

Wastewater treatment by nanofiltration membranes

R Mulyanti¹ and H Susanto²

¹ Master Program of Environmental Science, School of Postgraduate Studies
Universitas Diponegoro, Jl. Imam Bardjo SH No 5, Pleburan, Semarang, 50241,
Indonesia

² Departement of Chemical Engineering, Faculty of Engineering, Universitas
Diponegoro, Jl. Prof Soedarto SH, Tembalang, Semarang, 50275, Indonesia

E-mail: heru.susanto@che.undip.ac.id

Abstract. Lower energy consumption compared to reverse osmosis (RO) and higher rejection compared to ultrafiltration make nanofiltration (NF) membrane get more and more attention for wastewater treatment. NF has become a promising technology not only for treating wastewater but also for reusing water from wastewater. This paper presents various application of NF for wastewater treatments. The factors affecting the performance of NF membranes including operating conditions, feed characteristics and membrane characteristics were discussed. In addition, fouling as a severe problem during NF application is also presented. Further, future prospects and challenges of NF for wastewater treatments are explained.

1. Introduction

Increased human activities in all sectors, i.e. industry, food, medical, fishery, etc., demands availability of adequate clean water. Low fresh water stock, only 3 % of total water on earth, requires sophisticated technology to process water and wastewater to produce safe output for the environment and even to be reused for various purposes.

The membrane technology which offers high selectivity, low energy requirement, cost advantage and environmental sustainability, can be combined with other separation process, without adding any chemical and it's easier in up-scaling [1]. Membrane technology can solve existing problems, especially in wastewater treatment.

The common membrane filtration technology is pressure driven membrane processes which are based on pore size, consisting of four processes, i.e. microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

2. Nanofiltration Membrane

The development of nanofiltration membrane application in all fields is very rapid in recent years. This membrane was already used in filtration process the end of 1980s [2]. The characteristics of NF which are 1- 5 nm pore size and 7- 30 operating pressure [3] are used to separate solutes with low molecular weight, e.g. lactose, glucose, salt, and it's effective in rejecting hardness, dye and heavy metal. NF as a membrane technology with pressure driven process is a very promising membrane application for future waste treatment, ending dependency to fresh water usage [4], [5] and ground water by wastewater reuse which can't be performed by conventional waste treatment. Relatively low operating pressure and higher permeate flux allow NF to replace reverse osmosis (RO) in various



applications. Lower energy consumption compared to reverse osmosis (RO) and higher rejection compared to ultrafiltration (UF) make nanofiltration (NF) membrane get more and more attention for wastewater treatment.

3. Separation Mechanism of NF

Pollutant separation by NF membrane really depends on differences of particle sizes and charge effects (for ionic components) due to effects of steric and electrostatic interactions based on Donnan exclusion [2], [4], [6]. According to [3], components with high molecular weight are separated by sieving mechanism, unlike components with low molecular weight or ionic species which are separated by charge effect and solution diffusion mechanism.

4. NF Application

Nanofiltration is increasingly common in industry, pharmaceuticals, water purification, wastewater treatment, biotechnology, and brackish water desalination.

In industry, some uses of NF process are to separate colors in textile industry [7], [8], metal recovery, olive mill wastewater treatment [9], [10]. Integration of NF and RO effectively removed soluble monovalent and divalent ions in OME (olive mill Effluent) compared with conventional physicochemical process [11]. NF was also used in coke wastewater treatment [12], pulp and paper [13], oily wastewater treatment from oil and petroleum industries, acid sulphate removal from mine water [14].

There were also many applications on domestic sector, e.g. treatment of municipal wastewater [4], [15], Leachate [16], car wash wastewater [17], and restaurant effluent. NF-90 quite efficiently reduces BOD 5 and the conductivity was over 80 % compared with aerobic and anaerobic processes, chemical coagulation and electrocoagulation and electroflotation [18].

NF is also an alternative for separation in food processing, e.g. removal of phenolic compounds from pomegranate juice [19], wastewater treatment of instant tea powder [20], Combination of NF + RO with cascade operation in whey treatment gives optimal result for recovering protein and lactose [21]. NF is also used to concentrate coffee extract [22] and red wine [23]. In pharmaceuticals, NF process is selected in antibiotic separation process [24], [25].

Most commercial NF membranes have negative charge with varying Molecular Weight Cut Off (MWCO) e.g. 100-300 Da (ESNA1), 150 Da (TS80), 150 - 300 Da (DL, HL, NFX), 180 Da (UTC20), 200 Da (TS40, DK, TFC SR 100, SR3D, SPIRAPRO), 200-400 Da (NF270, NF200, NF 90), 300 - 500 Da (NFW), 400 Da (TR60), 500 Da (XN45), 600- 800 Da (NTR7450, NFG), 2000 Da (CK) [2].

5. NF Performance

NF performance is represented by flux (J) calculation which is measured from the volume of flow which passes membrane (permeate volume) divided by the size of membrane surface (A) at particular time (t), such as in Equation (1)

$$J = \frac{V}{A \cdot t} \quad (1)$$

and rejection (R), which is ratio of feed concentration reduced by permeate concentration (Cp) to feed concentration (Cf), can be calculated by Equation (2).

$$R = 1 - \frac{C_p}{C_f} \times 100\% \quad (2)$$

NF performance in rejecting COD is approximately 70 % [26] to 99,4 % [18] and it's able to separate dyes by 90,6 - 95 % on average [27]. NF ability to remove salinity parameter varies from 75 % to 95 % [28] depending on the membrane in use. Meanwhile, the conductivity rejection level is 82,3 % [18].

Significant factors which determine membrane performance, especially NF, are operating condition, membrane characteristic and feed characteristic.

5. 1 Operating Condition

Membrane performance is strongly affected by operating conditions, including temperature, operating pressure and flow rate.

5.1.1 Temperature. Permeate flux increases along with temperature increase because when temperature increases, viscosity and level of concentration polarization will decline [29]. Removal of COD and Electrical Conductivity in oily wastewater declines when temperature and permeate flux increase [6]. A study on rubber waste treatment [30] shows that membrane permeability will decline above 24°C, but if flux permeate is maintained at 11-12 Lm⁻²h⁻¹, the effect of temperature will be insignificant. However, if there is fouling, flux will decline despite increase of temperature [13]. Temperature change causes variation of diffusion coefficient and component absorption, and then influences flux.

5. 1.2 Operating Pressure. Increased pressure is essentially directly proportional with flux increase, but at certain point this doesn't apply due to fouling and concentration polarization phenomenon [31]. The study by [27] shows that increased operation pressure will increase dye rejection and transport rate of solvent.

5. 1.3 Flow Rate. Increased flow rate impacts increased permeate flux and mass transport, as well as declining possibility of concentration polarization [27].

5. 2 Membrane Characteristic

Membrane characteristics, such as charge, pore size, and hydrophilicity, are closely associated with membrane performance. Separation process by membrane must consider the charges of the membrane and solute. If membrane charge is different from solute charge, there will be gravitational force, so there's bigger chance of fouling. Fouling will eventually reduce flux and change membrane selectivity. Pore size of membrane is a determinant of membrane rejection level on uncharged contaminant. Meanwhile, hydrophilicity is related to very weak interaction to solute, but high to water, the opposite of hydrophobicity. The advantage of hydrophilic membrane compared by hydrophobic is it's not vulnerable to fouling, but hydrophobic materials tend to produce high flux [31].

5. 3 Feed Characteristic

Similar to membrane characteristic, feed characteristic significantly affects membrane performance, e.g. related to chemical structure, pH, charge, geometry and hydrophilicity of solute. Feed pH can influence membrane charge, even changing it.

"The occurrence of an isoelectric point means that at lower pH than the isoelectric point, the membrane is positively charged and vice-versa by [32]. Isoelectric point may be different for each membrane type. For example, the isoelectric point on TFCS and NF 70 is 3 and 4, whereas TFCL is 5,2 [33]. while membrane FM NP010 is 4,2 [34]. pH change also influences hydrophilicity of membrane [35]. Furthermore, temperature of feed will increase mass transfer process in membrane [6].

6. Wastewater Reuse

Waste as a result of human activity is a challenge and has great potential to be reused for various needs. Waste is a renewable resource and can be a new water source alternative as sustainability point in minimizing environmental impact, and a solution for clean water scarcity. Application of wastewater reuse has spread beyond Middle East and United States as countries with the highest levels of wastewater reuse [36]. In Asian and European countries, wastewater reuse is increasing. Membrane

technology can produce high quality effluent, enabling reuse for various purposes, e.g. irrigation [4], tourism, public park, processed water [30], toilet, with certain criteria that are given in table 1.

Table 1. Application and wastewater reuse of NF.

Application	Type Of NF Membrane	Operating Condition	Membranes Performance	Wastewater Reuse
Rubber wastewater treatment [30]	Integrated process of NF270 and evaporation	NF : Pilot scale (continuous) Permeate flux 11L/m ² h Evaporator : pilot scale (batch), capacity of full size drum 5 m ³ /d with the boiler blowdown.	COD removal was over 95 % and water recovery was 80-90 % if permeate flux maintain less than 12 L/m ² h , energy costs decline until 55 %	Permeate could be reused as boiler feed water with reduction of total hardness concentrate.
Dairy industry [37]	Membrane Bioreactor (MBR) and NF	MBR : The flow rate was 0.80 L/h, and the permeate flux was 18.2 L/(h m ²). Cross-flow velocity of 7.8 m/s	MBR as secondary process was followed by NF process had rejected 99 % of COD, 93.1% of total solids	For boiler and cooling water
Coking wastewater treatment [38]	A combination of biological (full scale plant) processes with MBR and NF-RO integrated system (pilot scale)	<u>Full scale</u> : T : 35 – 38°C, average flow rate 200 m ³ /h, pH and DO were maintained at 6.5-6.8 and 5-6 mg/L(in oxic reactor) <u>Pilot scale</u> : MBR :flow rate 10 m ³ /h, 4 modules (flat-sheet submerged), DO & MLSS concentration were maintained 6 mg/L & 8500 mg/L NF +RO : feed pressure : 0.6 Mpa & 1,0 Mpa , pore size : 0.001 µm & 0.0001µm, filtration time : 2-3 months in 1 cycle	Removal of COD, hardness , conductivity, fluoride, TN, T-CN and chloride ion meets the standards for industrial reuse	Industrial reuse
Secondary effluent of textile wastewater treatment [28]	NF 90, NF 200, NF 270	The temperature and pressure of experiment were at 25°C and 6 – 22 bar, with recirculation flow were at 340 L/h	Best result was given by NF 90, which COD removal and salt retention were 99 % and 75 – 95 %	Textile industry reuse
Wastewater treatment of rendering plant [39]	Combination of SBR, sand filtration, UF (MW,CQ,GM), NF(NF279, NF90), RO (XLE)	laboratory scale (batch). Six UF / RO/NF cells connected in parallel. Operating pressure of MW, CQ, GM, were 2, 4, and 5 bar. Then NF270, NF90, XLE were at 10 bar	Best rejection was showed by combination of UF (MW) with NF90 and RO (XLE)	steam generation, washing factory and vehicle

7. Fouling Phenomena

Fouling is the main and inevitable problem in membrane application, including NF, beside it reduces membrane performance by flux reduction over time, as well as reducing cost efficiency [11]. Fouling

can be defined as blockage on the surface and pores of membrane by soluble material or suspended material, such as colloid, organic component, inorganic component and biological component [2], [6].

Fouling can be solved physically, chemically and hydrodynamically. Fouling control by chemical cleansing will cause long term damage to membrane structure, reducing membrane performance [18].

8. Future prospects and challenges of NF

NF is the latest technology alternative for waste treatment which is very innovative, economical, and environmentally friendly. The integration of NF with other separation processes potentially yields optimal result in wastewater treatment, so the quality of the produced effluent can be reused. Beside saving resources, waste reuse has great prospects in long term water provision and it's more economical than desalination process. The future challenges and prospects of NF application is very great considering the broad range of selectivity of organic solute and salt, enabling further studies for various applications.

9. Conclusions

NF characteristics which are between UF and RO makes NF application increasingly favors across sectors due to low energy requirement and much better selectivity. Beside the size difference of the components to be separated, charge effect also influences separation process by NF. NF performance is also determined by membrane and feed characteristics, as well as operation condition.

Separation process by membrane technology, especially NF, has bright prospects in wastewater treatment and great potentials for further development. Integration with other processes potentially produces higher quality effluent.

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