Membrane selection for organic contaminants removal from Hartebeespoort dam water in South Africa

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Abstract

Membrane filtration of raw water obtained from Hartebeespoort dam in South Africa and spiked with four different organochlorides pesticides (4,4-DDT 10.4 μg/L; Heptachlor 10.4 μg/L; Aldrin 26.05 μg/L; Endosulfan sulfate 10.4 μg/L) and three polyaromatic hydrocarbons (Pyrene 5.2 μg/L; Naphthalene 4.15 μg/L; Acenaphthene 10.4 μg/L) was done using three different commercially available membranes (AFC 40, AFC80 and AFC99). The purpose was to determine important membrane characteristics for removal of organic contaminants and enhance water recovery. The FTIR analysis of the membranes indicated a significant presence of amides group (peak at 1650 cm^{-1}) and acyl and phenyl C-O groups in all the membranes (peak at 1150 cm^{-1}). AFC40, a nanofiltration membrane, showed a modular structure, has 2.9% porosity and average roughness 0.76. AFC80, a reverse osmosis membrane, showed little modular structure, has 2.9% porosity and average roughness 0.79. AFC99, another reverse osmosis membrane was tight and showed no nodular structure, percentage porosity was 0.2 while average roughness was 0.67. All the membranes are hydrophilic and gave more than 99% rejection of organic solutes however water recovery was higher with AFC40 which is more hydrophilic (Contact angle 30°- 40°). AFC40 had little effect on the conductivity of the feed water. Membrane with higher nodular structure has higher porosity. The presence of nodular structure increases water recovery but also allows the passage of some dissolved solids.

Keywords: Hartebeespoort dam, organic solutes, membranes, reverse osmosis, nanofiltration

1. Introduction

Chemical pollution of natural waters has already become a major public concern in almost all parts of the world, since it has largely unknown long-term effects on aquatic life and on human health [1]. Most of these chemical pollutants can be removed by the conventional treatment method of coagulation and sedimentation. However, the occurrence of micro-pollutants in both surface and underground water is a major concern to water practitioners all over the world [2,3]. There are two major reasons for this, the first one is the fact that the adverse effect of these micro-pollutants is significant and the extent of damage to human is not well document if taken through drinking water [4]. The other reason is that the conventional treatment methods may not be adequate for the removal of these micro-pollutants [2,5]. The technology options available for the removal of these micro-pollutants are advanced treatment methods such as Advance Oxidation Processes (AOP), Granular Activated Carbon (GAC) or Membrane Technology [5]. The addition of more advanced final treatment steps (usually involving oxidation by H_2O_2 or O_3, and granular activated carbon – GAC – filtration) is generally considered to be effective, although significant problems still arise, mainly related to saturation of activated carbon, and to toxic chemical by-products, which may develop in the GAC filters under some conditions [3]. When a high water quality is desired, membrane processes such as reverse osmosis (RO) and nanofiltration (NF) might be used as tertiary treatment [6].

Hartebeespoort dam located in South Africa is a major source of drinking water. There is a water purification plant located near the dam which uses the conventional treatment method. However recent analysis of the dam water indicated the presence of micro-pollutants [7]. Membrane technology is being consider as an option in order to remove these micro-pollutants. The purpose of this work is to investigate three membranes for filtration of water obtained from Hartebeespoort dam in order to determine important membrane characteristics for removal of organic contaminants and enhance water recovery.

2. Material and method

2.1 Material

2.1.1 Membrane

Three membranes obtained from Xylem UK were used for the experiments. They are all made from 1,2-benzisothiazol-3(2H)-one, sodium salt. They are tubular membranes of about 32cm in length and 1.4cm in diameter. The trade names are AFC40, AFC80 and AFC99. AFC40 is a nanofiltration membrane while AFC99 and AFC80 are Reverse Osmosis membranes

2.1.2 Source and characterization of dam water

Raw water sample was obtained from Hartebeespoort dam 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. Turbidity measurement was done using portable microprocessor turbidity meter HI93703) from HANNA. pH of process water was measured using Jenway 3510 pH meter obtained from Lansec. Conductivity of water was determined with conductivity meter HI8033 obtained from HANNA while Total Dissolved Solid (TDS) was calculated from conductivity values with chemiasoft [8]. The raw water was pretreated using sand filtration and ultrafiltration.

2.1.3 Preparation of organic solutes

Four organochloride pesticides (OCPs) and three polyaromatic hydrocarbons (PAHs) solution were prepared by dissolving a certain mass of the organics in either ethanol or methanol. This is because the organics were insoluble in water so each of them was dissolved in an organic solvent that is highly soluble in water. The organics were added to the raw water obtained from the dam after pretreatment. The organic solute and source, the solvent and the concentration in process water is as shown in Table 1.

Table 1: Organic solutions and final concentration in process water

Solute	**Source and purity**	**Solvent and solute concentration in solvent**	**Solute concentration in water**
Heptachlor	Dr. Ehrenstorfer GmbH 99.0%	0.5g/L Methanol	10.4µg/L 0.5ml in 24L water
Aldrin	Dr. Ehrenstorfer GmbH 99.0%	1.25g/L Methanol	26.05µg/L 0.5ml in 24L water
4,4-DDT	Dr. Ehrenstorfer GmbH 98.5%	0.5g/L Ethanol	10.4µg/L 0.5ml in 24L water
Endosulfan sulfate	Dr. Ehrenstorfer GmbH 99.0%	0.5g/L Methanol	10.4µg/L 0.5ml in 24L water
Pyrene	Dr. Ehrenstorfer GmbH 99.0%	0.25g/L Methanol	5.2µg/L 0.5ml in 24L water
Naphthalene	Dr. Ehrenstorfer GmbH 99.5%	0.2g/L Ethanol	4.15µg/L 0.5ml in 24L water
Acenaphthene	Dr. Ehrenstorfer GmbH 99.5%	0.5g/L Methanol	10.4µg/L 0.5ml in 24L water

2.1.4 Process Equipment

A laboratory scale reverse osmosis pilot plant manufactured by Elettronica Veneta, Italy was used for the process experiment.

2.2 Method

2.2.1 Membrane characterization

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy was performed on the membrane samples using a PerkinElmer Spectrum 100 spectrometer (PerkinElmer, USA) between 500cm^{-1} and 4000 cm^{-1} wave number.

Scan Electron Microscopy- Energy Dispersive X-Rays (SEM-EDX)

The surfaces of the membranes were scanned using Joel Field Emission Electron Microscope JESM-7600F. The virgin membranes were mounted on a double-sided carbon tape and the surfaces were coated with iridium (about 5 nm thickness) in order to make it conductive before SEM analysis. The sample was exposed to electron beam at an accelerating voltage of 15 KV. EDX data was obtained during SEM measurement. The SEM images were analyzed with the aid of WSxM 5.0 Develop 8 [9] and ImageJ [10] for surface roughness, percentage porosity and pore identification.

Contact angle

Contact-angle measurements for the membrane were done using Sessile drop water measurement. The equipment used was Dataphysics Contact Angle Instrument (SCA 20, OCA 15EC). This was done by depositing sessile drops of deionized water on the dry surfaces of the membranes at room temperature. Images were captured five seconds after depositing the water drop onto the sample just before measurement of the contact angles. Three measurements were taken at different locations of the membrane sample. The average was calculated to obtain the membrane's contact angle.

2.2.2 Membrane Preparation

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 and AFC80 membrane, they were cleaned with a solution of 2ml/l (70% Nitric Acid) at temperature (55°C) and was also recirculated for 30 minutes.

2.2.3 Process experiment

The pretreated raw water was spiked with the organic solutes at concentration stated in Table 1. The water was then treated in a cross-flow laboratory pilot plant at pressures of ranges from 5 to 45bars. The flow rate was 1018 L/h. The flow diagram is shown in Figure 1. The permeate flow rate was taken against the applied pressures.

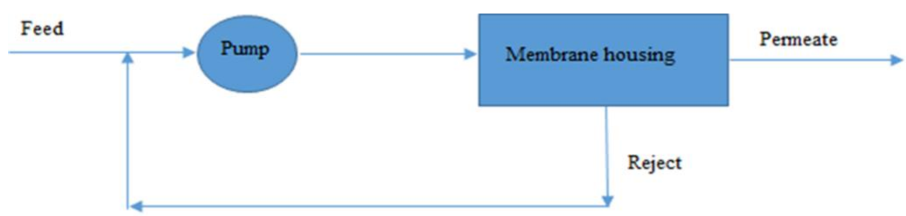


Figure 1: Flow diagram of the filtration process

2.2.4 Organic contaminants rejection

Two 500 ml sample of permeate were taken for every filtration run. The organic solutes present in the permeate were extracted using liquid-liquid extraction. Solvent used for the extraction was 100ml of dichloromethane (99+% purity). The extraction was done three times and the process done in duplicate. Excess water was remove from the extracted solvent using anhydrous sodium sulphate (99% purity). The sodium sulphate was activated in furnace before use. This was done by heating the anhydrous sodium sulphate in the furnace at 600°C for 72 hours. The solvent was concentrated using a vacuum evaporator to about 2ml. This was further concentrated to 0.5µL using

Nitrogen gas. before being analyzed using Gas Chromatography Mass Spectrometry (GCMS). The clean extracts were analyzed for selected PAH and OCPs by Shimadzu model 2010 plus gas chromatograph coupled with a model QP 2010 ultra, mass spectrometer (Shimadzu, Japan) using electron ionization and injected by a Shimadzu A0C-20i auto sampler. Equation 1 was used to calculate the rejection coefficient.

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

Where R is Rejection coefficient; C_p is the solute concentration in permeate; C_f is the solute concentration in the feed.

3. Results and discussion

3.1 Membranes Characteristics

The FTIR results for each of the membrane reveal similar patterns as shown in Figure 2. There is strong presence of saturated amides group and weak amines group in each of the membranes with equal intensity as indicated by peak at 1650 cm^{-1}. This is expected because the membranes are made from 1,2-benzisothiazol-3(2H)-one, sodium salt, a polyamide. There is also the presence of amines group with equal intensity for AFC99 and AFC40 but higher than the intensity of AFC80 (peak at 3310 cm^{-1}). There is strong presence of acyl and phenyl C-O groups in all the membranes (peak at 1150 cm^{-1}). There is the presence of ortho disubstituted aromatic group in each of the membranes (peak at 740 cm^{-1}) but the fact that it is not clearly shown in AFC99 is unexpected.

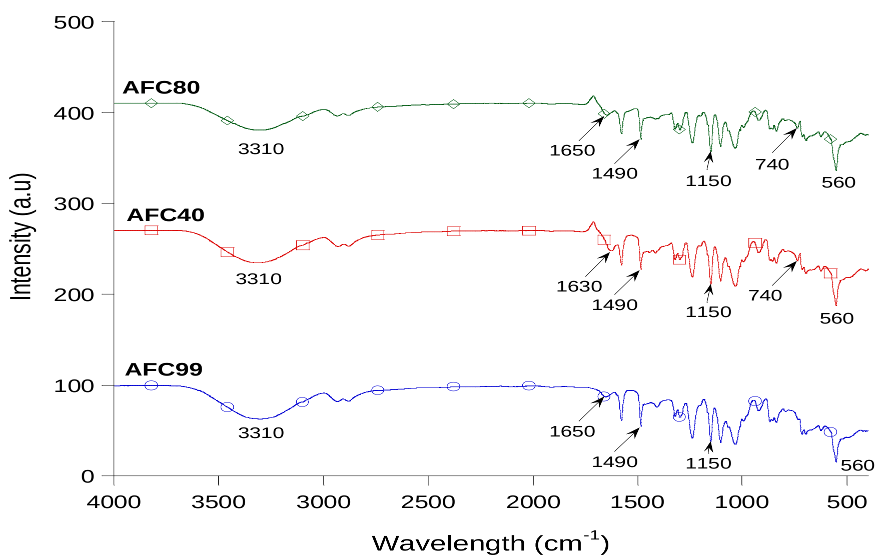


Figure 2: FTIR results for the membranes

Figure 3 shows the qualitative EDX analysis of the membranes. AFC40 contain Carbon (75.31wt %), Oxygen (14.66wt%), Sodium (0.46 wt %) and Sulphur (9.57 wt %). AFC80 contains Carbon (61.19 wt %), Oxygen (11.88 wt %), Sodium (0.32 wt %), Sulphur (25.14 wt %). AFC99 contains Carbon (74.02 wt %), Oxygen (19.04 wt %), Sodium (0.26 wt%), Sulphur (6.06 wt %). Actually, the composition of the membranes was expected to be the same because they were made from the same material. However, the EDX is showing that there is a possible change in composition due to membrane processing and this may have effect on the performance of the membranes. It is of note that although the sodium contents of all the membranes are low, AFC40 has the highest sodium content.

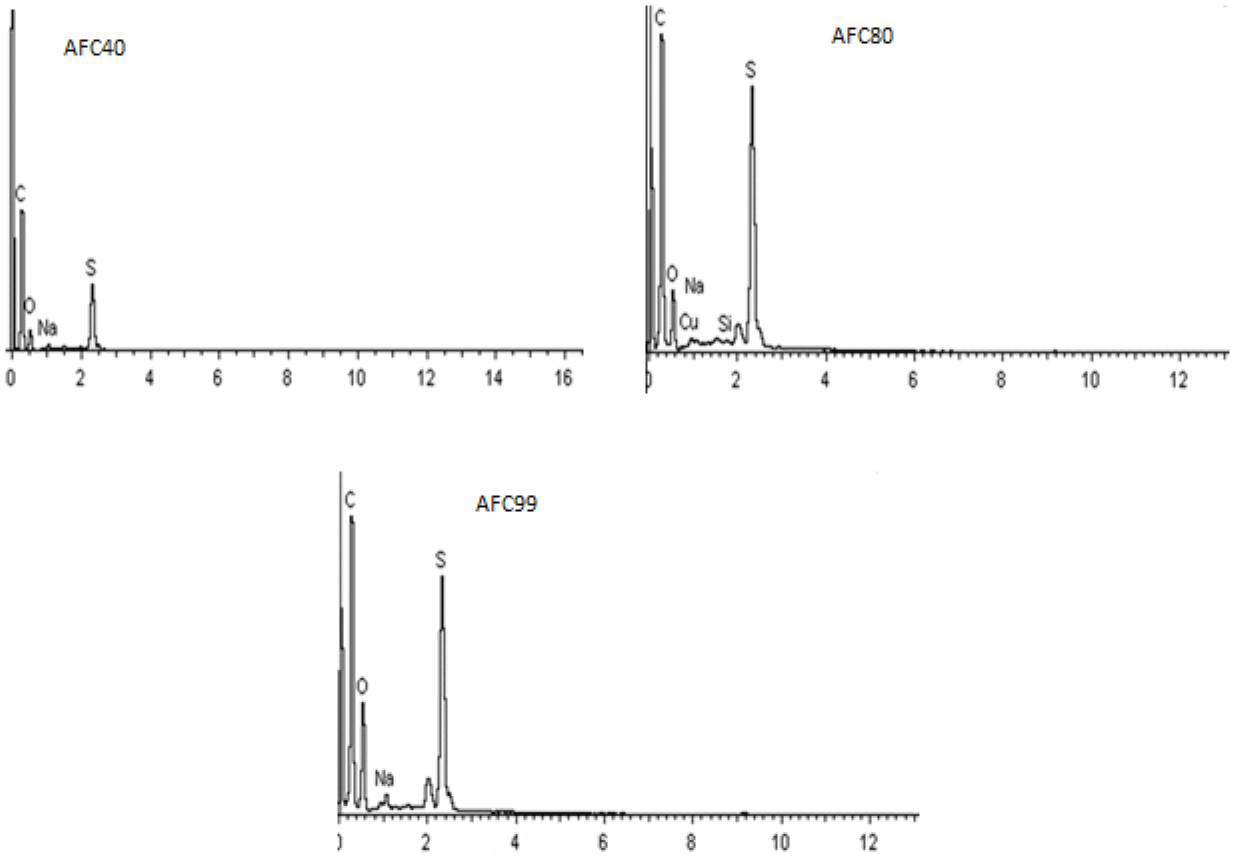
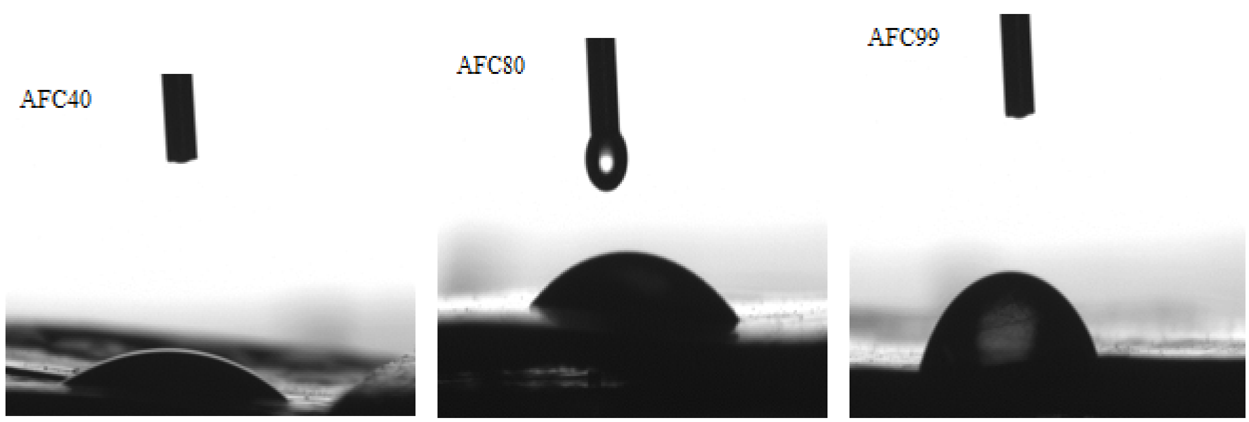


Figure 3: EXD results

The contact angle is a measure of hydrophilicity of the membranes, the lower the values of contact angles, the more hydrophilic the membrane is. Materials that are hydrophilic generally have contact angles less than 90° while hydrophobic materials have contact angles greater than 90°. All the membranes investigated are hydrophilic, however, AFC40 exhibits more hydrophilicity than AFC80 and AFC99 as indicated by the lower values of contact angle.



30°- 40° 32°-50° 40°- 63°

Figure 4: Contact angle results

SEM images are as shown in Figure 5. Both AFC40 and AFC80 showed a nodular structure but nodules of AFC40 are bigger than that of AFC80. AFC99 showed no nodular structure. A progressive disappearance of the nodular structure is observed form AFC40 to AFC99. AFC40 a Nanofiltration membrane has the highest nodules while AFC99 a Reverse Osmosis membrane has none. However, although AFC80 is a Reverse Osmosis membrane, it has some nodular structures but not as big and as pronounced as that of AFC40. This is likely to have effect on the rejection of solute and water flux obtained from each of the membranes. None of the images showed visible pores. All the images showed a dense finely dispersed structure with AFC99 showing higher density and fineness than AFC80 and AFC40.

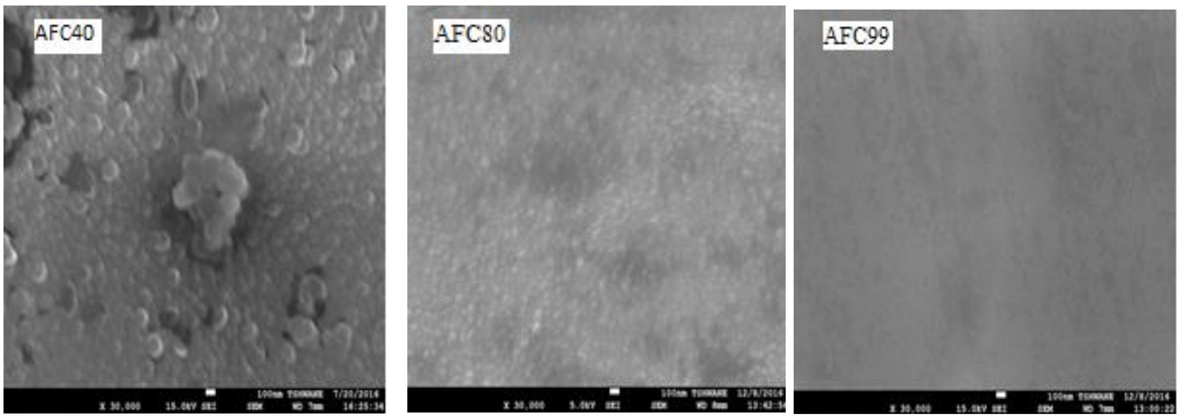


Figure 5: SEM images of the membranes at 3000x

The SEM images were processes using ImageJ. The threshold images which separates the background from the objects are as shown in Figure 6. The Figure showed that AFC40 is more porous than AFC80 and AFC99, while AFC99 showed a totally dense membrane. The porosity and roughness analysis of each of the membranes as determined using WSxM 5.0 Develop 8 software are shown in Table 2 and the roughness analysis shown in Figure 7. AFC40 is more porous but less rough than AFC80. AFC99 has the lowest porosity and roughness, however the porosity and roughness of each of the membranes are low.

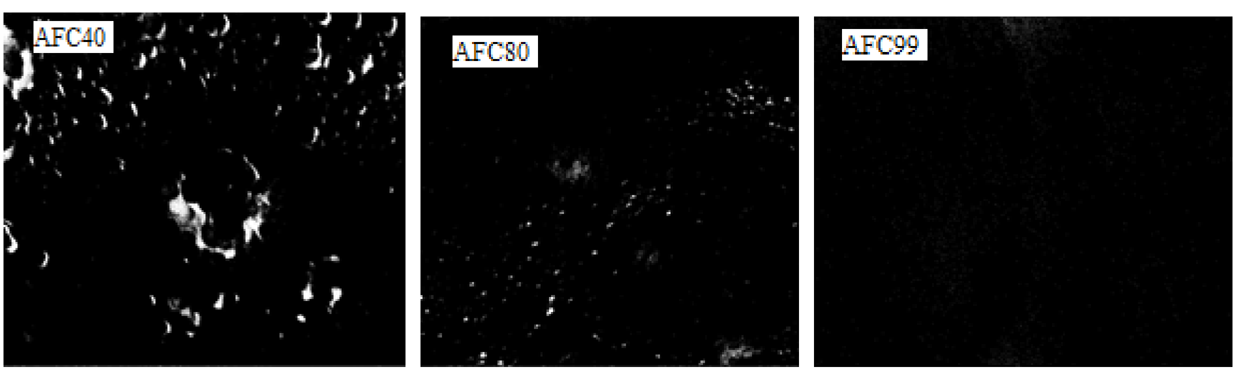


Figure 6: ImageJ threshold images of membranes

Table 2: Comparison of porosity and roughness

	Percentage porosity	**Roughness average**
AFC40	2.90%	0.76
AFC80	0.90%	0.79

AFC99	0.20%	0.67

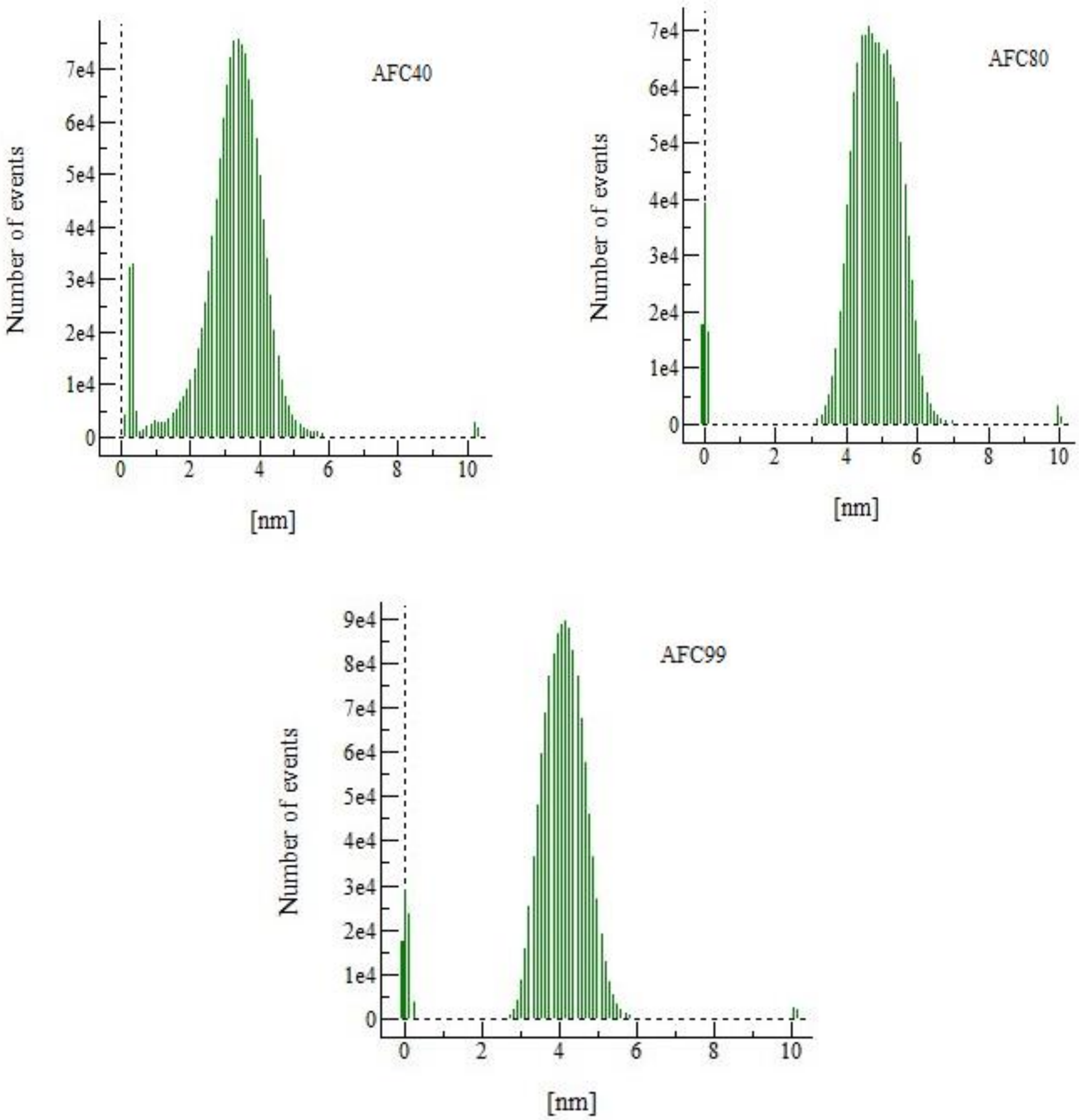


Figure 7: Roughness analysis of the membranes

3.2 Process water

The raw water used for the experiment was characterized for Conductivity, TDS, pH and Turbidity. The results are shown in Table 3. The Conductivity of the raw water was low and hence the low value of the total dissolved solid (TDS). This means the water is of low ionic strength [11]. The sand filtration process increased the TDS and turbidity. The ultrafiltration process reduced the turbidity significantly as expected but has no effect on the Total Dissolved Solids. The final water fed into the membranes system is slightly alkaline, it is less turbid and also has low TDS.

Table 3: Process water characterization

Parameter	Raw water	Sand filtration	Ultrafiltration
Conductivity (µS/cm)	590	610	580
TDS (mg/L)	306	317	301
pH	8.23	7.97	8.22
Turbidity (NTU)	4.16	4.95	1.13

Table 4 shows the comparison of the effect of each membrane on the Conductivity, TDS, pH, and Turbidity of the feed water. Both AFC 99 and AFC80 significantly reduced the turbidity of the process water. It is observed that only AFC99 has significant effect on the TDS and this is due to the tightness of the membrane.

Table 4: Comparison of Conductivity, TDS, pH and Turbidity measurements

	Conductivity (µS/cm)	**TDS (mg/L)**	**pH**	**TURBIDITY (NTU)**
Ultrafiltration permeate	580	301	8.22	1.13
AFC40 permeate	550	285	7.56	0.92
AFC80 permeate	500	259	7.62	0.46
AFC 99 permeate	260	133	7.42	0.38

3.3 Solute Rejection

The water obtained after the ultrafiltration stage was spiked with the organics before treatment on a reverse osmosis laboratory pilot plant. Results are as shown in Tables 5. All the membranes exhibit greater than 99% rejection of the organic solutes. This may be due to low porosity of the membranes and high molecular weight of the organic solutes.

Table 5: Comparison of rejection

	Raw dam water spiked with PAH and OCP						
Membrane	Heptachlor 10.4µg/L	Aldrin26.05µg/L	4,4-DDT 10.4µg/L	Endosulfan sulfate 10.4µg/L	Pyrene 5.2µg/L	Naphthalene 4.15µg/L	Acenaphthene 10.4µg/L
AFC40	>99%	>99%	>99%	>99%	>99%	>99%	>99%
AFC80	>99%	>99%	>99%	>99%	>99%	>99%	>99%
AFC99	>99%	>99%	>99%	>99%	>99%	>99%	>99%

3.4 Water recovery

Water recovery increases with pressure as indicated by progressive increase in permeate flow with pressure (Figure 8). This is expected but at higher pressure the rate of increase in permeate flow for each of membranes dropped. This is because the ionic strength of the process water is low and consequently, the osmotic pressure is also low. This means high pressure is not needed for the filtration process. Figure 8 actually showed that a pressure greater than 30bars is not needed. Generally, AFC40 showed higher water recovery than AFC80 and AFC99. This may be due to higher porosity which is attributed to the nodular structure of the membrane. The fact that the membrane has high hydrophilicity may also contribute to increase in permeate water flux.

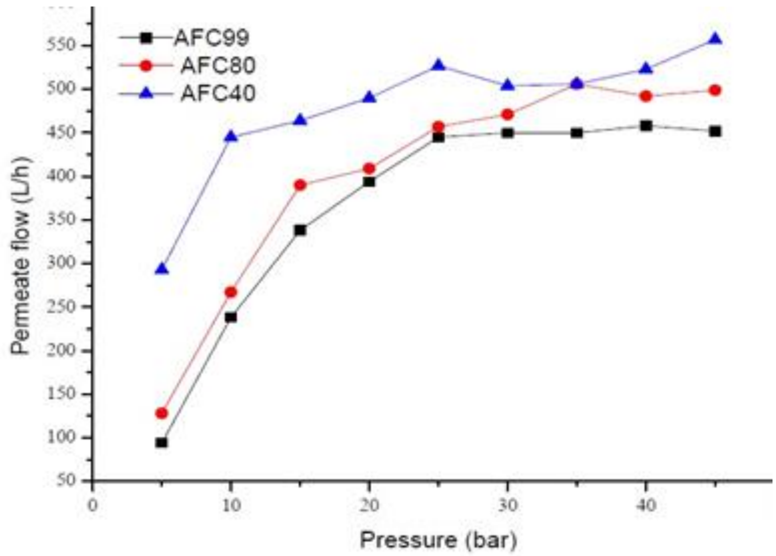


Figure 8: Comparison of permeate flow rates

4. Conclusion

All the membranes showed a significant presence of amides group because the membranes are made from polyamides. All the membranes are of low porosity and roughness. However, AFC40, a nanofiltration membrane, has high nodular structure which causes increase in porosity. AFC40 has higher porosity than AFC80 and AFC99, and gave highest permeate water flow. All the membranes gave adequate rejection of the organic solute although AFC40 has little effect on the conductivity of the process water. The nodular structure in AFC40 and its high hydrophilicity may have increased permeate flow, but the nodular structure allows the passage of some dissolved solids.

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References

1. Loos, R., Gawlik B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio. G.: EU-wide survey of polar organic persistent pollutants in European river waters. Environmental Pollution 157, 561–568 (2009)

2. Bolong, N., Ismail, A.F., Salim, M.R., Matsuura, T.: A review of the effects of emerging contaminants in wastewater and optional for their removal. Desalination 239:229–246 (2009)

3. Karabelas, A., Plakas, K.: Membrane Treatment of Potable Water for Pesticides Removal, Herbicides, Theory and Applications. Prof. Marcelo Larramendy (Ed.), ISBN: 978-953-307-975-2, InTech, Available from: http://www.intechopen.com/books/herbicides-theory-and-applications/membranetreatment-of-potable-water-for-pesticides-removal (2011)

4. McKinlay, R., Plant J.A., Bell J.N.B., Voulvoulis, N.: Endocrine disrupting pesticides: Implications for risk assessment. Environment International, Vol. 34, No. 2, pp. 168–183, ISSN 0160-4120. (2008)

5. Chang, H., Choo, K., Lee, B., Choi, S.: The methods of identification, analysis, and removal of endocrine disrupting compounds (EDCs) in water. Journal of Hazardous Materials 172, 1–12 (2009)

6. Jacob, M., Guigui, C., Cabassud, C., Darras, H., Lavison, G., Moulin, L.: Performances of RO and NF processes for wastewater reuse: Tertiary treatment after a conventional activated sludge or a membrane bioreactor. Desalination, 250, p. 833- 839. (2010)

7. Amdany R., Chimuka. L, Cukrowska E., Kukučka P., Kohoutek J. Vrana B.: 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 (2014)

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

9. Horcas, I., Fernandez, R., Gomez-Rodriguez, J.M., Colchero, J., Gomez-Herrero, J., Baro, A.M.: WSXM: A software for scanning probe microscopy and a tool for nanotechnology. Rev. Sci. Instrum., 78, 1 (2007).

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

11. Sarkar, B.N., Venkateswralu, R. Rao, N., Bhattacharjee, C., Kale, V.: Treatment of pesticide contaminated surface water for production of potable water by a coagulation–adsorption–nanofiltration approach. Desalination 212, 129–140 (2007)