Available online at www.sciencedirect.com

ScienceDirect

Procedia CIRP 26 (2015) 792 – 796

www.elsevier.com/locate/procedia

12th Global Conference on Sustainable Manufacturing

Membrane distillation technology for treatment of wastewater from rubber industry in Malaysia

N.M. Mokhtar [a,b], W.J. Lau [a,b*], A.F. Ismail [a,b], D. Veerasamy [c]

[a]*Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.*
[b]*Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.*
[c]*Rubber Research Institute of Malaysia, Malaysian Rubber Board, Technology and Engineering Division, Rubber Research Institute of Malaysia, Malaysian Rubber Board, 47000 Sungai Buloh, Selangor, Malaysia*

* Corresponding author. Tel.: +60 75535926; *E-mail address:* lwoeijye@utm.my/ lau_woeijye@yahoo.com (W.J. Lau)

Abstract

The possibility of using direct contact membrane distillation (DCMD) for the treatment of rubber processing effluent (DCMD) has been investigated in this work. The in-house made polyvinylidene fluoride (PVDF) mixed matrix membrane incorporated with inorganic material of Cloisite® 15A was employed as MD membrane and its performance was characterized with respect to permeate flux and rejection against several important water quality parameters. The obtained results showed that the DCMD process was able to reduce significantly the levels of total organic carbon (TOC), total dissolved solid (TDS), sulphate, colour, turbidity and conductivity in rubber industry wastewater, recording at least 96% removal efficiency irrespective of parameters. Nevertheless, flux decline was experienced in DCMD and this could be mainly caused by the concentration polarization, temperature polarization and membrane fouling itself.

Peer-review under responsibility of Assembly Technology and Factory Management/Technische Universität Berlin.

Keywords: Membrane distillation; rubber industry; wastewater treatment; polyvinylidene fluoride; Cloisite 15A

---

1. Main text

Malaysia has represented as the fourth largest rubber producer in the world after Thailand, Indonesia and India [1,2]. The industry of rubber is one of the most important industries in Malaysia and plays a vital role in the nation's economy. There are two types of processes in raw natural rubber processing; the production of natural rubber latex (NRL) concentrate and the Standard Malaysian Rubber (SMR) [3]. However, it must be noted that the production process of the rubber industry always leads to a large amount of contaminated wastewater generated, as a result of large quantity of water needed during processing. Untreated effluents from rubber industries are usually associated with malodour problem and contain a considerable amount of contaminants and pollutants. Table 1 shows the typical characteristics of effluents from rubber processing in Malaysia. As the effluent consists of a complex mixture of chemicals, high concentration of organic matters (major ions, organic solvents, nutrients, etc.), suspended solids and nitrogen, treatment of this wastewater under controlled conditions is necessary in order to prevent the release of harmful wastes to the environment. Stringent environmental regulation for the control of rubber effluents is enforced in Malaysia in which the wastewater treatment plant must comply with the Environmental Quality (Industrial Effluents) Regulations 2009 under standard A and standard B. Both standards consist of discharge temperature, pH, biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and other heavy metals, but with different parameter limits, depending on the location of discharge after treatment process.

With a new global trend towards a sustainable development, the rubber industry needs to focus on cleaner production technology, waste minimization, utilization of waste, resource recovery and recycling of water. Among various treatment approaches, biological methods especially aerobic, anaerobic and facultative ponds are widely used for treatment of rubber wastewater in Malaysia [2]. These systems are inexpensive and have a high efficiency for organic load reduction, but required large areas to implement. Recently, membrane based separation processes have

Peer-review under responsibility of Assembly Technology and Factory Management/Technische Universität Berlin.
doi:10.1016/j.procir.2014.07.161

gradually become an attractive alternative to the conventional separation processes in the treatment of wastewater. Several approaches have been proposed to implement membrane technology to the treatment of wastewater from rubber industry. Of them, ultrafiltration (UF) is generally considered as the competitor against the conventional methods in the processes of waste NRL recovery and SMR processing mill effluent treatment [4–7]. UF membrane is not only able to operate at very low pressure (less energy consumption) but also shows promising results to recover and recycle waste raw materials. Currently, membrane distillation (MD) process which uses microporous membrane similar like UF has also attracted the interest of academic and scientific communities due to its excellent properties to retain the non-volatile solutes and produce treated water of high quality. The excellent performance of MD in desalination and wastewater treatment processes has been documented in literature [8–10]. As a new member of membrane separation family, MD can be operated at atmospheric pressure and lower temperature than traditional evaporation. Furthermore it features very little loss of effective components and requires only low grade thermal energy or waste heat [11]. To date, there is no technical work reporting on the possible use of MD system for rubber processing effluent treatment. In view of this, the objective of this work is to study the potential of MD process in treating rubber processing effluent and how this relatively new membrane technology could contribute to rubber industry, in particular in Malaysia.

Table 1 Characteristics of process effluents from rubber processing [2]

Parameter	[a]Typical range
pH	3.7-5.5
Biological oxygen demand (BOD)	1500-7000
Chemical oxygen demand (COD)	3500-14000
Suspended solids (SS)	200-700
Total nitrogen (TN)	200-1800
Sulphate	500-2000

[a]All units are mg/L except pH

2. Basic principles of direct contact membrane distillation (DCMD)

An insight into DCMD process, this emerging membrane technology has been recognized as liquid-liquid separator where feed and permeate solutions are maintained in direct contact with the membrane surfaces throughout the entire operation in which the separation mechanism is based on vapor-liquid equilibrium (VLE) principle [11]. The membrane acts as a physical barrier and holds the liquid-vapor phases at the entrance of membrane pores. By applying aqueous solution colder than the feed solution at the permeate side, a difference of partial pressure is created across the membrane and both water vapor and volatile species starts to permeate through the membrane pores. In this case, both evaporation and condensation processes occur simultaneously inside the membrane module.

Among different types of MD configurations, special attention is paid to DCMD process and this process is particularly studied for desalination of seawater and brackish waters, owing to its simple operation mode and less maintenance cost [8,10,12–15]. . In addition to desalination process, the potential of DCMD is also examined for industrial wastewaters e.g. textile wastewater [16,17], radioactive wastewater [18,19], pharmaceutical wastewater [20] and olive mill wastewater [21,22]. The findings revealed that DCMD technology is an attractive alternative to the conventional treatment processes due to its potential to either produce high-quality water (permeate) or allow reuse of the concentrate solution (retentate) which can reduce the overall production costs.

2.1 Rubber effluent samples

The NRL wastewater was collected from a rubber industry in Negeri Sembilan, Malaysia. Table 2 shows the basic quality parameters of the wastewater samples which were analyzed in our laboratory. The wastewater sample was preserved at a temperature less than 4˚C, but above freezing point in order to prevent the wastewater from undergoing biodegradation due to microbial action.

Table 2 Physico-chemical analysis of the feed wastewater

Parameter	Unit	Value
pH	-	3.9
BOD	mg/L	1500
COD	mg/L	1650
Total organic carbon (TOC)	mg/L	6765
Total dissolved solid (TDS)	mg/L	18710
Sulphate	mg/L	3339
Colour	Pt/Co	1306
[a]Turbidity	NTU	332
Conductivity	µS/cm	31700

[a]NTU = Nephalometer turbidity unit

2.2 Analytical methods

The organic strength of the wastewater was determined by TOC analyzer (TOC LCPN, Shimadzu) meanwhile the clarity of the wastewater was determined by portable turbidimeter (2100Q, Hach). The ionic conductivity and TDS of the sample solutions were determined using a benchtop conductivity meter (4520, Jenway). Colour and sulphate concentration of the sample solutions was detected by a UV-vis spectrophotometer (DR5000, Hach).

2.3 DCMD experiments

The DCMD experiments were conducted on a laboratory-scale circulating unit, as illustrated in Figure 1. An in-house made composite hollow fiber membrane consisted of organic polyvinylidene fluoride (PVDF) and inorganic Cloisite 15A® was used. Figure 2 shows the Scanning Electron Microscope (SEM) micrographs of the prepared membrane. The DCMD system was designed to have two circulating streams, i.e. hot stream was fed through the shell-side while cold stream was circulated through the lumen-side of the hollow fiber membrane in counter-current flow. The DCMD was maintained at feed and permeate temperatures of 55.5±0.1˚C and 20.0±1˚C, respectively. Both solution temperatures were controlled using coiled heater (830, PROTECH) and chiller (F26-ED, JULABO), respectively. Table 3 presents the information on the hollow fiber membrane used as well as the membrane module.

Table 2 Details of membrane and membrane module

Membrane	PVDF-Cloisite 15A
Pore size (μm)	0.088
Porosity (%)	83.70 ± 0.67
Number of fibers	10
Module inner dia. (mm)	10
Fiber outer dia. (μm)	763 ± 19
Fiber inner dia. (μm)	511 ± 15
Module length (mm)	220
Effective fiber length (mm)	190
Effective membrane area (m^2)	0.005

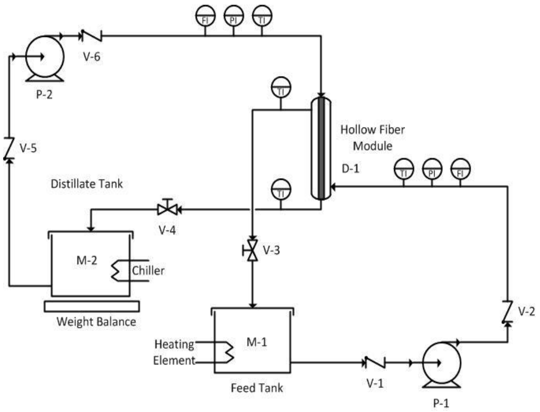

Figure 1 Schematic DCMD experimental setup

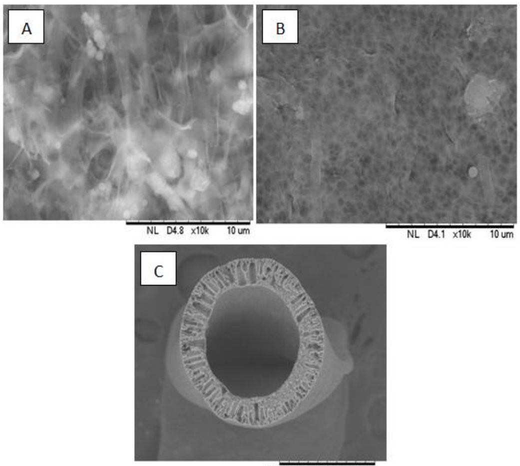

Figure 2 SEM micrographs of PVDF-Cloisite 15A hollow fiber membrane, (A) inner surface, (B) outer surface and (C) cross-section.

The pure water flux, J_v of membrane ($kg/m^2.h$) was determined using Eq. 1.

$$J_v = \frac{\Delta W}{A \Delta t} \qquad (1)$$

where ΔW (kg) is the volume of permeate collected over a predetermined time Δt (h) of process and A (m^2) is the effective membrane area. To determine solute rejection, R (%) of the membrane, Eq. 2 was employed.

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100 \qquad (2)$$

where C_p and C_f are the solute concentration (mg/L) in the bulk permeate and feed solution, respectively.

3. Result and Discussion

Figure 3 shows the calculated permeate fluxes by DCMD process for rubber wastewater as a function of time. The initial permeate flux was recorded at 7.19 $kg/m^2.h$. However, the permeate flux was decreased rapidly to 5.05 $kg/m^2.h$ within the first 30 min and continued to decrease until it achieved almost stable at the end of the experiment. This performance decline could be explained by several factors such as concentration polarization, temperature polarization and fouling phenomenon. As reported in Table 2, the feed wastewater is a mixture of complicated composition, including small amount of uncoagulated latex, serum with substantial quantities of proteins, carbohydrates, sugars, lipids, carotenoids, as well as inorganic and organic salts and also includes washing water from the various processing stages [2]. It is believed that the major reason for this severe flux decline is due to membrane fouling.

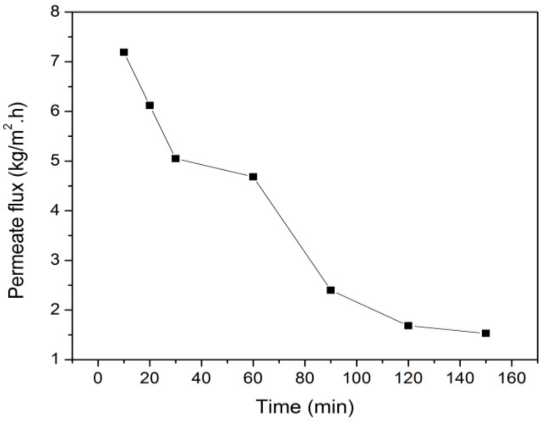

Figure 3 Permeate flux versus time

Generally, fouling can be categorized in four types; inorganic fouling, biological fouling, organic fouling and particulate or colloidal fouling. Among these types of fouling, inorganic fouling or scaling is widely reported in MD process [23]. Scaling occurs when the concentrations of some of the sparingly soluble salts (i.e. calcium sulfate, calcium carbonate) in the feed solution reach supersaturation due to high product water recovery, and the salts crystallize directly on the membrane surface or crystallize in the bulk solution and deposit on the membrane surface [24]. Meanwhile, biofouling is usually occurred during municipal wastewater treatment or other applications that have biological compounds such as protein in their solutions [25]. For this study, a possible mechanism behind these fouling problems for rubber wastewater is given in Figure 4. It is explained that hydrophobic interaction tends to occur between the polymeric membrane and the proteins and other organic materials in the rubber wastewater. It is thus proposed that, fouling is dominated by the deposition of the milky uncoagulated latex, proteins and carbohydrates colloidal onto the membrane surfaces. The complex chemistries between the organophilic compounds in the feed solution and the hydrophobic membranes have led to a fouling cake formation at the membrane outer layer. Thus, a lower evaporation area is anticipated due to the presence of foulants that cover the membrane surface. In addition, the latex precipitation is likely to cause the clogging of the membrane pores, which leads to an increase in flow resistance and lower feed flow rate [26,27]. The decreasing in feed flow rate would then induce temperature polarization effect and finally decreases the temperature difference between the feed and permeate side. Because of this, low permeate fluxes were obtained in this study. Another reason for the discernible flux decline can be governed by the increasing of non-volatile solute concentration in the feed solution with increasing of operation time. As reported by previous studies, the increasing in solute concentrations has led to a decrease in partial water vapor pressure which is the main driving force for this non-isothermal system [28]. This is called as concentration polarization effect.

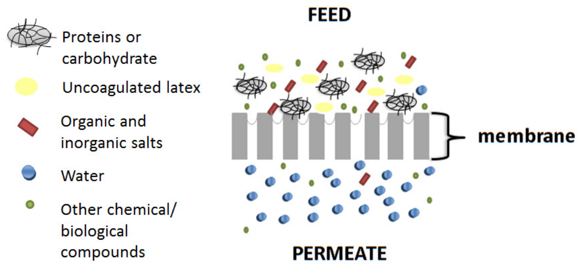

Figure 4 Possible fouling mechanisms in treating rubber effluent via DCMD

Figure 5 shows the results of the physico-chemical analysis of the permeate solution. Prior to TOC removal efficiency, it was found that more than 99% rejection was obtained which indicate that almost all the large macromolecular organic carbon had been retained from passing through membrane matrix. Meanwhile, the overall TDS and conductivity removal efficiency of the DCMD system were very similar, showing approximately 98.7%. With respect to colour and turbidity separation efficiency, at least 97% rejection could be achieved using DCMD system. Another unique feature of this attractive technology is its capability in reducing the sulphate content in the rubber effluent to a very low level. With these excellent performances, the permeate produced is of high quality and could be reused for industrial process.

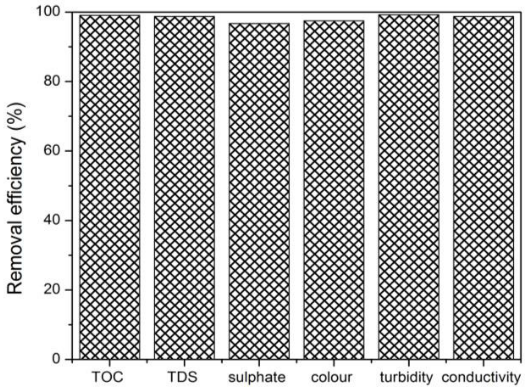

Figure 5 Removal efficiency of the PVDF-C15A membrane.

4. Conclusion

As the wastewater from rubber industry is contaminated with a complex set of oxygen demanding materials, its discharge to environment must comply with the local regulations. MD is found to be a feasible process for rubber wastewater treatment which allows production of high purity water. Major findings of this work include the significant reduction of several important parameters in rubber processing effluent i.e. TOC, TDS, conductivity, sulphate, colour and turbidity to a very low level of concentration. Although MD demonstrated excellent performance in producing treated water of high quality, its water production rate was deteriorated against the operation time, owing to the severe fouling problem. The main reason of this severe flux decline is due to the presence of complex components e.g. latex and protein in the rubber effluent, which plays a role blocking/covering the pore of membrane and further decrease the evaporation area. Other possible explanation for this phenomenon includes the concentration and thermal polarization effect in the DCMD process.

Acknowledgements

The authors are grateful to the Ministry of Education for granted research funding under Research University Grant Scheme (Vot No. Q.J130000.2509.05H10) and Research Management Centre Universiti Teknologi Malaysia (RMC UTM).

References

[1] Vijayaraghavan, K., Ahmad D., Yazid A.Y.A., 2008. Electrolytic treatment of Standard Malaysian Rubber process wastewater, Journal of Hazardous Materials 150, p. 351.

[2] Mohammadi, M., Man, H.C., Hassan, M.A., Yee, P.L., 2010. Treatment of wastewater from rubber industry in Malaysia, African Journal of Biotechnology 9, p. 6233.

[3] Sulaiman, N.M.N, Ibrahim, S., Abdullah, S.L., 2010. Membrane Bioreactor for the treatment of natural rubber wastewater, International Journal of Environmental Engineering 2 (1–3), p. 92.

[4] Veerasamy, D., Supurmaniam, A., Nor, Z.M., 2009. Evaluating the use of in-situ ultrasonication to reduce fouling during natural rubber skim latex (waste latex) recovery by ultrafiltration, Desalination 236, p. 202.

[5] Veerasamy, D., Ismail, A. F., 2012. Rehabilitation of fouled membrane from natural rubber skim latex concentration through membrane autopsy and ultrasonication enhanced membrane cleaning procedure, Desalination 286, p. 235.

[6] Ersu, C.B., Braida, W., Chao, K.P., Ong, S.K., 2004. Ultrafiltration of ink and latex wastewaters using cellulose membranes, Desalination 164, p. 63.
[7] K. Konieczny, W. Engineering, Ultrafiltration of latex wastewaters, 104 (1996) 75–82.
[8] S. Bonyadi, T.S. Chung, R. Rajagopalan, R & D NOTES A Novel Approach to Fabricate Macrovoid-Free and Highly Permeable PVDF Hollow Fiber Membranes for Membrane Distillation, 55 (2009). doi:10.1002/aic.
[9] Wang, K.Y., Foo, S.W., Chung, T.S., 2009. Mixed Matrix PVDF Hollow Fiber Membranes with Nanoscale Pores for Desalination through Direct Contact Membrane Distillation, Industrial & Engineering Chemical Research 48, p. 4474.
[10] Prince, J.A., Singh, G., Rana, D., Matsuura, T., Anbharasi, V., Shanmugasundaram, T.S., 2012. Preparation and characterization of highly hydrophobic poly(vinylidene fluoride) – Clay nanocomposite nanofiber membranes (PVDF–clay NNMs) for desalination using direct contact membrane distillation, Journal of Membrane Science 397-398, p. 80.
[11] Khayet, M., Matsuura, T., 2011. Membrane Distillation: Principles and Applications, first ed. Amsterdarm, The Netherlands.
[12] He, K., Hwang, H.J., Woo, M.W., Moon, I.S., 2011. Production of drinking water from saline water by direct contact membrane distillation (DCMD), Journal of Industrial and Engineering Chemistry 17, p. 41.
[13] Qtaishat, M., Rana, D., Khayet, M., Matsuura, T., 2009. Preparation and characterization of novel hydrophobic/hydrophilic polyetherimide composite membranes for desalination by direct contact membrane distillation, Journal of Membrane Science 327, p. 264.
[14] Singh, D., Sirkar, K.K., 2012. Desalination of brine and produced water by direct contact membrane distillation at high temperatures and pressures, Journal of Membrane Science 389, p. 380.
[15] Khayet, M., Cojocaru, C., García-Payo, M.C., 2010. Experimental design and optimization of asymmetric flat-sheet membranes prepared for direct contact membrane distillation, Journal of Membrane Science 351, p. 234.
[16] Calabro, V., Drioli, E., Matera, F., 1991. Membrane Distillation in the Textile Wastewater Treatment, Desalination 83, p. 209.
[17] Mozia, S., Morawski, A.W., Toyoda, M., Tsumura, T., 2010. Integration of photocatalysis and membrane distillation for removal of mono- and poly-azo dyes from water, Desalination 250, p. 666.
[18] Zakrzewska-Trznadel, G., Chmielewski, A.G., Miljević, N.R., 1996. Separation of protium/deuterium and oxygen-16/oxygen-18 by membrane distillation, Journal of Membrane Science 113, p. 337.
[19] Zakrzewska-Trznadel, G., Harasimowicz, M., Chmielewski, A.G., 1999. Concentration of radioactive components in liquid low-level radioactive waste by membrane distillation, Journal of Membrane Science 163, p. 257.
[20] Gethard, K., Sae-Khow, O., Mitra, S., 2012. Carbon nanotube enhanced membrane distillation for simultaneous generation of pure water and concentrating pharmaceutical waste, Separation and Purification Technology 90, p. 239.
[21] El-Abbassi, A., Hafidi, A., García-Payo, M.C., Khayet, M., 2009. Concentration of olive mill wastewater by membrane distillation for polyphenols recovery, Desalination 245, p. 670.
[22] El-Abbassi, A., Hafidi, A., Khayet, M., García-Payo, M.C., 2013. Integrated direct contact membrane distillation for olive mill wastewater treatment, Desalination 323, p. 31.
[23] Gryta, M., 2008. Alkaline scaling in the membrane distillation process, Desalination 228, p. 128.
[24] He, F., Gilron, J., Lee, H., Song, L., Sirkar, K.K., 2008. Potential for scaling by sparingly soluble salts in crossflow DCMD, Journal of Membrane Science 311, p. 68.
[25] Goh, S., Zhang, Q., Zhang, J., Mcdougald, D., Krantz, W.B., Liu, Y., Fane, A.G., 2013. Impact of a biofouling layer on the vapor pressure driving force and performance of a membrane distillation process, Journal of Membrane Science 438, p. 140.
[26] Hausmann, A., Sanciolo, P., Vasiljevic, T., Weeks, M., Schroën, K., Gray, S., Duke, M., 2013. Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation, Journal of Membrane Science 442, p. 149.
[27] Gryta, M., 2005. Long-term performance of membrane distillation process, Journal of Membrane Science 265, p. 153.
[28] Goh, S., Zhang, J., Liu, Y., Fane, A.G., 2013. Fouling and wetting in membrane distillation (MD) and MD-bioreactor (MDBR) for wastewater reclamation, Desalination 323, p. 39.