

Fouling Subsequent Cleaning Performance of Spiral Wound Nanofiltration Membrane Module

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ABSTRACT: Fouling Subsequent Cleaning Performance of Spiral Wound Nanofiltration (NF) Membrane Module was done. The membrane modules consisted of polyamide (PA) with cross sectional area of 1 m². NF membrane fouled by Humic acid with different doses (200, 300, 500 ppm) and calcium ions (0.5 to 2 mM) and three pH selected for this study were (6.5, 7.5, 8.5) adjusted by NaOH and HCl. When the concentration of Humic acid was increased approximately from 200 to 500 ppm, retention increased from 87.5 to 89%. Initial flux at 200 ppm Humic acid of $2.667 \times 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$ decline flux $2.0724 \times 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$ with increase Calcium ion (2mM) with constant flow rate 979kPa and pH 6.5. Flux was decline with influence of Humic acid 200 ppm solution increasing pH up to 8.5 because adsorption of Humic Acid decreased at higher pH. It was obtained to electrostatic repulsion between Humic acid and the membrane surface. Fouled membrane modules were cleaned by using different cleaning agent such as anionic surfactant, e.g., sodium dodecyl sulphate (SDS) and metal chelating agent e.g., ethylenediaminetetraacetic acid (EDTA). With constant flow rate 9 lpm and transmembrane pressure drop of 69 kpa. And Comparison of flux restoration (membrane fouled with and without calcium ions).

KEYWORDS: Nanofiltration membrane, Humic acid, Calcium ions, Sodium dodecyl sulphate, Ethylene diamine tetra acetic.

I. INTRODUCTION

Spiral wound membrane module nanofiltration (NF) membrane processes are becoming increasingly popular as a result of the impressive improvements of membrane properties and the corresponding reduction in treatment cost, the significant stress to meet the ever increasing water demand, and the increasingly stringent water quality regulations. Nanofiltration membranes are used to remove organic matter and hardness from surface water and groundwater. In Membrane filtration process, spiral wound membrane module fouling depends on the foulant available in the feed stream. Wastewater filtration process, wastewater contains three type of membrane fouling categories, microbial (bacteria, viruses, etc.), organic (NOM) and inorganic (minerals) contents [7]. Depending on the physicochemical properties of the membrane, composition of feed solution and process conditions, membrane loses its performance with time. Fouling not only decreases the flux but also changes the rejection of solutes [1]. Fouling layer are general terms for deposits on or into the membrane that unfavourably affect filtration. In this study Spiral wound membrane module fouled by Nature organic matter (NOM) such as Humic acid.

Humic acid which is primarily a product of the microbiological degradation of vegetation as well as animal decay, enter surface and ground water rainwater run-off from surrounding catchment[12]. The presence of Humic acid in water is often regarded as a simple colour problem, is considered to be one of the major causes of membrane fouling. Numerous studies have reported the physical and chemical aspects of fouling of NF by Humic acid. Divalent ions such as calcium and magnesium that are naturally present in raw waters may make increase the

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problems in system. These ions which have a strong potential to form complexes with NOM are capable of forming bridges between membrane surface and NOM.

Humic acid comprising heterogeneous and unruly polymeric organic degradation products are profusely in natural waters. Humic acid molecules are highly polydispersed. The typical molecular weight spans from several kDa to a few hundred kDa with a great dependence on their sources. Humic acid is negatively charged over a wide pH range due to deprotonation of carboxylic and phenolic functional groups, and the charge density increases at higher pH [7]. Typical total acidity for Humic acids is around 8 meq/g. Compared to Humic acid, polysaccharides are larger macromolecules whose molecular weight range (200-2000kDa), typical polysaccharides have rigid fibrillar or rod-like structures and they are generally weakly negatively charged (total acidity 0–0.8 meq/g). Many polysaccharides can form an extensive three-dimensional cross-linked structure (known as a gel) in the presence of some multivalent metal ions.

Membrane cleaning is more direct and quick to restore the permeability of spiral wound nanofiltration membrane modules. In general, chemical cleaning can be broadly classified based on cleaning agents into six categories: acids (such as citric acid, HCl), alkaline (such as NaOH), Alkaline solutions remove organic foulants on membrane by hydrolysis and solubilisation of the fouling layer. Alkaline solution also increases the solution pH and there for increase the negative charges and solubility of the organic foulant [11].

II. EXPERIMENTAL

2.1 Materials

Humic acid (MW 6000 to 10,000Da); cleaning agents, namely, sodium dodecyl sulphate (SDS) and ethylenediaminetetraacetic acid (EDTA) were purchased from Loba Chemie Pvt. Ltd., Mumbai India. All the analytical grade chemicals were used without further treatment. Calcium carbonate was used as divalent calcium source.

2.2 Methods

2.2.1 Experimental set-up

The schematic flow diagram of the Perma Pilot Plant (a spiral wound configuration with nanofiltration (NF) membrane module for research purpose) was shown in Fig. 2.1. The experimental setup was supplied by M/s Permionics Membranes Pvt. Ltd., Gujarat, India. Spiral wound membrane module was connected with a feed tank (20 L). A cooling tank (20 L) was provided to control the temperature of retentate. Two rotameter were connected with retentate and permeate line to measure flow rates of retentate and permeate, respectively. To manipulate feed flow rate and pressure in membrane module, a part of feed was recycled through a by-pass line. High pressure (up to 4136 kPa) triplex plunger pump was attached with the pilot plant to circulate the feed in NF membrane module. Spiral wound NF polyamide membrane module was procured from M/s Permionics Membranes Pvt. Ltd., Gujarat, India. The NF hydraulic membrane permeability (L_p) was measured as $3.62 \times 10^{-11} \text{ m/Pa}\cdot\text{s}$. respectively. Polyamide NF membrane module with effective membrane cross sectional area of 1 m^2 , length of 510 mm and diameter of 73 mm was housed in stainless steel (SS 316) cylindrical shell. Flow rate (up to 10 lpm) of the feed was controlled with the help of rotameter and control valve. One control valve was attached at the outlet of the retentate line to maintain the desired pressure inside the membrane module. To measure the electrical conductivity of permeate; one conductivity meter was attached with the module. Temperature had influence in the permeate flux. Therefore, a cooling tank was provided to maintain the temperature of feed tank. Before experiment, NF membrane module was compacted with deionised water at 100 for 1 h.

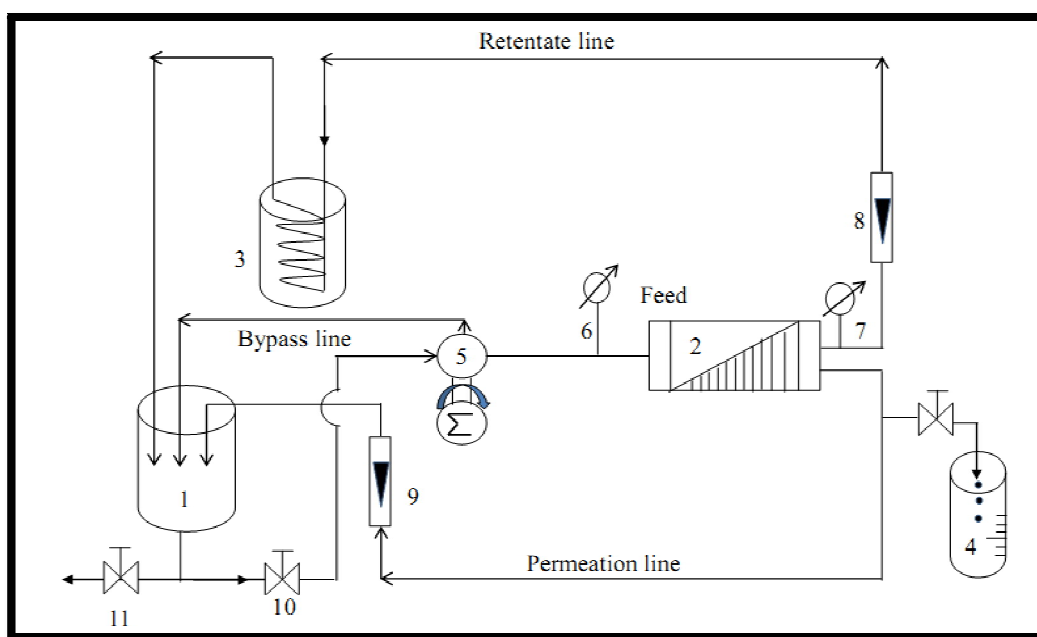


Fig.1.1. Schematic diagram of spiral wound membrane setup

- (1) Feed tank (2) NF spiral wound membrane Modules(3) Cooling tank (4) Measuring cylinder (5) Plunger pump (6) Inlet pressure gauge (7) Outlet pressure gauge (8) Retentate flow rate (9) Permeate flow rate (10) Feed control valve (11) Drainage valve

2.3 Experimental methods

2.3.1 Fouling operations

Organic fouling tests conducted using the small lab scale NF membrane modules. NF membrane module fouled by Humic acid, solution were prepared 200, 300 and 500 ppm by using stirred at 200 rpm for 30 min duration, calcium ions different concentration added in feed and pH adjusted by NaOH, HCl. Prepared feed was put in feed tank. NF membrane experiment was conducted 979 kPa, and flowrate 9 lpm. Constant feed flow rate was maintained by adjusting the control valves. Permeate samples were collected at a definite time interval for analysis of purpose and the remaining amount of permeates was recycled to feed tank. Total time to run these experiments was 90 min. To maintain the transmembrane pressures (TMP) inside the membrane module, feed and retentate outlet control valves were adjusted. The temperature of the feed tank was measured periodically and maintained at $25 \pm 2^\circ\text{C}$ with the help of cooling tank by circulating coolant.

2.3.2 Cleaning experiments

Membrane cleaning is carried out to recover the permeate flux. The cleaning process started with the circulation of selected cleaning solution for 15 at 69kPa and cross flow velocity of 9 lpm. DI water, SDS and EDTA used cleaning of fouled membrane module. Cleaning agent used with different physical and chemical operating conditions. Make a Cleaning solution and adjusted pH with used NaOH and HCl and fixed feed temperature. Feed put in tank after started set up and measured the flux. Flux is recovered at cleaning process. The restored flux using organic-free test solution at identical operating conditions used in the fouling experiment determined the efficiency of the membrane cleaning. All the operations were carried out at a temperature of $30 \pm 2^\circ\text{C}$.

2.3.3 Humic acid concentration measurement

Humic acid concentration was measured using a UV-vis spectrophotometer (Thermo scientific UV 2300). In this method, the samples were placed in a quartz cuvette and the absorbance value of the sample was measured at a

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wavelength of 254 nm. A standard calibration curve of UV 254nm absorbance vs Humic acid concentration. Was produced from which the concentration of unknown sample could be obtained, pH 6.5 and temperature 25°C. Humic acid concentration is plotted versus absorbance and the results were linear fitted. The value of regression (R^2) is found to be as 0.98. Feed and permeate concentration show in next section.

III. RESULTS AND DISCUSSION

3.1 Nanofiltration membrane fouling

3.1.1 Effect of Humic acid and Calcium ions concentration on flux reduction

NF membrane module fouled by 200 ppm Humic acid at TMP 979 kPa and 6.5 pH. In filtration process investigated flux decline with and without calcium ions concentration. Shown in Fig.3.1 initial $2.6667 \times 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$ and final $2.31214 \times 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$ flux for Humic acid solution filtration process without calcium ions, flux is less decline and with 2 mM calcium ions final flux $2.0724 \times 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$. Calcium ions presence in feed flux decline rate higher as compare to absence of calcium ions. In the absence of calcium ion, flux was not so much lowered inspite and some amount of adsorbed Humic acid. It was considered that the deposited layer might have loose structure because there does not exist calcium ion which connects different Humic acids. Membrane fouling by colloid particles has been explained by van-der Waals force, electrostatic interaction between the colloidal particles and the membrane surface.

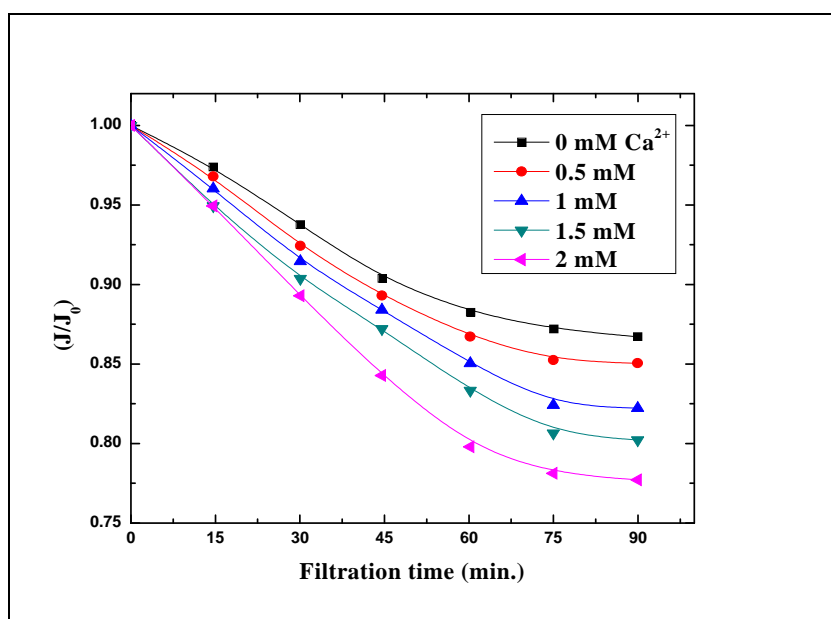


Fig. 3.1. Variation of Flux decline with calcium ions concentrations.

3.1.2 Effect of solution pH

The influence of Humic acid 200 ppm solution pH (6.5, 7.5, 8.5) on membrane fouling, pH adjusted by adding NaOH and HCL. The rejection efficiency increased with an increase in pH. The possible reason is that the membrane surface charge and Humic charge was been more negatively due to deprotonation functional groups under alkaline condition. Under these conditions, Humic accumulation on the membrane surface decrease. It was observed that the relative flux declines (J/J_0) shown in Fig.3.2. A more significant decline in permeate flux is observed at pH 6.5 compared to pH 8.5. This behaviour rare attributed to the less electrostatic repulsion among the Humic acid molecules and between Humic acid molecules and the membrane surface at this pH. In generally, flux decline at pH 6.5 to 8.5 is very small because all the functional groups are already deprotonated and the membrane is negatively

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charged. As a result, Humic accumulation on the membrane surface is not substantial. The shape of Humic acid molecules are different with pH, due to increased electrostatic repulsion between negatively charged near carboxyl groups and thus form asperser fouling layer. Similar trends of increased flux decline with decreasing pH for charged natural organic matter (NOM). The amount of Humic acid to be adsorbed should decrease with increasing pH because the electrostatic repulsion between the Humic acid and the membrane surface would increase with the increasing pH.

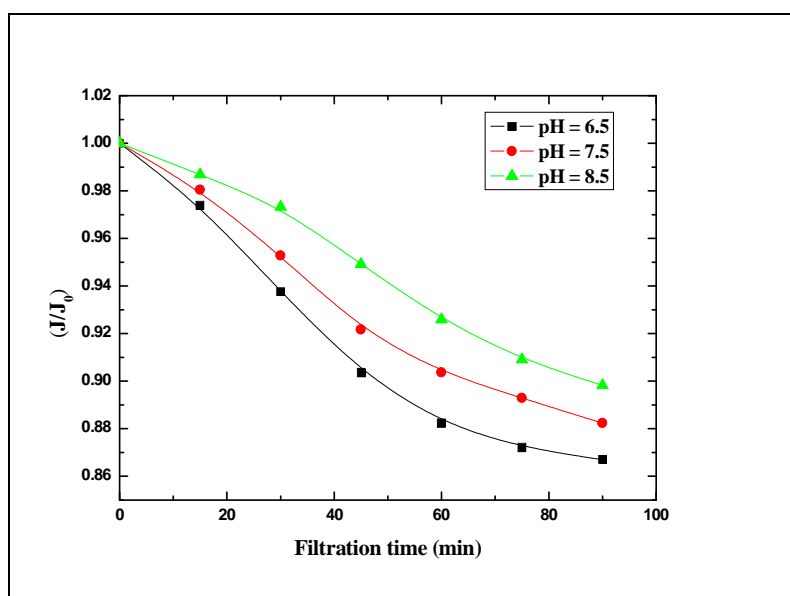


Fig.3.2. Variations of flux decline at deferent pH of 200 ppmHumic acid

3.1.3 Humic acid Rejection

Foulant (Humic acid), different concentrations (200 to 500 ppm) at TMP drops 979 kPa were used to foul the spiral wound NF membrane module. With increased of Humic acid concentration from 200 to 500 ppm, rejection will increase from 87 to 89%. Rejection percentage with different concentration shown in table 3.1 the result is at high concentration rejection rate high. Because at high concentration Humic acid molecules will pass less from membrane, maximum Humic particles deposited on membrane surface and make a gel layer. These deposited particles created some problems in filtration process; membrane fouled on after some time.

Table 3.1 Humic acid Concentration in permeate

Feed (ppm)	Permeate (ppm)	Rejection (%)
200	25	87.5
300	42	86
500	65	89

Feed and permeate sample (Humic acid)

Solution has been filtered 200 ppm Humic at 6.5 pH, acid solution by using spiral wound NF membrane module and later found that the permit Humic acid concentration decrease to 25 ppm Humic acid as shown in the Fig.3.3. So the rejection percentage was calculated to be 87.5%.

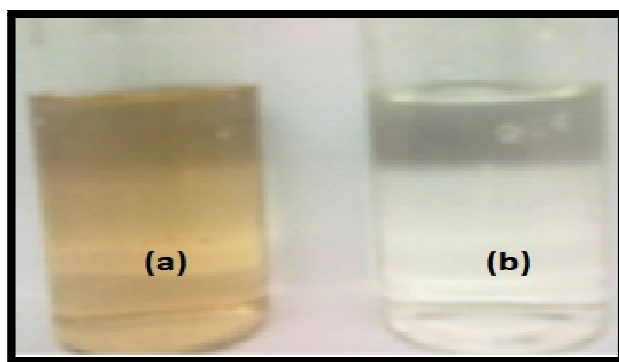


Fig.3.3. The photographs for (a) feed and (b) permeate solutions

3.2. Nanofiltration membrane cleaning

3.2.1 Study of cleaning dose

To optimize the dose of SDS (pH = 11) and EDTA (pH = 11) in terms of original flux recovery SDS concentration was varied from 2 to 10 mM whereas EDTA concentration was varied from 0.5 to 2 mM. Pure water flux at TMP 69 kPa was $21.73 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$ and after fouling membrane flux was reduced to $5.5 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$. The variation of permeate flux values with SDS concentration was shown in Fig.3.5 (a). It was observed from the figure that with the increase of SDS dose, permeate flux was found to increase. When SDS concentration was increased permeate flux recovery was increased from $5.5 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$ to $14.85 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$, when dose was 8 mM. Flux recovery was observed when SDS concentration was further increased to 8 mM. Beyond this concentration, recovery of permeate flux was marginal [10]. Hence, 8mM SDS concentration was taken as optimum surfactant dose. With EDTA the recovery of permeate flux was increased from $5.5 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$ to $17.85 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$, when dose was 1 mM. The results were shown in Fig.3.5 (b). Like SDS dose, further increase in permeate flux was observed with increase in EDTA dose. When EDTA dose was 1mM, the recovery of flux was 92%. Further increase in EDTA dose to 2 mM could not increase the permeate flux recovery. So 1mM EDTA was considered as the optimum dose.

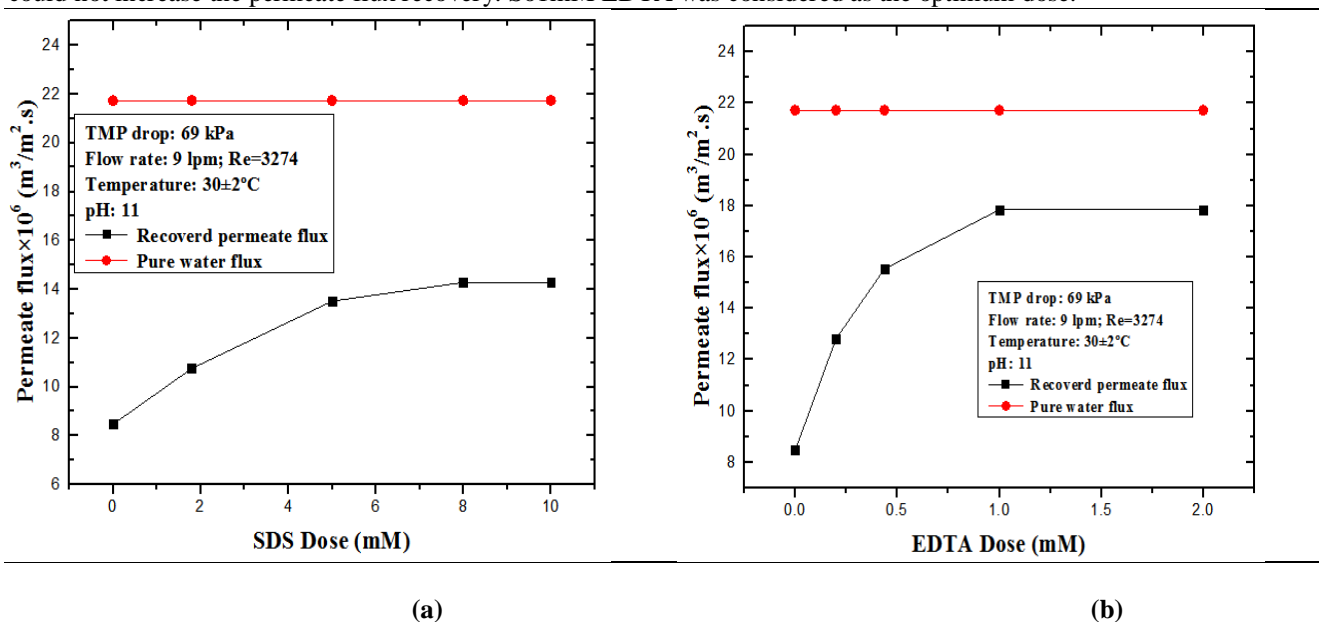


Fig.3.5. Optimization of SDS and EDTA concentration to recover the permeate flux.

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3.2.2 Effects of with and without calcium on membrane cleaning

Spiral wound NF membrane filtration process 200 ppm Humic acid solution module was fouled after 90 min. Before filtration NF membrane permeability 3.62×10^{-11} m/Pa.s, and pure water flux 21.73×10^{-6} m³/m².s after 90 min flux decline with calcium ions flux 5.5×10^{-6} m³/m².s at 69 kPa without calcium ions flux 6.25×10^{-6} m³/m².s shown in Fig.3.6. With calcium ions flux is more declines. Fouled spiral wound NF membrane module (200 ppm HA and 2 mM Ca²⁺) clean with cleaning agents such as DI water, SDS and EDTA. At DI water cleaning process flux was recover 8.142×10^{-6} m³/m² and optimum dose SDS cleaning process flux was recover 14.85×10^{-6} m³/m².s. EDTA cleaning efficiency is high as compare to SDS optimum EDTA dose 1 mM flux recover to 17.85×10^{-6} m³/m².s and efficiency 92%. This is due to the fact that EDTA in contact with the membrane during the cleaning process may make the membrane more hydrophilic and increase the water permeability [5], on the other hand, was able to almost restore the flux to its initial level. The excellent performance of EDTA as a cleaning agent for alginate removal is due to its strong metal chelating property that can preferentially bond calcium in alginate-calcium gel through legend-exchange reaction to form soluble calcium-EDTA complexes [3]. As a result, the cross linked alginate calcium structure was destroyed and the alginate chains were easily separate and removed from the membrane surface. But without calcium fouled membrane cleaning efficiency is high to compare with calcium, the same shear rate was not sufficient to physically remove the strongly bonded alginate-calcium gel from the membrane surface when calcium was present in the feed.

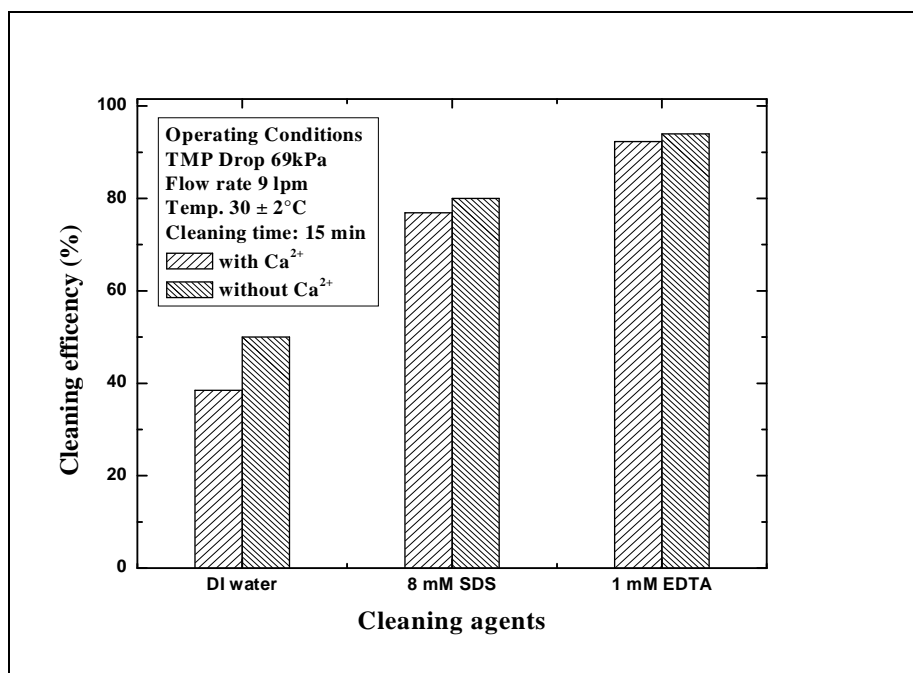


Fig.3.6. Comparison of flux restoration with and without calcium ions.

IV. CONCLUSION

- In this present work organic pollutants Humic acid were treated with the help of NF membrane modules. The maximum removal efficiency of Humic acid is 77% after it reaches its steady state value after 90 min of operation.
- EDTA was shown to be a better cleaning agent as compare to SDS for alginate fouling in the presence of calcium because of its ability to form soluble complexes with calcium from the sodium alginate calcium gel layer.

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- In Humic acid solution fouling is more pronounced at low pH as compare to high pH. Amount of Humic acid to be adsorbed should decrease with increasing pH because the electrostatic repulsion between the Humic acid and the membrane surface increases with the increasing pH.
- For cleaning of Fouled spiral bound membrane modules, we took different doses of SDS and EDTA and we found that 8 mM SDS and 1mM EDTA gives maximum cleaning efficiency.

REFERENCES

1. Ang, Tiraferri and Elimelech “chemical cleaning of RO membrane fouled by wastewater effluent: Achieving higher efficiency with dual-step cleaning”, *Journal of Membrane Science*, Volume 376, pp. 100–106, 2011.
2. Lee and Elimelech “chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes” *J membrane sci*, Volume, 272(1-2), pp. 198-210, 2006.
3. Mohammadi, Madaeni and Moghadam “Investigation of membrane fouling”, *desalination*, Volume 153(1-3), pp. 155-160, 2003.
4. Lee and Elimelech “Salt cleaning of organic-fouled reverse osmosis membranes”, *water resource*, Volume 41(5), pp. 1134-1142, 2007.
5. Sun and Listiari “Organic fouling of nanofiltration membranes: Evaluating the effects of Humic acid, calcium, alum coagulant and their combinations on the specific cake resistance”, *Journal of Membrane Science*, Volume 332, pp. 56–62, 2009.
6. Sun and Chun “Fouling mechanism and resistance analyses of systems containing sodium alginate, calcium, alum and their combination in dead-end fouling of nanofiltration membranes”, *Journal of Membrane Science*, Volume 344, pp. 244–251, 2009.
7. Yoon and Lee “Effect of calcium ion on the fouling nanofilter by Humic acid in drinking water production” S0043-1354, 00416-8, 1997.
8. V. Singh and C.Das “Performance of spiral wound ultrafiltration membrane module for with and without permeate recycle: Experimental and theoretical consideration”, *Desalination*, Volume 322, pp. 94–103, 2013.
9. Ahmed and Robert “Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency”, *Journal of Membrane Science*, Volume 303, pp. 4–28, 2007.
10. Hong and Elimelech “Chemical and physical aspect of natural organic matter (NOM) fouling of nanofiltration membrane”, *Journal of Membrane Science*, Volume 132, 159-18, 1997.
11. Rathore H, Kushwaha P and Singh V “Fouling Subsequent Cleaning Performance of Spiral Wound Reverse Osmosis Membrane Module”, *International Journal of Chemical Studies*, Volume 4(2), pp. 66-69, 2016.
12. Kushwaha P, Rathore H and Pandey L K “Removal of Chromium Ions from Synthetic Tannery Wastewater by using Untreated Neem Sawdust as an Adsorbent”, *International Journal of Engineering Trends and Technology*, Volume 34(1), pp. 32-34, 2016.