CHEMICAL ENGINEERING TRANSACTIONS
VOL. 63, 2018

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jeng Shiun Lim, Wai Shin Ho, Jiří J. Klemeš

ISBN 978-88-95608-61-7; **ISSN** 2283-9216

DOI: 10.3303/CET1863117

Industrial Nickel Wastewater Rejection by Polyimide Membrane

Jing Ying Chuah[a,*], Kok Chung Chong[a], Soon Onn Lai[a], Woei Jye Lau[b], Sze Shin Lee[a], Hang Meng Ong[c]

[a]Universiti Tunku Abdul Rahman, Lee Kong Chian Faculty of Engineering and Science, Jalan Sungai Long, Bandar Sungai Long, 43000 Kajang, Malaysia
[b]Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Malaysia
[c]Singapore Polytechnic, School of Chemical and Life Science, 500 Dover Road, Singapore 139651
ichbinir.cjy18@1utar.my

Membrane distillation (MD) is one of the emerging thermal driven membrane separation processes in wastewater treatment attributed to its lower energy requirement and able to couple with waste heat relative to pressure driven process. In this study, polyimide was used as the polymeric materials in hollow fiber membrane fabrication whereas 1-methyl-2-pyrrolidone (NMP) was use as solvent for synthesize industrial wastewater in nickel removal. The properties of the fabricated membrane were found to possesses the optimum characteristic in terms of LEP, porosity, inner diameter and morphology as reported in literature for the application of DCMD. The permeate flux performance in the range of 67 to 79 kg/m^{2}h with the rejection rate of more than 98.80 % suggested that the PI membrane possesses the potential to be applied in the industrial wastewater treatment in nickel removal.

1. Introduction

There is a wide variety of heavy metals such as Ni, As, Cr, Cu, Cd, Hg, Zn present in the wastewater. Due to its high solubility in aquatic environment, living organisms will absorb the heavy metal compounds, which will consequently cause serious health disorder. The amount of nickel components present in the wastewater solution is approximately 0.05 g/l (Babel and Kurniawan, 2004) where the main sources of nickel wastewater are industrial activities or products such as printed circuit board manufacturing, plastics manufacturing, metal finishing and plating, semiconductor manufacturing, production of nickel-cadmium batteries, pigments, fertilizers and etc. An uptake or exposure to large quantities of nickel can cause severe health problems such as lung embolism, birth defects, respiratory failure, asthma and chronic bronchitis, allergic reactions e.g. skin rashes, sickness and dizziness as well as higher chances of development of lung cancer. Therefore, clearly, there is a need to develop efficient, effective and inexpensive methods to treat the wastewater. Through some approaches studied, technologies such as conventional methods, for example, activated carbon adsorption, chemical precipitation, flocculation, biosorption, evaporation, filtration, solvent extraction, reverse osmosis and membrane distillation are typically employed to remove nickel from wastewater.

Membrane distillation (MD) is one of the nascent thermal driven membrane separation process that water exists as the major component in the feed solution. The first patent was being filed since 1963 (Khayet and Payo, 2016), currently still being developed for its industrial implementation. MD refers to the transportation of vapor through a non-wetted porous hydrophobic membrane where the thermal driven force is vapor pressure difference created by the temperature different between two side of the membrane pores.

During MD separation process, both heat and mass transfer occur simultaneously where different configurations of MD are applied with different method of condensation (Khayet et al., 2005). Under these conditions, evaporation takes place at the hot feed side, migration of vapor through the membrane pores and condensation takes place at the cold permeate side, inside the membrane module (Banat and Simandl, 1998).

Please cite this article as: Jing Ying Chuah, Kok Chung Chong, Soon Onn Lai, Woei Jye Lau, Sze Shin Lee, Hang Meng Ong, 2018, Industrial nickel wastewater rejection by polyimide membrane, Chemical Engineering Transactions, 63, 697-702 DOI:10.3303/CET1863117

MD is a promising liquid separation technology which is widely used for water treatment in industry due to the attractive feature it possesses. For instance, low operating temperature is required comparing to the temperature normally applied in conventional distillation (Khayet, nd,), the feed solution is not necessary to heat up until boiling point, the temperature is typically set at 40 °C to 60 °C. Moreover, unlike other pressure-driven processes such as reverse osmosis, lower operating hydrostatic pressure is needed in MD, generally near to the atmospheric pressure (Tijing et al., 2014). Thus, MD is envisaged to be an economical process as the desired membrane mechanical properties are relatively lesser and inexpensive material such as polymer can be used in order to avoid the corrosion problem. Furthermore, according to the principle of vapor-liquid equilibrium, higher rejection factor is achieved when there are no volatile components in the feed solution and. This characteristic tends to overcome the largest concern which is the shortage of fresh water in the modern era. Membrane fouling resistant is relatively higher than in the pressure-driven separation process (Tijing et al., 2014). Nevertheless, MD has a limitation of low permeability on to the other pressure-driven separation process.

2. Materials and methods

2.1 Membrane fabrication

Dope solution was formulated and undergoing a series of preparation steps before the fabrication process. Meanwhile, hollow fiber membrane spinning parameters were determined.

2.1.1. Dope preparation

N-Methyl-2-pyrrolidone (NMP, >99.5 %) was obtained from Sigma Aldrich while PI pellet was obtained from Alfa Aesar. Dope solution is a membrane-forming solution, which N-Methyl-2-pyrrolidone containing certain amount of PI. 77 wt% of NMP and 23 wt% of PI were mixed and stirred for at least 24 h until the PI was fully dissolved in the NMP solvent, where a homogeneous mixture was eventually formed. It is then degassed to remove the air bubbles that were existed within the dope solution during mixing and stirring.

2.1.2. Hollow fiber membrane spinning

The technique used in hollow fiber membrane fabrication in this work is by dry wet phase inversion spinning technique. Spinning parameter such as the size of the spinneret, bore fluid rate and air gap were determined carefully due to the parameters affected the performance of the membrane Phase inversion principle was implemented, where the solution and bore fluid were fed into tube-in-orifice and inner tube of spinneret respectively. Fibers passed through a considerable air gap and coagulated in the water bath. The collecting fibers were then soaked in water for three days, so that the solvent remained in the membrane fibers were rinsed out. The hollow fiber membrane was air-dried vertically at room temperature before testing.

2.2 Membrane characterization

2.2.1. Liquid entry pressure

The purpose of study the LEP is to understand the pressure limit where the feed liquid will start to penetrate the microporous membrane pores. LEP analysis was carried out by filling up the deionized (DI) water in a module, where the bottom of the test module was attached with 5 unit of hollow fiber membranes whilst a diaphragm pump was connected to another end (Chong et al., 2014). The pressure was applied to the membrane in stepwise function until the first drop of the liquid is seen.

2.2.2. Membrane porosity

Membrane porosity, ε was resolved by gravitational method (Ahmad et al., 2012). Membrane samples was analyzed by taken the reading of membrane dry weight followed by immersing the samples in 2-butanol (Fisher Scientific, >99 %) solution for 2 h. The reading of wetted membrane weight was then measured in order to determine the membrane porosity. Based on the Equation. (1) given, membrane porosity can be estimated:

$$\varepsilon = \frac{(w_1 - w_2)/\rho_w}{(w_1 - w_2)/\rho_w + w_2/\rho_w} \times 100\% \quad (1)$$

where w_1 is the wetted membrane weight (g), w_2 is the dry membrane weight (g), ρ_w is the density of 2-butanol used to immerse the membrane, ρ_b is the density of polymer material of the membrane. Three times of measurement is taken for each sample in order to ensure the reproducibility of the data.

2.2.3. Membrane morphology

HITACHI S3400N Scanning Electron Microscope (SEM) has been used to collect the images of the cross sectional, inner and outer surface. The measurements such as diameter of the membrane has been marked in the images captured. Prior to SEM analysis, sample was prepared by immersing the membrane in the liquid nitrogen for cryogenic cracking. The samples were then attached onto a sample holder with carbon double-sided tape. A thin layer of gold coating was applied on the samples with the use of sputter coater machine (SC7620, Emitech, UK). In sample analysis, the purpose of a gold layer coating is to enhance electronics conductivity. The size of pore was determined based on the SEM image while distribution of pore size was determined through the graph with spreadsheet application program.

2.3 Experimental setup

The schematic diagram for the experimental setup for this work was shown in Figure 1. The synthesized nickel wastewater was filled in the feed tank and heated to the temperature at the range of 40 °C to 55 °C with the using of the heating plate. Wastewater solution and distilled water were then pumped into the membrane module at constant flow rate for both feed and permeates at 0.4 L/min, respectively. Meanwhile, the chiller was set at the permeate tank in order to maintain the permeate tank temperature at 18 °C. The vapor was thermally driven from feed to the permeate side by the temperature difference across the membrane pores. The vapor was then condensed and collected in the permeate tank. Temperature sensor maintained the feed solution temperature due to the major heat loss across the membrane module which caused the recycled feed solution temperature decreased. The permeate volume in the permeate tank increased over time and increased volume readings were taken to calculate the flux and used for other performance tests.

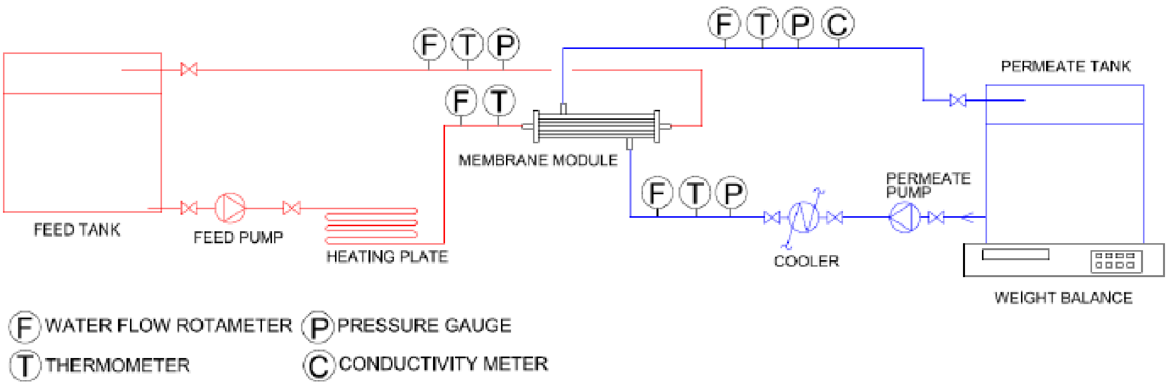


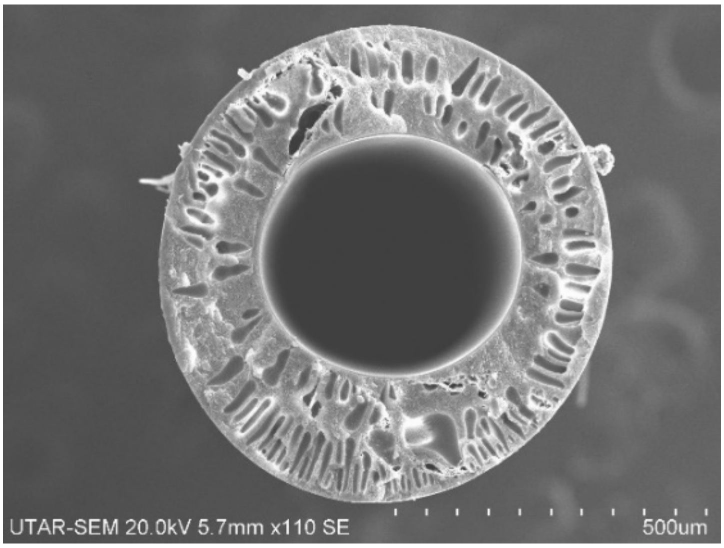
Figure 1: Schematic diagram of MD experiment

3. Results and findings

3.1 Membrane characteristics

Liquid entry pressure (LEP) play a vital role in the MD application as it defined the maximum allowable pressured applied on the membrane before wetting. The LEP for the PI membrane was recorded at 2.5 bar which is optimum in MD study as reported by Mokhtar et al. (2015). which will lead to higher resistance to pore wettability. The membrane porosity of the PI membrane used in this work was 61 ± 57 % which is well agree with reported by El-Bourawi et al. (2006) where the membrane porosity that required in a MD process is within the range of 30 % - 85 %. Based on the characteristics of PI membrane in term of LEP and porosity, it is expected that the membrane possesses good characteristic for MD application possesses good characteristic for MD application.
The morphology of the PI membrane is tested by using the scanning electron microscope (SEM). The PI membrane inner diameter and thickness was recorded at 400 μm and 170 μm, respectively from the SEM image measurement. As shown in Figure 2 (a) and (b), the cross-section of the PI hollow fibre membranes used in this study. From the images, it can be observed that finger-like structures were formed from inner surface to the outer surface of the hollow fiber membrane. Pores with different sizes can be seen where mostly appeared at the upper layer of the porous layer inside membrane. The formation of the structure is attributed to the prolong contact time of the extruded dope solution in the air before it immersed into the coagulation bath. The interaction between NMP and water coagulation bath triggered the rapid diffusion of NMP and the formation of surface layer. Meanwhile, the NMP diffusion rate slowed down, encouraged the

growth of membrane pores and led to formation of finger-like layer (Young and Chen, 1995). This type of morphology is in favour to the permeate flux performance due to the lower membrane resistance.



(a)

(b)

Figure 2: Membrane morphology of (a) Cross sectional view (b) Membrane thickness enlargement view

3.2 Effect of feed temperature on permeate flux

Figure 3 shows the permeate flux of membranes with respect to different feed inlet temperature. The membrane illustrated a trend where permeate flux increasing with respect to the feed inlet temperature. The inlet temperature for cold side is maintained at 18 °C whereas the inlet temperature for hot feed is adjusted from 40 °C to 55 °C throughout the experimental studies. This trend formation may attribute to the increase the feed temperature that lead to a greater vapor difference which drive more flow across the membrane. Figure 4 depicted the nickel rejection rate of membranes with respect to different feed inlet temperatures. As observed from the figure, the rejection rate decreases as the feed inlet temperature increases. It is noteworthy to mention that in this study, the permeate flux possesses an inversely proportional relationship with the rejection rate where the higher the permeate flux performance, the lower the rejection rate. Nevertheless, the rejection rate for all the feed inlet temperature was close to the MD theoretical rejection rate which is more than 99 %. The decrease of the rejection rate across feed inlet temperature was considered as insignificant (<0.5 %) which indicated the membrane had a stable rejection rate (Hou et al., 2010). These stability tests clearly implied that the self-fabricated membranes were suitable for DCMD application in nickel wastewater treatment.

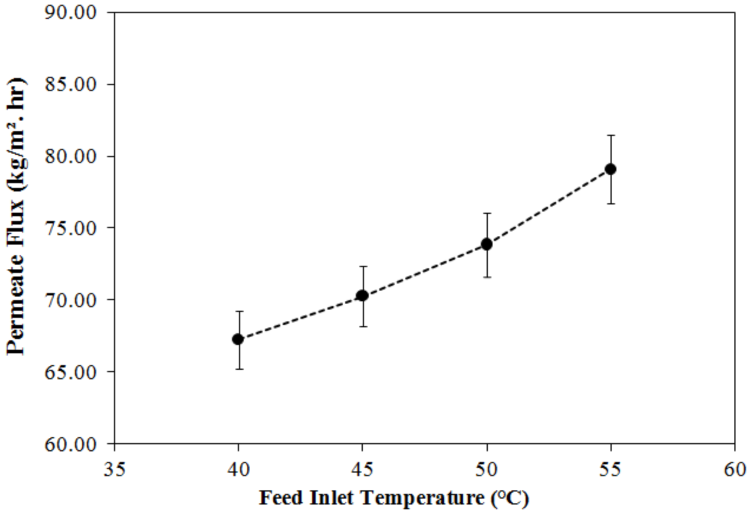


Figure 3: Membrane permeate flux as a function of feed inlet temperature with the operation condition of feed and permeate inlet flow rate at 0.4 L/min, permeate inlet temperature at 18 °C.

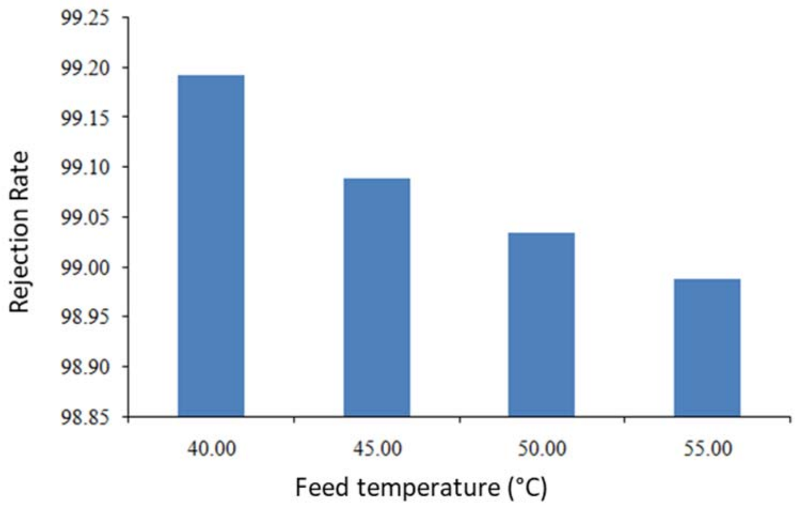


Figure 4: Membrane rejection rate as a function of feed inlet temperature with the operation condition of feed and permeate inlet flow rate at 0.4 L/min, permeate inlet temperature at 18 °C.

4. Conclusion

The PI hollow fiber membranes were successfully fabricated by phase inversion spinning technique using NMP as solvent. The membrane characteristic test illustrated that the membrane possesses optimum LEP, porosity, inner diameter and morphology for the application of DCMD. The experimental study on nickel wastewater rejection depicted a good permeate flux performance in the range of 67 to 79 kg/m^{2}h with the rejection rate of more than 98.80 %. The results from this work suggested that the permeate flux increase with the increase of feed inlet temperature. Additionally, the PI membrane was found to yield a potential in rejecting nickel metal in wastewater treatment.

Acknowledgements

The authors would like to thank Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia especially Professor A.F. Ismail for supplying membrane samples for this research project.

References

Ahmad A., Ideris N., Ooi B., Low S., Ismail A., 2012, Synthesis of Polyvinylidene Fluoride (PVDF) Membranes for Protein Binding: Effect of Casting Thickness. Journal of Applied Polymer Science, 128(5), 3438-3445.

Agency for Toxic Substances and Disease Regis, 2017, Nickel – Ni, Chemical properties of nickel – Health effects of nickel – Environmental effects of nickel. c1998-2017 <lenntech.com/periodic/elements/ni.html> accessed 10.05.2017.

Agency for Toxic Substances and Disease Regis, 2015, Toxic Substances Portal – Nickel. c2005-2017, Agency for Toxic Substances and Disease Regis <atsdr.cdc.gov/phs/phs.asp?id=243&tid=44> accessed 10.05.2017.

Babel S., Kurniawan T.S., 2004, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and Commercial Activated Carbon Modified with Oxidizing Agents and/or Chitosan, Journal of Chemosphere, 54(7), 951-967.

Banat F., Simandl J., 1998, Desalination by Membrane Distillation: A Parametric Study, Journal of Separation Science and Technology, 33(2), 201-226.

Chong K., Lai S., Lee K., Lau W., Ismail A., Ooi B., 2014, Characteristic and performance of polyvinylidene fluoride membranes blended with different additives in direct contact membrane distillation, Journal of Desalination and Water Treatment, 54(12), 3218-3226.

Dhokpande S.R., Kaware D., Jayant P., Kulkarni S.J., 2013, Research for Removal of Nickel from Waste Water – A Review, International Journal of Science, Engineering and Technology Research, 12(2), 2278-7798.

El-Bourawi M.S., Ding Z., Ma R., Khayet M., 2006, A framework for better understanding membrane distillation separation process, Journal of Membrane Science, 285, 4-29.

Hou D.Y., Wang J., Zhao C.W., Wang B.Q., Luan Z.K., Sun X.C., 2010, Fluoride removal from brackish groundwater by direct contact membrane distillation, Journal of Water Science and Technology, 22(12), 1860-1867.

Khayet, M., Matsuura, T., 2011, Membrane Distillation Principles and Application, Elsevier, New York, USA.

Khayet M., Matsuura T., Mengual J., Qtaishat M., 2005, Design of novel Direct Contact Membrane Distillation Membranes, Journal of Desalination, 192(1-3), 105-111.

Khayet M., Payo G.C., 2016, Progress on Membrane Distillation and Related Technologies, Journal of Membrane Science and Research, 2, 161-162.

Mokhtar N.M., Lau W.J., Ismail A.F., 2015, Dye wastewater treatment by direct contact membrane distillation using polycinylidene fluoride hollow fiber membranes, Journal of Polymer Engineering, 35(5), 471-479.

Ramboll, 2013, Heavy Metals in Wastewater Removal and Analyses, Ramboll <www.ecoprofi.info/docs/event_2013-03-22_presentation_Ramboll_Varpula_en.pdf> accessed 10.05.2017.

Lacroix R., Chåtelain R., Kvita P., 1989, Process for the preparation of concentrated aqueous dye formulations of water-soluble organic dyes by membrane separation and with cross-flow micro-filtration to remove suspended or colloidal solids. United States Patent US 4851011 A.

Tijing L., Woo Y., Choi J., Lee S., Kim S., Shon H., 2014, Fouling and its control in membrane distillation — A review, Journal of Membrane Science, 475, 215-244.

Young T.H., Chen L.W., 1995, Pore formation mechanism of membranes from phase inversion process, Journal of Desalination, 103: 233-247.

Zoungrana A., Mehmet C., Zengin I.H., Inoglu O., Elcik H., 2016, Treatment of metal-plating waste water by modified direct contact membrane distillation, Journal of Membrane Science, 70(9), 1185-1195.