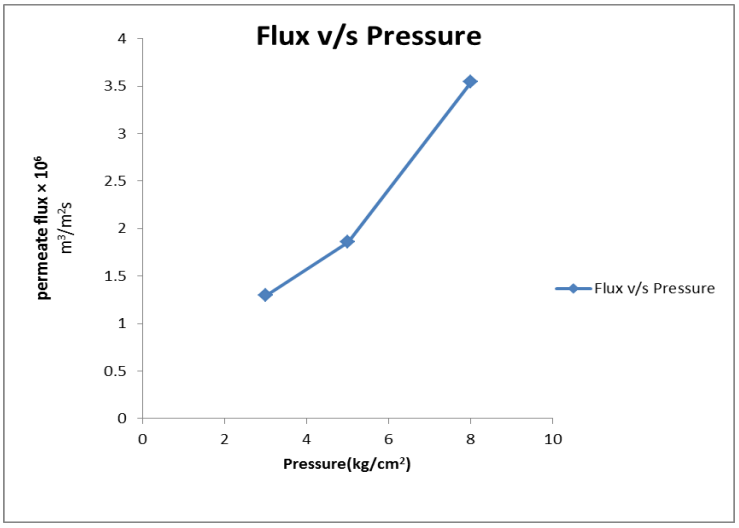

Fig. 3: Permeate flux v/s pressure

5.2 Effect of dilution

Treatment of the waste-water with 5 times dilution

Instead of cleaning the membrane every hour, we dilute the solution 5 times to make it more aqueous so that the salts don't deposit on the membrane. The pressure is maintained at 5 kg/cm^2, permeate is obtained in sufficient quantity and the flux is maintained. The TDS in permeate reduces to a range of 2000-2500 ppm after around 2 hours. Diluting the feed 5 times that is ratio of feed to water will be one part of feed and four parts of water. The distribution of solids is more thus giving a higher flux than that with no dilution.

Treatment of waste-water with 10 times dilution

Similar to 5 times dilution, 10 times dilution makes the solution even more aqueous. The TDS in permeate is in the range of 4000-4500 ppm. The flux will increase as the amount of water increases in the solution. The flux initially remains constant and later reduces after long time, due to concentration polarization and membrane fouling.

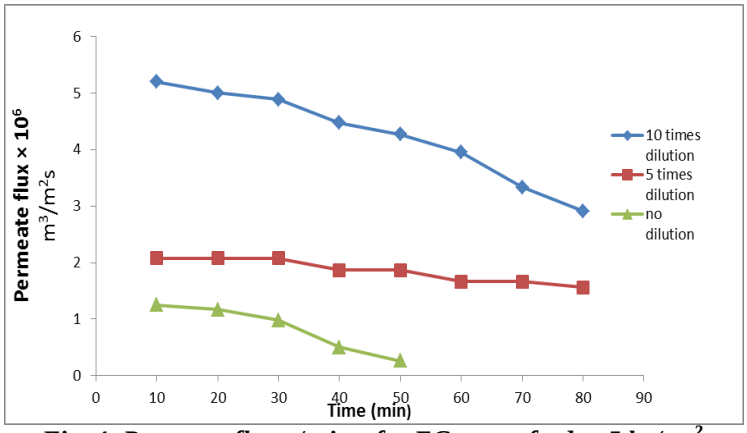

Fig. 4: Permeate flux v/s time for EG-water feed at 5 kg/cm^2

As seen in fig. 4, the flux increases as the dilution increases.

It can be said that the flux decreases with increase in concentration of the solute in the feed. Hence to obtain higher flux, the solution is to be diluted. As the dilution factor increases, the solvent flux also increases. This is due to reduction in concentration of the solutes in the feed. The solutes as not accumulated on the membrane surface as much as in undiluted feed. Hence the formation of polarized layer is less and so the resistance to the flow of solvent is less. As a result we get increased permeate flux. The rejection of solutes depends on the concentration of feed. As the feed is diluted the retention of solutes decreases. Rejection will decrease with the dilution factor of the feed. Rejection is around 97% for no dilution but membrane is clogged, 92% for 5 times dilution and 85% for 10 times dilution.

5.3 Chemical cleaning of membrane

Chemical cleaning of membrane is widely used in various membrane industries. The selection of chemicals for cleaning is critical. The chemicals used for cleaning can also be a mixture of various chemicals in defined composition, chemicals at defined pH, different temperature, etc. the chemicals should be selected in such a way that they dissolve the deposited solids on the membrane. The chemicals should not harm the membrane and should not affect the membrane properties or change them. Chemicals are selected depending on the membrane material and foulant. Cleaning can be done in two ways, acid cleaning and alkali cleaning. Acid cleaning is done to remove salt deposits or scales and alkali cleaning is done treat organic foulants. Since EG-water solution is containing sulphates, acid cleaning is preferable.

Membrane cleaning with 2% citric acid solution

Permeability of HPA-150 membrane was calculated with distilled water. So we have the water flux of distilled water at 5 Kg/cm^2. The EG-water solution was passed through the membrane for one

hour at 5 Kg/cm^2. Then the fouled membrane was water washed for about 10-15 minutes by passing water through the NF pilot plant. Next it was cleaned with 2% citric acid for one hour at room temperature and atmospheric pressure. After cleaning, again it was water washed for 10-15 minutes. Then the flux was calculated for distilled water run for one hour. Flux recovery due to cleaning was calculated. The flux recovery is calculated using equation (3).

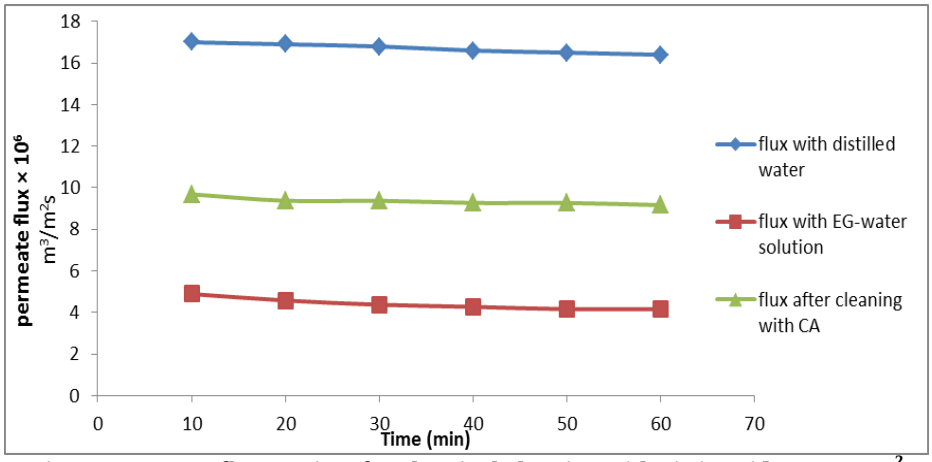

Fig. 5: Permeate flux v/s time for chemical cleaning with citric acid at 5 Kg/cm^2

Flux recovery after cleaning with Citric Acid =55.77%.

When the fouled membrane is cleaned with citric acid, due to the interactions between the sodium sulphate and other foulants retained on the membrane and the citric acid solution, the citric acid will dissolve the salts in it and thus the adsorbed salts from the membrane are removed. Since the salts adsorbed on the membrane surface blocking the pores, are removed, the solvent passage through the membrane will increase and hence the permeate flux.

Membrane cleaning with 2% EDTA(Ethylene diamine tetraacetic acid).

Permeability of HPA-150 membrane was calculated with distilled water. The EG-water solution was passed through the membrane for one hour at 5 Kg/cm^2. Then the fouled membrane was cleaned with 2% EDTA solution for one hour at room temperature and atmospheric pressure. After cleaning, flux was calculated for distilled water run for one hour. Flux recovery due to cleaning was calculated.

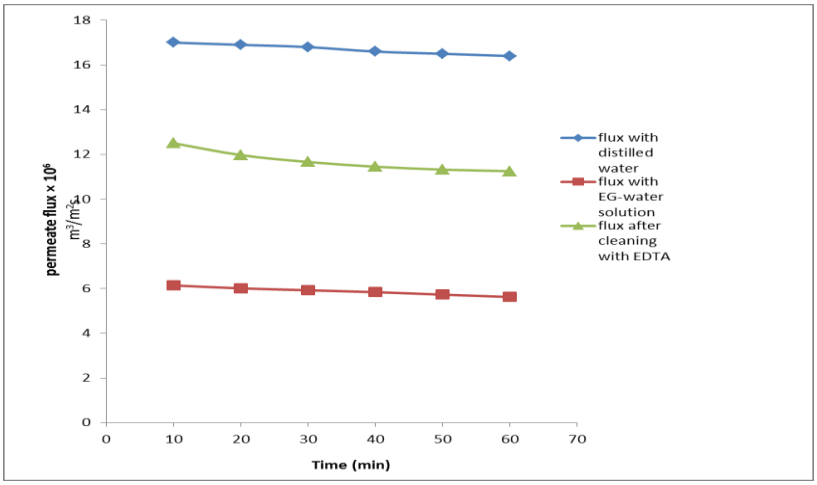

Fig. 6: Permeate flux v/s time for chemical cleaning with EDTA at 5 Kg/cm^2

Flux recovery after cleaning with EDTA = 69.84%.

As seen from fig. 6 the flux recovery is more with EDTA as compared to citric acid. This may be due to the better ability of dissolving or more interactions of the solutes with EDTA solution. EDTA will form some complexes with the solutes and hence the solutes will be detached from the membrane.
The flux increases as compared to the flux with EG-water as the chemical cleaning will remove the solids deposited on the membrane due to the salts in the solution which is reversible. The flux is not completely recovered as the initial flux, due to adsorption and permanent fouling.

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