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Nanofiltration as Pretreatment to Reverse Osmosis for Paper and Pulp Mill Effluent

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Annotation
The paper and pulp industry produces effluent which is high in organic content and salinity, typically making is difficult to treat. For reclamation of this wastewater, the process should be designed such that the water is 'fit for purpose'. Agricultural reuse of this waste stream is a potential option as the treatment requirements are less intense than for other reuse opportunities. This papers forms part of a larger project for developing an integrated UF-NF-RO system fir reclaiming the biologically treated effluent from a thermo-mechanical pulp and paper mill in rural Australia. The current work has characterised the waste water and investigated a suite of commercially available NF membranes as a pre-treatment method for RO. Dead-end stirred cell filtration has been used to evaluate the selective removal of multivalent ions and low molecular weight organics in the NF stage. The result demonstrate the importance of the NF stage to the reclaimed water and show a SAR reduction of between 30-60% is achievable in this system. Of the commercially available membranes tested the membrane which performed the best was the NTR-7450 membrane from Hydranautics.

Keywords
Effluent, Nanofiltration, Pulp and Paper Mill, Reclaimed water.

INTRODUCTION
A global water scarcity coupled with the uncertainty created by climate change has resulted in increasing pressure for improved water management. This trend is being driven by both growing public awareness and more stringent regulation imposed by authorities. Water reclamation is seen as a major alternative source of water, in particular, for industrial and agricultural purposes.

The paper and pulp industry consume large quantities of water in the pulping, bleaching and paper making processes. Typically between 10-40 litres of fresh water are used per kilogram of paper produced (Pizzichini et al. 2005) and there is limited scope for further in-process recycling without increased risk of scale deposition on process equipment, corrosion, reduced production capacity and loss of operational flexibility (Integrated Pollution Prevention and Control (IPPC) 2001). However, there is still significant scope to lower the intake of fresh water via external recycling. In Australian, the current practice in many pulp and paper mills is to biologically treat the pulp and paper effluent (PPE) prior to, in most cases, discharge to local waterways. At the current levels of treatment this effluent places further strain on waterways which are already showing signs of distress and they are not sufficiently clean for reuse purposes, as it is still high in colour, organic content and salinity.

Due to the rural nature of many pulp and paper mills in Australia, reclamation for agricultural application may represent the most obvious reuse option. The agricultural sector is consistently the largest water consumer in Australia and in 2004/2005 represented 64% of all water use (ABS 2006; Stevens 2006). Water reclamation and reuse for agricultural purposes is an advantageous practice because intense treatment is often unnecessary and the wastewater often contains nutrients and compounds that are beneficial to the soil.

In the reclamation of any wastewater source the end use of utmost importance and the final product water should be 'fit for purpose'. That is, the water treatment process should be tailored for the particular reuse application and adhere to state and national guidelines outlining acceptable physic-chemical parameters (Leslie et al. 2005).

The feasibility of water reuse in agricultural applications is contingent upon the sodicity and salinity of the soil, the residual nutrients such as nitrogen and phosphorus and heavy metals. Where irrigation is applied the reuse volumes that can be applied also vary according to the soil and crop types (SA 1999). The sodicity describes the condition of the soil, where a soil with a 'high' sodicity restricts the water entry and reduces the ability of the soil to conduct water and is evaluated by the sodium absorption ratio (SAR) which is the ratio of sodium ions compared calcium and magnesium ions.

$$SAR = \frac{\left[Na^{+}\right]}{\sqrt{\dfrac{\left[Ca^{2+}\right]+\left[Mg^{2+}\right]}{2}}}$$

It is typically recommended that irrigation water have an SAR less than 5 (ANZECC 2000). The salinity describes the total salt content of the water, which when high can have a detrimental effect on crops by lowering the nutrient uptake, reducing crop yields and accumulating within the soil and is typically described by the electrical conductivity (EC).

It is important to note that whilst high level of both SAR and salinity are detrimental to soil and crop wellbeing waters may have a low SAR but high salinity and still be suitable for irrigation use, however the same is not applicable for waters that have a high SAR and low salinity (ANZECC 2000).

The current research project proposes to use a UF-NF-RO system (Figure 1) to create reclaimed water that is both high in nutrients and low in monovalent salts. The primary pre-treatment of the feed water is by the UF, which removes any, remain suspended solids and some of the large molecular weight (MW) organic matter. The NF unit has been used to recover the multi-valent ions and mush of the remaining organic material whilst allowing most of the monovalent salts to pass through the membrane. The RO unit will remove the remaining salts and organics. The reclaimed water will be a blend of the retentate from the NF and the RO permeate.

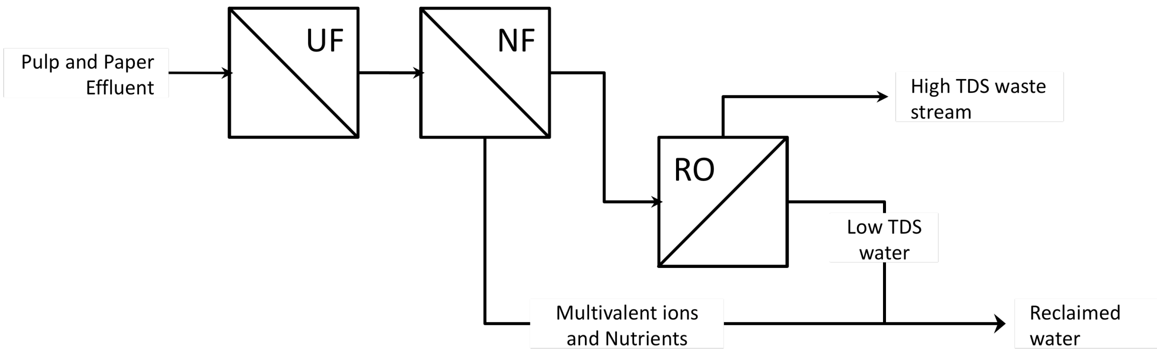

Figure 1: UF-NF-RO process

The benefit of using both NF and RO compared to an RO only system is the ability to operate the RO unit at higher recoveries as the ions removed in the NF stage reduce the propensity for fouling or scale on the RO membrane.

The focus of this paper has been limited to the selection of the NF membrane for this hybrid system. The selection criteria is based on the ability of the NF membrane to produce a retentate stream high in multivalent ions and an overall SAR reduction across the entire process. The work includes an initial assessment of three wastewater samples from a thermo-mechanical pulp and paper mill, from which synthetic wastewater samples were created in the lab to test the selectivity of a range of NF membranes. This was followed by validation of these results with real wastewater from the mill.

METHODS & MATERIALS

Nanofiltration membranes

This study has evaluated six commercial membranes sourced with the NF-270 and NF-90 sourced from DOW Filmtec, ESNA1-LF2 and NTR-740 obtained from Hydranautics and the HPA-150 and HPA-250 obtained from Permionics, India.

Experimental Operation & Analysis

Nanofiltration experiments with synthetic and actual wastewater was conducted in a dead-end flow cell with a membrane area of $0.00126m^2$ and a batch volume of 300mL. All the experiments were conducted at a constant pressure of 600kPa, and a stirring rate of 600rpm, up to a recovery of 75%. Pre-compaction of the membranes was conducted with milli-Q water under the same experimental conditions.

The concentrations for Calcium, Sodium and Magnesium in the permeate were analysed with ion specific electrode and confirmed by ICP-AES. DOC analysis for the fouling test were carried out with a Shimadzu TOC-VCSH TOC analyser and colour measurements were conducted using a standard colorimetric method (Clesceri et al. 1998).

RESULTS AND DISCUSSION

Wastewater Characteristics

The initial phase of this work involved the characterisation of a variety of waste streams within the pulp and paper mill in order to determine which would be the most suitable for reclamation. The three streams sampled were from the outlet of the secondary clarifier from the mills wastewater treatment facility (WWT), the outlet from the paper machine (PM) and finally the waste stream from the recycled fibre facility (RCF). General characteristics of the waters have been provided in Table 1 and are typical of those reported in literature for other thermo-mechanical mills (Pokhrel and Viraraghavan 2004; Manttari and Nystrom 2007)

Further characterisation of the organic matter was completed by high-performance size exclusion chromatography (HPSEC). The MW distribution of the organic for the WWT, PM and RCF are given in Figure 2. The MW distribution for the PM and RCF sample are quite similar and show a significant portion of organic matter with a MW less than 200. These low molecular weight constituents represent organic acids, which are readily broken down in the biological treatment processes, and this explains their absence in the WWT water sample. This is also a justification for the significantly lower TOC for the WWT sample compared to the PM and RCF waters and it would be expected to result in lower membrane fouling for the WWT water.

Initial screening of the NF membrane was conducted using synthetic wastewater replicating the ionic balance of the waste waters supplied by the paper mill. It was found that the rejection of monovalent ions (Na^+) varied widely for both membrane and water type. For water type the rejection for WWT (46% rejection average across all membrane) and RCF (49%) wastewaters were approximately equal whereas the rejection for PM waste was substantially higher at 62%. For each of the membrane types the average rejection for the three waters was 19%, 39%, 43%, 67%, 73%, 73% respectively for NTR-7450, NF-270, ESNA1-LF2, HPA-250, HPA-150 and NF-90.

Table 1: Physico-Chemical Properties of Feed Waters

Property	Units	WWT	PM	RCF
Physical Parameters				
pH		7.75	6.89	7.69
Colour	PCU	400	120	100
TDS		1630	1640	2120
Alkalinity	mg/L	620	153	322
Conductivity	µS/cm	2420	1940	2580
Turbidity	NTU	6.1	44.9	38.3
Dissolved Organic Carbon	mg/L	79	531	461
Nutrients				
Total Nitrogen	mg/L			
Ammonia	mg/L	0.369	0.018	0.488
Total Phosphorus	mg/L	0.12	0.44	0.78
Chemical Oxygen Demand	mg/L	218	2130	2300
Ionic Balance				
Calcium	mg/L	81	59	39
Magnesium	mg/L	15	7	5
Potassium	mg/L	52	36	44
Chloride	mg/L	50	55	53
Sulphate	mg/L	464	55	53
Sodium	mg/L	383	289	412
Silica	mg/L	100	584	556
Manganese	mg/L	0.39	0.79	0.83
Iron	mg/L	0.29	0.07	0.10

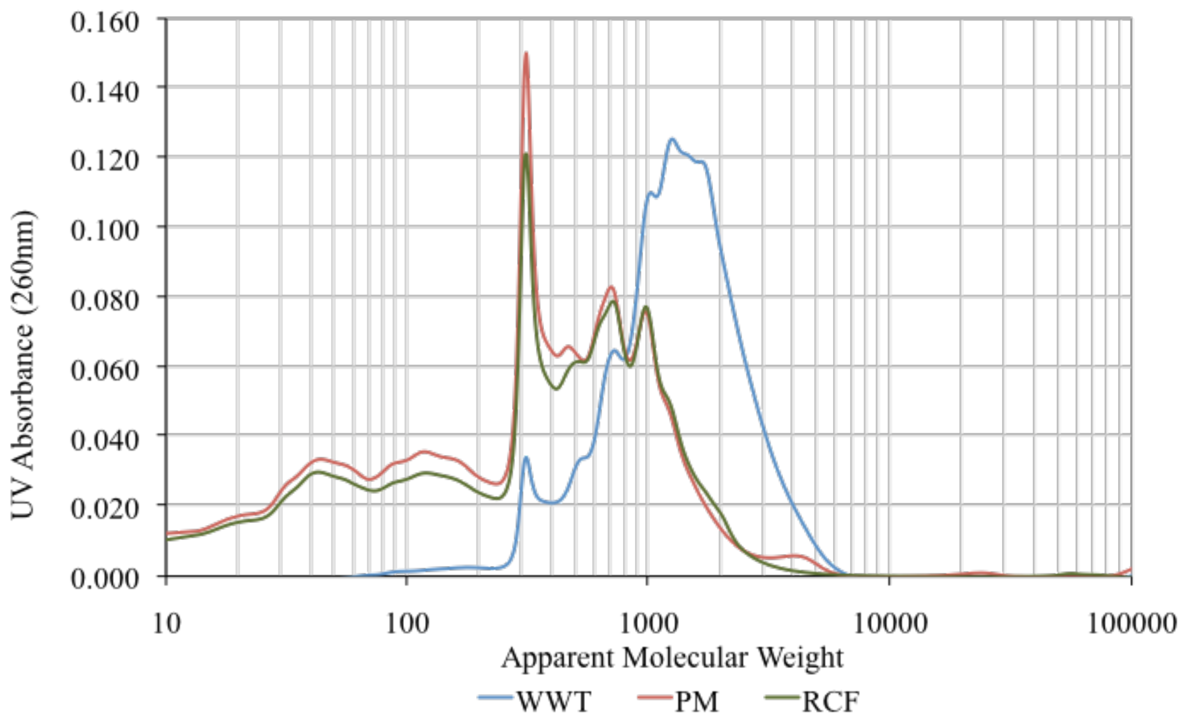

Figure 2: HPSEC of wastewater samples

Membrane Rejection and Selectivity

The objective of the proposed hybrid UF-NF-RO process is to produce a retentate stream that is proportionally higher in multi-valent ions concentration compared to monovalent ion, The selectivity between monovalent (Na^+) and divalent salts (Ca^+, Mg^+) has been reported in Figure 3 where that the selectivity has been given by the equation

$$\text{selectivity} = \frac{R_{Na^+}}{R_{Ca^{2+}+Mg^{2+}}}$$

For these applications, a low selectivity is desirable, which indicate a greater retention of divalent salts. It can be seen that for the six commercial membrane examined they can be broadly divided into two groups based on performance, with the NF-270, NTR-7450 and ESNA1-LF2 have a substantially lower selectivity's than the other membranes. This is consistent with the Na^+ rejection where those membranes that have a sodium rejection less than 50%, also have low selectivity in the range 0.4-0.6.

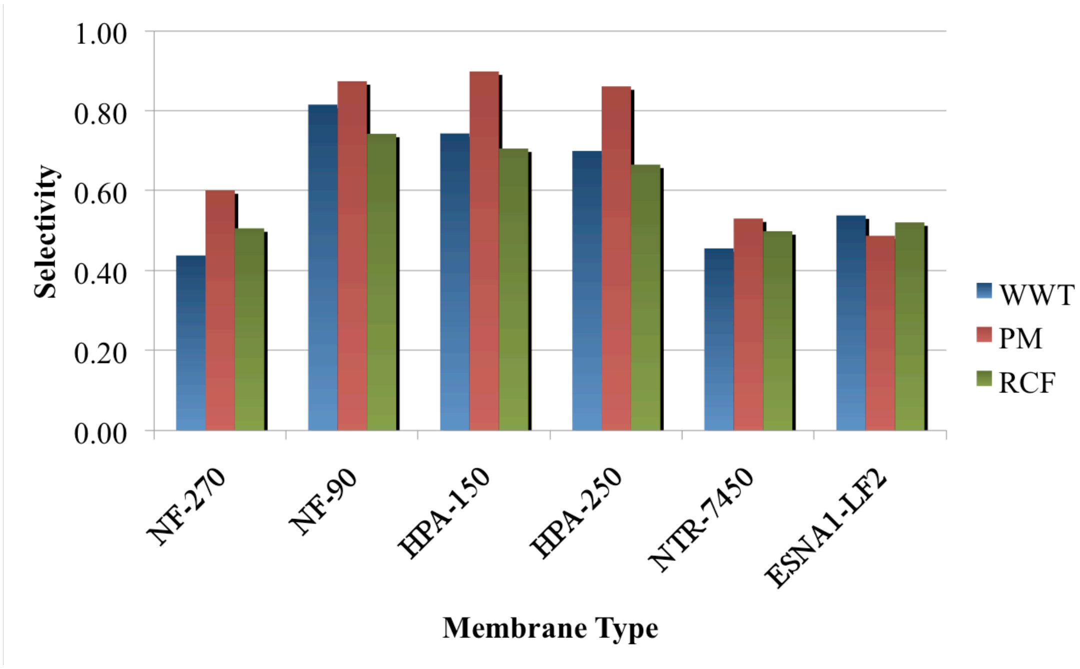

Figure 3: Monovalent rejection selectivity

Evaluation of the SAR reduction.

For the hybrid MF-NF-RO system the final reclaimed water for irrigation uses is a blend of the permeate from the RO unit and the retentate from the NF unit. In order to assess the overall reduction in SAR the system has been modelled assuming recovery values of 80% for the NF unit and 75% for the RO unit. The rejection for the NF unit is based on the above selectivity's whilst the RO unit was assumed to have a uniform rejection of 97% for all ions.

Figure 4 shows the product SAR values for the three synthetic wastewaters. For the WWT sample the SAR was reduced from an initial value of 7.35 to between 4.0 and 6.5. Comparatively rhe PM and RCF waters were altered from initial values of 9.30 and 20.35 to 5.4 – 9.5 and 12.0 – 18.0 respectively. In each of these cases the NTR-7450 membrane demonstrated the greatest ability to reduce the SAR. The NF-270 and ESNA1-LF2 membranes also performed well.

Therefore it may be expected that by using an NF-RO system with the assumed recoveries used specifically for lowering the SAR such that the reclaimed water can be used for irrigation purposes reductions between 30-60%. Hence to achieve an SAR of less than 5 the maximum SAR for the NF feedwater would be between 7.15 and 12.50. On this basis, the WWT wastewater stream was considered as the only water applicable for treatment under this process, further work was not conducted with the other two wastewater streams.

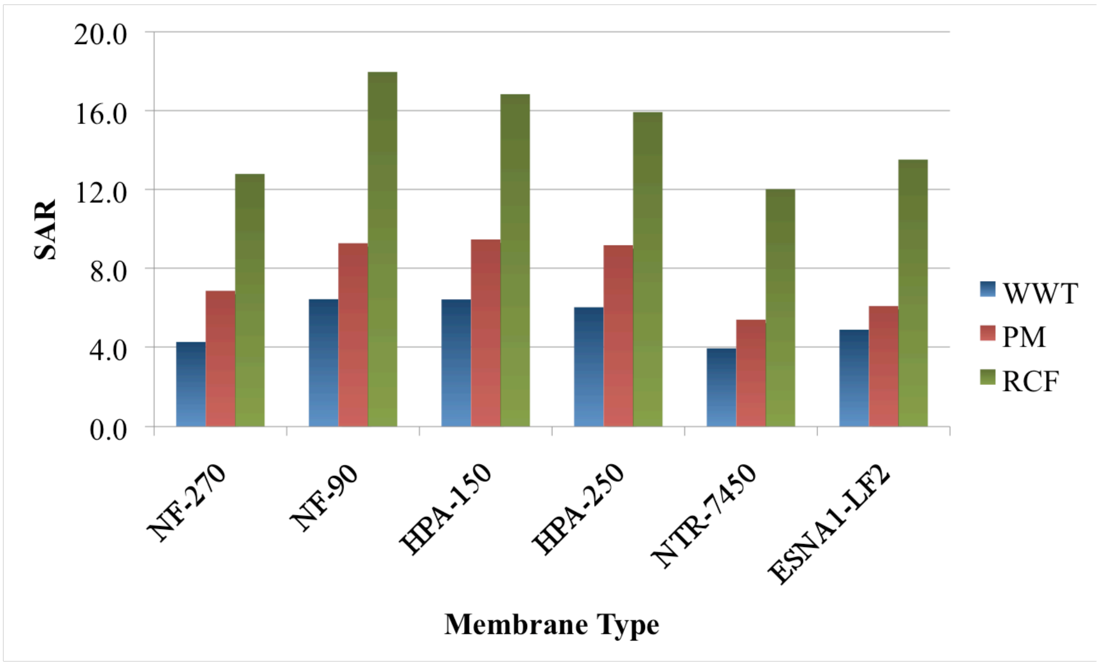

Figure 4: SAR reduction in hybrid process

The results in Figure 4 report the product SAR for recoveries of 80% and 75% for the NF and RO respectively. However, for the RO, at least, it may be expected that recoveries greater than this may be achieved due to reductions in the scale propensity as a result of calcium removal in the NF stage. Figure 5 illustrates the effect of altering the recovery rate for both the NF and RO units for the NTR-7450 membrane on the WWT synthetic wastewater. This figure demonstrates the greater dependence on the NF recovery for lowering the SAR compared to thee RO recovery. Therefore whilst the ability to operate at higher RO recoveries will improve the quantity of reclaimed water it does not appreciably improve its quality.

Comparing Synthetic with Real Water

In order to provide validation of the results observed with synthetic wastewater a comparison has been made with real WWT water. The experiments were conducted in exactly the same manner as for the previous experiment, however, DOC removal and colour reduction (Table 2) were also measured. Additionally, fouling in the dead-end cell for each of the three most promising membrane products is reported in Figure 6.

The selectivity for the real wastewater is significantly better than for the synthetic water, in particular for NTR-7450, which is effectively zero, indicate almost no rejection of Na^+ ions. This results in higher reduction in the SAR ratio, however still only up to a reduction of approximately 60%. In terms of the SAR reduction the NTR-7450 as before preformed best with the NF-270 membrane also performing well. However, for the DOC and Colour removal the NTR-7450 membrane only removes 53% and 42% respectively, compared to the ESNA1-LF2 and NF-270 which remove 95% and 80% of the DOC and 80% and 54% of the colour respectively. The removal rate are indicative of the fouling performance of each of the membranes as the fouling resistance for the ESNA1-LF2 membrane is substantially higher than that for the NF-270 membrane and the NTR-7450 which appears to foul very little up to a recovery of 80%.

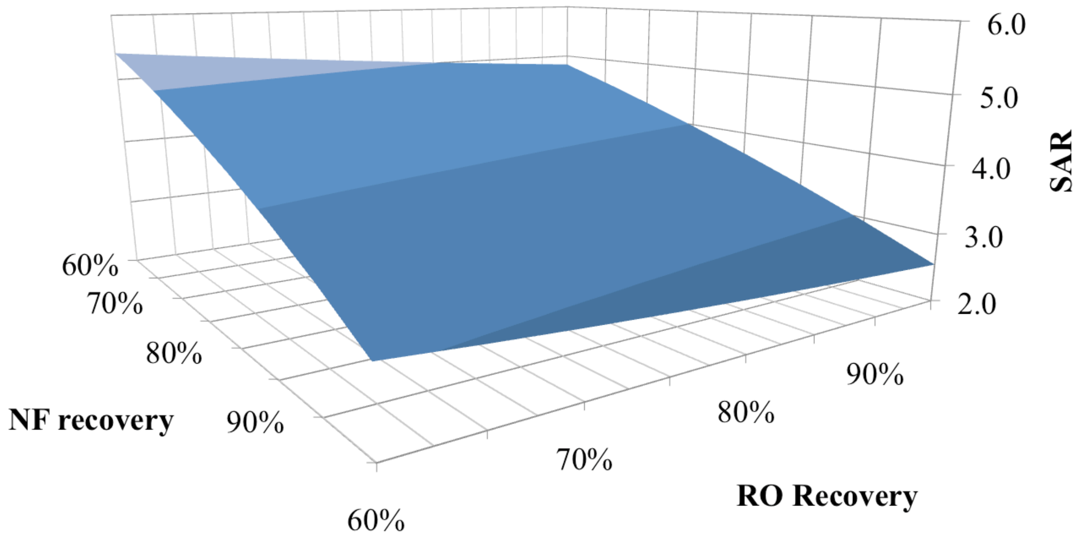

Figure 5: SAR dependency on NF and RO recovery

Table 2: Membrane performance with real wastewater

Membrane Type	Selectivity	SAR reduction (%)	DOC removal (%)	Colour Reduction (%)
NF-270	0.26	54	80	58
NF-90	0.68	17	94	84
HPA-150	0.49	35	91	74
HPA-250	0.44	39	90	67
NTR-7450	-0.01	62	53	42
ESNA1-LF2	0.44	39	95	80

CONCLUSIONS

For the current UF-NF-RO system and based on this experimental work with synthetic and real PPE, it is apparent that the performance of the NF unit is critical in producing reclaimed water that is adequate for irrigation use. It has been shown that SAR reduction between 30 and 60% are achievable in such a system and therefore only adequate for waste streams that have an SAR lower than 12.5. Of the size commercial membranes investigated in this research the NTR-7450 has shown most promise in terms of it multivalent selectivity and therefore ability to reduce the SAR.

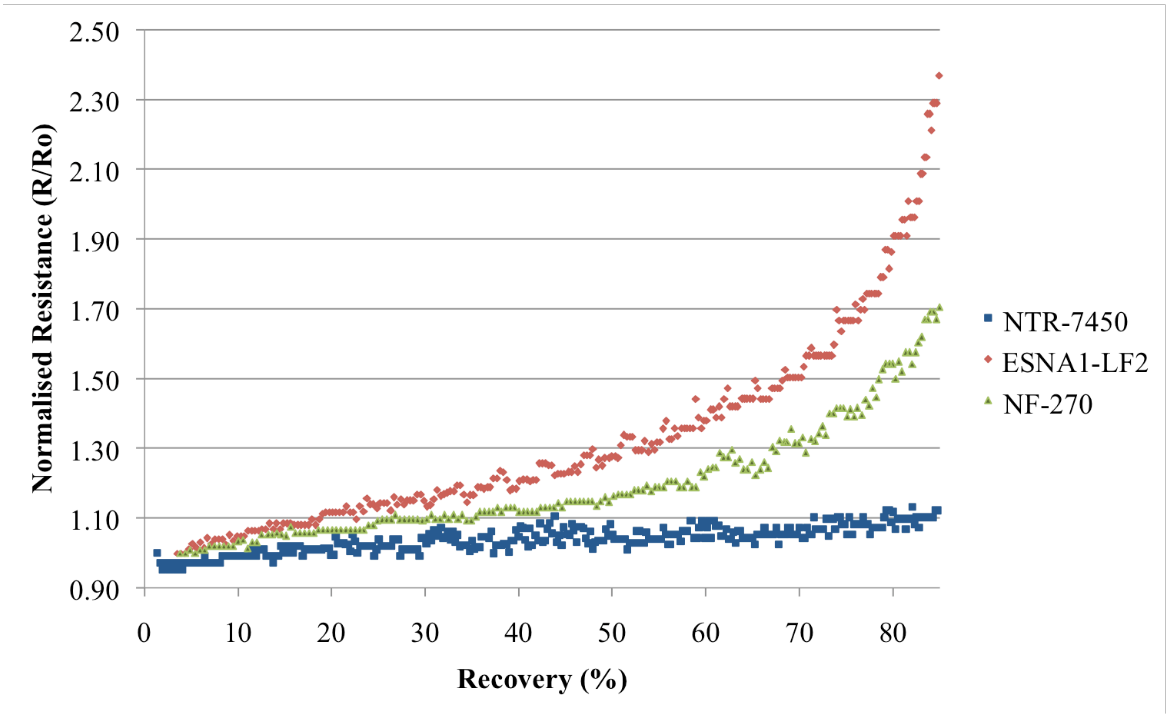

Figure 6: Dead-end cell fouling profiles

However, this membrane has low removal rates of DOC and colour compared to the NF-270 which also had good selectivity. This may pose fouling problems in the RO unit and further work is required to look at the overall performance of UF-NF-RO system for both of these membranes.

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