Design & Fabrication of Nanofiltration Unit: A Review

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Abstract - This review comprises of various methods and materials used for design of nanofitration unit for diverse applications. Nanofiltration is an advance membrane separation technique for water and wastewater treatment as well as concentration & separation of antibiotics and pharmaceuticals due to its unique charge-based repulsion property and high rate of permeationrelies on the ability of membranes to discriminate between the physical size of particles or species in a mixture or solution and is primarily used for water pre-treatment, treatment, and purification. The membranes are key to the performance of nanofiltration systems. Recent developments of membranes for NF have greatly extended their capabilities in very high or low pH environments, and in their application to non-aqueous liquids. Some methods are summarized showing their driving force, membrane structure and the approximate time of introduction for technical filtration. The effect of various nanofiltration membranes on different water samples are described so as to ensure proper fabrication of nanofiltration unit for diverse purposes such as in waste water treatment.

Keywords - NF-Nanofiltration; Molecular weight cut off(MWCO); MF-Microfiltration; UF-Ultra filtration; UV-Ultraviolet; TDS-Total Dissolved Solids;RO-Reverse Osmosis ; ED-Electro dialysis; AFM-Atomic Force Microscope; Scanning Electron Microscope; DMAc-dimethylacetamide ;PVP- polyvinyl pyrrolidone; mine influenced water; nanofiltration; feed pH; iso-electric point; ion rejection; metal recovery; discharge criteria Pollutants Asymmetric Polyethersulphone ; Optimum condition.

I. INTRODUCTION

Nanofiltration (Pore size: Particles in the molecular range from 0.0001 µm to 0.001 µm or 250 to 400 MW) is the newest of the major methods, serving as an intermediate between ultra filtration and reverse osmosis. This process allows some salts through the membrane, allowing monovalent ions to pass while rejecting high percentages of divalent cations and multivalent ions. Nanofiltration membranes are rated in terms of percent salt rejection and flow. Pre-treatment of seawater feed to RO/thermal processes using nanofiltration prevents scaling by removal of scale forming hardness ions, prevents membrane fouling in RO processes by removal of turbidity and bacteria and is expected to lower the required pressure to operate RO plant by reducing seawater [7]. Nanofiltration can be used for partial and/or selective demineralization of brackish water, and is more suitable for producing drinkable water directly without the need for remineralisation compared to RO. The separation process for NF requires that the water be forced through a semi-permeable membrane in the opposite direction of natural osmotic flow, leaving contaminants in the more highly concentration solution (reject water) [12,13]. Nanofiltration is a low- to moderately high-pressure (typically 50 to 450 pounds per square inch [psi]) process in which monovalent ions will pass freely through the membrane but highly charged, multi-valent salts and low molecular weight organic molecules will be rejected to a much greater degree. NF employs very high pressures and thin film membranes to filter particles of sizes on the order of 10 nanometres (nm). NF membranes used for potable water applications typically use molecular weight cut-offs of 200 to 400 daltons (i.e., approximately 2 to 4 nm). NF systems employ pressures between 70 psi and 150 psi and flux rates ranging from 15 to 25 gallons per day per square feet (gpd/ft2) An NF membrane system train consists of chemical addition for pre-treatment and pH adjustment, a cartridge filter for removal of large particles that may foul the membrane system, medium to high pressure booster pumps for the feed water, membrane vessels, a disposal system for concentrate, degasifier, a clearwell for the addition of post-treatment disinfection and softening agents, and a transfer pump to water storage or to the distribution system. Operation of an NF facility requires cleaning the pre-treatment filters, disinfecting and cleaning the membrane to prevent fouling, and checking the system to ensure proper operation. Membranes are expected to have at least a 3 to 5-year lifespan. NF membranes have up to a 90 percent recovery rate [9,10].

II. MATERIALS AND METHODS

The simplest NF system for POU/POE consists of a prefilter, an NF membrane filter, a booster pump, a storage tank for the treated water, and a flow regulator for the reject water, just like any RO system design [11]. Benefits of water treatment nanofiltration include: Lower operating costs, Lower energy costs, Lower discharge and less wastewater than reverse osmosis, Reduction of total dissolved solids (TDS) content of slightly brackish water, Reduction of pesticides and VOCs (organic chemicals), Reduction of heavy metals, Reductions of nitrates and sulfates, Reduction color, tannins, and turbidity, Hard water softening, Being chemical-free (i.e., does not use salts or chemicals), and Water pH after nanofiltration is typically non aggressive.

METHOD	DRIVING FORCE	MEMBRANE	PERMEATION
Dialysis	Concentration	Porous	Solutes
Electro dialysis	Electrical	Porous	Ions
Cross flow filtration	Pressure/concentration	Porous	Water
Pervaporation	Partial pressure	Dense	Liquid
Membrane distillation	Partial pressure	Porous	Liquid

Table1. Properties of various methods for membrane filtration [11].

III. DIFFERENT NANOFILTRATION MEMBRANES

A. Antifouling nanofiltration membrane prepared from MWCNTs-

The multi walled carbon nano tubes (MWCNTs) were oxidized by sulfuric acid and nitric acid to generate functionalized groups in structure of MWCNTs in order to increasing dispersivity of carbon nanotubes in polymer matrix. The treated MWCNTs exhibited good compatibility between MWCNTs and polyethersulfone components. Cross sectional SEM images of membranes top-layer showed initially by adding /increasing of oxidized MWCNT, size of top-layers pores enhanced until 0.2 wt% of MWCNT and again reduced by further increasing of MWCNT amount. In addition, fouling of membrane resulting from BSA filtration could be reduced by importing MWCNTs to the blend membrane. The results confirmed that the surface roughness of membranes plays an important role in antibiofouling resistance of MWCNT membranes, which 0.04 wt% MWCNT/PES membrane with lower roughness had the best antifouling properties [14,15]. The behavior of the MWCNT blended membranes in salt retention experiments indicated that the mechanism of salt rejection is Donnan exclusion, which membranes surface are negatively charged. In the last several years, considerable attempts have been made to develop new composite polymeric materials to improve both performance and antifouling properties of nanofiltration membranes. Selection of an appropriate membrane, pretreatment of the process fluid, adjustment of operating design, and conditions are all recognized to control fouling to some extent. It is generally accepted that an increase in hydrophilicity provides better fouling resistance because protein and many other foulants are hydrophobic in nature. Most nanofiltration membranes are electrically charged, which significantly reduces the scale-formation. Dimethylacetamide was used as solvent in preparation of oxidized MWCNT blended PES membranes. The antifouling performance of the pristine polyethersulfone and modified MWCNT/PES nanofiltration membranes was characterized by means of measuring water flux recovery after fouling by BSA solution.

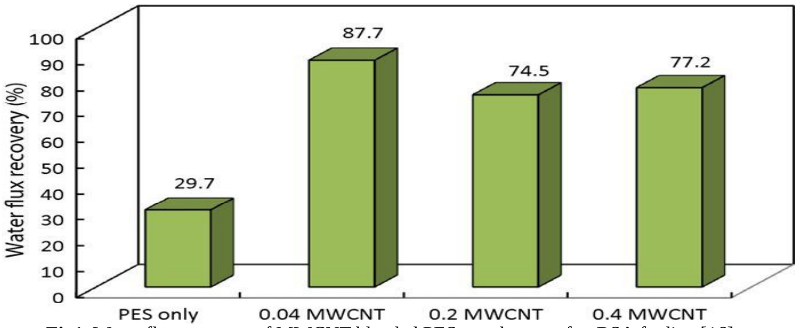


Fig1. Water flux recovery of MWCNT blended PES membranes after BSA fouling [16].

B. Dow NF 270 polyamide membrane and a TriSep TS 80 polyamide membrane-

Two nanofiltration membranes, a Dow NF 270 polyamide thin film and a TriSep TS 80 polyamide thin film, were investigated for their retention of ionic species when filtering mine influenced water streams at a range of acidic pH values. The functional iso-electric points of the membranes, characterized by changes in retention over a small pH range, were examined by filtering solutions of sodium sulphate. Both membranes showed changes in retention at pH 3, suggesting a zero net charge on the membranes at this pH.

Authors	**Membrane**	**pH range**	**Solution**	**IEP**
Childress and Elimelech [3]	NF 70	2–9	0.001 M NaCl	4
			0.001 M NaCl + 0.001 M CaCl2	3- 3.5
			0.001 M NaCl + 0.001 M Na2SO4	4
			0.001 M NaCl + 0.001 M MgSO4	-
	TFCS	2-9	0.001 M NaCl	3
			0.001M NaCl + 0.001 M CaCl2	3.5
			0.001 M NaCl + 0.001 M Na2SO4	3
			0.001 M NaCl + 0.001 M MgSO4	3
Hagmeyer and Gimbel [4]	Desal 5 DK	3–11	0.002 M KCl	4
	NTR-729]	3–11	0.002 M KCl	4
Childress and Elimelech [2]	NF 55	3–9	0.001 M NaCl	3.2
			0.001 M NaCl + 2 mg L−1 humic acids	no IEP
			0.001 M NaCl + 1 mM surfactants	
				no IEP
			0.001 M KCL	
Tanninen *et al.* [5]	NF 270	-	0.001 M KCL	3.3
	Desal 5 DK	-	0.001 M KCL	4.1
	Desal KH	-	0.001 M KCL	4.9
	BTP-NF-1	-	0.001 M KCL	6
	BTP-NF-2	-		5.4
			0.001 M NaCl	
	NF 270	2.5–7	0.001 M $CaCl_2$	2.8
Artug [1]				3.5
	NF 90	2.5-7	0.001 M NaCl	
			0.001 M $CaCl_2$	4.3
	NF PES 10	2.5-7		4.3
			0.001 M NaCl	
	NF 2 2.5–7	2.5-7	0.001 M $CaCl_2$	3.4
				3.5
			0.001 M NaCl	
			0.001 M $CaCl_2$	3.2
				2.9

Table2. Iso-electric point (IEP) of different commercial nanofiltration (NF) membranes as measured in the existing literature.

IV. EXPERIMENTAL ANALYSIS OVER MINE WATER SAMPLE

Two NF membranes were tested in this study. A Dow NF 270 polyamide thin film composite NF membrane was used, because of the availability of published work describing its zeta potential and IEP and, therefore, the ability to compare the current results. NF 270 is considered a “loose” NF membrane, with nominal MgSO4 rejections of about 97% and molecular weight cut-off of 270 Da. The published NF 270 IEP range is between pH 2.5 and 4. A TriSep TS 80 polyamide thin film composite NF membrane was also assessed as an example of a “tight” NF membrane [1,5,6]. It is characterized by a nominal monovalent ion rejection of 80%–90%, a higher than 99% rejection of polyvalent ions and has a molecular weight cut-off between 100 and 200 Da. The IEP of TS 80 has been found at about pH 3.

IEP Tests-

Type of Test	Feed Sample	NF membrane	Feed Flow (L h−1)	Feed Temperature (°C)	Feed Pressure(bar)	Permeate Flux Rate (L m−2 h−1)
IEP Test IEP Test	NaCl-Na2SO4 NaCl-Na2SO4	NF270 TS 80	200 225	37 ± 4.1 25 ± 0.0	20 ± 0.0 10 ± 0.5	130 ± 0.0 33 ± 5.8
Feed pH Test Feed pH Test	MW A MW B	NF 270 TS 80	200 225	25 ± 0.6 25 ± 0.5	7 ± 1.2 19 ± 2.8	32 ± 2.5 35 ± 4.6
Recovery Test Recovery Test Recovery Test Recovery Test	MW C MW C MW D MW D	TS 80 NF 270 TS 80 NF 270	225 225 225 225	25 ± 1.2 25 ± 0.5 25 ± 0.5 25 ± 0.8	23 ± 5.0 10 ± 2.7 22 ± 6.2 10 ± 1.9	32 ± 2.0 34 ± 0.9 33 ± 1.6 34 ± 1.5

Table3. Three sets of tests were conducted on four mine water samples and on two NF membranes [17,18].

The IEP tests were carried out with feeds ranging from pH 5 to pH 2 in 0.2 pH decrements by dosing hydrochloric acid. Test details, *i.e.*, the feed flow rate, feed temperature, feed pressure and permeate flux rate, are listed in table. The results of the IEP Tests are shown in Figure, where the relationship between ion rejection and feed solution pH is presented [1,5,6].

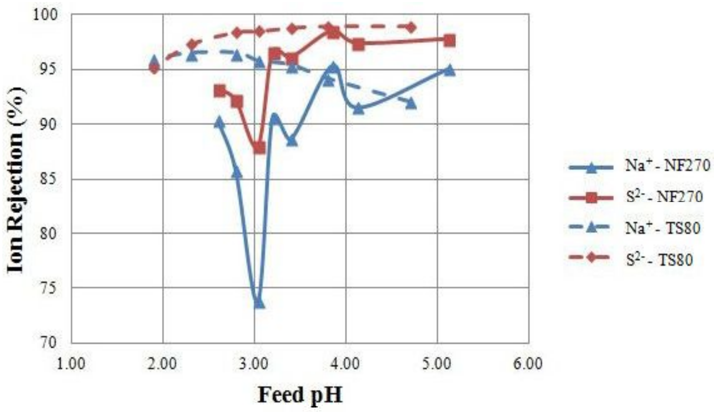
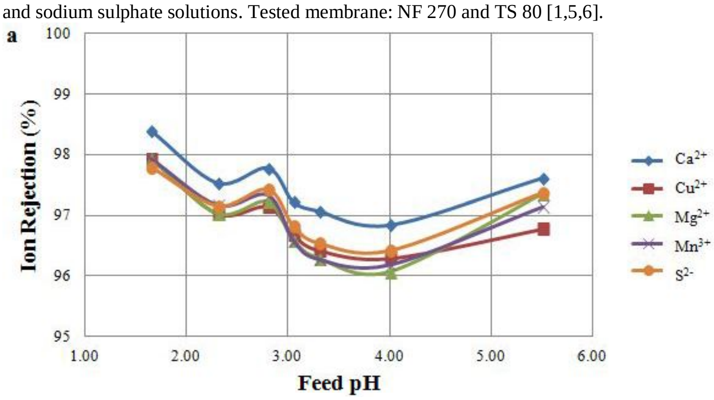


Fig2. Ion rejection as a result of the IEP Tests. Tested feed solution: sodium chloride and sodium sulphate solutions. Tested membrane: NF 270 and TS 80 [1,5,6].



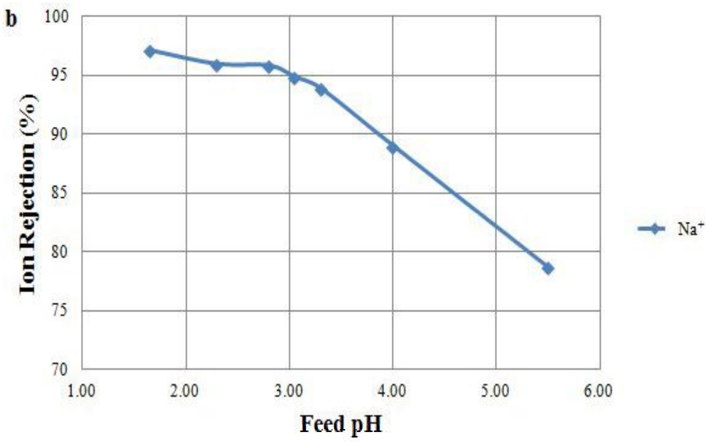


Fig3.Tested feed solution: MW B. Tested membrane: TS 80 membrane, (**a**) Rejection of multivalent ions; (**b**) Rejection of sodium ion [21].

V. EFFECT OF PH ON DYE REJECTION WITH ASYMMETRIC N23 MEMBRANE

Balik wastewater contains high concentration of pollutants such as high colour, carcinogenic dyes and toxic heavy metals. Due to low cost operation required as well as high selectivity achieved, separation using membrane technology has becoming promising alternatives to treat coloured wastewater. Locally fabricated asymmetric membrane coded as NF23 was prepared from locally made aromatic polyethersulphone (PES) polymer with 23% of concentration, using N-*Methyl*-2-*Pyrrolidone* (NMP) and water (H_2O) as solvent and non solvent, respectively. This membrane was prepared using dry-wet phase inversion process; with casting speed of 10 seconds (over 300 mm length) and 50°C coagulation bath temperature with permeability coefficient of 3.64 l/m2.h.bar. The membrane was found to be best operated at pH 7.4. The rejection of heavy metals elements such as Mn, Cd and Cu were more than 90%, meanwhile the COD rejection was of about 80%. The molecular weight cut off (MWCO) for NF23 which was obtained from Polyethylene glycol (PEG) permeation experiment was approximately 3000 Da. In spite of the high MWCO, the self-made membranes showed similar or even higher rejections when filtrating dyes and other pollutants from Batik industry effluent, combination with high permeate fluxes. In order to evaluate the behavior of NF23 for rejection of dye at different pH in wastewater, the filtration of RB5 (anionic dye) was performed and the effect of pH was investigated. Increase or decrease the pH of solution will contribute significant effect on ion rejection in charged membrane where the charge of membrane is also changed [22].

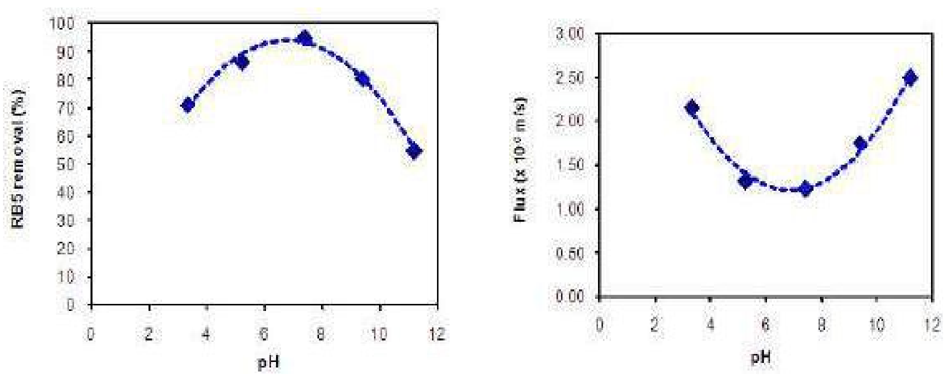


Fig4. (a) RB5 rejection versus pH and (b) Flux versus pH using NF23 at P=10 bar [22].

VI. APPLICATIONS

Applications are mainly in water treatment, the food industry, and the pharmaceutical and biomedical industries. For point-of-use and point-of-entry (POU/POE) applications, NF systems have become widely available only in the past few years. Typical NF applications include water softening, desalination of dyestuffs, acid and caustic recovery, and colour removal. Additionally, NF is very efficient in simultaneously controlling THM precursors, hardness, and microbial contamination. Because of its very small pore size, NF can remove both large and very small microorganisms (e.g., enteric viruses). NF membranes can also remove some colloidal material and organics, and are extremely effective in removing disinfection by-product precursors. NF is a common technology for water softening and NOM reduction.

VII. CONCLUSION

Nanofiltration can lower TDS and hardness, reduce colour and odour, and remove heavy metal ions from ground water. The need to remove or recover metal ions from industrial wastewaters is necessary by both financially in terms of cost savings through metal reuse or sale, and environmentally as heavy metal toxicity can affect organisms throughout the food chain, including humans. n. Softening and NOM-removal are major applications, but NF is frequently applied for the combined removal of NOM, micropollutants, pesticides, arsenic, iron, heavy metals, sulphate, nitrate and bacteria and viruses. The main challenge in NF for water treatment is to control fouling of the membrane by NOM, silt, scaling etc. Regardless of other conditions there will always be a maximum flux that can be applied in long term stable operation and therefore the flux should be limited and not exceed this value. More knowledge of the rejection of typical and specific and important water pollutants and groups of pollutants for various types of membrane material would be useful. There is a need for evaluation of waste disposal options and to assess the environmental impact of discharge.

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