An Overview of NRC Projects in Waste Water Treatment by Membrane Processes

Dr. Kumar

(National Research Council Canada)

An Overview of NRC Projects in Wastewater Treatment by Membrane Processes

Ashwani Kumar
Group Leader, Separation Technologies
Institute for Chemical Process and Environmental Technologies
National Research Council of Canada
M-12, Montreal Road
Ottawa, Ontario, K1A 0R6

Summary

A brief introduction to NRC's research activities will be given with special emphasis on membrane processes. NRC's membrane research group has been involved in many membrane research projects with industrial clients in various sectors of the industry. These projects generally were focused on using membranes for treating industrial wastewater streams for recycling process water, recovering of valuable components and meeting the environmental regulations. The group looked in to various aspects of process development dealing with membrane performance evaluation, optimization of operational parameters, determination of fouling propensities of membranes and simple cost analyses in some cases. Case studies dealing with process development for effluent treatment for the pulp & paper, mining & mineral processing and poultry processing industries will be discussed briefly.

Introduction

Separation technologies group is involved in strategic research in the general areas of polymer membrane formation, characterization, performance evaluation, design of modules and application development for the chemical process and environmental industries. As membrane fouling plays an important role in wastewater application development, researchers in our group are working on analyzing the fouling phenomena and developing fouling resistant membranes. During the last six years, the group has worked on several industrial projects utilizing the membrane based wastewater treatment approach. A brief description of selected projects from various industrial sectors is given below.

Pulp and Paper

Kraft Pulp Bleach Plant Effluent

In this process lignin decolourizing and breakdown is achieved by treating the pulp with chlorine gas or chlorine compounds. This treatment produces significant amounts of chlorinated compounds (for example. chlorinated lignin, phenolics, dichlorodimethylsulphone) in addition to lignin and resin acids. These compounds are reported (1, 2) to be major contributors to water pollution measured as COD, AOX (adsorbable organic halogens), colour and toxicity. Biological treatment can effectively treat only the lower molecular weight components in the effluent (< 1000 Da). In one approach, ultrafiltration can be used to remove high molecular weight compounds followed by biological treatment of permeate to reduce toxicity and BOD before discharge.

Effluent in the study was a mixture from the chlorination stage and caustic extraction stage and had a pH of 7. The TOC, COD, TDS, AOX were 3150, 3100, 6500 and 305 mg/L, respectively. Several commercial and NRC membranes (NMWCO ranges 200-200,000 Da) were tested in a Pellicon system and NRC standard test cells. The effects of operating parameters, membrane types and cleaning procedures were studied.

After many preliminary experiments the optimum operating condition for testing were established. It was observed that temperature cycling of the membranes between 20-50^{0}C produced permanent changes in more open membranes whereas changes in tighter membranes were reversible. It has been reported (3) that chlorinated organic compounds with molar mass greater than 8,000 Da are non-biodegradable. Consequently, in this study 8,000 Da was selected as the boundary between membrane and biological treatment. A set of three membranes was evaluated in greater detail for treating the effluent. The resulting reduction in pollutants is listed in Table 1. Also it was observed that the toxicity of permeate did not decrease significantly. Subsequent tests involved treating permeate from UF membranes by tighter NF membranes that produced lower toxicity and desired reductions in the pollutants (Table 2). Limited tests for cleaning these membranes showed that a proper cleaning solution could restore the performance of the membranes.

Plug Screw Feeder Pressate (PSFP)

This effluent is a complex mixture of inorganic and organic compounds, suspended fine particles, sugars and acids, having molecular weights in the range of 1 to greater than 100 kDa. Further processing of this stream is required as it contains many components that cannot be discharged into waterways. A consortium of research and development groups including a major pulp and paper manufacturer was interested in the feasibility of membrane application for treating this effluent. This project was managed by NRC for the consortium. The purpose of the study was to evaluate commercially available membranes, to investigate fouling of membranes in these application and possibly to develop new membranes with lower propensity for fouling. A comprehensive evaluation of membranes in laboratory as well as in the mill was done following an established protocol.

All tests were done on membrane coupons in NRC test cells. A partial list of the membranes and their performance for treating this effluent in once flow-through at $50^{0}C$ is given in Table 3. A large variation in the product rates and separation (based on TOC) was observed with different type of membranes, indicating that some material types are more prone to fouling than others for treating this stream (4).

A procedure for adsorption tests to study fouling of membranes with PSFP was developed. Membranes were characterized by determining pure water permeation rate and polyethylene glycol separations before and after contacting with the feed at $50^{0}C$. Continuous effluent tests were performed to determine the final product rates and pure water permeation of the exposed membranes. These data were used to estimate the contribution of different types of fouling mechanisms for a particular type of membrane. It was clear from the data analysis that different membranes show a varying degree of fouling due to factors like adsorption and pore plugging. These data were further used to develop a series resistance model for different membrane (4).

Table 1: Pollution reduction using a series of UF membranes.

Run #	Membrane	Product rate, (m^3/m^2.d)	Module ΔP, (kPa)	% Pollution reduction for each stage				Toxicity (EC_{50}) raw=9 %
				TOC	COD	TDS	AOX	
1	V222	2.7	14	50.7	57.3	25.9	76.7	11
	V226	4.0	165	67.6	71.0	38.1	-	17
	V227	2.4	124	76.8	79.8	46.9	88.3	12
2	V222	2.7	14	52.5	56.3	25.9	-	13
	V226	4.1	250	69.1	70.4	38.3	-	17
	V226	5.2	300	69.0	70.4	38.1	-	15
	V227	2.5	150	78.1	78.4	48.8	-	15
3	V222	2.7	14	50.9	58.2	26	-	13
	V226	4.0	165	65.8	69.6	37.5	-	18
	V226	4.1	270	67.8	72.3	38.0	-	19
	V227	2.7	124	78.8	79.9	46.7	-	23

Table 2: Pollution reduction of UF permeate by NF membranes. (ΔP=517 kPa)

Membranes	Product rate (m^3/m^2.d)	% Pollution reduction			Toxicity (EC_{50})
		TOC	COD	AOX	
R83	0.7	45.0	40.3	-	100
MRC2	1.8	22.0	21.1	49.1	75
DSS64	0.8	66.0	59.9	89.4	100
DSPS1	0.4	54.9	53.0	-	100

Membrane ID	Material	Product rate $m^3/m^2.d$	Separation, % (TOC)
U1	acrylamide on PS	1.7	72
T1	polyamideimide (PAI)	1.8	73
H1	TFC	2.0	85
D5	TFC	2.0	88
F1	cellulose triacetate	2.3	97
FI1	polysulfone	0.5	70
PC1	polysulfone	0.2	54
C1	cellulosetriacetate	0.3	41
P10	polyacrylonitrile (PAN)	0.3	36

Mining and Mineral Processing

Separation technologies group has worked on several projects in this sector in the areas of process water recycling, concentration of dilute streams and removal of toxics for environmental compliance. One such study dealt with the removal of nitrogen from mill water. Ammonium and nitrate ions are generated from the degradation of cyanide in the case of gold mill effluent, use of ammonium nitrate fuel oil, blasting agents and other reagents used in mineral processing. The concentration of nitrogen in the effluent exceeds the allowable limits set by regulatory agencies. Also, high concentration of nitrogen in effluent has other undesirable effects e.g. corrosion, algal growth and interference with aquatic life in receiving water bodies. In addition to natural chemical and/or biological treatment, several other chemicals and physical methods (ammonia stripping, ion exchange, oxidation and membranes) have been used for treating these wastewaters (5).

Membrane technology offers several advantages (ability to remove both cationic and anionic species, energy efficient, compact, modular). However, the concentrate containing metal and other toxics needs to processed for safe disposal. The present work reports the use membranes for removal ammonium and nitrate from simulated and actual wastewater including discussion on treatment of concentrate and simple economic analysis.

The form of ammonia is dependent on the pH of the effluent. Consequently, the separation of ammonia by membranes will be pH dependent. In order to investigate the effects of free and complexed ammonia on separation three different (two simulated A, B and one actual C) feed samples were used. Feed sample A, had 31mg/L ammonia in distilled water. Feed sample B had the composition in mg/L: NH_3, 25; Ca, 288, Fe, 599; SO_4, 63 and Zn, 63 whereas composition in mg/L: NH_3, 25; Ca, 288, Fe, 599; SO_4, 63 and Zn, 63 whereas actual field sample had the composition: NH3, 51.1; NO3, 207; SO4 707.1; Na, 214a and Ca, 266. Selected commercial reverse osmosis and nanofiltratrion membranes were tested. Permeation rates at 2.1 MPa for RO and NF membranes were in the range of 0.68-2.65 $m^3/m^2.d$. The separations of NH3 for different membranes are listed in Table 4.

Table 4: Separation (%) of ammonia for various membranes

Membranes	Feed A	Feed B	Feed C
DS-3B (RO)	25.8	97.1	95.1
FT-30 (RO)	26.5	82.4	93.9
DS-5 (NF)	25.0	94.7	54.8
HPVD (NF)	18.1	75.9	65.8

It is clear from the above table that a very high separation of ammonia could be achieved by RO membranes. It is interesting to note that in the case of Feed B the separations by NF membranes are also very high. This is due to the fact that ammonium ions are able to make a complex with iron and sulphate that was rejected by NF membranes (6).

The concentrate from this process contains significant amount of ammonium, sulphate and nitrate that are nutrients for soil. This by-product can be a source of additional revenue. Assuming the standard cost of membrane systems ($100/$m^2$, 20-30 % of the system cost) of $500/$m^2$, a cost estimate for processing a 1,000 USG of wastewater (7) of $1.80-2.20 was given which is less than the typical brackish water treatment cost of $2.30. Recovery of fertilizer by-product will further add to the profitability of this process.

Poultry abattoir wastewater treatment

The procurement of clean water and the treatment of wastewater are essential for the operation of an abattoir. Water use for poultry slaughtering has been estimated to range from 18 to 30 m^3/t of finished product while water use for poultry processing is about 15 to 100 m^3/t of finished product. This may limit the potential production and profitability of an abattoir, particularly the rural slaughterhouses. Significant reduction in wastewater can be achieved by adopting recycling technologies. In poultry processing, live birds are slaughtered, scalded, de-feathered, eviscerated, cleaned, and chilled. Scalding and chilling generate a large amount of wastewater. Since the chiller effluent has lower biological oxygen demand (BOD) and chemical oxygen demand (COD) than scalder effluent, this stream was selected for the present study.

The main contaminants in chiller water are blood, fats/oils, grease and micro-organisms. Typically, total suspended solids are reported in the 600-800 mg/L range. Approximately 30% of these solids (200-250 mg/L) are large floating particles of grease and fat. The major portion of the suspended solids (55% of the 20-50 μm range particles) form an opaque haze and are believed to be emulsified oils of entrapped proteins and lipids as well as the bulk of the micro-organisms. The remaining 5-10% of the particles are less than 5 μm in size and seem to be even more tightly bound with emulsified globules.

Due to their capabilities to remove all the microorganisms and suspended matter, membrane processes are a potential alternative for reconditioning process water. Furthermore, membrane technology allows the minimization of chemical usage and in turn, disposal costs. The objective of this study was to determine the applicability of ultrafiltration and nanofiltration membrane systems to treat poultry abattoir wastewater in order to obtain a recycle stream that will meet the Canadian poultry wastewater reuse criteria. A variety of membranes were tested to find a suitable membrane which could provide the desired separation and flux.

Ultrafiltration membranes

Several ultrafiltration membranes were first characterized by pure water permeation rate (PWP), the product rate (PR) and separation of a probe solute (polyethylene glycol (PEG), 6 kDa). Regenerated cellulose membrane had the highest PEG separation (90%) and the lowest flux (83.6 LMH). Udel PS membranes were considered to have the "larger" pore size. Radel A PS membranes had intermediate membrane performances with flux and separation of 67% and 156.8 LMH, respectively.

The results from the static adsorption test for adsorptive fouling showed that, there were no significant changes (< 2%) in the flux and separation for regenerated cellulose. For Udel polysulfone membrane adsorptive fouling on the surface was significant. Consequently, the permeation rates decreased by 23 to 13 % of the original while the separations increased by 1.2 to 1.6. The experimental results indicate that Radel A polysulfone membrane have fouling propensities that are intermediate between that of regenerated cellulose and Udel polysulfone.

The effects of pore size on the treatment of poultry waste effluent stream was studied with five different Radel A PS membranes with molecular weight cut-off of 4.5, 10, 35 and 100 kDa. An additional membrane with substituted hydroxyl group on polysulfone material was also evaluated using a typical feed (540 mg/L TOC) and operating pressure (345 kPa). As the experiment progressed, a steady decrease in flux was observed for all membranes. This flux decline was due to both membrane fouling as well as the increase in concentration of the feed as experiment was performed in concentration mode.

In general, all membranes tested showed the same level of total organic carbon (TOC) separation (50%). It was observed that separation increased with the processing time. However, relative insensitivity of separation to membrane material and the weak correlation with membrane pore size suggested that a "gel" layer is controlling the separation rather than the membrane. The examinations of feed exposed membranes were found to have gel like deposits on their surface.

An important criterion of recycled water concerns micro-organism concentration and percent light transmission. Based on a visual test, all permeates were completely clear and colorless. Permeate obtained with membranes of greater than 10 kDa MWCO had a foul odour. This odour might be due to the poor separation of low molecular weight components like amines and sulfur compounds. The microorganism analysis showed that total coliforms, faecal *Streptococci*, faecal coliforms and *E. coli* were all undetectable in the permeates from the 4.5 kDa MWCO membranes.

The light transmission rate at 500 nm was 98% using tap water as a reference. The above microorganism analysis results and other permeate properties were expected because UF/NF membranes should effectively retain all the molecules which have larger molecular sizes than membrane pore sizes. Depending upon the specific membranes (e.g. UF and NF), solute molecules larger than 1.0 nm (> 0.2 kDa MWCO) are retained, so bacteria with molecular size > 100 nm (> 30 kDa) should be retained. The results confirmed that permeate was able to meet a majority of the regulations governing water reuse for poultry industry.

The major limitation in the use of ultrafiltration membranes was the TOC content of permeate above the required Agriculture Canada meat inspection regulations of 100 mg/L. This criterion was not met with ultrafiltration membranes. Using the series of Radel A PS and hydroxyl substituted Radel A PS membrane, the TOC separation ranged from 35 to 55% (Figure 3) for a feed concentration of 580 to 780 mg/L. The TOC concentration in permeate was therefore at least 260 mg/L. Nanofiltration membranes with lower MWCO rating than ultrafiltration were then investigated to meet these stringent rquirements.

Nanofiltration membranes

Two commercial nanofiltration membranes were chosen for this series of tests. Effects of time of operation on permeation rates and TOC separations were evaluated and it was shown that the permeation rates go down with time that is indicative of some fouling experienced by membranes. However, the rate of fouling is not very high. Also, the permeation rates could be fully recovered after cleaning the membranes. The values for TOC separations were not significantly affected with time of operation. It appears that fouling of the membranes is taking place at the surface of the membranes probably by an adsorption mechanism. As the surface of membrane is cleaned by the post trial in line cleaning technique that consisted of successive washing with warm water (50°C), alkaline solution and water, the performance was restored.

Under the operating pressure of 345 kPa, the TOC separation and flux of thin film composite (NF 45) membranes were 72 - 82% and 17.2 LMH, respectively, compared with that of 4.5 kDa Radel A polysulfone UF membranes at 30 - 50% and 65.5 LMH respectively. Both of these thin film composite membranes (NF 45 and DS5) could produce permeate quality which meets the guidelines of less than 100 ppm of TOC. Also, the total *coliform*, faecal *strptococci*, *E. coli* and standard plate count were undetectable in the permeate. It was found that the light transmission through permeate at 500 nm was higher than 98%. The permeation rates can be increased by increasing the trans-membrane pressures. For example a change of pressure from 345 to1069 kPa increased permeate flux from 18.6 to 63.8 LMH while the TOC separations did not change significantly.

As discussed earlier, the untreated feed caused fouling of the membranes resulting in performance decline. It was decided that a pretreatment of feed prior to membrane treatment should be explored. For this work, we selected lime and phosphoric acid for pretreatment. Basically, lime will enhance the settling of suspended solids/haze containing blood and fat. A subsequent treatment by phosphoric acid was done. The lime treatment is inexpensive and lime sludge so produced might be usable for agricultural applications. The effects of three pretreatment options with lime/phosphoric acid on TOC removal are listed in Table 5.

As expected the feed TOC was reduced dramatically after pretreatment. It is clear from the data those pretreatment decreases the fouling of membranes significantly. The recovery of flux after cleaning is clearly very close to the original values.

Table 5: Comparison between different chemical pretreatment for NF operations.

Pretreatment	TOC_{Feed}	$TOC_{Permeate}$	% Sep	PWPi	$PR_{0.5 hrs}$	PWP_{clean}
					(LMH)	
No pretreatment	726.5	115.1	84.2	47.0	32.9	59.0
4% lime treatment +1% Phosphoric acid	222.8	41.6	81.3	70.7	63.6	72.2
1% lime treatment +1% Phosphoric acid	297.6	87.4	70.6	72.0	48.3	74.2
5% lime treatment	237.5	66.2	72.1	72.2	44.6	73.1

REFERENCES

1. G. E. Carlberg et. al *Sci. Total Environ.* 48, (1986) 157-67.
2. K. Lindstrom et. al *J. Chromatog.* 128 (1976) 13-26.
3. M. Haggblom and M. Salkinoja-Slonen *Wat. Sci. Technol.* 24 (1991) 161-70.
4. M. Dal-Cin et. al *Desalination and Water Reuse*, in press (1994).
5. Randol International Ltd., Water Mamnagement and Treatment for Mining and Metallurgical Opeartions, Vol. 4, Golden, Colorado, USA, June 1985.
6. F. T. Awadalla, C Striez and K. Lamb, "Removal of Ammonium and Nitrate Ions from Mine Effluents by Membrane Technology", Sepr. Sci. Technol., 29 (1994) 483-495.
7. R. J. Ray, "Cost estimates" in Membrane Handbook (W.S.W Ho and K. K. Sarkar, Eds), Van Nostrand Reinhold, 1992, pp355-390.
8. S. Q. Zhang, O. Kutowy, A. Kumar and I. Malcolm, "A laboratory study of poultry abattoir wastewater treatment by membrane technology", Can Agriculture Engineering, 39 (2) (1997) in press.

ACKNOWLEDGEMENT

Special thanks to my colleagues in the separation technologies group.