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Treatment of High TDS Liquid Waste: Is Zero Liquid Discharge Feasible?

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ABSTRACT

A zero liquid discharge treatment system for the disposal of saline industrial liquid waste was proposed and evaluated in this study. Microfiltration was selected as a pretreatment process after a qualitative assessment against 'conventional' options. Two reverse osmosis (RO) membranes were examined for the pre-concentration of liquid waste using a laboratory scale membrane rig. The results were used to validate the use of the ROSA simulation package. ROSA simulation was conducted with liquid waste having a range of salinity of up to 100,000 ppm of total dissolved solid (TDS). Results reported here indicated that RO membranes were highly suitable for liquid waste of up to 25,000 ppm of TDS. Several techniques suitable for the treatment of RO concentrate were also identified and evaluated. These include spray dryers, scraped surface evaporators and forced circulation crystallisers/evaporators. Overall, the treatment train was deemed to be preliminarily feasible based on the robust and modular nature of the design, the theoretical ability to achieve the desired output, and the relatively economical use of the integrated membrane system for pre-concentration, reducing dryer/evaporator capital and operational expenditure.

Keywords: liquid waste; zero liquid discharge (ZLD); membrane filtration, reverse osmosis (RO)

1. INTRODUCTION

The treatment and disposal of saline industrial liquid waste are notoriously difficult and challenging. Environmental regulations in Australia prohibit the landfilling of liquid waste. Disposal of industrial liquid waste to the marine environment is also strictly prohibited in Australia. Sewer disposal is only possible after treatment for the removal of total dissolved solid (TDS) and other toxic constituents. While usually small in volume, the treatment and subsequent disposal of industrial waste can be particularly expensive. In this study, a zero liquid discharge treatment train is proposed and evaluated for the disposal of saline liquid waste from a liquid waste plant near Wollongong, Australia. The plant currently has a discharge licence to the sewer for liquid waste of less than 10,000 ppm in TDS. Most saline liquid waste must be diluted or trucked to another treatment facility over a long distance. Zero liquid discharge (ZLD) provides a landfill based disposal technique for the liquid waste if economically practical.

Zero liquid discharge separates waste from wastewater, resulting in a solid (or near solid) waste stream and a product water stream capable of being used for further application (Dalan, 2000; Dixon, 2004). ZLD has typically been applied using several stages of thermal concentrating process to reduce in volume industrial wastewaters. With the in-

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creasing use and develop of membrane filtration techniques, volume reduction by reverse osmosis has become generally more economically practical than thermal techniques (Heijman *et al.*, 2009; Mickley, 2001). Pre-concentration by RO reduces the volume of wastewater to be treated by energy intensive super concentrators (Dalan, 2000; Dixon, 2004; Heijman et al., 2009; Wilf, 2007). Super concentrators such as spray dryers, crystallises and evaporators then volume reduce the waste liquid by removing the remaining water resulting in a product suitable for disposal by landfill (Dalan, 2000; Dixon, 2004; Wilf, 2007). Industrial applications of ZLD include disposal of high TDS textiles wastewater (Vishnu *et al.*, 2008), treatment and disposal of power generation cooling water using integrated membrane process (Seigworth *et al.*, 1995), and disposal of desalination concentrate from membrane filtered recycled and groundwaters (Erdal *et al.*, 2008). However, ZLD treatment of saline industrial liquid waste has rarely been reported in the literature. Because of the high disposal fee of up to \$300/m^3 and the strict regulation regarding the treatment and disposal of liquid industrial waste, ZLD treatment is not only sustainable approach but also economically attractive.

2. METHODS AND MATERIALS

The proposed treatment train consists of microfiltration (MF) for pre-treatment, reverse osmosis (RO) for pre-concentration of waste solutions prior to the application of a super-concentrating evaporator with the objective of producing a solid product for land based disposal and a relatively clean permeate stream for blending with high TDS streams to facilitate sewer discharge (Figure 1).

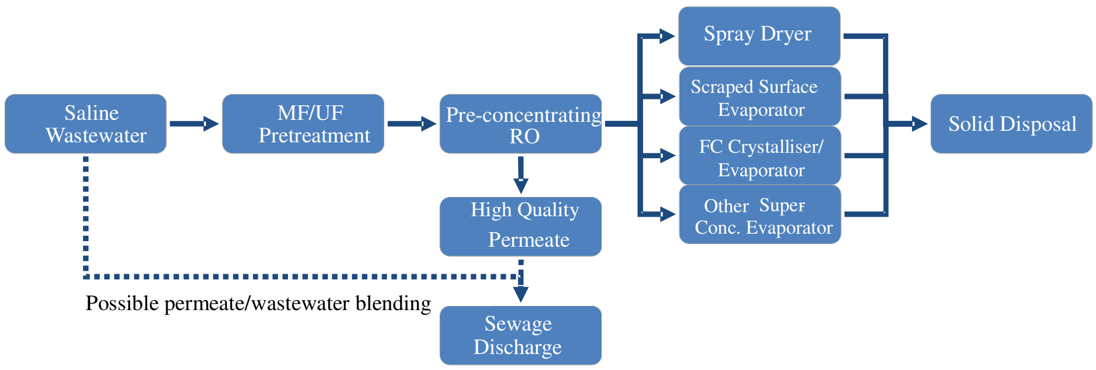


Figure 1 Proposed treatment train for disposal of highly saline liquid waste (note: only one of the concentrate handling techniques would be used)

Pre-concentration design and assessment were conducted by computer simulation, yielding required assets, energy consumption and output quantities and qualities. Prior to simulation, laboratory scale experiments were conducted using a low TDS liquid waste. The experimental results were used to validate the computer simulation output. Following the validation of the simulation program, membrane systems were designed to achieve the design objectives for a range of TDS concentrations. Feasibility was assessed on the ability of the membrane system to achieve the design outcomes in an efficient and effective manner.

2.1 Saline Solution

Processed liquid waste of 18,000 ppm TDS was collected from a Liquid Treatment Plant near Wollongong. Detailed composition and characteristics of this liquid waste are presented in Table 1.

Table 1 Key liquid waste characteristics and key constituents of test sample

Characteristics	TDS, mg/L	Conductivity, µS.cm^{-1}	Turbidity, NTU	pH
	18,000	21,100	131	12.0
Key Constituents	Ion	mg/L	Ion	mg/L
	Aluminium	2.5	Copper	0.28
	Ammonia	17	Iron	21
	Arsenic	0.14	Lead	0.27
	Barium	0.73	Manganese	0.08
	Boron	0.10	Nickel	0.20
	Chromium	0.11	Tin	0.59
	Cobalt	0.24	Zinc	7.2

2.2 Pretreatment

A stainless dead end stirred cell MF set-up was used for the pretreatment of the liquid waste. Detailed description of this MF set-up is available elsewhere (Mariam & Nghiem, 2010). Unadjusted pH liquid waste and liquid waste with pH adjusted to 7 were tested against two Millipore polypropylene microfiltration membranes (nominal pore size of 0.45 and 0.22 µm).

2.3 NF/RO Filtration Protocol

Experiments were conducted using a laboratory scale crossflow membrane filtration rig. Detailed description of this experimental rig is available elsewhere (Nghiem & Hawkes, 2007). Two commercially available RO membranes – namely BW30 and SW30 – were selected for investigation. These membranes were kindly donated by Dow Chemical.

The effects of operational variables (temperature, pH and pressure) on membrane performance were investigated for all membranes using a consistent liquid waste sample. Membrane performance was assessed using the two primary performance indicators of TDS (measured by conductivity) rejection and permeate flux. Permeate sample were collected for metal analysis to observe component by component rejections.

The following experimental protocol was used for the experimental series:

1. Membrane compaction for 1 hr using MilliQ water at 20 bar pressure, 25 °C, 30.4 cm/s crossflow
2. Empty the feed reservoir then introduce 7 L of test solution to the reservoir
3. Run the system at a specified condition (pH, pressure, temperature) for at least 1 hour
4. Sample collection for conductivity and metal analysis by an inductive coupled plasmas atomic emission spectrometer (ICP-AES).

2.4 ROSA Simulation

Computer simulation of the RO process was conducted using ROSA 6.1 by Dow; the package is for the design of systems using the Filmtec™ range of membranes by Dow. Initially the program was used to replicate the conducted experiments, providing comparative data for the validation process. Analysis of the membrane pre-concentration process using the simulation package was conducted for three TDS concentrations: 24,400; 48,500 and 75,500 ppm and for a system capacity of 100 m^3/day. These concentrations were chosen in order to establish system requirements (i.e. number of membrane stages and passes), achievable system recoveries and permeate qualities, based on the analytical breakdown of liquid waste streams.

2.5 Disposal of Concentrated Brine

The disposal goal for the volume reduced liquid waste was the land base disposal of a solid output; zero liquid discharge. Technique selection was determined through qualitative assessment based on literary research comprised particularly of ZLD case studies and manufacturers information. The recommended options were based on the ability of the technique to achieve solid/near solid output and be of robust design.

3. RESULTS AND DISCUSSION

Assessment was based on practical results, computer simulation, literature, and manufacturers information. Key information and results used to determine the feasibility of the proposed treatment train are as follows.

3.1 Pretreatment

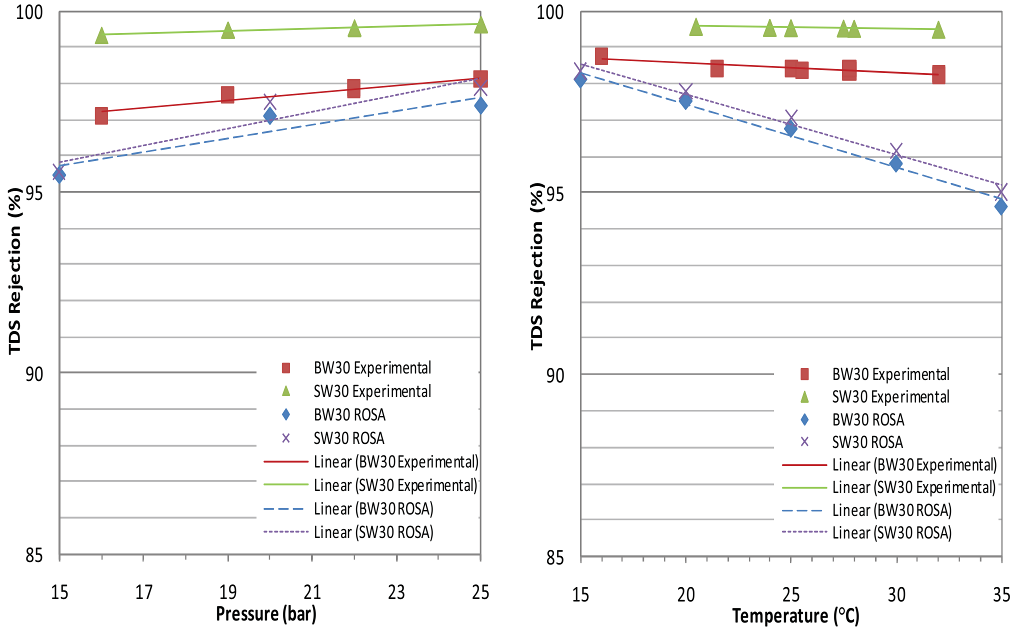
RO membranes are highly sensitive to fouling due to colloids, inorganic scale and biofilm formation (Bonnelye *et al.*, 2008; Durham, 2002; Durham & Walton, 1999; Wilf, 2007). The key requirement of the pretreatment stage is to provide a consistent feed of a quality suitable for long term reverse osmosis membrane operations. Membrane pretreatment of liquid waste prior to RO pre-concentration was found to be qualitatively more efficient and effective due to:

- Higher and more consistent rates of foulant removal: microfiltration and ultrafiltration have pore size of 0.01 to 0.1 μm compared to 5 to 10 μm for media filters (Durham & Walton, 1999).
- Membrane pretreatment removal mechanisms minimally affected by overloading and variations in feedwater quality (Durham & Walton, 1999; Wilf, 2007).
- Membrane pretreatment processes are generally compact: in general, MF/UF provides a saving of 33% in plant area compared to conventional techniques such as chemical coagulation and sand filtration.

Further comparison between and the benefits of membrane pretreatment over conventional pretreatment are presented in a study by Vedavyasan (2007). Experimental results obtained from various pretreatment conditions indicated that with the same applied pressure of 1 bar the 0.45 μm MF membrane could deliver a larger permeate volume than the 0.22 μm MF membrane before backwashing was required while there was no discernible difference in the permeate quality (measured by turbidity). In addition, severe membrane clogging was observed when the liquid waste pH was adjusted to 7. In contrast, satisfactory pretreatment was obtained at pH 12 (unadjusted). This can be attributed to the high solubility of organic matter in the liquid waste at high pH. As a result, the 0.45 μm MF membrane was selected for the pretreatment step and pH of the liquid waste was not adjusted.

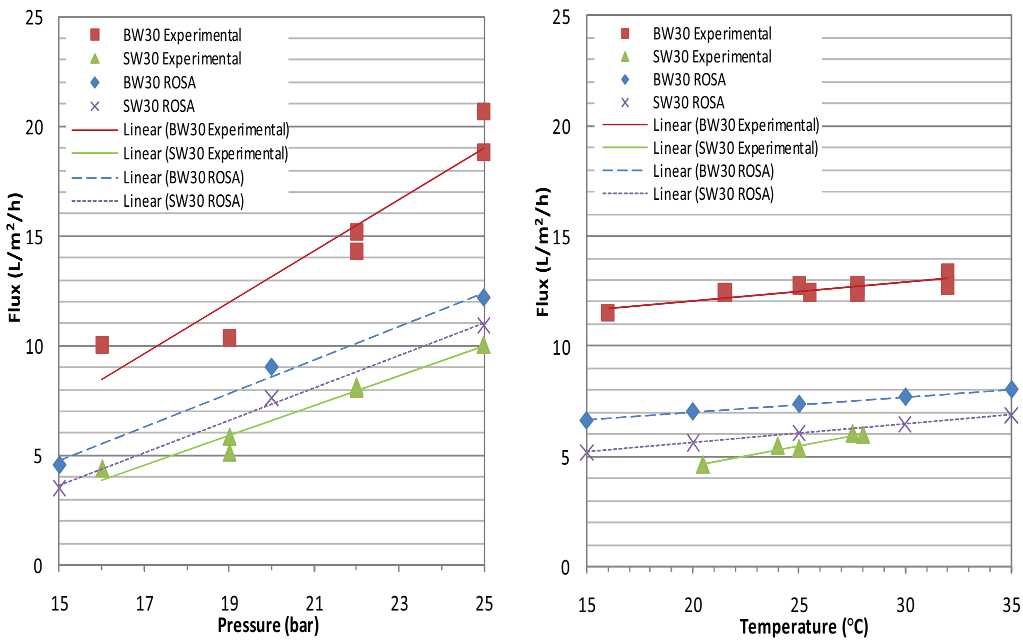
3.2 Experimental Validation of Simulation

The resulting experimental and simulation trends for the effect of the three main variables tested on the key performance indicators of TDS rejection and flux were compared for the two Dow membranes. On a qualitative basis the overlaying trends in the experimental performance indicators were equivalent to those of in simulation data. The experimental and simulation data trends are evident in Figures 2 – 3.



(a) (b)

Figure 2 (a) Experimental and simulated TDS rejection as a function of pressure (T=25 °C, pH=7 and TDS feed=18,000ppm); (b) Experimental and simulated TDS rejection as a function of temperature (P=18 bar, pH=7 and TDS feed=18,000ppm)



(a) (b)

Figure 3 (a) Experimental and simulated membrane flux as a function of pressure (T=25 °C, pH=7 and TDS feed=18,000ppm); (b) Experimental and membrane flux as a function of temperature (P=18 bar, pH=7 and TDS feed=18,000ppm)

Samples were collected for analysis by an inductive coupled plasmas atomic emission spectrometer (ICP-AES) for the purpose of ensuring sufficient removal of individual components. ICP-AES analysis revealed that heavy metals in the permeate were either completely removed or only existed at trace level concentrations that are below environmental concerns. Summary of the ICP-AES analysis data for the operational effect of temperature and pressure, presented in the Table 2, clearly shows the high mean removal of key constituents by the two membranes.

Table 2 ICP-AES analysis results of average permeate concentrations and rejection rates of key constituents by experimental testing of BW30 and SW30 membranes for effect of temperature and pressure.

Constituent	**C_{Feed} (μg/L)**	**BW30 $C_{P.Ave}$ (μg/L)**	**BW30 R_{Ave} (%)**	**SW30 $C_{P.Ave}$ (μg/L)**	**SW30 R_{Ave} (%)**
Aluminium	2500	201	92.0	62	97.5
Arsenic	140	3	100.0	3	100.0
Barium	730	0	100.0	0	100.0
Boron	100	0	100.0	0	100.0
Chromium	110	0	100.0	0	100.0
Cobalt	240	10	91.1	2	98.4
Copper	280	75	73.3	40	85.7
Iron	21000	0	100.0	0	100.0
Lead	270	14	93.1	0	100.0
Manganese	80	0	100.0	0	100.0
Nickel	200	0	100.0	0	100.0
Tin	590	160	73.0	62	89.6
Zinc	7200	0	100.0	0	100.0

C_{Feed}: feed concentration of constituent; $C_{P.Ave}$: average concentration of constituent in permeate; R_{Ave}: average rejection rate of constituent by membrane. Note: values of zero given when constituent is below detection limit (1 μg/L) and a rejection rate of 100% assumed.

In the pH varied experiments ICP-AES analysis showed general adherence to the common trends but significant variations in the rejection of several ions; notably the metals arsenic, barium, cadmium, chromium, iron, manganese, nickel, lead and zinc, and also the metalloid boron. Variation in pH causes speciation of certain molecules; this is known as pH dependent speciation. pH dependent speciation of constituents has been shown to affect the retention of constituents by reverse osmosis membranes (Richards *et al.*, 2009). For example magnesium transitions from a primarily species of $MgSO_4$ to $MgCO_3$ between pH 9-10; the $MgCO_3$ may then precipitate on the membrane face given sufficient concentrations at the boundary layer (Richards *et al.*, 2009). Overall the use of the ROSA software package for preliminary analysis and initial system design was deemed reasonable for the liquid waste in question.

3.3 Membrane Simulation Results and Application Assessment

Preliminary system design was conducted with ROSA 6.1 simulation by Dow. Designs based on the standard 4 inch membrane modules from the DOW Chemical (i.e. SW30-4040 and BW30-4040) yielded reasonable results, especially for the lower TDS concentrations. The system was designed on an influent flow of 100 m^3/d and RO concentrate of greater than 100,000 ppm in TDS. It is obvious on inspection of the following table (Table 3) that as the feed TDS concentration of the stream increases:

- Required membrane area increases: i.e. more pressure vessels, stages required
- Permeate quality decreases: requires a second pass to achieve low TDS permeate concentrations
- Energy consumption increases: greater pressure over a greater membrane area is needed to overcome higher osmotic pressures
- Recovery rates decrease: less permeate is able to be practically recovered

Comparison between system recoveries and energy demands for the low and high TDS streams clearly demonstrate there is a practical limit to the feed concentration of TDS that should be pre-concentrated using the RO technique.

A secondary benefit to RO pre concentration is the use of the permeate to dilute TDS containing streams. This allows discharge limits with respect to TDS concentration to be met while minimising the system size. The following mass balance simulations are based on the simulated system details as seen in Table 3 and are used to demonstrate the possible application of such a method.

The low TDS bypass/permeate blending scheme in Figure 4 shows to the ability of the system to allow for bypass of the brine concentrating process. At this concentration, approximately a third of the stream does not require treatment and can be blended with the relatively clean permeate to meet the TDS discharge limit of 10,000ppm. Figure 5 demonstrates the use of permeate from the more efficiently treated lower range TDS streams to dilute very high TDS streams. The relatively high volume, low TDS permeate from the 24,400 ppm stream is combined with a very high TDS (75,000 ppm) stream. The low TDS permeate provides a means for the dilution of high range TDS streams (i.e. 50,000-75,000 ppm) which is impractical for the application of RO pre-concentration.

The mass balance simulations simple present a possible application of the relatively clean permeate to further facilitate the disposal of TDS containing liquid waste. The arrangement and system design would be dependent on operational requirements and the stock and range of TDS containing waste liquids to be disposed.

3.4 Disposal of Concentrated Brine

The objective of the concentrate handling phase is to produce a solid discharge from a high concentration (>100,000 ppm TDS) lower volume feed. As such it was determined that the evaporative system should:

- have a high concentrating factor (semi-solid or solid)
- be immune to, or able to mitigate fouling/scaling
- be economical for small system operation

A range of evaporative techniques for the super-concentrating/drying of RO concentrated streams were identified and investigated. It was determined that a super-concentrating technique would be required to produce a solid or near solid product. Mechanical systems are minimally influenced by environmental variables (i.e. temperature, humidity) (Mickley, 2001; Pankratz, 1994), providing more reliable performance. Assuming relatively small volumes were to be treated (i.e. < 50 m^3/d), high energy consuming techniques become economically practical as high operating costs are surpassed by the high capital costs of more energy efficient techniques (Mickley, 2001). The following evaporating techniques were deemed potentially feasible for application:

- Spray dryer: produces dry powder product, high energy consumption but economically competitive for feeds of less than 50 m^3/d (Mickley, 2001)
- Scraped surface evaporator: high energy consumption, scraped surface reduces fouling and promotes heat distribution, produces solid of semi-solid product (LED Italia for Veolia Water)
- Forced circulation crystalliser/evaporator: can be seeded to promote solid formation, reduced fouling formation in fluidised bed design, may have limited concentrating effect (may not produce required objective)

A major design constraint in the consideration of the evaporation technique is the potential for fouling and scaling. The liquid waste stream being studied has a very high fouling potential, as such evaporators for consideration should be able to handle high fouling potential liquids; systems that cannot will require very high maintenance and suffer from reduced performance and potentially system damage.

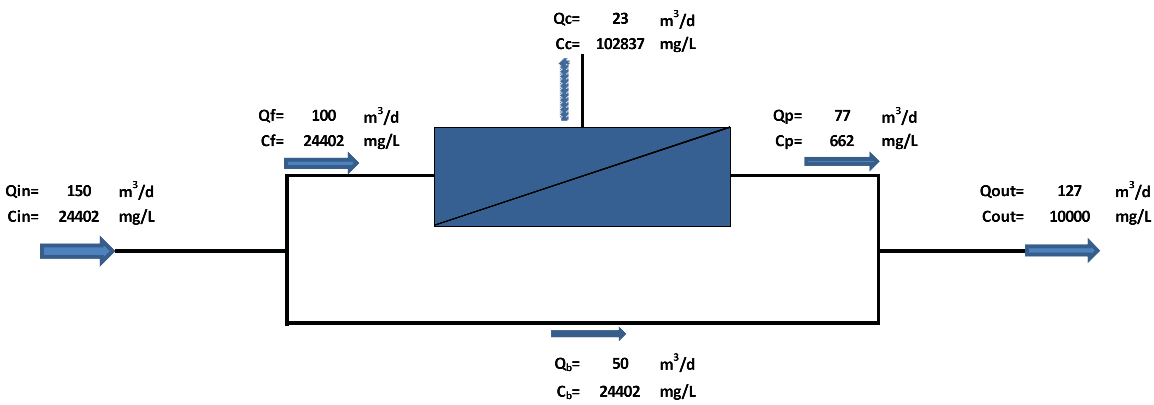


Figure 4 Mass balanced low TDS RO system with bypass/permeate blending

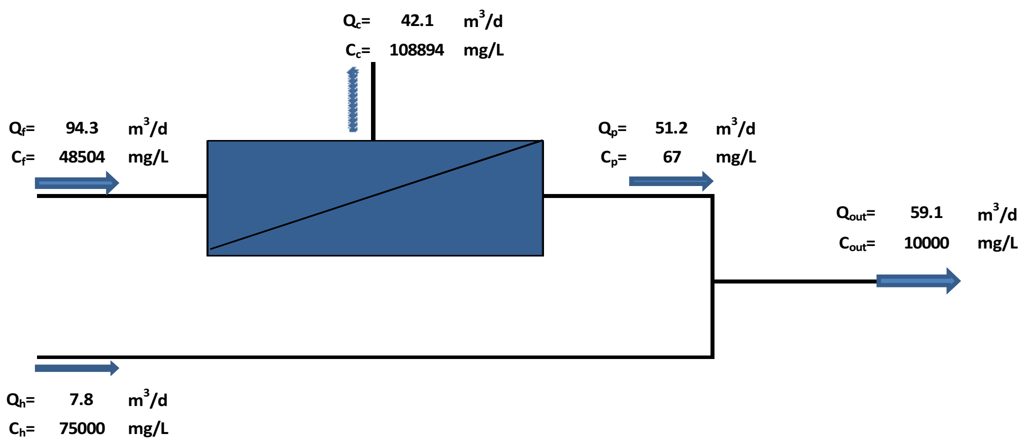
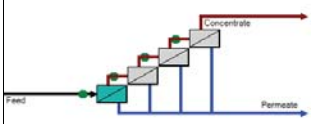
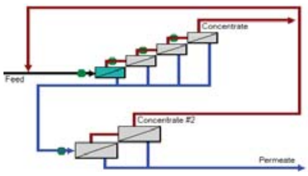
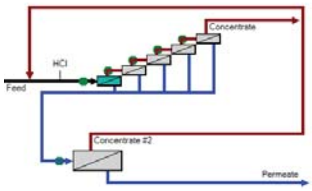


Figure 5 Mass balanced high TDS stream diluted to discharge requirements with permeate from low TDS stream brine concentrating process

Table 3 Summary of simulated brine concentrating reverse osmosis system

TDS (mg/L)	**24400**			**48500**			**75000**		
System Design	Pass 1	SW30	2 PV[1], 6 elem./PV	Pass 1	SW30	3 PV, 6 elem./PV	Pass 1	SW30	3 PV, 6 elem./PV
		SW30	1 PV, 6 elem./PV		SW30	2 PV, 6 elem./PV		SW30	3 PV, 6 elem./PV
		SW30	1 PV, 6 elem./PV		SW30	2 PV, 6 elem./PV		SW30	3 PV, 6 elem./PV
		SW30	1 PV, 6 elem./PV		SW30	2 PV, 6 elem./PV		SW30	3 PV, 6 elem./PV
		-	-		-	-		SW30	3 PV, 6 elem./PV
	Pass 2	-	-	Pass 2	SW30	1 PV, 6 elem./PV	Pass 2	BW30	1 PV, 6 elem./PV
		-	-		SW30	1 PV, 6 elem./PV		-	-
System Layout									
System Flows		Flow, m^3/d	TDS, mg/L		Flow, m^3/d	TDS, mg/L		Flow, m^3/d	TDS, mg/L
	System Feed	100.0	24400	System Feed	94.3[2]	48500	System Feed	90.2	75500
	Feed 1	100.0	24400	Feed 1	100.0	47070	Feed 1	100.6	70110
	Permeate 1	76.8	660	Permeate 1	57.9	2120	Permeate 1	34.5	6710
	Conc. 1	23.2	102840	Conc. 1	42.1	108890	Conc. 1	66.2	103170
	Feed 2	-	-	Feed 2	57.9	2120	Feed 2	34.5	6710
	Permeate 2	-	-	Permeate 2	51.2	70	Permeate 2	23.9	170
	Conc. 2	-	-	Conc. 2	6.7[3]	17780	Conc. 2	10.6[4]	21460
	System Permeate	76.8	660	System Permeate	57.9	70	System Permeate	23.9	170
	System Conc.	23.2	102840	System Conc.	42.8	107470	System Conc.	66.2	103170
System Recovery	76.8 %			54.4 %			26.5 %		
Energy Demand	2.4 kWh/m^3			4.6 kWh/m^3			8.2 kWh/m^3		

[1] PV: Pressure Vessel (elem./PV: number of membrane elements in each pressure vessel)
[2] System feed and second pass concentrate total 100 m^3/d
[3] 6.03 m^3/d returns to Pass 1 feed and 0.67 m^3/d to disposal
[4] 10.59 m^3/d returns to Pass 1 feed

CONCLUSIONS

It was ascertained from the experimentally verified computer simulated results that the RO process could achieve volume reduction of feed waters by recovering relatively high quality permeates from feed wastewaters. Although limited to the medium to low TDS concentrations (i.e. <50,000 ppm), RO pre-concentration is more efficient than thermal alternatives. The proposed treatment train would have a reasonably small footprint and a lower predicted energy consumption than a fully thermal evaporative system. Permeate and waste stream blending is also a viable option for further dilution and disposal of high TDS waste streams for sewer discharge; reducing the required ZLD system capacity.

In summary, the application of an integrated membrane system in combination with a small scale super-concentrator, to achieve ZLD for the liquid waste in question is preliminarily feasibly. Further assessment is required for the determination of system feasibility. This should be based on pilot studies, analysis of system designs from relevant technology manufacturers, economic assessment of proposed systems, and current operational costs; to compile a thorough cost-benefit analysis to compare options.

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REFERENCES

Bonnelye, V., Guey, L., & Del Castillo, J. (2008). UF/MF as RO pretreatment: the real benefit. *222*.

Dalan, J. A. (2000). 9 things to know about zero liquid discharge. *Chemical Engineering Progress, 96*(11), 71-76.

Dixon, G. N. (2004, January/February). Distillation Process Can Yield Zero Liquid Discharge System. *Industrial Water World.*

Durham, B. (2002). Membranes as pretreatment to desalination in wastewater reuse. *Membrane Technology, 143*, 8-12.

Durham, B., & Walton, A. (1999). Membrane pretreatment of reverse osmosis: long-term experience on difficult waters. *Desalination, 122*, 157-170.

Erdal, U. G., Lozier, J., Lynch, A., & Schindler, S. (2008). Evaluating Traditional and Innovative Concentrate Treatment and Disposal Methods for Water Recycling at Big Bear Valley, California *Membrane Technology, Proceeding of the Water Environment Federation*(21), 411-431.

Heijman, S. G. J., Guo, H., Li, S., van Dijk, J. C., & Wessels, L. P. (2009). Zero liquid discharge: Heading for 99% recovery in nanofiltration and reverse osmosis. *Desalination, 236*(1-3), 357-362.

LED Italia for Veolia Water. Evaled PC Heat Pump Technology (Publication. Retrieved January 2009, from LED Italia: www.veoliawaterst.com

Mariam, T., & Nghiem, L. D. (2010). Landfill leachate treatment using hybrid coagulation-nanofiltration processes. *Desalination, 250*(2), 677-681.

Mickley, M. C. (2001). Membrane Concentrate Disposal: Practices and Regulations (Publication. Retrieved January 2009: www.usbr.gov/pmts/water/publications/reportpdfs/report123.pdf

Nghiem, L. D., & Hawkes, S. (2007). Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size. *Separation and Purification Technology, 57*(1), 176-184.

Pankratz, T. M. (1994). Evaporation: A Wastewater Treatment Alternative. *Water Engineering & Management, 9*(141), 42-47.

Richards, L. A., Richards, B. S., Rossiter, H. M. A., & Schäfer, A. I. (2009). Impact of speciation on fluoride, arsenic and magnesium retention by nanofiltration/reverse osmosis in remote Australian communities. *Desalination, 248*(1-3), 177-183.

Seigworth, A., Ludlum, R., & Reahl, E. (1995). Case study: Integrating membrane processes with evaporation to achieve economical zero liquid discharge at the Doswell Combined Cycle Facility. *Desalination, 102*, 81-86.

Vishnu, G., Palanisamy, S., & Joseph, K. (2008). Assessment of fieldscale zero liquid discharge treatment systems for recovery of water and salt from textile effluents. *Journal of Cleaner Production, 16*, 1081-1089.

Wilf, M. (2007). *The Guidebook to Membrane Desalination Technology*: Balaban Desalination Publications.