Performance evaluation of membrane technology for removal of micro pollutants in Hartbeespoort dam water in South Africa

Amos Adeniyi[1], Thabo Brooms[1], Richard Mbaya[1], Maurice Onyango[1], Patricia Popoola[1], Olukunle Olubiyi[2]

[1]Department of Chemical, Metallurgical and Materials Engineering, [2] Environmental Chemistry Research Group, Department of Environmental, Water and Earth Sciences. Tshwane University of Technology (TUT), Private Bag X680, Pretoria 0001, South Africa. adeniyia@tut.ac.za, amosadeniyi7@yahoo.com

Abstract The performance of a reverse osmosis (AFC99) and nanofiltration (AFC40) membrane was evaluated for the removal of micro pollutants from Hartbeesppoort dam water, found to have low ionic strength. The Reverse osmosis (RO) membrane was found to have percentage porosity of 0.2%, average roughness (0.67), and contact angle (40°-63°) gave a water recovery of about 43%. As for Nanofiltration (NF) membrane, the percentage porosity was found to be 2.9%, average roughness (0.76) and contact angle was in the ranges (30°-40°) gave a water recovery of about 48%. Both membranes performances gave a rejection > 99% for all the micro pollutants.

Keywords micro pollutants, dam water, Hartbeespoort dam, reverse osmosis, nanofiltration

Introduction

The emergence of micro-pollutants such as polyaromatic hydrocarbons (PAHs) and organochloride pesticides (OCPs) in both surface and underground water, is of a major concern to the water practitioners and nations of the world (Loose et al. 2009). The potential health risks of these emerging micro-pollutants can lead to damaging of immune system, cancer, genetic malformations and development of neuro disorder (McKinlay et al. 2008). However, the existing conventional water treatment plants were not designed for these unidentified contaminants; and this situation has become a threat to water supply network (Bolonga et al. 2009). Currently used conventional treatment techniques such as coagulation, precipitation, and activated sludge processes, may not be highly effective in removing these contaminants, but more advanced wastewater treatment options namely: granular activated carbon (GAC), membrane technology, and advanced oxidation processes (AOPs), have shown some satisfactory results (Chang et al. 2009). The AOPs and GAC are considered effective even though significant problems still arise mainly due to saturation of activated carbon, and other toxic chemical by-products which may develop in the GAC filters under some conditions (Karabelas and Plakas 2011). Membrane processes such as RO and NF can be included as a tertiary treatment when high water quality is desired (Jacob et al. 2010).

Hartbeespoort Dam is located 25°45″09.97″S, 27°53´04.39″E, about 37 km west of Pretoria and on the Crocodile River in North West Province, South Africa (Amdany et al. 2014). Micro pollutants such as organochloride pesticides and polyaromatic hydrocarbons (PAHs) have previously been detected in the water obtained from the dam which serves as a drinking water source (Amdany et al. 2014; Cukic and Vender 2010). Concentrations ranged from

30.0 *ng/L* to 51.5 *ng/L* for PAHs and 0.3 to 0.8 *ng/L* for OCPs (Amdany et al. 2014). Although these pollutants have been detected at low concentration level, they still possess potential health risks (McKinlay et al. 2008). The aim of this work was to investigate the performance of RO and NF membrane for the rejection of micro-pollutants emanating in Hartbeespoort dam, water recovery and for a good quality drinking water purpose.

Methods

Raw water obtained from Hartbeespoort dam was used for the investigation of the study. The raw water was pretreated using sand filter and microfiltration before being spiked with three different organochlorides pesticides (4,4-DDT 10.4 µg/L; Heptachlor 10.4 µg/L; Aldrin 26.05 µg/L) and three polyaromatic hydrocarbons (PAHs) (Pyrene 5.2 µg/L; Naphthalene 4.15 µg/L; Acenaphthene 10.4 µg/L). Each micro-pollutant was dissolved in either organic solvent (ethanol or methanol) before being added to the raw water due to low water solubility. Tubular membranes, RO (AFC99) and NF (AFC40) were both obtained from Xylem (Ltd) in the United Kingdom (UK). Length of each membrane is 32cm and diameter is 1.4cm. The AFC99 membrane was cleaned with a solution of 3ml/l (70% Nitric Acid) at temperature (55°C) and was recirculated for 30 minutes. As for AFC40 membrane, it was cleaned with a solution of 2ml/l (70% Nitric Acid) at temperature (55°C) and was also recirculated for 30 minutes.

The raw feed water and permeate were tested for pH, turbidity, and conductivity. TDS was estimated from the value of electrical conductivity using chemiasoft (2015). The investigation was done in a crossflow separation system shown in Figure 1. The membrane housing is a stage of two units of membranes in series. The membranes were investigated for water recovery at pressures ranging from 5 to 45 bars and at feed constant flow rate of 1018 L/h.

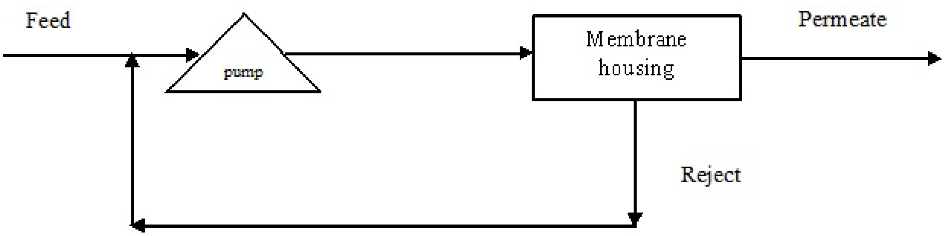

Figure 1 *Process flow diagram*

Analytical

For each run, 3 data of permeate flow rates were taken and 500 mL sample of the permeate was taken for analysis. The organic solute was extracted from the permeates samples using dichloromethane and the extracted solute was further concentrated to 0.5µL using Nitrogen gas, before being analyzed for concentration using Gas Chromatograph Mass Spectrometer (GCMS) (Olukunle et al. 2014). This was done in duplicates. The membranes were characterized for morphology using Scan Electron Microscopy (SEM) (Agboola et al. 2014), and for contact angle using sessile drop water measurements (Mbuli et al. 2014). The SEM image was analyzed using imageJ (Broeke et al., 2015) and WSxM 5.0 Develop 8.2 software (Horcas et al. 2007).

The permeate and rejection data were analyzed using the following equations:

$$W_R = \frac{Q_{permeate}}{Q_{feed}} \times 100\% \quad [1]$$

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

Where is water recovery; is the permeate flow rate; is the feed flow rate; is Rejection coefficient; is the solute concentration in permeate; is the solute concentration in the feed.

Results and discussion

Raw water characterization

Table 1 shows the results of the conductivity, TDS, pH, turbidity of the raw water and pretreated raw water. The raw water was high in turbidity, but low in ionic strength. Pre-treatment process significantly reduces the turbidity as expected, but with little effect on the pH, conductivity and TDS.

Membrane characterization

Figure 2 show the morphology of both membranes before use. The images were analyzed using image J as shown in Figure 3 and the 3-dimenisonal images using WSxM 5.0 develop 8.2 are shown in Figure 4.

Table 1 *Characterization of raw water and permeate from sand filter and ultrafiltration*

Parameter	Raw water	Sand filtration	ultrafiltration
Conductivity (µS/cm)	590	610	580
TDS (mg/L)	308	317	301
pH	8.23	7.97	8.22
Turbidity (NTU)	4.16	4.95	1.13

The SEM image (Figure 2) of AFC40 shows a nodular structure while that of AFC99 shows a tight, finely dense structure. Both images show no visible pores. Thresholding the SEM image of both membranes gives the idea to separate the background of an image from the object. This is due to the fact that that gray levels of pixels belonging to the object are substantially different from the gray levels of the pixels belonging to the background (Broeke et al. 2015). The threshold images (Figure 3) revealed the pores in AFC40, however the pores in AFC99 could not be identified The analysis of the images with regards to percentage po-

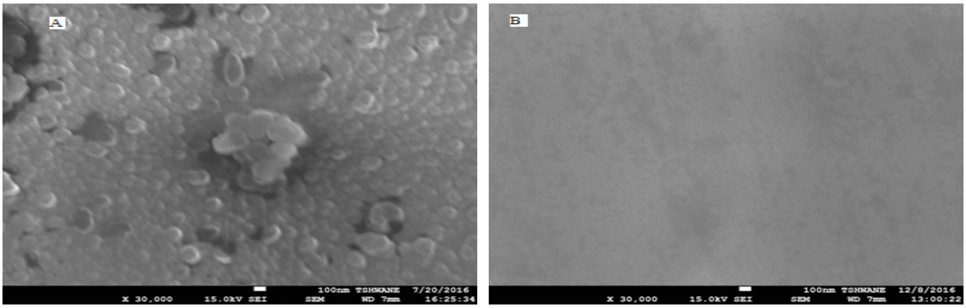

Figure 2 *SEM images of AFC40 (A) and AFC99 (B)*

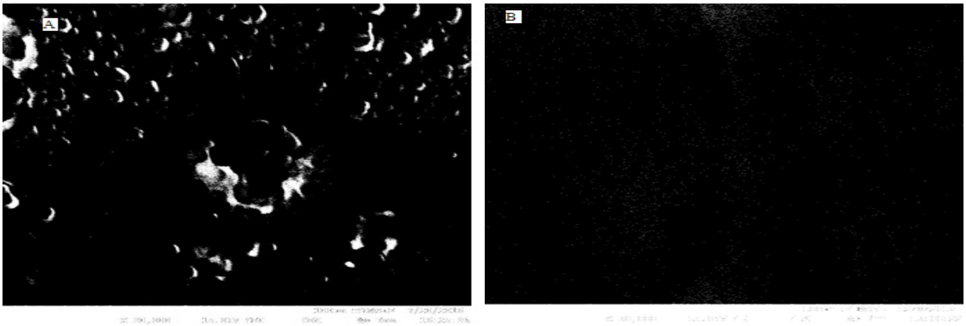

Figure 3 *Threshold images of AFC40 (A) and AFC99 (B) using image J*

rosity and average roughness indicates that AFC40 has porosity of 2.9% and average roughness of 0.76, while AFC99 has porosity of 0.2% and average roughness of 0.67, respectively. This is confirmed by the 3D images which showed that AFC40 is more rough and porous. Nanofiltration membranes are generally more porous than reverse osmosis membranes.

Both membranes were also characterized for contact angle. The contact angle for the NF ranged from 30° – 40°, while for RO ranged from 40°- 63°, respectively. This indicates that the NF membrane was more hydrophilic than RO membrane.

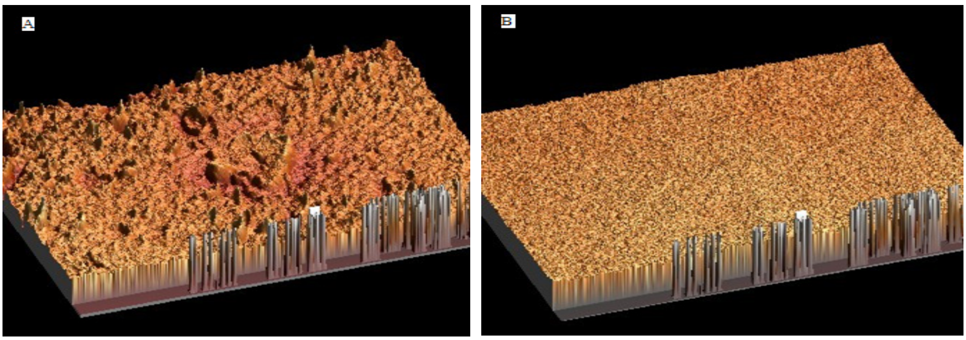

Figure 4 *3D images of AFC40 (A) and AFC99 (B) using WSxM 5.0 Develop 8.2*

Process results

The results of the water recovery are as shown in figures

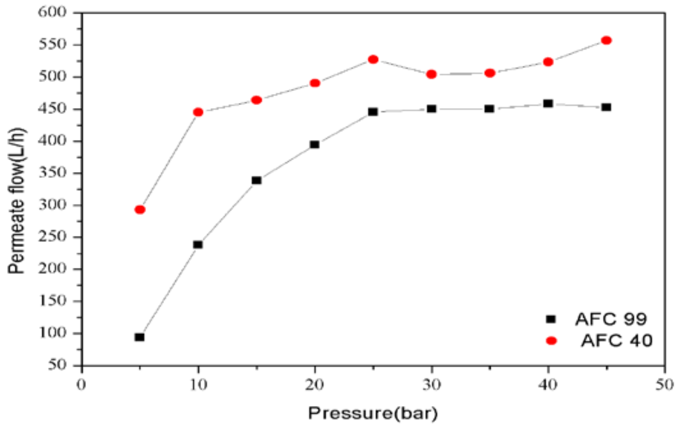

Figure 5 *Permeate flow*

Figure 5 indicates that permeate flow increases with an increase in pressure as expected, however, permeate flow shows a slight increase after 30bars. In all the results, permeate flow rate was higher for AFC40 as compare to AFC99. An average water recovery for AFC40 is 48%, while water recovery is 43% for AFC99. The reason for a higher water recovery in favor of AFC40 could have primarily be due to its higher percentage porosity. However, higher average roughness and hydrophilicity as well as lower contact angle could have also played a role in enhancing water recovery and solute rejection. Water recovery can be improved by adding more stages to the treatment process.

The investigation of rejection of organic was done in pressure ranges of 20-30 bars. Table 2 shows that RO membrane significantly reduced the TDS and turbidity of the feed water, while the NF membrane has no effect on the reduction of TDS, with minor effect on reduction of turbidity. This implies that if water has higher ionic strength, the NF membrane cannot be used.

Table 2 *Characterization of the permeate*

	AFC40			AFC99		
	20bar	25bar	30bar	20bar	25bar	30bar
Conductivity (µS/cm)	550	580	580	260	260	270
TDS mg/L	285	301	301	133	133	138
pH	7.56	7.63	7.69	7.42	7.8	7.56
Turbidity (NTU)	0.62	0.59	0.6	0.38	0.32	0.38

Table 3 shows the concentration of the organic solutes in the permeate in ng/L. The rejection coefficient of both RO and NF membranes was greater than 99% for each of the organic solute investigated. The reason for high rejection coefficient could have been due to low porosity between two membranes. Molecular weight of the organic solutes investigated ranges from 128 to 422. This implies that the molecular weight and the porosities of the membranes are favorable for steric exclusion on the solutes, and this implies that both membranes are adequate for the removal of micro pollutants.

Table 3 *Solute concentration in permeate (ng/L)*

	AFC40			AFC99		
	20bar	**25bar**	**30bar**	**20bar**	**25bar**	**30bar**
4,4-DDT	0.09	0.09	0.07	0.07	0.09	0.07
Endosulfan-sulfate	0.70	0.89	0.46	0.9	1.05	0.45
Heptachlor	0.06	0.05	0.06	0.05	0.05	0.05
Pyrene	0.49	0.20	0.24	0.28	0.51	0.17
Naphthalene	0.13	0.22	0.12	0.16	0.37	0.08
Aldrin	2.44	1.65	1.17	1.05	1.97	0.89
Acenaphthene	0.72	0.79	0.63	0.62	1.30	0.38

Conclusion

The application of membrane technology for the removal of micro-organic pollutants at Hartbeespoort dam, was investigated in a stage of two-unit membrane process. The RO and NF membrane gave rejection coefficient greater than 99%, however the NF membrane offered a better advantage in terms of water recovery. Average water recovery for RO and NF membranes was 43% and 48%, respectively. A performance improvement on both membranes for water recovery, can be achieved by increasing number of stages during membrane filtration process.

Acknowledgement

The authors would like to acknowledge Tshwane University of Technology for funding, providing research facilities and laboratory equipment(s); and also Rand Water for funding. A word of gratitude goes to Prof Jonathan Okonkwo for giving us permission to use the organic chemistry laboratory facility

References

Agboola O, Jannie M, Mbaya R (2014) Characterization and performance of nanofiltration membranes. A review. Environ Chem Lett, 12, 241-255, doi:10.1007/s10311-014-0457-3

Amdany R, Chimuka L, Cukrowska E, Kukučka P, Kohoutek J, Vrana B (2014) Investigating the temporal trends in PAH, PCB and OCP concentrations in Hartbeespoort Dam, South Africa, using semipermeable membrane devices (SPMDs). Water SA Vol. 40 No. 3, http://dx.doi.org/10.4314/wsa.v40i3.5

Bolong N, Ismail AF, Salim MR, Matsuura T (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. Des 239, 229–246, https://doi.org/10.1016/j.desal.2008.03.020

Broeke J, Pérez JMM, Pascau J (2015) Image Processing with ImageJ. Second Edition. Packt Publishing.

Chang H, Choo K, Lee B, Choi S (2009) The methods of identification, analysis, and removal of endocrine disrupting compounds (EDCs) in water. JHM 172, 1–12, doi: 10.1016/j.jhazmat.2009.06.135.

Cukic Z, Venter P (2010) Characterization and managing of internal nutrient load (sediments) of hartbeespoort dam. www.ewisa.co.za/literature/files/339_265%20Cukic.pdf (accessed:10-05-2015)

Horcas I, Fernandez R., Gomez-Rodriguez JM, Colchero J, Gomez-Herrero J, Baro AM (2007) WSXM: A software for scanning probe microscopy. Sci. Instrum., 78, 1, doi: 10.1063/1.2432410

http://www.chemiasoft.com/chemd/TDS (accessed: 03:08:2015)

Jacob M, Guigui C, Cabassud C, Darras H, Lavison G, Moulin L (2010) Performances of RO and NF processes for wastewater reuse: Tertiary treatment after a conventional activated sludge or a membrane bioreactor. Des 250, 833–839, doi: 10.1016/j.desal.2008.11.052

Karabelas A, Plakas K (2011) Membrane Treatment of Potable Water for Pesticides Removal, Herbicides, Theory and Applications, Prof. Marcelo Larramendy (Ed.), ISBN: 978-953-307-975-2.

Loos R, Gawlik BM, Locoro G, Rimaviciute E, Contini S, Bidoglio G (2009) EU-wide survey of polar organic persistent pollutants in European river waters. Environ Pollut, Vol. 157, pp. 561–568, doi: 10.1016/j.envpol.2008.09.020.

Mbuli BS, Nxumalo EN, Mhlanga SD, Krause RW, Pillay VL, Oren Y, Linder C, Mamba BB (2014) Development of Antifouling Polyamide Thin-Film Composite Membranes Modified with Amino-Cyclodextrins and Diethylamino-Cyclodextrins for Water Treatment. J. Appl. Polym. Sci., doi: 10.1002/APP.40109, doi: 10.1002/app.40109

McKinlay R., Plant JA, Bell JNB, Voulvoulis N (2008) Endocrine disrupting pesticides: Implications for risk assessment. Environ Intl, Vol. 34, No. 2, pp. 168–183, ISSN 0160-4120.

Olukunle OI, Sibiya IV, Okonkwo OJ, Odusanya AO (2014) Influence of physicochemical and chemical parameters on polybrominated diphenyl ethers in selected landfill leachates, sediments and river sediments from Gauteng, South Africa. Environ Sci Pollut Res, doi:10.1007/s11356-014-3443-1.

Sharpe RM, Irvine DS (2004) How strong is the evidence of a link between environmental chemicals and adverse effects on human health? Brit. Med. J., 328, 447–451, doi: 10.1136/bmj.328.7437.447