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**Nitrate removal from potable water using immersed
membrane bioreactors**

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ABSTRACT

Nitrate is practically ubiquitous in waters abstracted for municipal potable water production in Europe due to decades of intensive agricultural practice. Ion exchange is principally selected to target abstracted waters with elevated nitrate concentrations. However, the cost associated with disposal of the waste stream has re-ignited interest in destructive rather concentrative technologies. This thesis explores the potential of membrane bioreactor (MBR) technology for the removal of nitrate from potable water. Two configurations are considered: an MBR to replace ion-exchange completely; and an MBR to treat the ion-exchange waste stream in-situ for re-use.

For the replacement MBR, permeate quality can be affected by nitrite accumulation, micro-organism and carbon breakthrough. However, at steady-state and provided substrate addition was controlled, permeate quality was consistently high. Selection of an appropriate substrate was observed to improve permeability by a factor of three. Permeability was sustained within the MBR by adopting a dead-end filtration strategy having identified a relationship between filtered volume, flux and suspended solids concentration. Provided the filtered volume within a single filtration cycle did not exceed a set volume, the accumulated deposit was reversible. For the ion-exchange waste stream MBR, organic carbon breakthrough was considerable. However, the impact upon resin capacity was apparently limited when permeate was re-used for resin regeneration. Salt shocking did not induce permeability decline although some denitrification capacity was lost. Cost evaluation demonstrated that operating ion-exchange in parallel with MBR regenerant treatment was more cost effective than ion exchange with direct disposal.

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ABBREVIATIONS AND NOTATIONS

ABBREVIATIONS

AOC	Assimilable organic carbon	
ASP	Activated sludge process	
BER	Biofilm electrode reactor	
COD	Chemical oxygen demand	(mg.L ⁻¹)
CSTR	Continuous stirred tank reactor	
DBP	Disinfection by-product	(µg.L ⁻¹)
DO	Dissolved oxygen	(mg.L ⁻¹)
DOC	Dissolved organic carbon	(mgC.L ⁻¹)
ED	Electrodialysis	
EEM	Excitation emission matrix	
EPS	Extracellular polymeric substances	(mg.L ⁻¹)
EU	European Union	
GAC	Granular activated carbon	
HF	Hollow fibre	
HPC	Heterotrophic plate count	
HP-SEC	High performance size exclusion chromatography	
HRT	Hydraulic retention time	(hours)
IEX	Ion exchange	
MBfR	Membrane biofilm reactor	
MBR	Membrane bioreactor	
MF	Microfiltration	
MLSS	Mixed liquor suspended solids	(kg.m ⁻³)
MW	Molecular weight	(kDa)
MWCO	Molecular weight cut off	(kDa)
PAC	Powdered activated carbon	
PVDF	Polyvinylidene fluoride	
RO	Reverse Osmosis	
SAD _m	Spec. aeration demand per unit mem. area	(m ³ .m ⁻² .h ⁻¹)
SAD _p	Spec. aeration demand per unit permeate	(m ³ .m ⁻³)
SBR	Sequencing batch reactor	
SGD _m	Spec. gas demand per unit mem. area	(m ³ .m ⁻² .h ⁻¹)
SMP	Soluble microbial product	(mg.L ⁻¹)
SRT	Solids retention time	(days)
SUVA	Specific UV absorbance	(m.L.mgC ⁻¹)
Temp.	Temperature	(°C)
THMFP	Tri-halo methane formation potential	(µg.L ⁻¹)
TMP	Trans-membrane pressure	(mbar)
TOC	Total Organic carbon	(mgC.L ⁻¹)
UF	Ultrafiltration	
UMCCA	Unified multi-component cellular automation	
US	United States	
USBR	Upflow sludge blanket reactor	
UV	Ultraviolet	(cm ⁻¹)
VFA	Volatile fatty acids	
Vol.	Volume	(m ³)

NOTATIONS

ρ	Density	(kg.m^{-3})
μ	Viscosity	($\text{N.s}^{-1}.\text{m}^{-2}$)
α	Specific resistance	(m.kg^{-1})
A_{Bio}	Acetic acid derived biomass	
$b_{d,b}$	Bubble drag coefficient	
d_{10}, d_{50}, d_{90}	Particle diameter below which lies a % of the total volume of all particles in the sample	(μm)
dP/dt	Rate of TMP increase	(mbar.min^{-1})
C:N	Carbon to nitrogen ratio	
CHCl_3	Tri-chloromethane	($\mu\text{g.L}^{-1}$)
CHClBr_2	Chlorodibromomethane	($\mu\text{g.L}^{-1}$)
CH_3OH	Methanol	
Cl	Chloride	(mg.L^{-1})
ClO_2^-	Chlorite	
ClO_3^-	Chlorate	
ClO_4^-	Perchlorate	
D_i	Effective internal diameter	(m)
E_{Bio}	Ethanol derived biomass	
f	Fibre number	
g	Gravity constant	(m.s^{-2})
G	Shear	(s^{-1})
H_2	Hydrogen gas	
J	Flux	($\text{L.m}^{-2}.\text{h}^{-1}$)
J_c	Critical flux	($\text{L.m}^{-2}.\text{h}^{-1}$)
K	Permeability	($\text{L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$)
M_{crit}	Critical deposited mass	(g.m^{-2})
Mg^{2+}	Magnesium	
n	Impeller speed	(rev.s^{-1})
N_2	Nitrogen gas	
Na^+	Sodium	(mg.L^{-1})
NaCl	Sodium chloride	(mg.L^{-1} , %w/v)
NaHCO_3	Sodium bicarbonate	
NaOCl	Sodium hypochlorite	(mg.L^{-1})
NH_4OH	Ammonium hydroxide	
NO	Nitric oxide	
N_2O	Nitrous oxide	
NO_2^-	Nitrite	(mgN.L^{-1})
NO_3^-	Nitrate	(mgN.L^{-1})
P	Power	
P_{ave}	Average pressure	(mbar)
R_c	Hydraulic resistance of the cake layer	(m^{-1})
R_f	Hydraulic resistance of the fouling layer	(m^{-1})
R_m	Hydraulic resistance of the membrane	(m^{-1})
R_{res}	Residual resistance	(m^{-1})
SO_4^{2-}	Sulphate	(mg.L^{-1})
t_{crit}	Critical filtration time	(hours)
V	Volume	(m^3)
V_{crit}	Critical filtered volume	(L.m^{-2})

CHAPTER 1

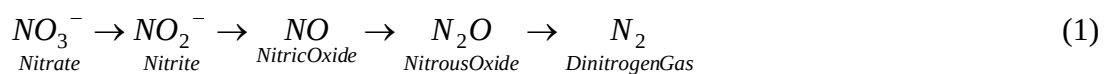
INTRODUCTION

1 INTRODUCTION

1.1 BACKGROUND

Decades of chemically assisted agriculture have significantly increased environmental concentrations of nitrate (NO_3^-), which is a major component of many fertilisers (Peyton et al., 2001). Nitrate possesses a poor binding capacity to soil which improves transmission to underlying aquifer resources (Glass and Silverstein, 1998). As a result, groundwater in many European regions now exceeds $100 \text{ mgNO}_3^-\cdot\text{L}^{-1}$ (Urbain et al., 1996). A 2005 Environment Agency survey indicated that surface water NO_3^- concentrations are now also elevated with an estimated 28% of UK Rivers exceeding $30 \text{ mgNO}_3^-\cdot\text{L}^{-1}$ (Environment Agency, 2006). Nitrate has been directly linked to blue baby syndrome or methaemoglobinaemia. This corresponds to the conversion of nitrate to nitrite in the gastrointestinal tract which impedes the oxygen capacity of haemoglobin in the blood causing a number of vasodilatory/ cardiovascular problems (Matějů et al., 1991; Soares, 2000). The drinking water regulatory limit has been set based on incidence data and ranges $10\text{-}11.3 \text{ mgNO}_3^-\cdot\text{N}\cdot\text{L}^{-1}$, dependent upon geographical location.

The first wave of technologies for the treatment of potable source waters high in nitrate was biologically oriented. Biological treatment facilitates the destruction of the nitrate ion through a series of intermediate steps to nitrogen gas (Eq. 1).



The original technology was based on a packed bed design and although successful, problems such as channelling and nitrite accumulation due to excess or irregular

biofilm development were reported which led to insufficient treatment quality (Gayle et al., 1989; Soares, 2000). Additionally, due to the process footprint and extensive downstream polishing requirement to target nitrite, micro-organisms, turbidity and excess carbon (Figure 1.1), the process was several times more expensive than ion-exchange resins (Richard, 1989). Ion-exchange has since been principally selected for nitrate removal.

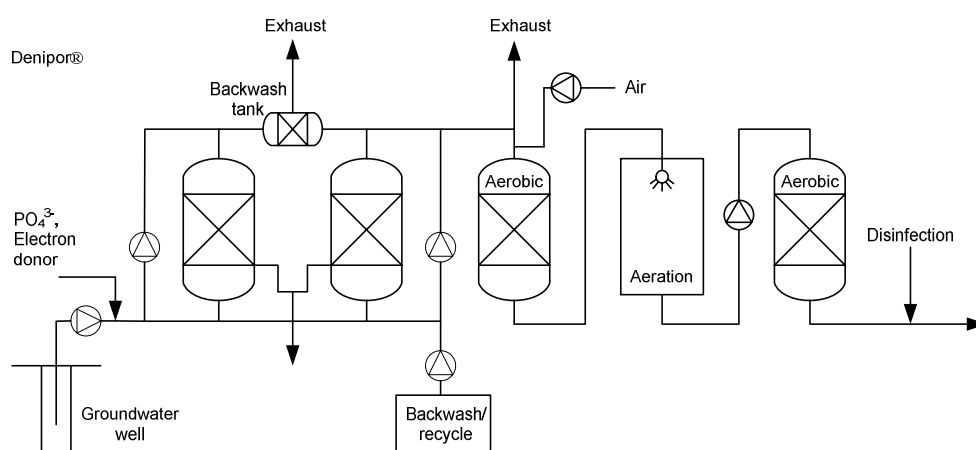


Figure 1.1 *Denipor® was one of the main designs adopted in the 1980's for biological denitrification of potable water.*

Ion-exchange is a concentrative process creating a waste stream of c.2% which is both high in nitrate and salt. The route for disposal is subject to increasing scrutiny. Regulation is now forcing many water providers to tanker waste off-site for disposal. Considering the cost involved (c. £13.m⁻³), the current volatility of oil prices and the impact on carbon footprint, in-situ destructive technologies are again being considered in place of ion-exchange. Several biological demonstration plants have been constructed in the US however, regulators have requested subsequent membrane filtration to safeguard against microbial breakthrough (Sanders, 2004). Membrane bioreactors integrate membrane technology into the biological reactor. Although development for municipal wastewater treatment has been extensive, relatively few

studies exist for this application (Nuhoglu et al., 2002; Delanghe et al., 1994; Urbain et al., 1996).

1.2 AIM AND OBJECTIVES

The present thesis reports work funded by the Engineering and Physical Sciences Research Council (EPSRC), Anglian Water, Severn Trent Water and Yorkshire Water. This thesis aims to assess the suitability of membrane bioreactor technology for its implementation into the potable treatment process, specifically for the destruction of the nitrate ion. Accordingly, the following objectives were identified:

1. To assess the current knowledge of membrane bioreactors applied to drinking water denitrification and identify areas that require further understanding.
2. To evaluate the permeate quality produced by membrane bioreactors for the replacement of ion exchange.
3. To determine an appropriate exogenous substrate to support nitrate removal within the membrane bioreactor.
4. To evaluate the hydrodynamics of immersed hollow fibre membranes applied in anoxic conditions and the resultant fouling potential.
5. To review and assess the application of immersed membrane bioreactor technology to work in parallel with ion-exchange by recovering the waste brine for re-use.

1.3 DOCTORATE OF ENGINEERING (EngD) PROGRAMME

Two distinctions can be made between an EngD programme and a conventional PhD. Firstly the research should address a problem of direct relevance to the industrial sponsor. Secondly, up to 20% of the thesis is to focus on business and commercial aspects related to the theme of the thesis. On this basis, Chapter 7 of the thesis places in context the impact that standardisation can have on the implementation of membrane technology in municipal applications. A preliminary costing is also appended (Appendix A) to evaluate the merits of the three options:

- Ion exchange with disposal;
- Ion exchange with MBR brine regenerant treatment and re-use; and
- MBR for the replacement of ion exchange.

1.4 THESIS PLAN

This thesis is presented in paper format. All papers were written by the first author, Ewan J. McAdam, and edited by Professor Simon J. Judd. All experimental work was undertaken by Ewan J. McAdam, with the exception of Chapter 3 where the THMFP GC-MS analysis was conducted by Dr. Emma Goslan.

This thesis begins with a review of the literature (Chapter 2) on the application of membrane bioreactor technology to replace ion exchange for potable water nitrate removal (2a, published in *Desalination* (2006) 196, 135-148: *McAdam, E.J., Judd, S.J., A review of membrane bioreactor potential for nitrate removal from drinking water*). A second review then summarises the literature to date on bacterial adaptation

for the denitrification of ion exchange waste brines (2b, published in Separation and Purification Technology (2008) 62, 264-272: McAdam, E.J., Judd, S.J., *Biological treatment of ion-exchange brine regenerant for re-use: A review*).

Chapters 3 to 6 cover the technical content of the thesis. Chapters 3 to 5 are based on the development of MBR technology for the replacement of ion exchange. Chapter 3 evaluates the permeate quality produced by a membrane bioreactor operated at nitrate concentrations similar to that faced during ion-exchange of potable source waters (Published in Water Research (2007) 41, 4242-4250: McAdam, E.J., Judd, S.J., *Denitrification from drinking water using a membrane bioreactor: chemical and biochemical feasibility*).

Chapter 4 evaluates the suitability of two exogenous carbon substrates to support denitrification and considers their impact on membrane performance (Published in Water Research (2007) 41, 3859-3867: McAdam, E.J., Judd, S.J., Cartmell, E., Jefferson, B., *The influence of substrate on fouling in anoxic immersed membrane bioreactors*).

Chapter 5a examines the optimisation of hydrodynamics for anoxic membrane bioreactors (5a, submitted to Journal of Membrane Science: McAdam, E.J., Judd, S.J., *Optimisation of dead-end filtration conditions for an immersed anoxic membrane bioreactor*). Chapter 5b optimises filtration conditions further and compares performance versus continuous gas scouring (5b, In preparation for Separation Science and Technology: McAdam, E.J., Judd, S.J., *A comparison of constant and intermittent (dead-end) gas scouring for anoxic immersed MBR operation*).

Following results from a preliminary cost evaluation reported in Appendix A (Published in Desalination (2008) 231, 52-60: McAdam, E.J., Judd, S.J., *Immersed membrane bioreactors for nitrate removal from drinking water: Cost and feasibility*) and for comparison with the ion exchange replacement MBR, Chapter 6 evaluates whether immersed membrane bioreactors can effectively treat ion exchange waste regenerant brine for re-use. The impact on resin capacity is also explored (In preparation for Water Research: McAdam, E.J., Pawlett, M. Judd, S.J., *Fate and impact of organics in an immersed membrane bioreactor for brine denitrification and ion exchange regeneration*).

Chapter 7 discusses the impact standardisation has on technology uptake and explores the role that standards have and can play in municipal membrane applications (McAdam, E.J., Judd, S.J., *Standardisation in the municipal membrane market: Current influences and future impact*).

The development of this thesis is summarised in the thesis road map (Figure 1.2). This thesis concludes in chapters 8 and 9 with a discussion on the implications faced for full scale implementation, before reaching conclusions and proposing further work.

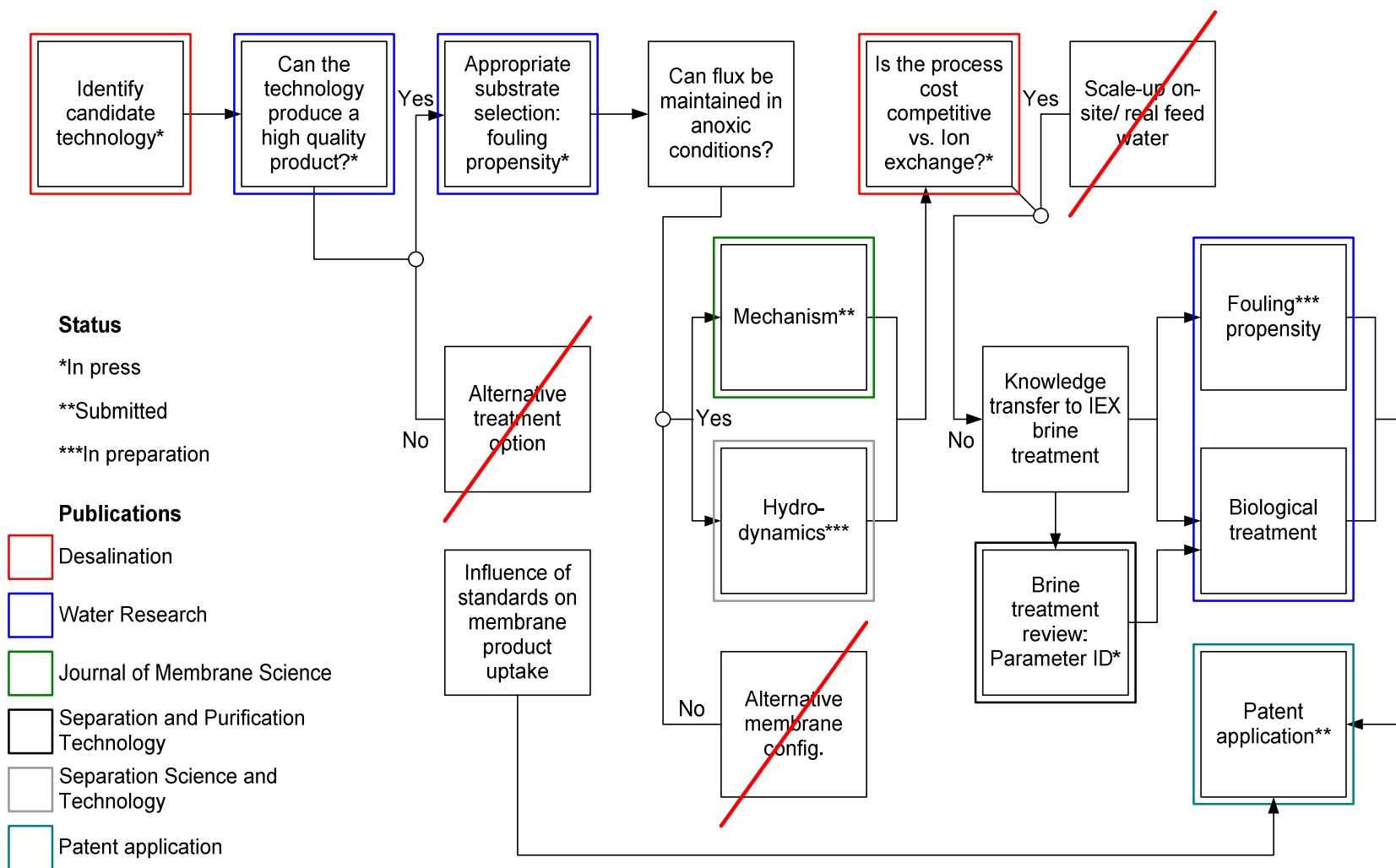


Figure 1.2 Thesis road map.

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CHAPTER 2a

LITERATURE REVIEW – A REVIEW OF MEMBRANE BIOREACTOR POTENTIAL FOR NITRATE REMOVAL FROM DRINKING WATER

PUBLISHED IN: *Desalination* (2006) 196, 135-148

2(a) A REVIEW OF MEMBRANE BIOREACTOR POTENTIAL FOR NITRATE REMOVAL FROM DRINKING WATER

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ABSTRACT

Continually elevated drinking water nitrate concentrations worldwide have increased focus on alternative nitrate removal processes accentuated by the limitations of current solutions, namely cost and complex waste generation. Biological denitrification is a comparatively low cost option, though its poor retention of bacteria and requirement for external carbon necessitates further downstream processing. To eradicate the associated disadvantages, the biological process can be integrated with membrane technology. Subsequently several membrane bioreactor (MBR) configurations have been trialled for this duty. Although the science behind each configuration has been justified, issues related to secondary contamination of the product water remain and require further investigation. This paper reviews the research to date appraising advantages and disadvantages associated with each configuration whilst also identifying areas that require further research and consequently assessing which nitrate removal MBR technologies will prevail for the future.

2.1 INTRODUCTION

A significant increase in nitrate (NO_3^-) levels in groundwater has been observed in many European countries, with levels exceeding $22.5 \text{ mg NO}_3^- \text{-N l}^{-1}$ in some areas (Urbain et al., 1996), well above regulated limits (Table 1.1). The accepted method for nitrate processing (ignoring blending (Oldani et al., 1992)) is ion exchange (IEX), although reverse osmosis (RO) using ultra low pressure membranes and extraction by electrodialysis (ED) have also been successfully demonstrated at full scale. All three processes, however, share the common disadvantage of yielding concentrated brine as a waste by-product which demands either further treatment or disposal.

Table 2.1 *Regulatory values*

	$\text{NO}_3^- \text{-N (mg l}^{-1}\text{)}$	$\text{NO}_2^- \text{-N (mg l}^{-1}\text{)}$
EU Regulations	11.3	0.03
US Regulations	10	1

An alternative to these technologies is biological denitrification, a relatively inexpensive process (Reising and Schroeder, 1996) which comprises an anoxic environment facilitating complete removal of nitrate by using the chemically bound oxygen in nitrate as a terminal electron acceptor, liberating nitrogen (N_2) as a gas (Fuchs et al., 1997) without generating a brine by-product.

The process is more typically associated with wastewater treatment but various configurations have been trialled for drinking water denitrification (Matějů et al., 1992; Soares, 2000). Its full scale application has been limited, however, because of poor retention of both the microbial biomass and the electron donor. Electron donors trialled have included methanol (Mansell and Schroeder, 1999), ethanol (Fuchs et al.,

1997), acetic acid (Barreiros et al., 1998), hydrogen (Haugen et al., 2002) and sulphur (Kimura et al., 2002), all designed to promote the appropriate heterotrophic or autotrophic conditions necessary for denitrification, each of which has its own drawback. Furthermore concerns over sociological implications, bacterial growth in the distribution system (from assimilable organic carbon), and formation of disinfection by-products (DBPs) slow developmental progress.

Consequently research has now refocused on combining the biological process with membrane technology in the form of a membrane bio-reactor (MBR) which can provide complete retention of the biomass. Questions none-the-less remain over appropriate electron donor selection and its retention in the reactor, as reflected in several of the MBR processes pioneered. Processes are either configured to selectively extract nitrate with porous (Mansell and Schroeder, 1999; Fuchs et al., 1997) or dense (Ion Exchange) membranes (Velizarov et al., 2003); supply gas (Lee and Rittmann, 2002; Ho et al., 2001) or reject biomass (Urbain et al., 1996; Nuhoglu et al., 2002). This text reviews the various membrane configurations with reference to investigations conducted to date and qualitatively determines the feasibility of each process whilst considering likely future developments of MBR technology for drinking water denitrification.

2.2 TRIALLED MEMBRANE TECHNOLOGIES

2.2.1 Extractive membrane bioreactor

In this configuration (Figure 2.1) also known as confined cell or fixed membrane biofilm reactor, nitrate is extracted from the pumped raw water by molecular diffusion through a physical barrier to a recirculating solution containing the denitrifying biomass. Ideally equal pressure is maintained to reduce the influence on diffusion (Mansell and Schroeder, 2002). Various materials have been researched to effectively separate the solutions, including calcium alginate gel, polyacrylamide/ alginate copolymer, an agar/ microporous membrane composite structure and various microporous membranes (Mansell and Schroeder, 2002). Membrane configurations have typically consisted of either flat sheet (Reising and Schroeder, 1996) or tubular (Ergas and Rheinheimer, 2004) type. The advantage of this process is that both the electron donor and the denitrifying biomass are separated from the product water. Whilst the membrane can permit electron donor transport, biofilm formation should theoretically aid donor retention (Fuchs et al., 1997).

Ergas and Rheinheimer (2004) used a tubular membrane yielding up to 99% removal efficiencies in high loading ($200 \text{ mg NO}_3^- \text{-N l}^{-1}$) environments, with other investigators reporting similar removals (90-99%) (Fuchs et al., 1997; Mansell and Schroeder, 1999) (Table 2.2). However, control of electron donor transfer into the product water has been less successful; Mansell and Schroeder (1999) and Ergas and Rheinheimer (2004) respectively reported $4 \text{ mg TOC (Total Organic Carbon) l}^{-1}$ and 8% methanol transfer under controlled addition experiments. Reising and Schroeder

(1996) conducted a batch study utilising a flat sheet membrane and methanol as the electron donor (CH_3OH) when comparing suspended growth and biofilm performance, noting significant transport of methanol across the membrane under suspended growth conditions, the authors postulating this to be a result of initial high concentrations and the lack of reaction and diffusion resistance associated with biofilm operation. The authors further predicted that the effect would be less significant in a continuous process and concluded that operation with a biofilm removal process resulted in a 25% effective diffusivity decrease compared to suspended growth operation (Reising and Schroeder, 1996). Later investigation by Fuchs et al. (1997) corroborated this hypothesis; determining ethanol to have a diffusion coefficient up to three times lower than that of nitrate due to the structure and thickness of the biofilm.

Subsequent autotrophic studies by Mansell and Schroeder (2002) used hydrogen gas as the electron donor and bicarbonate as the carbon source, thus removing shortcomings associated with organic carbon breakthrough, and reported removal efficiencies of up to 96% and minimal product water microbial content. Although this research implies that the process is viable, the risk associated with hydrogen gas dissolution (accumulation and explosion) has still to be addressed. Research suggests that this technology is effective in removing nitrate. However, pumping costs and the requirement for subsequent treatment stages (e.g. colour removal, taste, organic removal etc.), coupled with limited knowledge of the impact of fouling and fouling control in real time operation, suggest that further development of this technology is required. Evidence thus far suggests that this configuration has potential for niche applications such as hazardous waste treatment (Yang et al., 2005).

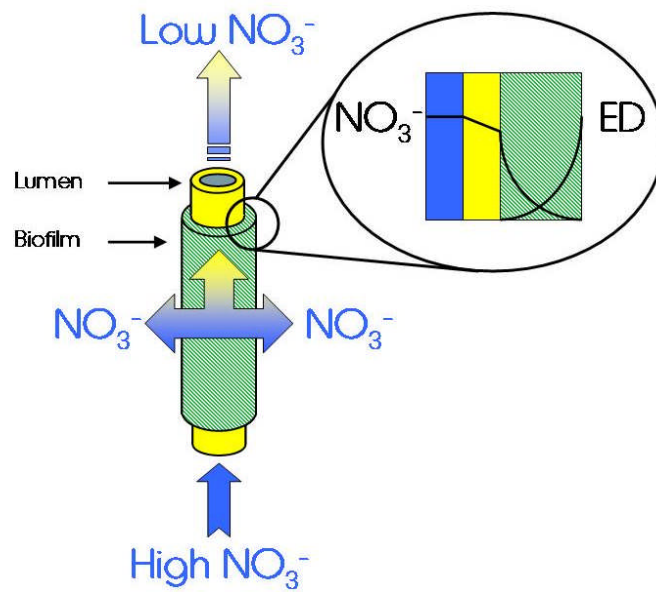


Figure 2.1 *Extractive MBR. Exploded view of mass transfer across the membrane biofilm interface.*

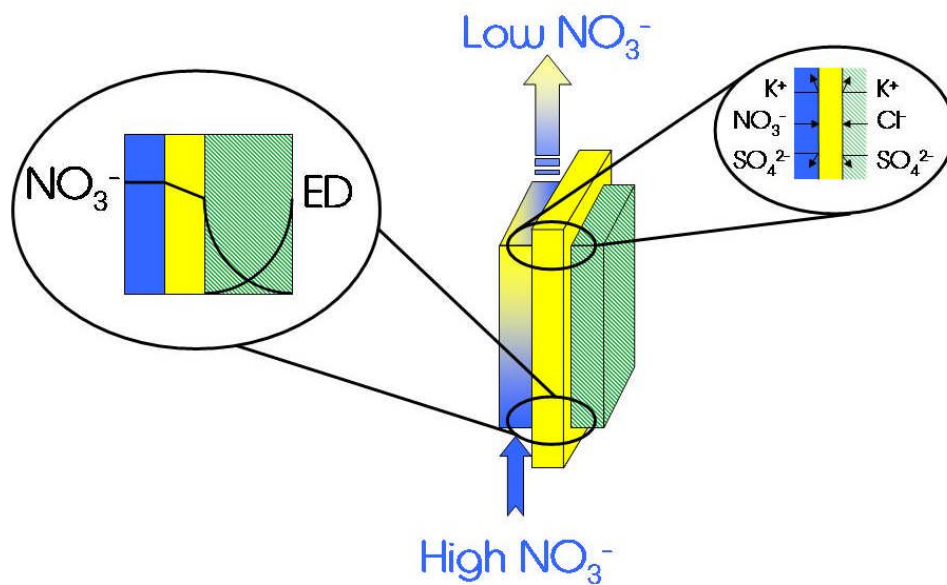


Figure 2.2 *Ion-exchange MBR. Exploded view of ion exchange at the membrane surface.*

2.2.2 Ion-exchange membrane bioreactor

This configuration (Fig. 2.2) is identical to the extractive process except microporous membrane technology is replaced by dense ion-exchange membrane technology, the advantage of which is that the nonporous membrane facilitates more specific extraction of nitrate from raw water and in principle hinders the transfer of organic and inorganic pollutants present in the biomedium (Fonseca et al., 2000). The process relies on the concentration and charge gradients of the ion species present as driving forces.

Table 2.2 *Biological characteristics of trialled MBR configurations for nitrate removal from drinking water*

Process/ Electron Donor	Vol.	C: N	Temp.	Alk.	pH	DO	MLSS	HRT	SRT	Nitrate Loading Rate (as N)	Nitrate Removal Rate (as N)	NO ₃ ⁻ -N (mg l ⁻¹)		NO ₂ ⁻ -N (mg l ⁻¹)	TOC (mg l ⁻¹)	Reference
	(m ³)	(g g ⁻¹)	(°C)	(mg l ⁻¹)		(mg l ⁻¹)	(kg m ⁻³)	(h)	(d)	(kg m ⁻³ d ⁻¹)	(g m ⁻² d ⁻¹)	In	Out	Out	Out	
Pressure Driven Ethanol	0.0025	1.2-1.4	20	N/a	8.0- 8.5	N/a	1.2-5	6	20	0.07-0.45	8.45- 56.45	16.9-113	<1.1	0.05	5-10	Delanghe et al., 1994
Pressure Driven Ethanol	0.02	1.15	N/a	N/a	N/a	N/a	1.8- 2.1	0.5-1	N/a	0.63	9.6-11.34	26.5	<4.5	<0.02	1.5- 2.1	Chang et al., 1993
Pressure Driven Ethanol	50	1.72	20	3.9	7.2	7 ^h	0.35- 0.85	2.5	5	0.2-0.7	12.95	10.2-15.4	<2.3	<0.015	<5	Urbain et al., 1996
Pressure Driven Ethanol	0.025	2.2	25±2	N/a	8±0. 2	N/a	1.8	1.79- 5.26	15	0.18-0.31	95-533	367	<4	N/d	N/a	Nuhoglu et al., 2002
Pressure Driven Sulphur	0.008	5 ^c	15.2- 29	N/a	6.7- 8.4	<0.3	1000 ^a	2.66	N/a	1.8	5.9	25	<1-20	<1	10-20 ^b	Kimura et al., 2002
Pressure Driven Acetic Acid	0.0005	1.37- 1.41	28	N/a	6.2- 7	N/a	0.6- 1.1	0.63-2.5	N/a	1.42-1.73	45.4-55.4	22.6-45.7	<1	<0.1	1.5- 2.0	Barreiros et al., 1998
Ion Exchange Ethanol	0.0003	N/a	24	N/a	8.5	N/a	N/a	2.67	2.5	0.08	7.45	30.5-79	9.4-45.6	N/d- 0.56	N/d- 7.02	Velizarov et al., 2000
Ion Exchange Ethanol	0.0007	N/a	24	N/a	7.2	N/a	N/a	4.2-4.4	3.5	0.81	6.5-7.5	32.2-50.4	4.2-9.1	0.014- 0.07	N/d	Fonseca et al., 2000
Gas Transfer Hydrogen	0.002	N/a	N/a	>9.5 ^d	7- 9.5	N/a	N/a	8.33	N/a	0.0001- 0.00004	1.6-5.4	225.8	N/a	<0.1	N/a	Ho et al., 2001
Gas Transfer Hydrogen	0.0004	1:7 ^m / 3:14 ⁿ	N/a	N/a	7.0	N/a	110- 179 ^e	0.7	N/a	0.096- 0.286	0.49-0.77	10-15	0.2-9	0.1-0.9	0.1 ^L	Lee and Rittmann, 2002
Gas Transfer Hydrogen	0.0012	N/a	N/a	250- 650	5.7- 7.0	N/a	500- 1000 ^e	4.1	N/a	0.02-0.77	2.2	65-200	0.6-13	N/d-<1	32	Ergas et al., 2001
Extractive Methanol	0.00002	1.13	21	N/a	7.0	N/a	0.3- 1.5	0.24- 0.55	N/a	0.8	4	20-30	2.3 - 16	N/a	4	Mansell and Schroeder, 1999
Extractive Methanol	0.0045	0.75- 6.4	N/a	N/a	7.2	N/a	N/a	1.2	N/a	4	1.1-6.1	200	<2-5.7	0.006- 0.023	9->10	Ergas and Rheinheimer, 2004
Extractive Ethanol	0.0005- 0.0009	1.9-4	20-25	N/a	8	N/a	0.14- 0.2	0.3-3.2	N/a	0.034- 0.048	0.27-1.23	22.5-45	<1 – 38.4	N/a	5-15 ^g	Fuchs et al., 1997
Hybrid Hydrogen	0.007	N/a	15.5-17	N/a	7.4- 8.0	N/a	N/a	9-12	20	0.02-0.19	1.76-2.87	13.6-72.3	<1 - 20.4	N/d	7.6- 8.1 ^j	Mo et al., 2005
Hybrid Hydrogen	0.008	N/a	10-12	N/a	8±0. 2	N/a	2-2.6	48-81.6	20	0.33	8.2-14.2	330	<1	N/d	26.8 ^k	Rezania et al., 2005
Hybrid Hydrogen	0.006	N/a	N/a	N/a	7- 11.9	<5	N/a	0.33-6	N/a	0.36-1.09	6.31	15 - 40	5	N/d-5	N/a	Prosnansky et al., 2002

^amg protein l⁻¹. ^bµg l⁻¹ assimilable organic carbon. ^cg d⁻¹ elemental sulphur addition. ^dpH rise in response to alkalinity formation. ^eµm biofilm thickness. ^gEthanol. ^hinfluent concentration. ^jDOC. ^kCOD. ^LHydrogen. ^mH₂:NO₃⁻. ⁿH₂:NO₂⁻. N/a - Not available. N/d - Not detected. Hybrid – Gas transfer&Pressure Driven.

Fonseca et al. (2000) used ethanol as the electron donor and subsequently opted for a membrane with the lowest permeability to ethanol. The subsequent apparent diffusion coefficient for ethanol through the membrane was found to be almost three orders of magnitude lower than that of ethanol in water (Fonseca et al., 2000). Corroborating these findings, Velizarov et al. (2000) reported ethanol concentrations in the effluent below the detection limit of 1 mg l^{-1} , although when ethanol concentrations exceeded 450 mg l^{-1} in the biocompartment (Table 2.2), ethanol could be determined in the product water. The authors postulated that use of a non-porous homogenous membrane minimises the penetration of low-molecular non-charged compounds into the treated water. The authors also concluded that by adjusting the co-ion ratio, nitrate flux can be easily controlled (Velizarov et al., 2000). Nitrite accumulation in the reactor and subsequent breakthrough observed during these studies ($<0.56 \text{ mg NO}_2^- \text{-N l}^{-1}$) corresponded to a period of carbon underdosing; under normal dosing conditions nitrite was not observed in the treated water above the detection limit. The inherent benefit of dense membranes is the ability, as demonstrated, to limit the transfer through the membrane of the electron donor. However, as with extractive technology, use of the MBR to simply extract and assimilate nitrate implies that further processing of the product water is required. Also the process has only been demonstrated in idealised conditions with synthetic water. As such the influence of fouling on exchange efficiency, as well as the potential for scaling from waters with high hardness levels (Oldani et al., 1992), complexity of operation and perhaps most importantly cost (given the expense of ion exchange membranes (Crespo et al., 2004)) has not yet been reported.

Table 2.3 Membrane characteristics of trialled MBR configurations for nitrate removal from drinking water.

Process Type	Membrane			Vol. (m ³)	Operating Flux (l m ⁻² h ⁻¹)	Permeability		TMP (bar)	Gas Flow Rate (ml min ⁻¹)	Cross-flow Velocity (m s ⁻¹)	Cleaning Frequency		Ref.
	Configuration/ Type/ Material	Pore Size (µm)	Area (m ²)			Initial (flux bar ⁻¹)	dK/ dt (flux bar ⁻¹ min ⁻¹)				Backwash (mins)	Chemical (days)	
Pressure Driven	SS/HF PVDF	200,000 ^a	0.02	0.0025	20.83	N/a	0.0145 ^m	N/a	N/a	1	N/a	7	Delanghe et al., 1994
Pressure Driven	SS/HF Cellulosic deriv.	0.01	1	0.04	45-100	300	0.0004-0.0014 ^m	<2.5	N/a	2	12 sec. ea. 12 mins.	N/a	Chang et al., 1993
Pressure Driven	SS/HF Cellulosic deriv.	0.01	400	50	60-70	88.7	7.66x10 ⁻⁷	0.7	N/a	0.9	2 ea. 60 mins	Ea. 4 hrs	Urbain et al., 1996
Pressure Driven	SS/FS Cellulose Acetate	0.2	0.0024	0.025	82.5-242.5	196-220	N/a	0.42-1.1	N/a	4.5	N/a	N/a	Nuhoglu et al., 2002
Pressure Driven	S/Disc	750,000 ^a	0.3	0.008	20.8	240	0.0016	0.1-0.2	N/a	200 rpm	400 rpm for 15 mins ea. 3 days	N/a	Kimura et al., 2002
Pressure Driven	SS/HF Polysulphone	500,000 ^a	0.032	0.0005	24	875	0.25	0.15	N/a	1.52	0.1 sec ea. 5 sec.	N/a	Barreiros et al., 1998
Ion Exchange	S/IEX	2.1 ^b	0.003	0.0002	0.035-0.07 ⁿ	N/a	N/a	N/a	N/a	150 ^e	N/a	N/a	Velizarov et al., 2000
Ion Exchange	S/IEX	2.1 ^b	0.003	0.0007	N/a	N/a	N/a	N/a	N/a	150 ^e	N/a	N/a	Fonseca et al., 2000
Gas Transfer	S/HF Polyethylene+PU	N/a	0.075	0.0004	0.14-0.43 ^f	N/a	N/a	N/a	31.4-42.5 ^{c,g}	10 ^e	N/a	N/a	Lee and Rittmann, 2002
Gas Transfer	S/HF Polypropylene	0.05	0.37	0.001	N/a	N/a	N/a	N/a	30 ^{c,g}	0.007	N/a	N/a	Ergas et al., 2001
Gas Transfer	S/Tube Silicone	N/a	0.00004	0.002	N/a	N/a	N/a	N/a	20 ^c / 5 ^d	3 ^e	N/a	N/a	Ho et al., 2001
Extractive	S/Tube PVDF/ Cellulose	500,000 ^a	0.0067	0.0005-0.0009	N/a	N/a	N/a	N/a	N/a	0.42-0.47 ^e	N/a	N/a	Fuchs et al., 1997
Extractive	SS/HF Acrylonitrile	50,000 ^a	0.14	0.0045	N/a	N/a	N/a	N/a	N/a	0.0015 ^h / 0.00009 ^j	N/a	N/a	Ergas and Rheinheimer, 2004
Extractive	S/FS PTFE	0.02	0.004	0.00002	N/a	N/a	N/a	N/a	N/a	0.0005-0.001	N/a	N/a	Mansell and Schroeder, 1999
Hybrid	S/HF PVDF	0.04	0.093	0.007	6.2-8.4	N/a	N/a	N/a	N/a	N/a	30 sec. ea. 600 sec.	14 ^k	Mo et al., 2005
Hybrid	S/HF PVDF	0.04	0.093	0.008	14.3-24.6	N/a	N/a	N/a	55.7 ^{B,c} , 20-40 ^c	20 ^{e,L}	N/a	14	Rezania et al., 2005
Hybrid	S/FS Polysulphone	0.2	0.037	0.0006	83-229	376-6857	0.0083	0.007-0.04	1-7.3 ^d	0.34-2.02 ^L	Intermittent op. 8on/ 2off	170	Prosnansky et al., 2002

2.2.3 Gas transfer membrane bioreactor

To avoid potential secondary contamination associated with utilising an organic substrate, hydrogen (H_2) can be used as the electron donor combined with either carbon dioxide or bicarbonate as the carbon source (Mansell and Schroeder, 2002) for autotrophic denitrification (Fig. 2.3) - often termed hydrogenotrophic - and can be considered both inexpensive and non-toxic (Haugen et al., 2002). Furthermore autotrophic bacteria produce relatively low biomass yield (Table 2.1) and, because of the low solubility of H_2 , it does not remain in the treated water (Lee and Rittmann, 2002). Gas transfer membrane bioreactors typically employ gas permeable hollow fibres (HF), although gas permeable silicon tubes have been trialled (Ho et al., 2001), to deliver hydrogen gas and in some cases carbon dioxide (dependent upon inorganic carbon source selected) through the lumen to denitrifying bacteria which grow on the shell side of the membrane. Hollow fibre gas transfer eradicates previous problems with low solubility as it provides gas fed directly to the biofilm, some research claiming that up to 100% gas transfer efficiency is possible (Mo et al., 2005), thereby also reducing the risk associated with gas accumulation, concentration and explosion.

Ergas and Reuss (2001) reported that although a batch comparison of autotrophic (hydrogenotrophic) and heterotrophic denitrification indicated autotrophic bacteria to be slower for biodegradation ($18 \text{ g NO}_3^- \text{-N m}^{-3} \text{ d}^{-1}$ versus $30 \text{ g NO}_3^- \text{-N m}^{-3} \text{ d}^{-1}$), subsequent testing revealed high NO_3^- utilisation rates at an influent NO_3^- concentration of $145 \text{ mg NO}_3^- \text{-N l}^{-1}$. Similar high removal yields were also noted by other investigators (Ho et al., 2001; Haugen et al., 2002) though equally variable NO_3^- removal efficiency has been reported (Lee and Rittmann, 2002).

Key to maintaining high nitrate removal efficiency is sustaining H_2 gas mass transfer rates, the reduction of which is primarily due to fouling by either the formation of thick and dense biofilms (Roggy et al., 2002), or direct precipitation of mineral solids at the membrane surface (Lee and Rittmann, 2002). Precipitation is reported to be a major foulant of hydrogen diffusers (Ergas and Reuss, 2001) as a result of build up inside microbial aggregates and direct surface deposition (Lee and Rittmann, 2003). Lee and Rittmann (2003) studied the effects of pH and precipitation noting an optimum pH range 7.7-8.6 for NO_3^- removal and proposed that successful long term operation depended upon interaction between available calcium, pH and alkalinity (Lee and Rittmann, 2003) since mass transport resistance keeps basic species in the biofilm and accentuates pH increase (Lee and Rittmann, 2003). However, precipitation of mineral solids did not adversely affect H_2 transfer in this investigation. Similarly Roggy et al. (2002) also noted limited effects of precipitation and thick biofilm formation on mass transfer rate, whilst others (Ergas and Reuss, 2001) have noted mass transfer limitations to the extent that the introduction of a crossflow velocity was required to shear biofilm from the fibres. The contrast in findings indicates that much more work is needed to further understand biofilm formation and its influence on mass transfer. This requirement has subsequently generated studies such as that undertaken by Laspidou and Rittmann (2004). These authors have developed a unified multi-component cellular automation (UMCCA) model, which predicts quantitatively the development of the biofilms composite density utilising three biofilm components: active bacteria, inert or dead biomass and Extracellular Polymeric Substances (EPS). The authors based the model on the hypothesis that fluid flow over the biofilm creates horizontal and vertical pressures, leading to fibre vibration causing biofilm consolidation, or higher density packing (Laspidou and Rittmann, 2004).

Applying a similar principle to gas transfer for biofilm formation, Chang and Tseng (1998) supplied methanol by diffusion through a silicone tube, the purpose being to reduce the

concentration in the bulk liquid phase. However, limited control could be established over methanol diffusion into the reactor. With concentrations of up to 50 mg l⁻¹ in the reactor reported and no subsequent barrier, methanol was transported directly into product water, breakthrough obviously depending upon biofilm activity and concentration gradient (Chang and Tseng, 1998).

As with the extractive processes, the disadvantage of gas transfer MBR is that the membrane is not used for direct filtration, but it is also not employed to retain the denitrifying biomass. As such product water is prone to 'sloughed' biomass and soluble microbial product (SMP) increasing both turbidity and dissolved organic carbon (DOC) concentrations in the treated water, as noted in several investigations (Ergas and Reuss, 2001) (Table 2.2). In contrast when investigating in-situ gas transfer, Haugen et al. (2002) recorded relatively low total organic carbon residuals (<0.5 mg l⁻¹), as the membrane was placed at the front end of a simulated horizontal flow aquifer containing spherical media, thus the biomass was ostensibly removed by 'natural' attenuation. In addition to contributing to residual organic carbon, biofilm growth also contributes to fouling, reducing performance and increasing maintenance. High gas transfer rates are commonly cited by authors who confirm safe dissolution of H₂ gas is possible. Importance is also attributed to retention of H₂ gas by the biofilm thus reducing the possibility of accumulation in confined spaces (Mansell and Schroeder, 2002). Although potentially controllable on a small scale such as those reviewed, problems such as uneven growth driven by the partial pressure drop inside the hollow fibre (Ahmed and Semmens, 1992) are liable to lead to maldistribution of gases and hence increased risk. Finally the poor adaptability of the autotrophic bacteria under drinking water denitrification conditions demonstrated in several studies by long acclimatisation periods of 40 and 70 days (Ho et al., 2001; Ergas and Reuss, 2001) cast doubt on its suitability for full scale operation. Although not necessarily feasible for this specific duty, some research has been carried out on its suitability

for in-situ aquifer remediation (Fang et al., 2002; Haugen et al., 2002) and although several of the above issues remain, requirements for biomass retention and direct filtration are omitted.

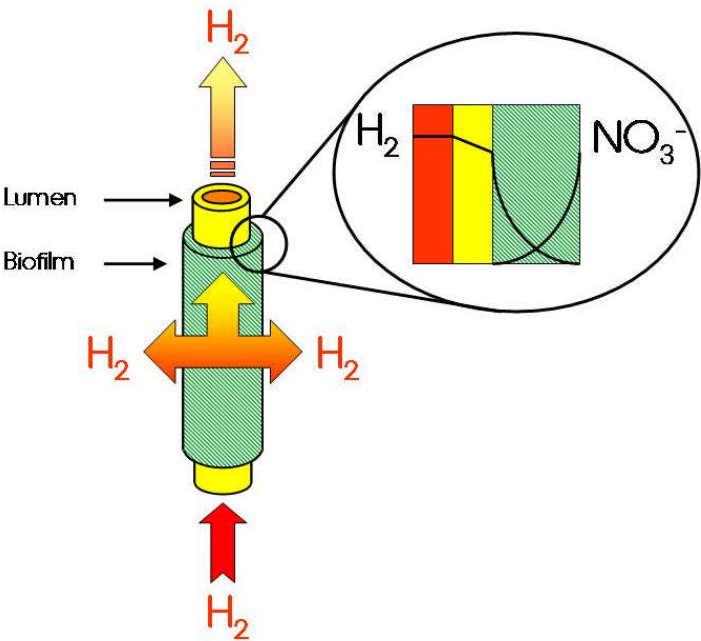


Figure 2.3 Gas transfer, diffusive or hydrogenotrophic MBR. Exploded view of mass transfer across the membrane/ biofilm interface.

Table 2.3 Stoichiometric reactions including biomass yields (Nerenberg et al., 2002).

Electron Donor	Stoichiometric Reaction	Yield (g cells g ⁻¹ N)
Ethanol	0.69 C ₂ H ₅ OH + NO ₃ ⁻ + H ⁺ → 0.14 C ₅ H ₇ O ₂ N + 0.43 N ₂ + 0.67 CO ₂ + 2.07 H ₂ O	0.689
Hydrogen	3.03 H ₂ + NO ₃ ⁻ + H ⁺ + 0.229 CO ₂ → 0.0458 C ₅ H ₇ O ₂ N + 0.477 N ₂ + 3.37 H ₂ O	0.306
Sulphur	0.98 S + NO ₃ ⁻ + 0.609 H ₂ O + 0.188 CO ₂ → 0.0375 C ₅ H ₇ O ₂ N + 0.48 N ₂ + 0.98 SO ₄ ²⁻ + 0.955 H ⁺	0.194

2.2.4 Pressure driven membrane bioreactor

This process relies primarily on a suspended denitrifying biomass rather than biofilm development and is thought to have the advantage of extended contact between the denitrifying culture and nitrate in the reactor medium, limited only by mixing rate (Nuhoglu et al., 2002). Rather than supplying the electron donor or acting as a channel for nitrate laden water, the membrane is placed within (Kimura et al., 2002) or external to the bioreactor (Urbain et al., 1996; Chang et al., 1993; Delanghe et al., 1994), physically rejecting the biomass (hence retaining active denitrifiers) and more refined species (Fig. 2.4). External (sidestream) MBRs are considered to be more suitable for wastewater streams characterised by high temperature, high organic strength, extreme pH, high toxicity and low filterability (Yang et al., 2005) and have been more commonly investigated in drinking water (Change et al., 1993; Tsai et al., 2004). Submerged membranes have more recently been considered for large scale MBR applications on the basis of their lower power costs (Yang et al., 2005) and improved mass transfer manifested as higher permeabilities (Judd, 2005). Permeate is subsequently extracted under an applied hydraulic or mechanical pressure and as permeate extraction continues, denitrifying biomass accumulates on the membrane surface in the form of a filter cake allowing further denitrification to take place while the product water passes through the membrane (Nuhoglu et al., 2002). Consequently this process is the only non counter ion configuration (Crespo et al., 2004, with both nitrate and electron donor entering the developed biofilm in the same direction.

Both heterotrophic and autotrophic systems have been investigated using acetate (Barreiros et al., 1998), ethanol (Urbain et al., 1996; Chang et al., 1993; Delanghe et al., 1994) and elemental sulphur (Kimura et al., 2002) as electron donors. Kimura et al. (2002) are currently the sole investigators of drinking water nitrate removal using submerged membrane bioreactors,

presumably because nitrate removal is dependent upon anoxic conditions and conversely submerged membranes require aeration to generate superficial liquid velocities to provide shear across the membrane surface. Possibly to circumvent this issue, the authors adopted rotating disc modules which apply rotational velocity to 'control' fouling thus with no reliance on aeration an anoxic environment could be maintained. Operation continued for 100 days at a flux of approximately $21 \text{ l m}^{-2} \text{ h}^{-1}$ with limited fouling (Table 2.3). The authors postulated that the different SMP materials produced had a low MBR membrane fouling propensity compared with conventional sewage (Kimura et al., 2002), though no supporting information was provided. Fouling control is critical to successful pressure driven MBR performance and, though the subject has received significant attention in MBR wastewater applications (Yang et al., 2005; Chang et al., 2002), investigations conducted in MBR applied to drinking water to date contain limited fouling data. Delanghe et al. (1994) reported a permeation decline of 7.5 - 15 % whilst operating at a flux of $6.25\text{-}8.33 \text{ l m}^{-2} \text{ h}^{-1}$ in a heterotrophic sidestream configuration. Urbain et al. (1996) also conducted pilot scale studies of a heterotrophic sidestream MBR, observing that biomass increased with loading rate and so required tangential crossflow velocities higher than 2 m s^{-1} to maintain reasonable flux values. Nitrate removal efficiencies of up to 98.5% are generally reported in these studies but, as with previous configurations reviewed, several investigators reported organic carbon (Delanghe et al., 1994) and elevated assimilable organic carbon (AOC) concentrations (Kimura et al., 2002) in the product water.

Urbain et al. (1996) reported on the successful development of a full scale heterotrophic sidestream MBR utilising ethanol as the electron donor. Although, as reported above, increased loading caused fouling as a consequence of increased biomass concentration, the process was considered viable at lower loading rates as crossflow velocities (generated by fluid velocity) could be reduced by a factor greater than two (Urbain et al., 1996). The full scale $400 \text{ m}^3 \text{ d}^{-1}$

nitrate removal process constructed in Douchy, France, comprised powdered activated carbon (PAC) dosing for pesticide removal. Stabilised fluxes between 60 and $70 \text{ l m}^{-2} \text{ h}^{-1}$ were obtained at full scale and, contrary to previous investigations, having optimised C: N dosing, treated water of low organic carbon concentration as well as tri-halo methane formation potential (THMFP) was reported. The author hypothesised that low effluent organic content was a consequence of effective membrane rejection of biomass by-products of high molecular weight (Urbain et al., 1996).

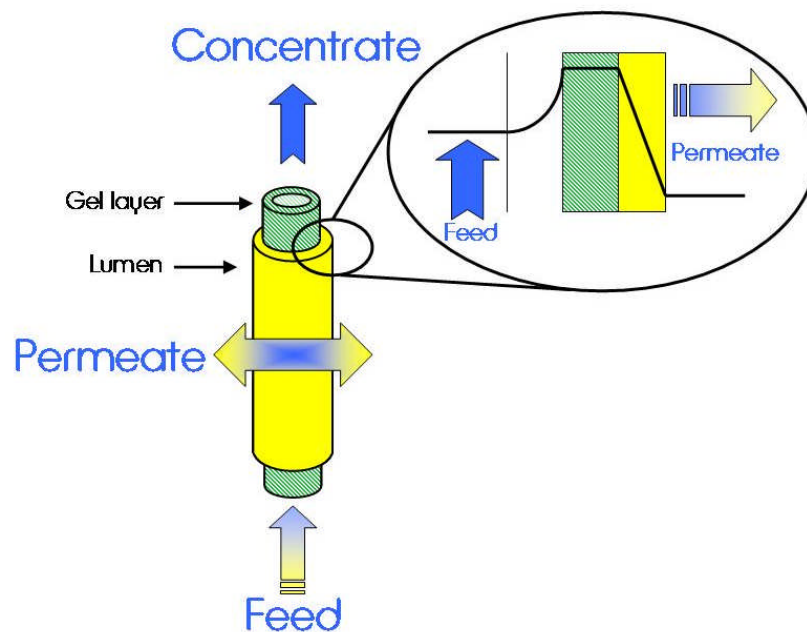


Figure 2.4 Pressure driven MBR. Exploded view of mass transfer and concentration polarisation at the membrane/ biofilm interface.

2.3 HYBRID SYSTEMS

Rather than incorporating gas permeable membranes to overcome the shortcomings of standard hydrogen gas dissolution, Prosnansky et al. (2002) produced hydrogen gas electrolytically in-situ to supply a biofilm grown at the cathode, the process being termed a Biofilm Electrode Reactor (BER). To enhance the surface area for biofilm growth, Granular Activated Carbon

(GAC) was packed tightly at the cathode surface and submerged membrane technology was employed in a separate follow-on chamber (Figure 3.1).

Following refinement of carbon dioxide flows to compensate for pH shift, improved NO_3^- and NO_2^- removal performance was noted although concentrations of 5-10 mg NO_3^- -N l^{-1} consistently appeared in the effluent throughout testing. Whilst specific removal rates were low compared to other MBR configurations, these were much improved when compared to previous BER studies, the authors attributing improvement to mass transfer improvement as a consequence of the increased surface area (Prosnansky et al., 2002). As the effluent NO_3^- concentrations indicate, the process is difficult to control fully due to influent dissolved oxygen concentration affecting hydrogen dissolution, difficulties with pH control, hydrodynamic limitations and the influence of the anode on nitrate migration upon increasing electric field intensity (nitrate escaped from the BER without treatment) (Prosnansky et al., 2002). Furthermore the process is comparatively limited due to an intensive energy requirement and, once again, formation of hydrogen bubbles which impose a safety risk.

More recent research (Mo et al., 2005) has focused on incorporating both gas transfer and submerged pressure driven membranes into the same reactor. The authors focussed treatment on suspended biomass rather than biofilms to minimise mass transfer problems previously reported with biofilm development (Crespo et al., 2004; Ergas and Reuss, 2001). Nitrate loading rates between 0.024-0.192 kg NO_3^- -N $\text{m}^{-3} \text{d}^{-1}$ were trialled with all but the higher loadings resulting in 100% removal performance. However, average effluent dissolved organic carbon (DOC) concentrations of approximately 8 mg l^{-1} were also observed. Mo et al. (2005) identified several possible sources of the elevated DOC concentrations (Table 2.2) including the generation and release of soluble microbial products (SMP), volatile fatty acids (VFA) produced by acetogenic bacteria in the biomass, and EPS. The regular removal of the

membrane biofilm (manual scraping, twice daily), known to act as a 'dynamic membrane' and improve rejection, would have been likely to have influenced the ease with which the organic matter was transported across the membrane. To evaluate biomass by-product removal the same research group operated a similar reactor under Sequencing Batch Reactor (SBR) conditions (Rezania et al., 2005) incorporating an anoxic period for hydrogenotrophic nitrate consumption followed by an aerobic period designed for permeate extraction and heterotrophic consumption of SMP. Steady state mass balance indicated 81% of the SMP to be retained by the membrane, 9% was biologically removed, 5% passed through the membrane and 5% was discharged during wasting. Although an interesting principle, as with several previous studies conducted, limited speciation of organic matter constrained the conclusions.

2.4 CONCLUSIONS

The science behind the reported processes appears to have been proven though full scale demonstration has been very limited and remains challenging. In brief, extractive process research to date focuses on high rate nitrate removal with little consideration of either nitrite formation, electron donor carry over or the implications of fouling (Table 2.4). It is considered that North American studies are less focused on nitrite formation compared with those conducted in Europe due to a less strict NO_2^- regulation (Table 1.1). Furthermore, if the membrane is not used for direct filtration, further downstream processing is required for colour, taste and turbidity improvements and for disinfection. Similarly gas transfer MBRs require downstream processing to remove sloughed biomass and SMP. Moreover its application is limited because, although efficient low bubble gas transfer has been reported, health and safety concerns remain. All research to date in this area, with the exception of one full scale pressure-driven study, has involved small scale reactors ($0.00002\text{-}0.04\text{ m}^3$) in idealised circumstance yielding little real-time information or attributable cost data.

Autotrophic growth conditions are conceivably preferable over their heterotrophic counterparts on the basis of low waste yields (Table 2.1, adapted from Nerenberg et al. (2002)) and substitution of organic carbon addition, though culmination of their lower adaptability, lower denitrifying rates and associated electron donor safety risks cast doubt on their applicability at full scale. The challenge with the application of heterotrophic electron donors is dose control, since under dosing produces nitrite (a more strictly regulated contaminant) and over dosing leads to secondary contamination. The latter may constitute direct health and sociological concerns, or indirect concerns over trihalomethane formation potential or stimulation of bacterial growth in the distribution network, though reports from a full scale pressure driven process implies dosing control to be achievable.

Where efficient sustainable gas transfer can be proven and fouling understood under low flow conditions, opportunities exist for in-situ gas transfer technology for groundwater remediation where breakthrough is irrelevant. Extractive and pressure driven configurations hold greater possibilities for mainstream treatment or blending, although further research into donor addition, the origin and control of biologically produced organics and their influence at the membrane surface is required. Reported success in France of a full scale pressure driven process would suggest that the process is both financially and technically viable. Greater consideration should be given to the development of submerged pressure driven MBR, which has proven to be more cost effective and have a lower fouling propensity than the sidestream process in municipal wastewater applications.

Table 2.4 *Summary of advantages and disadvantages of the trialled MBR configurations.*

Configuration	Advantages	Disadvantages
Extractive	<ul style="list-style-type: none"> - Separation of biomass and carbon source from product water - Biomass retention (thus retention of active denitrifiers) 	<ul style="list-style-type: none"> - Requires further downstream processing (e.g. filtration for bacteria/ viruses, colour, taste, turbidity) - Carbon source breakthrough - Pumping costs
Ion-Exchange	<ul style="list-style-type: none"> - Dense membrane significantly reduces risk of carbon source breakthrough - Biomass retention 	<ul style="list-style-type: none"> - Requires further downstream processing (as above) - Potentially complex operation - Unknown impact of fouling - Comparatively high membrane cost - Pumping costs
Gas Transfer	<ul style="list-style-type: none"> - Non-toxic and low cost electron donor - Good nitrate removal - Low biomass yield 	<ul style="list-style-type: none"> - Requires further downstream processing (pertaining to biomass removal specifically; also as above) - Biomass breakthrough - Potential for fouling to limit mass transfer - Health and safety risk with respect to hydrogen gas dissolution - Autotrophs, slow to adapt
Pressure driven	<ul style="list-style-type: none"> - Biomass retention - Direct filtration limits downstream processing requirements - Proven at full scale (including organic dosing control) - Comparatively low cost - Comparatively simple to operate 	<ul style="list-style-type: none"> - Potential for carbon source breakthrough - Limited knowledge of fouling - Pumping costs (more specifically for sidestream configuration) - Aeration costs (where air is used for fouling amelioration) - Downstream processing requirement (more limited due to direct filtration)
Biofilm Electrode Reactor	<ul style="list-style-type: none"> - Non-toxic and low cost electron donor - Potential for accurate dose control - Direct filtration potentially limiting downstream processing requirements 	<ul style="list-style-type: none"> - High energy requirement - Health and safety risk with respect to hydrogen gas dissolution - Low nitrate utilisation - Complex control - Efficiency impacted by dissolved oxygen concentration
Gas transfer/ Pressure Driven	<ul style="list-style-type: none"> - Combines benefits of pressure driven with gas transfer 	<ul style="list-style-type: none"> - Manual removal of biofilm to retain suspended biomass is labour intensive - Health and safety risk with respect to hydrogen gas dissolution - Aeration costs

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CHAPTER 2(b)

LITERATURE REVIEW – BIOLOGICAL TREATMENT OF ION-EXCHANGE BRINE REGENERANT FOR RE- USE: A REVIEW

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2(b) BIOLOGICAL TREATMENT OF ION-EXCHANGE BRINE REGENERANT FOR RE-USE: A REVIEW

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ABSTRACT

Ion exchange resins are typically selected to target anionic pollutants in drinking water treatment, however, the production of concentrated brine is a significant disadvantage as regulation of its disposal is becoming increasingly strict. Various destructive technologies have been trialled as a replacement for ion exchange, the most notable being biological reduction. Although several full-scale biological processes have been developed for drinking water treatment, regulators remain cautious about the introduction of microbes into the treatment process. Alternatively the bioprocess can be reconfigured to destruct the target anion in the concentrated waste brine, eliminating the bioprocess from direct treatment and reducing the waste volume and salt consumption associated with ion exchange. This paper reviews the difficulties faced when bio-processing complex, highly concentrated brine, evaluates the various process configurations trialled and presents an argument for the integration of membrane technology whilst also providing a précis of the literature available to date on membrane fouling for this application.

2.6 INTRODUCTION

Oxyanions (including perchlorate, nitrate and bromate) constitute a widespread problem in drinking water treatment. A specific focus on nitrate (NO_3^-) and perchlorate (ClO_4^-) removal has been stimulated by an increasing number of contaminated source waters, increasing pollutant concentration and associated health risks. Even low perchlorate concentrations ($\mu\text{g/L}$ range) interfere with the uptake of iodine by the thyroid which inhibits both the synthesis and secretion of thyroid hormones (Gingras and Batista, 2002). Though specific regulations are not currently available, target perchlorate concentrations ranging $2\text{--}6\ \mu\text{g/L}^{-1}$ have been recommended in various US states for treated potable water. Nitrate is converted to nitrite in the gastrointestinal tract which then reacts with haemoglobin in the blood converting it into methaemoglobin resulting in vasodilatory/ cardiovascular problems. Regulatory limits have been set on the basis of toxicological assessment and range $10\text{--}11.3\ \text{mgNO}_3^-\text{-N.L}^{-1}$ for treated potable water.

Sources of perchlorate include industries associated with rocket, missile and firework manufacture amongst others (Cang et al., 2004). Highly concentrated nitrate wastes are produced from various industries including nuclear fuel processing, cellophane, pharmaceutical and fertiliser manufacture and metal finishing (Glass and Silverstein, 1999; Pinar et al., 1997; Peyton et al., 2001). Both NO_3^- and ClO_4^- are readily soluble and bind poorly to soil, simplifying their transportation to ground and surface waters when discharged (Glass and Silverstein, 1999; Hiremath et al., 2006).

Ion-exchange is principally selected to target oxyanion removal from raw waters for potable water production due to its low cost and operational simplicity. As with other candidate technologies such as reverse osmosis (RO) and electro-dialysis (ED), a highly concentrated brine is produced containing the target pollutant, sulphate, bicarbonate and chloride (Clifford and Liu, 1993; Wisniewski et al., 2002). There is a reluctance to permit direct brine disposal to sewer, as it can cause problems in conventional municipal sewage systems (Romero Barranco et al., 2001). More conventional routes have been direct disposal to the environment by drainage ditch, river or coastal discharge (dependent upon consent). Evaporation ponds have also been used (Lauch and Guter, 1986), though this method relies on appropriate ambient temperatures and land availability. The use of brine evaporation ponds has been found to cause contamination of groundwater over a period of decades (Romero Barranco et al., 2001). Ion exchange brine disposal now often entails tankering, representing a considerable process cost and carbon footprint as brine waste can constitute between 0.8-2.4 % of treated product flow (van der Hoek et al., 1988).

The most promising alternative to brine disposal is the biological reduction of the concentrated anion and the subsequent re-use of the regenerant which provides reductions in waste volume, salt (NaCl) consumption and treated product loss. Biological reduction has been applied at full-scale to replace IEX completely. However, the risk of substrate or microbial carryover demanded significant downstream treatment, and the capital costs involved made the process relatively unattractive. By configuring biological reduction external to the treatment train to target the oxyanion in the IEX concentrate, process scale and cost can be significantly reduced and issues with permeate quality diminished. The first known combined IEX/

bio-process was reported for ammonium (NH_4^+) removal by Semmens and Porter (1979). The first combined IEX/ bio-process for oxyanion removal, and nitrate specifically, was reported nine years later (van der Hoek et al., 1987). The authors suggested a brine volume reduction of 95% was possible. Clifford and Liu (1993) subsequently argued that the saving might not be so great for IEX operated in partial regeneration mode. Since then, many laboratory-scale investigations have been undertaken, but no data published from full-scale applications.

Spent regenerant composition (Table 1) depends on resin type, removal/regeneration efficiency and influent characteristics (Gingras and Batista, 2002). Various IEX regenerants have been used including sodium chloride (NaCl), sodium bicarbonate (NaHCO_3) and ammonium hydroxide (NH_4OH) (Gingras and Batista, 2002; Yang et al., 1995). NaCl is the more commonly used regenerant. Though researchers are currently attempting to decrease NaCl concentrations required for regeneration (~0.5-1%) (Okeke et al., 2002), regenerants remain highly concentrated: generally 6-12 % (Gingras and Batista, 2002) and 3-12% (Clifford and Liu, 1993) for perchlorate and nitrate respectively and up to 15% in some instances (Chung et al., 2007). Cang et al. (2004) suggested that spent IEX regenerant from treating raw water with 50-100 $\mu\text{gClO}_4^-\cdot\text{L}^{-1}$ and 3-20 $\text{mgNO}_3^-\cdot\text{N}\cdot\text{L}^{-1}$ would contain 2.5-10 $\text{mgClO}_4^-\cdot\text{L}^{-1}$ and 150-500 $\text{mgNO}_3^-\cdot\text{N}\cdot\text{L}^{-1}$. It has been recognised that certain regenerant constituents impede biological performance (van der Hoek et al., 1988). On this basis Lahav and Green (1998) considered that the optimal NaCl concentration in the bio-process had to be much lower than the IEX regenerant concentration. However, dilution meant that there was insufficient ammonium extraction (the target pollutant) from the zeolite

resin to maintain reasonable nitrification; additionally, increased dilution could increase the volume of regenerant required.

This reviews focus is the bio-processing of waste brine generated from ion exchange. Included aspects are the impact, selection and tolerance of various biological communities, the influence of final effluent quality on IEX regeneration efficiency, process configurations (including membrane bioreactors) and areas for further research.

Table 2.5 *Characteristics of real and synthetic waste brines.*

Process/ App.	Influent (g.L ⁻¹)											Ref.
	NO ₃ ⁻ N	ClO ₄ ^{-(c)}	Na ⁺	Cl ⁻	SO ₄ ²⁻	Ca ^{2+(c)}	Mg ^{2+(c)}	TDS	Bicarb.	pH	Cond. ^(g)	
iMBR (Syn.) Sulphate	N/a	N/a	50 ^a	N/a	2-11.8	N/a	120	N/a	N/a	N/a	60-70	Vallero et al., 2005
extMBR (Real) ED Brine ^d	0.13	N/a	0.034	0.47	0.2	788	30	N/a	1.08 ^f	7.11	3.49	Wisniewski et al., 2001
SBR (Real) IEX ISEP [®] Brine ^K	0.35	3.5	N/a	N/a	1.6	22	2.5	68.3	N/a	N/a	91.6	Hiremath et al., 2006
SBR (Syn.) IEX Brine ^K	0.09-0.9	4.3	53-100 ^a	N/a	0.6-6	N/a	N/a	N/a	11.0	5-10	N/a	Hiremath et al., 2006
SBR (Syn.) IEX Brine ^d	0.61-0.84	N/a	29.25 ^a	8.4-11.2	1.7-2.1	N/a	N/a	N/a	5.8-9.1 ^f	N/a	N/a	Clifford and Liu, 1993
SBR (Syn.) High NO ₃ ^{-d}	2.7-8.2	N/a	35.6- 71.2	24.5- 49.03	2.5-5.0	N/a	N/a	48-180	15.8- 31.6 ^L	7.2	N/a	Glass and Silverstein, 1999
HF-MBfR (Syn.) IEX Brine ^e	1.0	500	10-40 ^a	N/a	0.08	0.0003	0.02	N/a	N/a	N/a	N/a	Chung et al., 2007
SBR (Syn) IEX Brine ^e	0.112	500	8-60 ^a	N/a	N/a	380	1320	N/a	0.2 ^L	N/a	N/a	Cang et al., 2004
Spent Brine (Real) IEX ^{h, d}	0.48	N/a	18.6	12.1	2.6	39.4	N/a	N/a	0.11 ^b	6.8	45.4	Site 1
Spent Brine (Real) IEX + Softener ^d	3.4	N/a	N/a	43.0	5.7	52	N/a	N/a	1.0 ^b	7.4	124.5	Site 1
Spent Brine (Real) IEX ^{h, d}	1.99	N/a	42.1	50.9	4.4	171.7	N/a	N/a	0.43 ^b	7.4	108.3	Site 2
Raw water Borehole	7.99 ^c	N/a	12.4 ^c	30.5 ^c	26.2 ^c	34.5	N/a	0.4 ^J	0.02 ^b	6.2	0.26	Site 1

N/a – Not applicable. Syn – Synthetic. ^aNaCl concentration. ^bAlkalinity as gCaCO₃.L⁻¹. ^cmg.L⁻¹. ^dNO₃⁻. ^eNO₃⁻ & ClO₄⁻. ^fAlkalinity as HCO₃⁻. ^gmS.cm⁻¹. ^hMean values.

^JOrganic carbon. ^KClO₄⁻. ^LAlkalinity as NaHCO₃.

2.7 BIOTREATMENT

2.7.1 Salinity and microbial community

The effect of salinity on traditional wastewater treatment is well known (Ludzack and Noran, 1965; Lefebvre and Moletta, 2006), and has been reported as impacting deleteriously on biological floc stability (Dan et al., 2002), BOD removal (Rinzema et al., 1988), anaerobic wastewater treatment (Lefebvre and Moletta, 2006; Rinzema et al., 1988), and generally a greater inhibition of denitrification (Clifford and Liu, 1993; van der Hoek et al., 1987) than nitrification (Dinçer and Kargi, 1999) at very high salinities ($>20 \text{ gNaCl.L}^{-1}$). Inhibition of denitrification within this salinity range (and up to 70 g.L^{-1}) has ranged from 10% (Clifford and Liu, 1993) to 100% (Glass and Silverstein, 1999; Lawson, 1981] depending largely on feedwater quality, microbial concentration and community structure. Inhibition of perchlorate and sulphate reduction has similarly been reported at salinities of $20\text{-}30 \text{ gNaCl.L}^{-1}$ (Cang et al., 2004; Vallero et al., 2005), with substantial ($>90\%$) reduction in perchlorate degradation rates reported when salinity was increased from 0 to 10-15% (Gingras and Batista, 2002).

Inhibition has been variously attributed to osmotic pressure effects across the cell wall (Vallero et al., 2005) as well as impacts on reaction pathways in substrate degradation (Dan et al., 2002). Variations in salinity tolerance (halotolerance) have been linked to loading conditions (Ludzack and Noran, 1965) and the growth phase of the microorganisms, the very young or very old cultures being more susceptible to salinity variation (Kincannon and Gaudy, 1966), as well as community diversity and

origin (Vallero et al., 2003). These reported studies have all been aimed at deriving a halotolerant community from activated sludge processes. Whilst halotolerance is usually achieved at high salinities following a period of acclimation, the communities are practically inactive at $>30 \text{ gNaCl.L}^{-1}$, i.e. seawater salinities (van der Hoek et al., 1987; Attaway and Smith, 1993). This implies that IEX regenerants would generally require dilution for effective bioprocessing.

As an alternative, some authors have developed either mixed (Cang et al., 2004; Okeke et al., 2002; Logan et al., 2001) or single *halophilic* cultures (Peyton et al., 2001; Cyplik et al., 2007] capable of withstanding higher salinities. Halophiles can be separated into three broad ranges: mild ($10\text{-}60 \text{ gNaCl.L}^{-1}$), moderate ($60\text{-}150 \text{ gNaCl.L}^{-1}$) and extreme or *extremophiles* ($150\text{-}300 \text{ gNaCl.L}^{-1}$) (Madigan et al., 2000).

Halophilic communities have been isolated from various sites, including salt evaporation facilities/salt marshes, sub-tidal sediments and salt marshes (Okeke et al., 2002; Logan et al., 2001; Lefebvre et al., 2004). Logan et al. (2001) found that not all locations yielded communities capable of perchlorate reduction at 30 gNaCl.L^{-1} . *Citrobacter sp.* has been identified as an effective halotolerant ClO_4^- reducer (Okeke et al., 2002) at concentrations up to 50 gNaCl.L^{-1} , and *Halomonas denitrificans* and *Halomonas Campisalis* have been shown to reduce nitrate at salinities up to 180 gNaCl.L^{-1} (Cyplik et al., 2007; Peyton et al., 2001) at rates comparable to those measured in non-halophilic studies (Foglar et al., 2005) (Table 2).

Table 2.6 *Specific denitrification rates from high salt and zero salt processes.*

NaCl Affinity/ Reactor type	NaCl Concn. (gNaCl.L ⁻¹)	Community origin	Specific rate (mgNO ₃ ⁻ -N.gVSS.h ⁻¹)	Reference
Non-halotolerant CSTR	0	ASP	2-50	Foglar and Briški, 2003
Non-halotolerant MBR	0	ASP	6.7 ^{a, b}	Delanghe et al., 1994
Non-halotolerant MBR	0	ASP	11.3 ^a	Chang et al., 1993
Halophilic Batch kinetic	125	<i>Halomonas</i> <i>Campisalis</i>	12.5-27.1	Peyton et al., 2001
Halophilic MBR	180	<i>Halomonas</i> <i>Denitrificans</i>	54.2 ^{a, b}	Cyplik et al, 2007

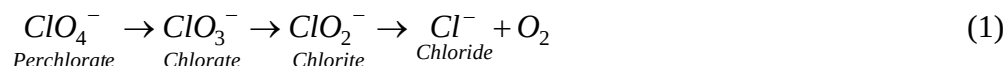
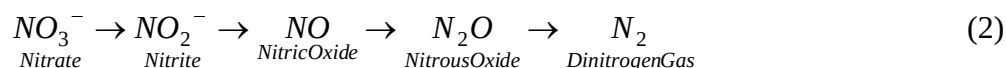
CSTR – Continuous stirred tank reactor. ASP – Activated sludge process. MBR – Membrane bioreactor. ^amgNO₃⁻-N.gSS.h⁻¹. ^bMax. rate observed.

2.7.2 Acclimatisation and shocking

Successful acclimation of inocula depends on type and growth phase of micro-organisms and the rate of increase in salt concentration (Lefebvre and Moletta, 2006). Increasing salinity rapidly to 60-70 gNaCl.L⁻¹ in non-halophilic communities has been shown to inhibit denitrification by between 60% (van der Hoek, 1987) and 100% (Glass and Silverstein, 1999); van der Hoek et al. (1987) observed some recovery over time (from 60% to 40% loss). Increasing salinity in smaller increments has been shown to reduce the deleterious impact on biological reduction in some cases (Glass and Silverstein, 1999), whilst other studies have demonstrated no impact (Vallero et al., 2003). Some authors have also shown that if the salinity drops, acclimation to NaCl is rapidly lost (Kincannon and Gaudy, 1968). In another case, specifically inoculum from marine sediment acclimatised to high salinities of 30 gNaCl.L⁻¹, shock loads between 53 and 80 gNaCl.L⁻¹ were found not to impair reduction of either perchlorate or nitrate (Hiremath et al., 2006).

2.7.3 Reduction mechanism

Both nitrate and perchlorate are degraded sequentially yielding end products chloride and di-nitrogen gas (Eq. 1 and 2).



It has been suggested that perchlorate and nitrate reduction are connected as one of the principal enzymes (nitrate reductase) is potentially used in both cases (Gingras and Batista, 2002) and at least two denitrifying Halophilic bacteria *Paracoccus halodenitrificans* and *Haloferax denitrificans* have been identified as reducing perchlorate (Okeke et al., 2002). However, it appears perchlorate reduction is not maximised by adapting denitrifying cultures (Logan et al., 2001) and furthermore not all denitrifiers can reduce chlorate (Logan, 1998). Similarly, only some perchlorate-reducing bacteria use nitrate (Coates et al., 1999), suggesting that the chlorate and nitrate reduction pathways may be unrelated.

In cultures capable of reducing both nitrate and perchlorate, both anions are degraded simultaneously, though perchlorate reduction is inhibited to some extent by nitrate (Hiremath et al., 2006; Herman and Frankenberger). It is unclear from the various publications whether the inhibition mechanism is specifically enzymatic or organism competition. The influence of NaCl concentration also remains uncertain, with some research suggesting nitrate reduction is more impeded by increasing NaCl concentration than ClO_4^- reduction (Hiremath et al., 2006) and vice versa (Cang et al., 2004). The nature of this interaction is dependent on community development, which

in turn is sensitive to salinity and acclimation conditions. However, it is apparent from some studies (Okeke et al., 2002; Yoshie et al., 2006) that it is beneficial to the reduction rate to develop mixed communities (halophiles, such as *Citrobacter sp.* with non-halophiles (Okeke et al., 2002)) rather than monocultures when treating brine containing either perchlorate or nitrate. In one study of a mixed denitrifying community, whilst the microbial diversity decreased on increasing the salinity from 20 to 100 gNaCl.L⁻¹, denitrification increased at the higher concentration (Yoshie et al., 2002).

2.7.4 pH

The pH of IEX brine is expected to be basic (pH 8-9) due to the accumulation of bicarbonate (Hiremath et al., 2006). Although maximum denitrification capacity is typically observed in the neutral range (Foglar et al., 2005; Delanghe et al., 1994), several authors (Glass and Silverstein, 1999; Peyton et al., 2001; van der Hoek et al., 1987; Mormile et al., 1999] have reported increased efficacy of halotolerant denitrifying communities at higher pH levels, with rapid denitrification reported at pH 9-9.5 by saline-acclimated activated sludge compared with none for the same saline-acclimated community at pH 7.5 (Glass and Silverstein, 1999). Similar efficiencies have been observed for halophilic communities at pH 9 (Peyton et al., 2001; Mormile et al., 1999]. Glass and Silverstein (1999) attributed inhibition in the neutral to acid pH region to the presence of nitrous acid, formed by association of nitrite and protons at the lower pH range.

2.7.5 Substrate and nutrient addition

A number of electron donors have been trialled successfully for anionic removal in non-saline conditions including methanol, ethanol and acetate (Matějů et al., 1992), with the efficacy depending upon conditions such as pH, salinity and culture. However, successful adaptation of halophiles to exogenous substrate has been more varied (Table 3). It has been postulated (Peyton et al., 2001) that the inability of halophilic organisms to take up various substrates was correlated to the limited organic variation in highly saline environments, thus the selection pressure on microbes to develop the necessary enzymatic systems was absent.

Cang et al. (2004) found the addition of Na_2S to improve ClO_4^- reduction, observing that sulphur was required for micro growth, oxygen scavenging and redox potential reduction which aids reduction. Hiremath et al. (2006) also recommended nutrient addition, finding magnesium was required at a molar ratio 0.11 ($\text{Mg}^{2+}/\text{Na}^+$) to maintain long-term ClO_4^- reduction in IEX brine and indicated that Mg^{2+} levels typically available in IEX brine are insufficient to maintain stable long-term performance.

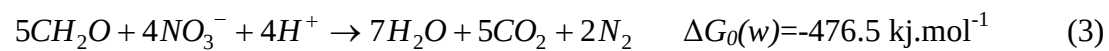
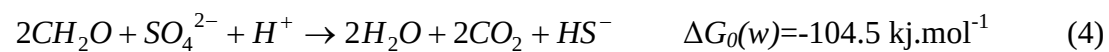
Table 2.7 *Substrate adaptation by halophilic bacteria.*

Oxyanion	Community derivation	pH	Salinity (g .L ⁻¹)	Substrate	Reactivity		Ref.
					Growth	Reduction	
NO ₃ ⁻	<i>Halomonas campisalis</i>	9	125	Acetate	✓	✓ ^a	Peyton et al., 2001
				Ethanol	✗	✗	
				Glycerol	✓	✓	
				Lactate	✓	✓	
				Methanol	✗	✗	
ClO ₄ ⁻	<i>Citrobacter sp.</i>	7.5	25	Acetate	✓	✓	Okeke et al., 2002
				Citrate	✓	✗	
				Ethanol	✓	✗	
				Formate	✓	✓	
				Fumerate	✓	✓	
				Glucose	✓	✓	
				Molasses	✓	✓	
				Yeast extract	✓	✓ ^{a, c}	
SO ₄ ²⁻	<i>Desulfobacter halotolerans</i>	7.2	50	Acetate	✓	✓	Vallero et al., 2005
				Ethanol	✓	✓ ^{a, b}	

^aHighest reduction rate observed. ^bbiotin and 4-aminobenzoate also added. ^cCombining yeast extract with sodium acetate yielded optimum reduction.

2.7.6 Impact of other passive anions

The influence of bicarbonate and sulphate concentration on bio-processing has also been studied since both species are concentrated by IEX. Bicarbonate has been found to exhibit less influence on denitrification capacity than NaCl (van der Hoek et al., 1987; Okeke et al., 2002), and has also been noted as suppressing nitrite accumulation (Okeke et al., 2002). Highly concentrated sulphate has been found to have no effect on perchlorate reduction (Hiremath et al., 2006, Attaway and Smith, 1993]. However, several cases (Clifford and Liu, 1993; Balderston and Siegburth, 1976) of complete nitrate removal at extended hydraulic residence times (HRT) have been reported, resulting in the subsequent reduction of lower-energy yielding electron acceptors such as sulphate (Butler et al., 2005) leading to sulphide production (Equation 4), which is undesirable.



2.7.7 Impact of processed brine regenerant on IEX regeneration

Bio-process permeate may contain microbes and high molecular weight organics which can lead to IEX resin fouling (Clifford and Liu, 1993) and treated water contamination. Yang et al. (1995) found that as NaCl and bicarbonate increased above 10 and 15 g.L⁻¹ respectively, increases in chemical oxygen demand (COD) and suspended solids were observed in the effluent. Other authors have also reported increasingly turbid effluent in the presence of salinity (Lefebvre et al., 2006; Dan et al., 2002) due to poor settleability. Some authors advocated post-treatment by granular activated carbon (GAC) to address this (Bae et al., 2002) which extended IEX operation by ~70 bed volumes versus untreated effluent. Clifford and Liu (1993) instead treated brine with standard microfiltration post-SBR denitrification and observed no difference in resin capacity when using the treated permeate as regenerant to freshly prepared brine. Several MBR investigations have also reported complete retention of both biomass and high MW organics by the membrane (Cyplik et al., 2007; Rosenberger et al., 2006; McAdam et al., 2007) providing a valid argument for its assessment for this duty. Such studies were all based on activated sludge, however; the impact of halophilic processes on permeate quality and IEX regeneration efficiency is uncertain.

Conventional anion IEX resin selectivity is hierarchical: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^-$, thus SO_4^{2-} out competes NO_3^- . Nitrate-to-sulphate selective resins are now capable of withstanding high sulphate concentrations; limited impact has been observed for the range 5-16 g SO_4^{2-} .L⁻¹ (van der Hoek et al., 1987; van der Hoek et al., 1988). However, the reduction of sulphate can potentially lead to the formation of sulphide

which is particularly toxic in its hydrogenated form H_2S . Bicarbonate is concentrated during IEX and is also generated during denitrification (Clifford and Liu, 1993). Though not significantly inhibitory to the reduction process, its use as a co-regenerant as suggested by Bae et al. (2002) also requires further investigation.

2.8 PROCESS

2.8.1 Configuration and performance

Resin can either be operated in complete (90-100 % nitrate removal) or partial (40-60 % nitrate removal) regeneration, dictating regenerant volume and so reactor size (Liu and Clifford, 1996). van der Hoek et al. (1988) pioneered anionic IEX-bioprocessing, using an upflow sludge blanket reactor (USBR) followed by sand filtration for bacterial removal. Following successful bench-scale demonstration, the authors built a 3.3 m^3 USBR pilot plant at a site with an average nitrate concentration $13.8 \text{ mgNO}_3^- \cdot \text{N} \cdot \text{L}^{-1}$ (Matějů et al., 1992; van der Hoek et al., 1990). The USBR was operated at an upflow rate $11 \text{ m}^3 \cdot \text{h}^{-1}$ and achieved 90% $\text{NO}_3^- \cdot \text{N}$ removal, resulting in a brine volume reduction of 40 to 80% (Matějů et al., 1992; van der Hoek et al., 1990). However, steady-state was difficult to achieve due to a considerable chloride concentration and a varying nitrate load resulting in nitrite accumulation (Matějů et al., 1992). Vallero et al. (Vallero et al., 2003) also reported difficulties in acclimating biomass to NaCl concentrations $>7.5 \text{ g} \cdot \text{L}^{-1}$ in a USBR due to washout and found growth of halotolerant species was only possible if the HRT was extended to 80 h (Vallero et al., 2003).

In an attempt to avoid sulphate accumulation, Bae et al. (2002) used two USBRs in series to process IEX brine, the first targeting NO_3^- and the second targeted SO_4^{2-} . Despite variations in influent concentration (30 gNaCl.L^{-1} , $0.6\text{-}1.7 \text{ gNO}_3^-\text{-N.L}^{-1}$ and $0.5\text{-}2.5 \text{ g SO}_4^{2-}.\text{L}^{-1}$) 96% removal was observed in the denitrifying reactor at a loading rate $5.4 \text{ g NO}_3^-\text{-N.L}^{-1}.\text{d}^{-1}$ whereas sulphate reduction efficiency remained at ~62% at a loading rate of $1.8 \text{ g SO}_4^{2-}.\text{L}^{-1}.\text{d}^{-1}$ (Bae et al., 2002). More recently, the same authors (Bae et al., 2004) explored the feasibility of sulphate sedimentation by the addition of barium chloride followed by enhanced coagulation with ferric chloride. However, chemical and capital costs pertaining to rapid mixing and separation stages probably outweigh the advantages offered.

Hollow fibre membrane biofilm reactors (MBfR) operate by supplying hydrogen gas (H_2) through the lumen of gas permeable hollow fibres to a biofilm developed on the shell side of the membrane (McAdam and Judd, 2006). This method has been trialed for nitrate removal from drinking water (Lee and Rittmann, 2002) and more recently for perchlorate and nitrate reduction in brine (Chung et al., 2007) (Table 2). Following inoculation from a salt pond, low reduction rates were observed for commercial (150 gNaCl.L^{-1} Purolite) brine. Subsequent dilution by 50% increased reduction significantly. Studies with synthetic brine (20 gNaCl.L^{-1}) containing nitrate, perchlorate or both produced rapid reduction, though the efficiency reduced by 40% when NaCl concentration was increased to 40 g.L^{-1} . H_2 pressure was not determined as the limiting factor and as salt concentration was reduced from 40 to 20 g.L^{-1} , reduction capacity significantly increased confirming that the micro-organisms were inhibited by high salt content (Chung et al., 2007). It was suggested that

improvements could be made by reducing salt concentration, increasing H_2 pressure, accumulating more active biomass, or otherwise enhancing the intrinsic biokinetics.

Externally configured pressure driven membrane bioreactors have also been studied for brine produced from electrodialysis (Wisniewski et al., 2001) and IEX (Cyplik et al., 2007). The inherent benefits of MBR are greater process control, complete biomass and high MW organics retention, which not only improves permeate quality but also safeguards against washout of halophiles as observed by Vallero et al. (2003). Cyplik et al. (2007) reported a maximum denitrification rate $1.3 \text{ g NO}_3^- \text{-N. g SS.d}^{-1}$ at an HRT 1.66 hours (solids retention time (SRT) 10 days) from a feed comprising 180 gNaCl.L^{-1} and $500\text{-}1000 \text{ mgNO}_3^- \text{-N.L}^{-1}$. The authors related this performance to high biomass concentration, opting for an extremophile as the monoculture (*Halomonas denitrificans*) and maintaining a highly saline environment reducing microbiological competition. A reasonable specific denitrification rate of $0.3 \text{ gNO}_3^- \text{-N. gVSS}^{-1} \text{.d}^{-1}$ was also observed by Wisniewski et al. (2001) treating ED brine, though the ionic concentrations of the concentrate flow were comparatively low.

Table 2.8 *Process characteristics and operating parameters.*

Reactor type	Scale (m ³)	Electron Donor	Principal Bacterium	Salinity Range (g.L ⁻¹)	mgNO ₃ ⁻ -N.L ⁻¹		Specific Denit. Rate (gN.gSS.d ⁻¹)	Loading Rate (kg.m ⁻³ .d ⁻¹)	Operating Parameters					MLSS (g.L ⁻¹)	Ref.
					In	Out			Temp. (°C)	pH	HRT (h)	SRT (d)	C:N (g.g ⁻¹)		
MBR Sulphate	0.006	Acetate Ethanol	<i>Desulfobacter halotolerans</i>	50	-	-	5.5 ^f	6.6 ^f	33	7.2	8-36	N/a	0.5 ^e	0.85 ^h	Vallero et al., 2005
MBR ED-Concentrate ^a	0.013	Ethanol	Adapted AS	34 ^j 476 ^k	106-534	0.6-1.7	0.29	0.48-0.72 ^r	20	6.3-9	5	7	1.3	0.5-2.5	Wisniewski et al., 2001
MBR IEX-Brine ^a	0.005	Methanol	<i>Halomonas denitrificans</i>	180	500-1000	N/a	0.7-1.3	12-48 ^r	N/a	7	1.25-5	7	1.3	10	Cyplik et al., 2007
SBR IEX-Brine ^a	0.0015	Methanol	Adapted AS	14.6-29.2	610-835	95%	N/a	0.65-0.89 ^r	22	9.1	10.5-22.5 ^m	N/a	0.9-1.3	3.2-4.4	Clifford and Liu, 1993
SBR High salinity ^a	0.03	Acetate	Adapted AS	35-71	2700-8200	0	0.46-1.2	2.7-8.2 ^r	N/a	9	24 ^L	12	1.5	12-38	Glass and Silverstein, 1999
USBR ^a	0.005	Methanol	N/a	5-25	N/a	N/a	0.38	12 ^{r, u}	N/a	8.8-9.2	0.3-0.55	N/a	0.8	32	Van derHoek et al., 1988
MBfR IEX-Brine ^b	11.7 mL	Hydrogen	Salt pond Inoculum	10-40	200-1000 ^r 500 ^s	57-692 ^r 184-499 ^s	N/a	0.032-0.087 ^q	N/a	N/a	108.6	N/a	3-5 ^t	N/a	Chung et al., 2007
IEX-Brine ^a	Batch Kinetic	Lactate Glycerol Acetate	<i>Halomonas campisalis</i>	125 (88 ^c)	113	0	0.3-0.65	N/a	4-45	9	N/a	N/a	<i>In excess</i>	25-43 ^d	Peyton et al., 2001
MBR High salinity	0.021	N/a	Mixed yeast/ Mixed bacteria	32	5000 ⁿ	N/a	0.93 ^p	N/a	N/a	3.5-4	4.5-16.1	15	N/a	4500	Dan et al., 2002

^aNO₃⁻. ^bNO₃⁻ & ClO₄⁻. ^cOptimum growth occurring at 88 g.L⁻¹. ^dmg.L⁻¹. ^eCOD/ SO₄²⁻. ^fSO₄²⁻. ^hVSS.L⁻¹. ^jNa⁺ concentration mg.L⁻¹. ^kCl⁻ concentration mg.L⁻¹. ^LBatch cycle: 22h reaction, 0.25h fill, 1.25h settle, 0.5 h withdraw. ^mFill 10 min, reaction 8-20 h, settle 2.5 h, draw 10 mins. ⁿCOD. ^pgCOD.gMLSS.d⁻¹. ^qnitrate flux g.m⁻².d⁻¹. ^rNO₃⁻-N. ^sClO₄⁻. ^tH₂ pressure (PSI). ^uMaximum concentration.

2.8.2 Membrane fouling

In non-halophilic communities, it is commonly acknowledged that salinity induces cell dehydration (Vallero et al., 2005) or plasmolysis (Reid et al., 2006), manifested as an increase in the soluble COD (Kincannon and Gaudy, 1968). Subsequently cell lysis or decay can result in release of carbohydrates, proteins and nucleic acids which are recognised membrane foulants (Judd, 2006) and can also affect surface charge, hydrophobicity and the flocculation process (Dan et al., 2002; Judd, 2006]. Reid et al. (2006) observed that both carbohydrate and proteins increased with increasing salinity and identified a weak negative correlation between permeability and SMP carbohydrate. Recent MBR studies have indicated that fouling associated with non-halophilic micro-organisms exposed to NaCl is more onerous than that from the use of halophilic bacteria, where larger biological flocs (and lower concentrations of fine particles) are generated (Vallero et al., 2005) and fouling can be controlled by physical means, rather than the use of aggressive chemicals to maintain membrane permeability (Cyplik et al., 2007) (Table 5).

Table 2.9 *Membrane operating parameters.*

Process/ Feed	Membrane			Reactor vol. (m ³)	Flux, <i>J</i> (l.m ⁻² .h ⁻¹)		Membrane Parameters				Cleaning		Ref.	
	Configuration/ type/ material	Pore size (μm)	Area (m ²)		TMP (bar)	<i>dP/dt</i> (mbar. min ⁻¹)	<i>K</i> (<i>J</i> .bar ⁻¹)	CFV (m.s ⁻¹)	Gas flow (l.min ⁻¹)	Phys.	Chem.			
												Op.		Crit.
MBR-PD Sulphate	Imm./ cylindrical/ Polysulphone	0.2	0.07	0.006	4.7- 17.1	18-21	N/a	0.009- 0.095	~235 ^a	N/a	1.4 ^c 1.2 ^d	Backflush ^j / Relaxation	NaOCl Citric acid ^k	Vallero et al., 2005
MBR-PD ED Brine	Ext./ tubular/ Ceramic	0.05	0.2	0.013	13	N/a	1.35	N/a	1000 ^a	1.32	N/a	N/a	Chemical Regen. ^L	Wisniewski et al., 2001
MBR-PD IEX Brine	Ext./ tubular/ Ceramic	0.22	0.26	0.005	24.6- 73	N/a	0.5-3	0.0014 ^m	21.5- 55.4 ^b	2	N/a	N/a	1M NaOH 0.1 M HCl	Cyplik et al., 2007
MBR-Df IEX Brine	Imm./ HF/ Polyethylene	0.4	0.53	11.7 ^e	N/a	N/a	N/a	N/a	N/a	150 ^f 570-766 ^g	3-5 ^h	N/a	N/a	Chung et al., 2007

CFV – Cross flow velocity. *K* – Permeability. Imm. – Immersed. Ext. – External. PD – pressure driven. Df – Diffusive. ED – Electrodialysis. HF – Hollow fibre.

^aApproximate Initial permeability. ^b*K* recorded at 2.5 bar for biomass concentrations ranging 5-15 g.L⁻¹. ^cN₂ gas sparge. ^dSpecific gas demand per unit membrane area (SGD_m), m³.m⁻².h⁻¹. ^emL. ^fRecirculation rate, mL.min⁻¹. ^gLiquid velocity, cm.min⁻¹. ^hHydrogen gas pressure, psi. ^jBackflush instigated when TMP>0.15 bar. When TMP <0.15 bar, relaxation was used. ^kChemical clean initiated when TMP>0.4 bar (1g NaOCl.L⁻¹ for 1 hour, 3g citric acid.L⁻¹ for 1 hour). ^LMembrane chemically regenerated until within 10% of its initial water *K*. ^mJ.min⁻¹.

2.9 CONCLUSIONS

- Halophilic denitrifying species can be collected from a series of hypersaline environments. The resultant bacteria are capable of high specific reduction rates in highly saline conditions (up to 180 g.L^{-1} reported). Their affinity to NaCl concentration is a function of the microbial community present, i.e. whether they can be classified as mild, moderate or extremely halophilic.
- Non-halophilic groups are limited to NaCl concentrations $<30 \text{ g.L}^{-1}$, require step-wise acclimation procedures and adapt poorly to NaCl variability.
- No finite conclusion can be reached to date on the influence of nitrate and perchlorate on reduction rate during simultaneous degradation or the microbial communities involved. Neither can an optimum substrate be suggested on the basis of current published research.
- The influence of extra concentrated anions (HCO_3^- , SO_4^{2-}) on biological performance is limited; bicarbonate can reduce specific reduction rates however, it also serves to create more alkaline conditions which improves biodegradation.
- Sulphate does not impact on the capacity of anion specific resins; accumulation can be hazardous if it is reduced to its sulphide form. Although biological and physical treatment of sulphate has been demonstrated, the added process complication and cost overshadows the advantages. Bicarbonate could be considered as a dual regenerant in some cases.
- A filtration/ separation step is essential to protect the resin from high molecular weight organics. MBR offers high MW organics retention and biomass retention thereby protecting permeate quality and facilitating uncomplicated acclimation conditions for halophilic bacteria.

- The fouling tendency of non-halophilic bacteria is significant in the presence of salt. In contrast, halophilic biomass appears to flocculate well and generate only small concentration of fine particles. However, solids concentration has a significant influence upon permeability decay.

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CHAPTER 3

DENITRIFICATION FROM DRINKING WATER USING A MEMBRANE BIOREACTOR: CHEMICAL AND BIOCHEMICAL FEASIBILITY

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3 DENITRIFICATION FROM DRINKING WATER USING A MEMBRANE BIOREACTOR: CHEMICAL AND BIOCHEMICAL FEASIBILITY

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ABSTRACT

Interest is growing in developing MBR to replace ion exchange for nitrate removal from drinking water. However, few published studies have successfully managed to retain exogenous or biologically derived carbon. This study determined an optimum C:N by substrate breakthrough rather than maximum nitrate removal. By dosing <C:N 1.52, ethanol (electron donor) could be retained and nitrate removal up to 92% observed. Carbon limited control led to nitrite formation $<0.35 \text{ mg NO}_2^- \text{-N}$ which was oxidised to $<0.02 \text{ mg NO}_2^- \text{-N.L}^{-1}$ by chlorination. Residual organics showed little competition with nitrite during short term chlorination thus chlorine demand could be predicted by the nitrite residual ($5.0 \pm 0.1 \text{ mg Cl}_2 \text{.mg NO}_2^- \text{-N}^{-1}$). Biomass was completely retained and low residual DOC ($0.4 \pm 0.7 \text{ mg.L}^{-1}$) indicated high rejection of influent DOC and soluble microbial products (SMP). Residual DOC exhibited low reactivity with long term chlorination (THMFP $72.7 \pm 7.7 \text{ } \mu\text{g.L}^{-1}$) however, the impact of substrate breakthrough on THMFP was significant. Immersed heterotrophic MBR produced consistent high quality product water at steady-state, comparing favourably to previously trialled heterotrophic fixed film membrane and packed bed processes.

3.1 INTRODUCTION

The nitrate concentration in many abstracted waters worldwide now exceeds regulatory standards (US and EU, 10 and 11.3 mgNO₃⁻-N.L⁻¹ respectively) specifically instigated to safeguard against the risk of methemoglobinaemia (blue baby syndrome). Following approval in the 1980's, several full-scale drinking water biological denitrification units were implemented in Europe (UK, France, Germany) to treat nitrate laden waters, with individual capacity ranging from 720 to 9600 m³.d⁻¹ (Richard, 1989). These were dominantly packed bed processes and were often subject to mass transfer problems associated with channelling (caused by clogging) and nitrite accumulation due to biofilm control issues (excess sludge age through insufficient washing) (Richard, 1989). Additionally, process scale and downstream processing required to remove nitrite, micro-organisms and biologically derived and exogenous carbon resulted in high capital investment.

As such, ion exchange has since been principally selected for nitrate removal. More recently, difficulties associated with brine disposal and concerns over energy conservation (as well as cost) have reduced the commercial attractiveness of ion-exchange, reverse osmosis or electrodialysis and consequently biological denitrification has again been considered, and, on a small scale, implemented. However, regulatory approval of full-flow denitrification has been hampered by the microbial contamination of the treated potable water, with regulators now demanding post filtration membrane technology as an effective microbial barrier (Sanders, 2004).

MBR offers a more integrated approach, though development for drinking water applications is still in its infancy and only limited research has been conducted (Nuhoglu et al., 2002; Delanghe et al., 1994); Urbain et al. (1996) have reported on the only full-scale ($400\text{m}^3.\text{d}^{-1}$) potable denitrification membrane bioreactor (MBR) which used pressure driven membranes, though laboratory scale extractive and diffusive MBR have also been evaluated (McAdam and Judd, 2006). Process feasibility is determined by balancing substrate addition; too much substrate leads to breakthrough, whilst too little results in nitrate leakage and nitrite formation (more strictly regulated by-product 0.03 and $1\text{ mg.L}^{-1}\text{ NO}_2^- \text{-N.L}^{-1}$, EU and US standards respectively). Ergas and Rheinheimer (2004) found that even when operating an extractive denitrifying MBR under substrate limited conditions, methanol (the applied electron donor) was detected in the permeate. Delanghe et al. (1994) determined an optimum C:N dose through batch trials but reported carbon breakthrough ($5\text{-}10\text{ mg Total Organic Carbon (TOC).L}^{-1}$) when operating an externally configured pressure driven MBR continuously, though the authors postulated that the carbon source was at least partially attributable to soluble microbial products (SMP) generated by the high shear requirement of the membrane module. Similarly, Change and Tseng (1993) reported an effluent COD $50\text{-}200\text{ mg.L}^{-1}$ when applying methanol to a diffusive MBR, though again the authors were unable to discriminate whether the source was excess methanol or SMP. Clearly membrane configuration and operating parameters are important in controlling both exogenous and biologically derived carbon, the retention of which is not only important in reducing downstream processing, but also because both forms of carbon can constitute disinfection by-product (DBP) precursors (Mo et al., 2005). Lee and Rittmann (2002) successfully developed an immersed hollow fibre membrane biofilm reactor (HF-MBfR) to circumvent the application of exogenous

carbon, which provided hydrogen gas (electron donor) dissolution through the lumen of the hollow fibres to a biofilm developed on the shell-side. Mo et al. (2005) continued this development by combining immersed hollow fibre gas dissolution with immersed pressure driven membrane separation (0.04 μm) to retain any sloughed biomass however, the authors reported carbon breakthrough up to 8 mg Dissolved Organic Carbon (DOC).L⁻¹, postulating the source to be SMP.

Although hydrogen gas dissolution has proven to be effective, mass transfer problems associated with biofilm formation (McAdam and Judd, 2006), membrane fragility (Rezania et al., 2007) and the absence of a biomass separation step potentially limit process application. Organic substrates are comparatively simple to implement however, retention of both substrate and SMP in the literature to date has been poor. The main objective of this paper is therefore to establish whether a definable 'breakthrough' substrate dosing point exists. The optimum C:N is typically defined in batch conditions and to solely maximise nitrate removal however, in this investigation, emphasis is on defining an optimum C:N under continuous steady-state conditions that provides substrate retention, rather than maximising nitrate removal. Of the few pressure driven MBR studies conducted, external configuration has been favoured to avoid aeration employed for immersed membrane scouring, thereby maintaining an anoxic environment. However, immersed membranes promote lower biomass shear, reducing the potential for SMP generation. Thus immersed membranes are employed in this study (scoured with nitrogen) and the permeate quality monitored to establish whether SMP and biomass impact upon permeate quality and finally whether the residual DOC (derived from feed, substrate or biomass) constitutes a DBP pre-cursor.

3.2 MATERIAL AND METHODS

3.2.1 Experimental Setup

The experimental setup consisted of a 5 L bioreactor with an immersed hollow fibre PVDF module (Zenon Env., ZW-1), nominal pore size 0.04 μm (Figure 3.1). The bioreactor lid was completely sealed using a 360° clamp. Permeate was extracted via peristaltic pump (Watson Marlow) at a flux of 9.4 $\text{L.m}^{-2}.\text{h}^{-1}$ yielding an HRT 5.75 hours. Nitrogen enriched air (>99%) generated from a nitrogen selective hollow fibre membrane (N_2 Gen Ltd., TN-210) was injected into the base of the module for membrane scouring. Gas flow was set to provide an intensity 0.011 $\text{m}^3.\text{m}^{-2}.\text{s}^{-1}$ (SAD_m 0.97 $\text{m}^3.\text{m}^{-2}.\text{h}^{-1}$). Backwashing was instigated every 30 minutes by reversing permeate flow using proprietary control software operated by a PC. Trans-membrane pressure was measured (Endress and Hauser, PMP-41), converted (Pico technology, ADC-16) and finally stored on the PC. Once trans-membrane pressure reached ~35 kPa, the membrane was removed, rinsed and soaked in NaOCl (500 mg.L^{-1}) for 5 hours. During this period, a spare module was inserted to maintain stable operation. Though gas injection provided mixing, complete mixing was ensured by adding a magnetic stirrer (Drehzahl, IKAMEG® REO). A conductivity probe (inserted and

sealed inside the reactor) measured reactor liquid level. Upon liquid level deviation (<50 mL), an integrated control unit (Broyce Control, B8LCR) actuated a solenoid valve sited at the base of the feed tank and restored reactor liquid volume. Off-gas was released via a non-return valve. Constant temperature (25°C) was maintained by submerging the reactor in a water bath controlled by a recirculation heater/ pump (Grant, VFP). pH was maintained with a phosphate buffer pair (pH 8±0.1).

3.2.2 Feed Solution and analysis

3.2.2.1 Feed solution, acclimatisation and sampling

A trace mineral solution adapted from Barreiros et al. (1998) was supplemented into the feed solution at 0.1% v/v to ensure non-limiting mineral conditions. Synthetic feed water comprised tap water (from a groundwater abstraction) (dissolved oxygen (DO) 5.3±1.1 mg.L⁻¹) amended by a nitrate concentrate. Ethanol was selected as an inexpensive, non-toxic exogenous carbon source and was delivered constantly via an ultra low flow (0.002 µL.min⁻¹) peristaltic pump (Masterflex, C/L).

Biomass was sampled from an activated sludge process and run in batch mode (5 L) for 45 days (10 day solids retention time (SRT)) to acclimatise the bacteria on a feed comprising nitrate amended tap water, ethanol and trace mineral solution. The bioreactor was subsequently seeded 10:1 (tap water: biomass) and allowed to acclimatise for 3 SRT (10 day SRT). Following this period, steady state was assumed to exist when MLSS, permeate nitrate and ethanol concentrations were stable. Sludge

was wasted daily using a peristaltic pump and measured with a volumetric cylinder. Each C:N setting was conducted by setting influent nitrate concentration constant and progressively increasing ethanol concentration. At each ethanol concentration, two weeks passed before sampling began. Sampling of the influent, biomass and permeate were carried out daily until steady state values were observed. Upon increasing nitrate concentration, a minimum 3 SRTs passed before testing began.

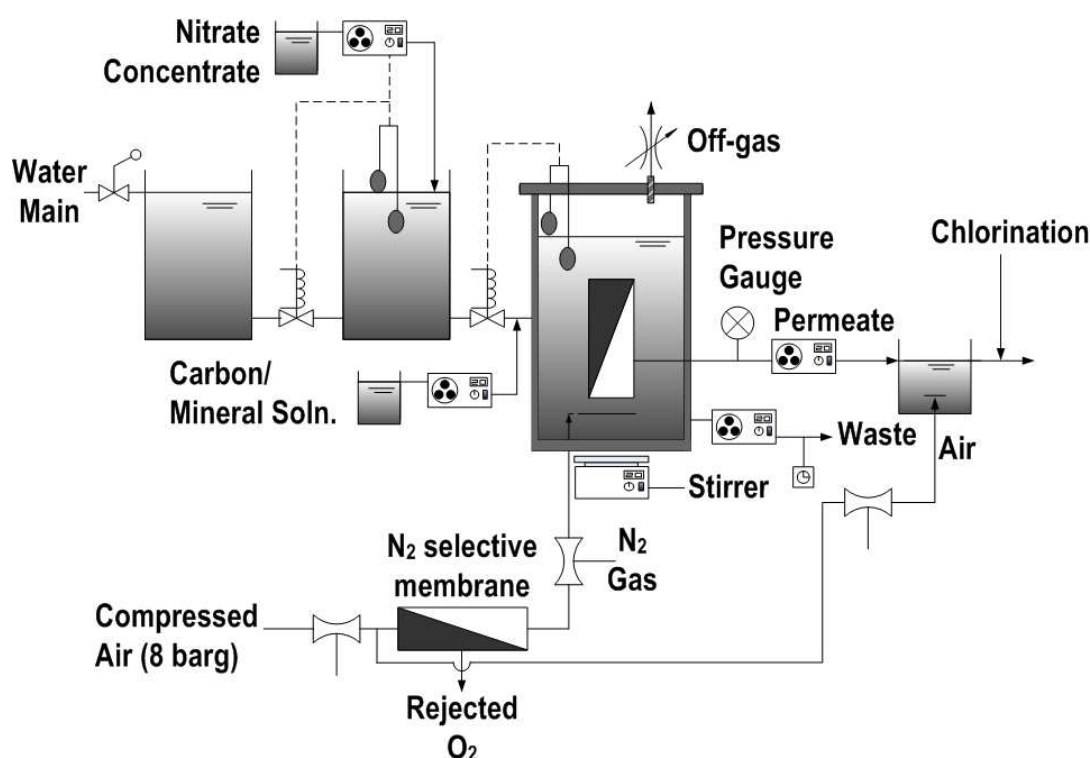


Figure 3.1 *Experimental reactor design.*

3.2.2.2 Standard analysis

Nitrate, nitrite and ammonia were analysed using a UV-spectrophotometric method (Spectroquant, NOVA 60). Ammonia concentrations were consistently low, in the range $<0.01\text{--}0.02\text{ mg NH}_4^+\text{-N.L}^{-1}$ and are therefore not reported in the text. Ethanol concentration was determined using the commercially available Boehringer-

Mannheim enzymatic method adopted by Velizarov et al. (2001) in another drinking water MBR investigation. Sample preparation prior to analysis involved the oxidation of ethanol and subsequent spectrophotometric determination at 340 nm. A linear calibration curve ($R^2 = 0.99$) was generated with a range of ethanol standards (0.5, 1, 2, 5, 10, 20 and 50 mg.L⁻¹) and validated the lower limit of detection (0.5 mg.L⁻¹) proposed in the original method. UV_{254nm} absorbance was determined by UV-spectrophotometric determination (Jenway, 6310). Mixed liquor Suspended Solids (MLSS) and heterotrophic plate counts (HPC) were determined by standard methods (APHA, 1998). Dissolved organic carbon was analysed using a total organic carbon analyser (Shimadzu, TOC-5000). Turbidity was measured using a HACH (2100N) turbidimeter. Serial fractionation was undertaken using an Amicon 8400 series stirred cell and standard Millipore membranes, size range 10, 30, 50, 100 and 300 kDa. Size exclusion chromatography (SEC) was performed with a Shimadzu *LC-10AD* liquid chromatograph fitted with a Phenomenex BiosepTM Sec-S column and subsequent UV_{254nm} detection. Floc size was measured with a Malvern Mastersizer 2000. Carbohydrates were measured using the phenol-sulphuric acid method with glucose as the standard. pH and DO were measured with Jenway submersible probes (pH 350; DO 970).

3.2.2.3 Chlorine demand and tri-halo methane formation potential analysis

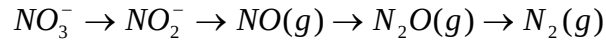
Chlorine demand was determined by adding a chlorine standard to samples followed by 30 minutes reaction time at 20±1°C. Free chlorine measurements were immediately determined using DPD powder pillows (Camlab Ltd., UK) and subsequent spectrophotometric determination (HACH, DR/2500). Prior to

chlorination, permeate samples underwent re-aeration to a target concentration of 8 mg.L⁻¹ (air flow rate 2 L.min⁻¹, HRT 2 minutes, tank volume 0.25L). Re-aeration did not impact the oxidation state of nitrite. THM-FP was carried out using a method adapted from standard methods (APHA, 1998) and involved buffering samples at pH 7, chlorinating samples with excess free chlorine (10mg Cl₂.mg DOC) and storing samples at 20°C for 7 days to allow the reaction to approach completion. Individual THM concentrations were measured using Gas chromatography-Mass Spectrometry (Perkin Elmer).

3.3 RESULTS AND DISCUSSION

3.3.1 Defining the optimum C:N

The target NO₃⁻ influent concentration was set at 14.7 mg NO₃⁻-N.L⁻¹ (actual, 14.8±0.4 mg NO₃⁻-N.L⁻¹). With sufficient nitrate supplied under anoxic conditions, bacterial growth is limited by the available organic carbon (Marazioti et al., 2003) therefore ethanol was progressively dosed step-wise to determine the appropriate C:N ratio by carbon limitation. A maximum nitrite concentration of 7.3 mg NO₂⁻-N.L⁻¹ was recorded when C:N was set at 0.85 (within 'carbon limited' conditions) and corresponded to approximately 50% of the initial nitrate concentration. Accordingly nitrate was reduced below the legislative limit (EU 11.3 mg N.L⁻¹) to 6.2 mg NO₃⁻-N.L⁻¹. Previous investigations have defined the reduction of nitrate to nitrogen gas (Eq. 1) as a two-step mechanism in batch mode which proceeds as follows: (1) complete NO₃⁻ reduction with simultaneous NO₂⁻ accumulation; followed by (2) nitrite conversion to dinitrogen gas (N₂) (Marazioti et al. (2003)).



(1)

Though analysis herein (Figure 3.2) is broadly characterised by this mechanism, in contrast to previous investigators, the separation of phases, caused by nitrate inhibiting the nitrite reductase enzyme (Foglar and Briški, 2003), is less apparent and nitrite and nitrate reduction occurred simultaneously in the second phase.

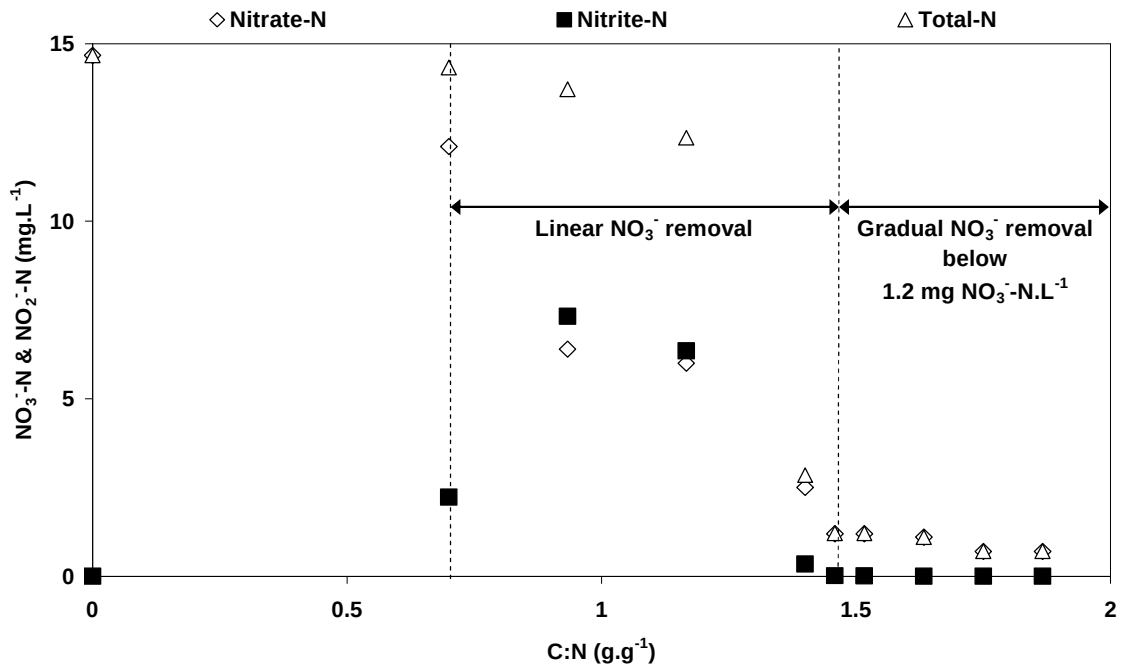


Figure 3.2 Nitrate removal mechanism with increasing carbon addition.

This effect is best characterised by the total N removal trend (Figure 3.2), where the sum of nitrate and nitrite nitrogen reduces with increasing applied C:N. This is particularly apparent when the C:N ratio is increased beyond the observed nitrite maxima. Whilst several operating conditions can be used to manipulate this relationship, it is considered that this simultaneous reduction is a response to continuous operation (lowering nitrite accumulation potential) and the presence of true denitrifiers. Minimisation of nitrite accumulation is important for regulatory

reasons but also, as Foglar and Briški (2003) observed, faster nitrate removal can be achieved where low nitrite accumulation occurs. Beyond a C:N ratio of 1.45, nitrite was reduced to $0.02 \text{ mg NO}_2^- \cdot \text{N} \cdot \text{L}^{-1}$ (below EU and US regulatory standards).

For C:N ratios ranging 0.72-1.45, nitrate concentration declined linearly and the percentage removed was directly proportional to the applied C:N ($0.89 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{mg C applied}$) (Figure 3.2, linear removal $R^2 = 0.93$). This corroborates the work of Glass and Silverstein (1998) who observed zero-order linearity when both carbon and nitrate or nitrite concentrations were non-limiting. Beyond C:N ranging 1.45-1.52, linearity was lost, indicating the commencement of nitrogen limited conditions (Mohensi-Bandpi and Elliott, 1998) and the definition of the optimum C:N ratio with respect to NO_3^- removal. At this dosing point, permeate nitrate and nitrite concentrations corresponded to 1.2 ± 0.1 and $0.02 \pm 0.005 \text{ mg} \cdot \text{L}^{-1}$ respectively. Beyond this C:N range (1.45-1.52), nitrate removal was best described as an exponent of the applied C:N ratio (Figure 3.4). Researchers have reported that activated sludge becomes nitrate-limited only below $0.07 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{L}^{-1}$ (Moore and Schroeder, 1971). However, in this study nitrate limitation was determined at $1.2 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{L}^{-1}$. This significantly higher value could be explained by inhibition of nitrate reduction by nitrite at low nitrate concentrations (Timmermans and Van Haute, 1983). Abeling and Seyfried (1992) found nitrate inhibition occurred when HNO_2 reached $0.13 \text{ mg} \cdot \text{L}^{-1}$ ($0.04 \text{ mg N} \cdot \text{L}^{-1}$). In the current study $\text{NO}_2^- \cdot \text{N}$ concentrations were below $<0.02 \text{ mg} \cdot \text{L}^{-1}$ when $\text{C:N} \geq 1.45$, suggesting that this bacterial community is more susceptible to inhibition than found in previous investigations. Once operating in nitrate limited conditions, ($\text{C:N} > 1.52$), ethanol breakthrough occurred (ethanol consumed = ethanol dosed - ethanol measured in effluent) (Figure 3.3). Even with a significant ethanol

concentration available in the bulk solution, the impact on nitrate removal was negligible and corresponded to a removal rate of 0.097mg N per mg C applied - an order of magnitude below that observed under carbon limited conditions.

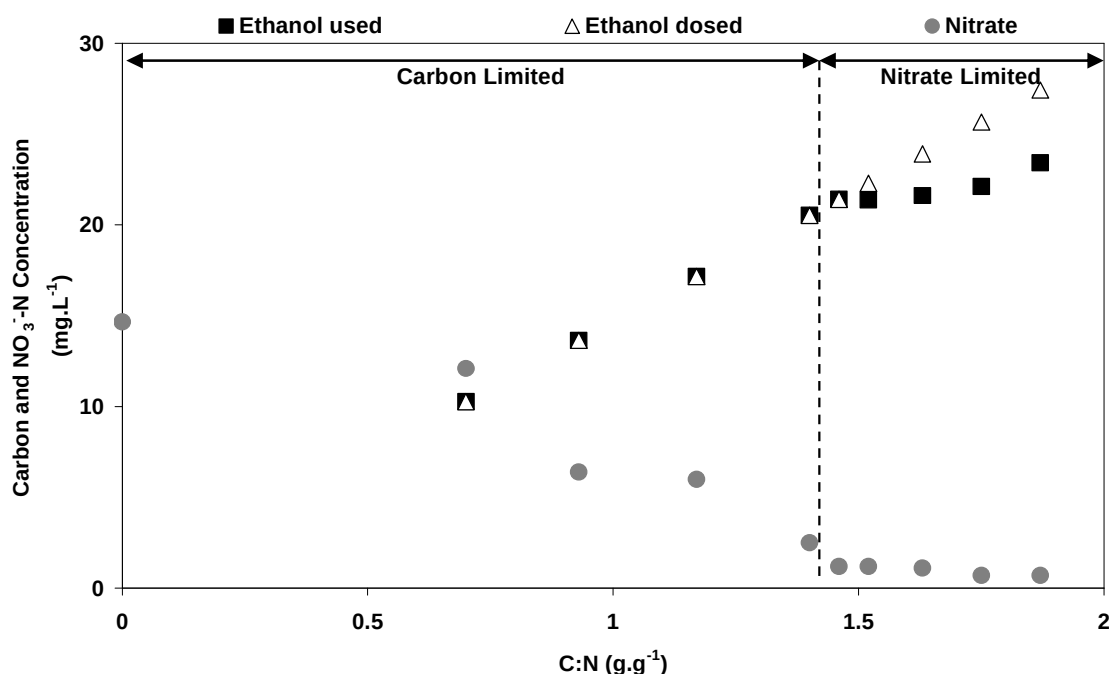
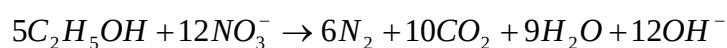


Figure 3.3 Definition of substrate breakthrough versus nitrate removal.

The optimum C: N ratio is above that typically reported bioenergetically for ethanol (Eq. 2, 0.71 gC.gN⁻¹, Gayle et al., 1989).



(2)

However, C:N ratios ranging 0.84-1.39 gC.gN⁻¹ have been reported (Green et al., 1994) suggesting significant variation. Following bioenergetic evaluation (based on 60% assimilation efficiency), Green et al. (1994) determined a C:N ratio of 1.46, correlating closely to that determined in this study and postulated that variation in C:N corresponded to metabolic pathway diversity, though this relationship can also differ with competing physical parameters. Nitrogen gas scouring was found to

principally purge the influent DO in this study, as was observed during nitrogen gas cessation.

Based on this study, MBR at full-scale could be operated at an optimum C:N ratio 0.7-0.85 (Figure 3.2) reducing nitrate below the regulatory limit ($7.9 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{L}^{-1}$), minimising ethanol consumption and introducing a significant factor of safety (2.05) for breakthrough. However, significantly more nitrite (up to $7.3 \text{ mg NO}_2^- \cdot \text{N} \cdot \text{L}^{-1}$) is produced when operating at low C:N ratios. Furthermore, as a replacement for ion exchange, the process is more likely to be implemented as a blending process treating partial flow thus nitrate removal must be maximised to reduce process scale. Rather than use C:N as a set-point, it is more plausible to define a process window (Figure 3.4) and control dosing by the permeate $\text{NO}_3^- \cdot \text{N}$ concentration (C:N 1.45; $1.2 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{L}^{-1}$). This permits an allowable process error of $\pm 1.03 \text{ mg C} \cdot \text{L}^{-1}$ or $1.97 \text{ mg ethanol} \cdot \text{L}^{-1}$ (i.e. C:N 1.52 minus 1.45) based upon maximum $\text{NO}_3^- \cdot \text{N}$ removal before breakthrough. In this case, nitrite ($< 0.35 \text{ mg NO}_2^- \cdot \text{N} \cdot \text{L}^{-1}$) arises in the permeate necessitating further downstream processing.

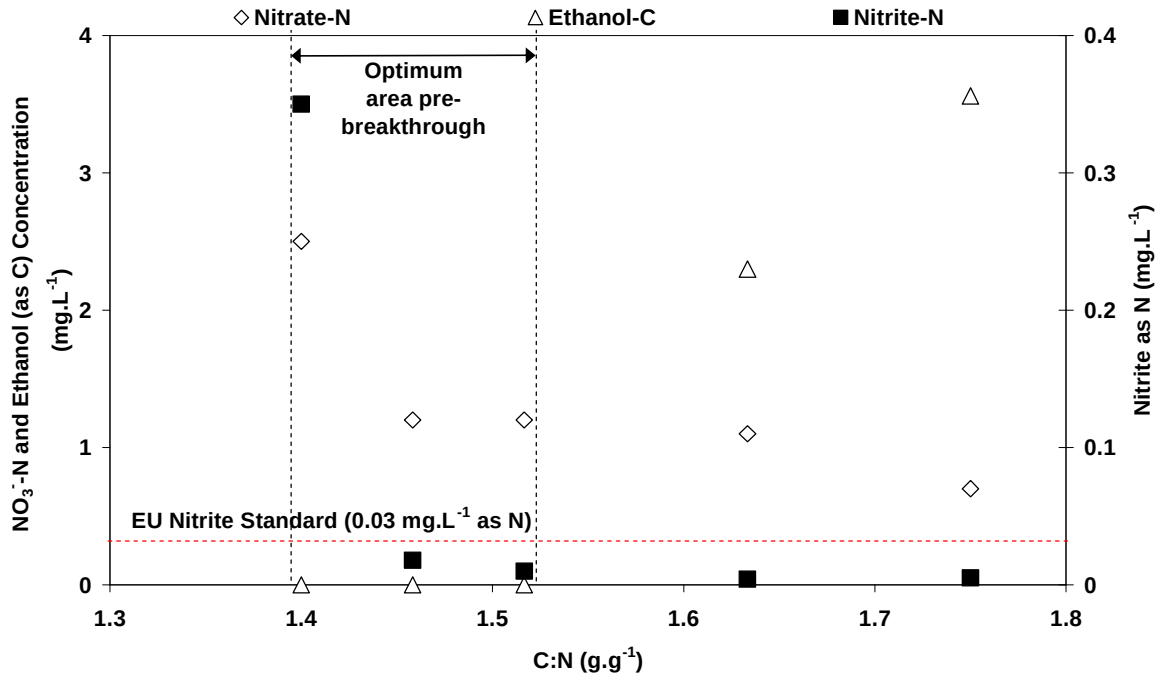


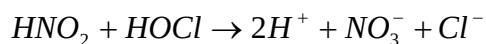
Figure 3.4 Defining an optimum area of operation which maximises nitrate and nitrite removal without permitting carbon breakthrough.

3.3.2 Chlorine addition

3.3.2.1 Nitrite demand

Diyamandoglu et al. (1990) demonstrated that nitrite could be oxidised to nitrate in aqueous solutions using chlorine gas. In this investigation, sodium hypochlorite (NaOCl) was used to oxidise nitrite in the MBR permeate at each C:N ratio to below the regulatory standard. The nitrite-chlorine demand ranged between 4.91 and 5.23 mg Cl₂.mg NO₂⁻.N⁻¹ (5.0±0.1 mg Cl₂.mg NO₂⁻.N⁻¹) yielding an approximate 1:1 stoichiometric molar ratio of chlorine/nitrite-nitrogen (Figure 3.5), in good agreement with the reactant molar ratio described in Eq. 3. This corroborates previous work

(Anbar and Taube, 1958; Diyamandoglu et al., 1990) and illustrates that the permeate organic residual consistently exerted a limited immediate chlorine demand.



(3)

Within the defined process window (i.e. maximising nitrate/ nitrite removal without yielding carbon breakthrough), a maximum chlorine demand of 2.5 mg.L⁻¹ was measured (Figure 3.6). Subsequent nitrate formation was <0.5 mg NO₃⁻-N.L⁻¹. Reduction in nitrite-chlorine demand was approximately linear beyond C:N 1.16 (Figure 3.5), with a demand corresponding to 125mg Cl₂.C:N⁻¹ (mass ratio). Beyond C:N 1.45, nitrite was reduced <0.02 mg NO₂⁻-N.L⁻¹ and no chlorine demand was observed. In practise, Urbain et al. (1996) operated a full scale drinking water MBR (groundwater; 400m³.d⁻¹) and reported permeate NO₂⁻-N consistently <0.015 mg.L⁻¹ despite regular breaks in process operation. The authors attributed this to superior substrate distribution however, it is unclear whether post-oxidation also contributed to this consistency.

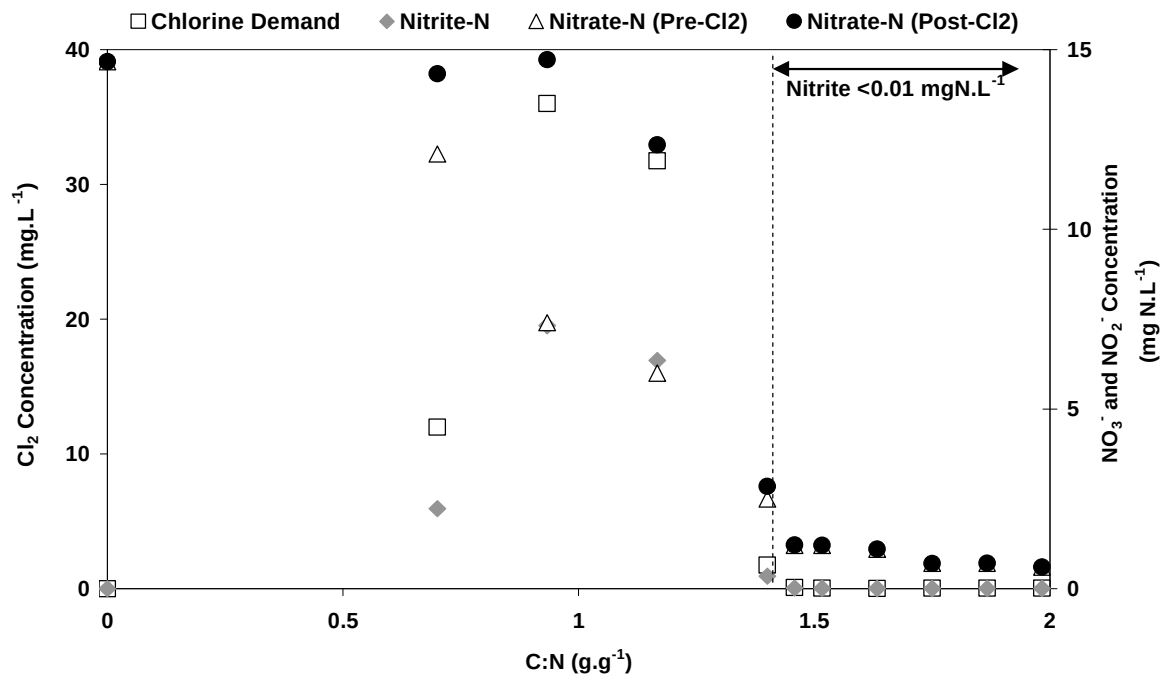


Figure 3.5 Chlorine demand for nitrite conversion.

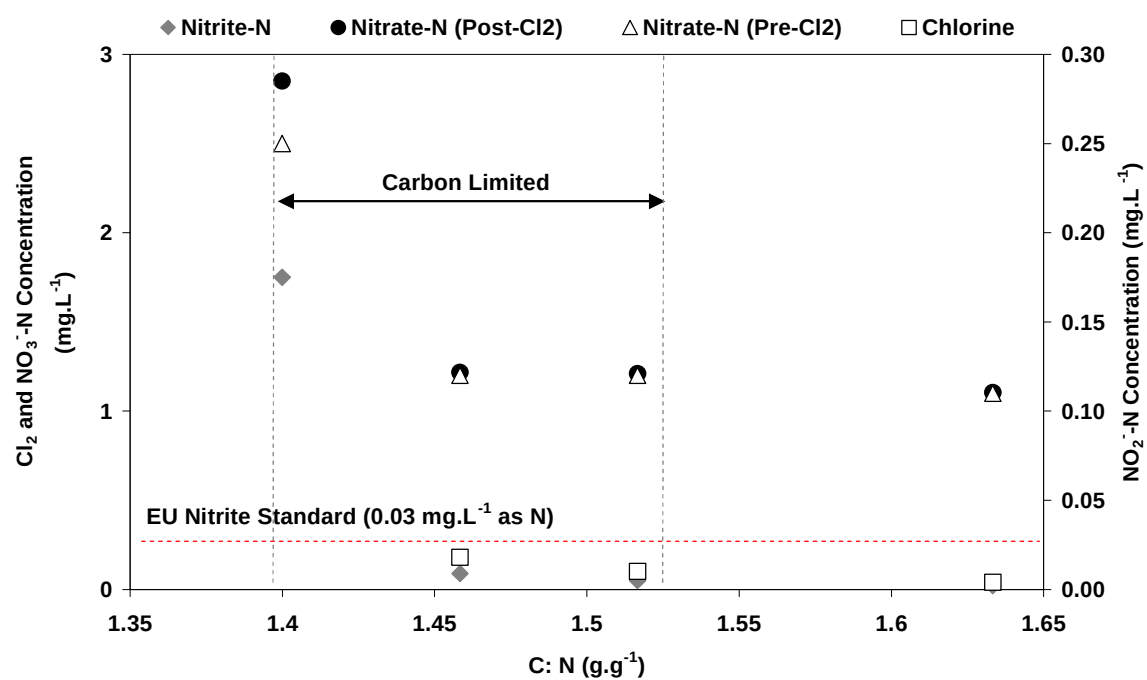


Figure 3.6 Chlorine demand within the arbitrarily defined operating window.

3.3.2.2 Tri-halomethane Formation Potential (THM-FP)

Biologically-derived DOC can have a significant impact on disinfection by-product formation (DBP) (Schmidt, 1998) as can the electron donor (Mo et al., 2005) and potentially the influent (Li et al., 2003). During carbon limited conditions (0.7 – 1.52), THMFP samples consisted primarily of trichloromethane (CHCl_3) ranging 19.71-57.28 $\mu\text{gTHMFP.L}^{-1}$ (27.4-71.6% conversion) and chlorodibromomethane (CHClBr_2) ranging 18.12-33.57 $\mu\text{gTHMFP.L}^{-1}$ (18.1-33.6% conversion) (Figure 3.7).

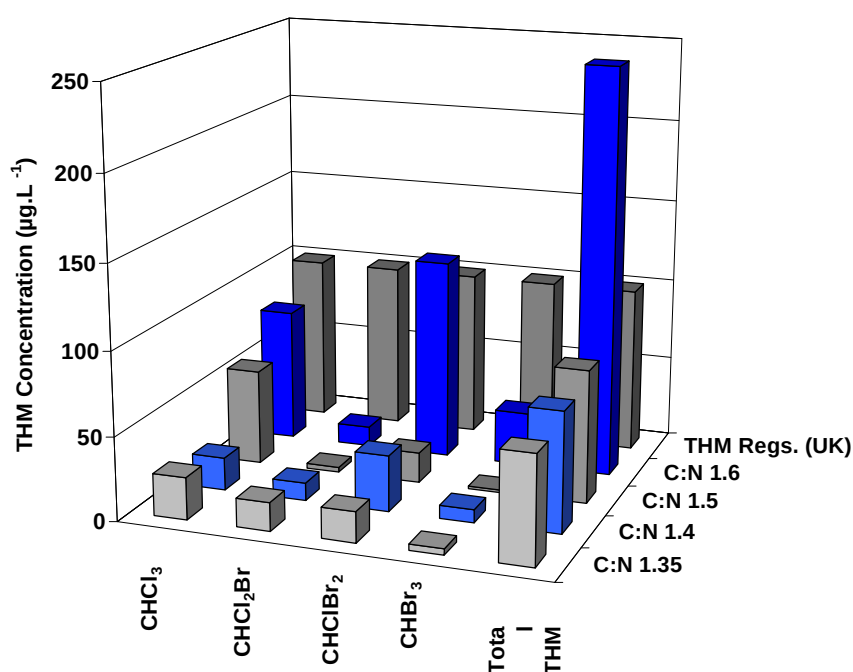


Figure 3.7 Tri-halo methane formation potential before (C:N 1.35-1.52) and after (C:N 1.63) substrate breakthrough.

Principal formation of CHCl_3 can be attributed to the feed water comprising low concentrations of available bromate (UK standard, 10 $\mu\text{g BrO}_3.\text{L}^{-1}$). Comerton et al. (2005) similarly reported THMs in MBR effluent to dominantly comprise CHCl_3 . Although THMs were formed, under carbon limited conditions, a mean total THM concentration $72.1 \pm 7.7 \mu\text{g.L}^{-1}$ was recorded, below both UK and US regulations.

Comparison with influent THMFP indicated a net removal of 44% (potable water, 129.4 $\mu\text{g.L}^{-1}$), though both influent and permeate possessed similar specific THMFP (76 and 62.3-73.4 $\mu\text{g THMFP.mg DOC}$ respectively) indicating that both sources were partially reactive to long-term chlorination.

Several feed water samples were spiked with known ethanol concentrations (1, 2, 5 and 10 mg ethanol.L⁻¹) and evaluated for THMFP. After correcting for background THMFP, ethanol derived THM formation was observed to be 64.7 $\mu\text{g THMFP per mg ethanol}$ (124 $\mu\text{g THMFP mg C}^{-1}$), the dominant compounds again comprising CHCl_3 (49.4-86.2 % or 2 % mean molar conversion) and CHClBr_2 (9.6-29.5 % or 1.5 % mean molar conversion). Ethanol-specific THMFP was considerably higher than that recorded for influent and permeate samples during carbon limited operation, and exceeded published values for raw water humic substances (regarded as the main source of THMFP in water treatment). Krasner et al. (1996) reported 51 and 21 $\mu\text{g THM mg DOC}^{-1}$ for the hydrophobic and hydrophilic humic fractions respectively, the net sum being comparable to the permeate in this investigation. However, given the higher reactivity associated with ethanol, it can be inferred that ethanol was not the sole contributor (if indeed a contributor at all) to the permeate THM formation observed. Once ethanol breakthrough had occurred, $\text{THMFP}_{\text{total}}$ increased to 246 $\mu\text{g.L}^{-1}$ (corresponding to C:N 1.61. This increase in $\text{THMFP}_{\text{total}}$ correlated closely to the relative carbon composition (measured ethanol and residual DOC), and as C:N increased, total THM concentration increased accordingly.

Permeate $\text{UV}_{254\text{nm}}$ ranged <0.01-0.02 cm^{-1} for samples at each C:N setting. Specific UV absorbance (SUVA) was consistently <0.08 cm^{-1} , implying the residual organics

to have low reactivity (Schmidt et al., 1998) and low molecular weight (Liu and Tseng, 1996) possibly as a result of rejection by the membrane. Li and Chu (2003) also attributed low permeate THMFP (3-day) ($60.4 \mu\text{g.L}^{-1}$) and $\text{UV}_{254\text{nm}}$ permeate absorbance ($0.04 \pm 0.01 \text{ cm}^{-1}$) to high MW membrane rejection when investigating the potential application of MBRs to polluted surface water treatment. However, contrary to Li and Chu (2003), a reduction in specific THMFP between feed and permeate was not observed, which is either due to the residual organics having similar characteristics as the influent, or the leakage of weakly $\text{UV}_{254\text{nm}}$ absorbing carbon containing molecules (e.g. carbohydrate) that exert some chlorine demand.

3.3.3 Permeate quality: carbon retention and membrane rejection

Over the duration of analysis, a mean influent DOC concentration of $1.3 \pm 0.3 \text{ mg DOC.L}^{-1}$ was recorded (Figure 3.8). During carbon limited conditions (at steady-state), the mean permeate DOC was $0.4 \pm 0.7 \text{ mg.L}^{-1}$ indicating that some of the influent DOC was retained within the bioreactor (Table 3.1). Influent DOC retention was further demonstrated during the transitional phase (unsteady-state) from C:N 0.93 to 1.17 when the influent DOC concentration increased (duration ~5 days) to $11.5 \pm 2.2 \text{ mgDOC.L}^{-1}$. Although the mean permeate DOC concentration increased to $1.4 \pm 0.9 \text{ mg.L}^{-1}$, approximately 88% of the influent DOC was retained. Hallin et al. (1996) found that a bacterial population that responded rapidly to ethanol as the electron donor continued to use influent COD simultaneously for denitrification. However, the variation in influent DOC concentration did not impact upon nitrate removal consistency during carbon limited conditions, indicating that influent DOC was bio-refractory. At steady-state, influent DOC retention was lower at $67.6 \pm 22.8\%$ and

comparison of feed and permeate sample HP-SEC chromatograms (Figure 3.9) consistently showed comparable (organic compound) elution profiles demonstrating both feed and permeate to have similar UV_{254nm} absorbing components.

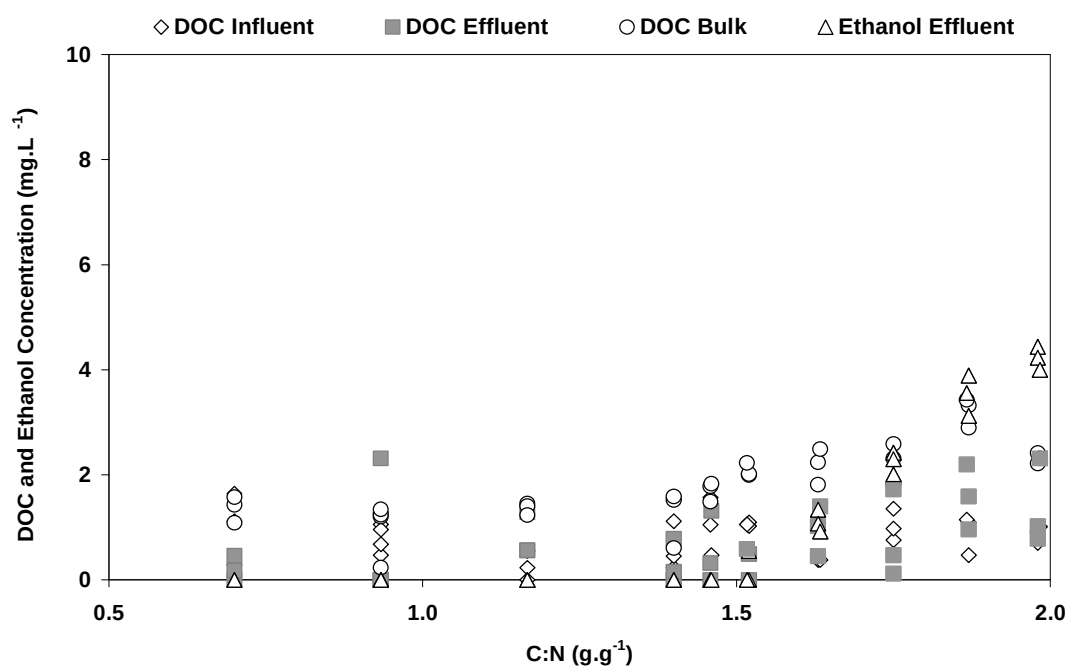


Figure 3.8 Influent, permeate and SMP DOC combined with ethanol (expressed as carbon) observed at increasing C:N concentration.

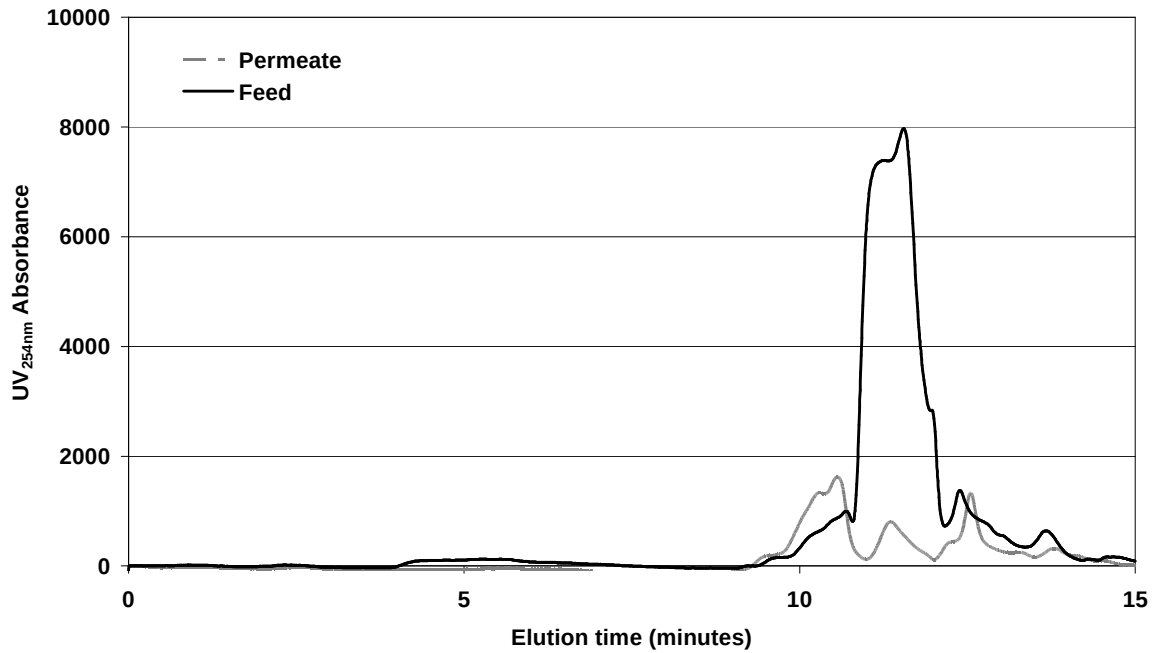


Figure 3.9. Comparison of feed and permeate samples using HPSEC analysis.

Reising and Schroeder (1996) reported that a pore size $<0.2 \mu\text{m}$ is necessary for denitrification as many soil bacteria (in which denitrifiers are abundant) are around this size. In the current investigation, none of the heterotrophic plate counts (HPC) exceeded 0 CFU.mL^{-1} , comparing well to the work of Barreiros et al. (1998) and Urbain et al. (1996) who also reported HPCs of 0 CFU.mL^{-1} using pressure-driven membrane separation for denitrification MBR studies (MWCO 500 kDa and 100kDa respectively). The authors ascribed the complete micro-organism retention to the pore size of the membranes used.

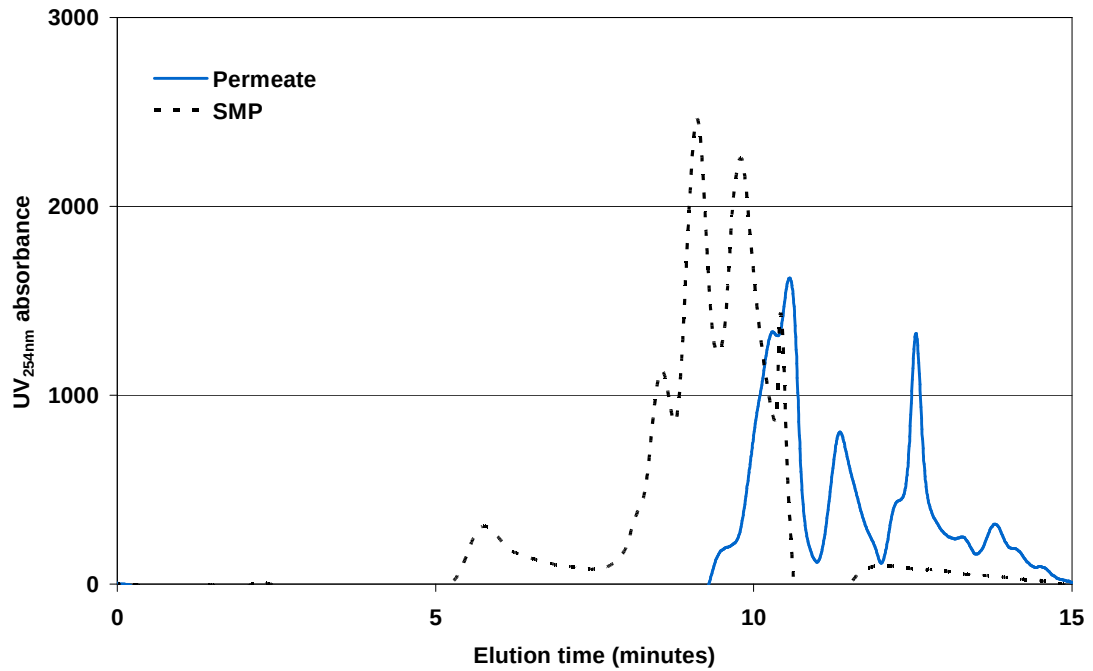


Figure 3.10 Comparison of SMP and permeate samples using HPSEC analysis.

In the current study, bioreactor SMP averaged $1.3 \pm 0.8 \text{ mg DOC.L}^{-1}$ (max. 3.1 mg.L^{-1}). Low permeate DOC ($0.4 \pm 0.7 \text{ mg.L}^{-1}$) indicated that SMP could be all or partially retained when using the membrane for biomass rejection. Serial membrane fractionation indicated that SMP principally comprised high MW organic material with $68.5 \pm 2.9\%$ DOC $>100 \text{ kDa}$. Retention of the high MW material was confirmed by comparing SMP and permeate HPSEC chromatograms (Figure 3.10), where a characteristic high MW peak observed between 5.4 and 6.4 minutes on the SMP chromatogram was absent in the permeate. Urbain et al. (1996) also reported low permeate DOC concentrations ($<1.0 \text{ mg DOC.L}^{-1}$) using ethanol as the electron donor, and suggested that SMP was retained due to its macromolecular size. Scouring of the fibres was limited to low flow conditions ($0.011 \text{ m}^3.\text{m}^{-2}.\text{s}^{-1}$) to ensure the purity ($>99\%$) of the nitrogen gas. Low shear conditions promote larger particle sizes (Wisniewski and Grasmick, 1998) as observed in this study, with particle sizes

reaching up to 1032 μm , comparing favourably to values cited in the literature (38.8-111 μm , Brookes et al., 2003), and these conditions contributed to the low SMP concentration observed.

The lower molecular weight organic material eluted at different times to the material in the permeate indicating that if the residual DOC is a result of the SMP, the source is likely to be non-or weakly UV absorbing components. Mo et al. (2005) recorded a high permeate DOC concentration up to 8.1 mg.L^{-1} . The authors ascribed this to generation of SMP below the molecular weight cut-off of the membrane (PVDF, 0.04 μm ; as used in this study). Differences in SMP composition (concentration and molecular weight) can arise from electron donor selection, biofilm rather than suspended processing or process conditions such as SRT. It should be noted that although carbohydrates in the SMP could not be quantified by either $\text{UV}_{254\text{nm}}$ or the phenol-sulphuric acid method, they were found to contribute to the biofilm formed on the membrane.

3.4 CONCLUSIONS

Many previous heterotrophic drinking water denitrification studies have reported difficulties with retaining either exogenous substrate or SMP however, by encouraging substrate distribution within suspended, well-mixed biomass and

defining C:N under continuous conditions, the point of exogenous breakthrough (C:N>1.52) was determined, below which both ethanol retention and high nitrate removal efficiencies (92%) were possible. Nitrite was formed as a by-product of carbon limited operation, and was effectively controlled by chlorine oxidation ($5.0 \pm 0.1 \text{ mg Cl}_2/\text{mg NO}_2^- \cdot \text{N} \cdot \text{L}^{-1}$). During the oxidation step, no competition from other potentially oxidisable substances was observed thus the chlorine requirement could be predicted. Low shear (N_2 intensity $0.011 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) encouraged the growth of large flocs and the release of low concentrations of high MW SMP which was retained by the membrane. The permeate DOC concentration was comparable to other drinking water processes ($0.4 \pm 0.7 \text{ mg} \cdot \text{L}^{-1}$) and shared similar HPSEC-UV and specific THMFP characteristics to the influent. When operating within carbon limited conditions, permeate DOC exhibited low reactivity with long term chlorination (THMFP $72.7 \pm 7.7 \text{ } \mu\text{g} \cdot \text{L}^{-1}$) however, the impact of ethanol breakthrough was significant. Product water quality in this study compares favourably to previous fixed film process studies however, the balance between sufficient nitrate removal and permeate quality in terms of ethanol, THMFP and nitrite remains sensitive. Further work is required to determine how close to breakthrough a feed-back dosing loop can be operated in unsteady-state to reduce scale and oxidation requirements.

Table 3.1 *Comparison of DOC concentrations in various full scale and pilot scale trials.*

Process/ e ⁻ donor	Scale/ Flow (m ³ ·d ⁻¹)	MLSS (g·L ⁻¹)	Influent (mg·L ⁻¹)		SMP _{DOC} (mg·L ⁻¹)	Eff. DOC (mg·L ⁻¹)	Reference
			NO ₃ ⁻ -N	DOC			

MBR ^a ethanol	LS 0.02	1.8-2.1	26.35	-	40-50	1.5-2.1	Chang et al., 1993
MBR ^b glucose	LS 0.002	1.5-2.5	N/a	4.35	4.17	1.78	Li and Chu, 2003
MBR ^a ethanol	FS 400	0.35	10.2-15.4	<5	5-27	0.8-1.2	Urbain et al., 1996
MBR ^{b,c} Hydrogen	LS 0.008	-	12-72	-	-	6-8.1	Mo et al., 2005
MBR ^b ethanol	LS 0.005	0.15- 0.54	14.8-34.8	0.2-13.7	1.3	0.4	Current study
Fixed bed ethanol	FS 2,400	-	12.5-15	1.9	-	4.5 ^d	Roennefahrt, 1986
Fixed Bed acetic acid	PS/ FS <150	-	6.9-8.4	0.69 ^e	-	>1.5 ^{e,f}	Sanders et al., 2004

^aExternally configured. ^bImmersed configuration. ^cUsed in combination with H₂ gas dissolution hollow fibre membrane. ^dDOC concentration post packed bed, 2.5 mg.L⁻¹ post aerobic filter (1), 1.1 mg.L⁻¹ post aerobic filter (2). ^eNPOC – non-purgeable organic carbon. ^fNPOC concentration after fixed bed breakthrough, roughing filter and sand filters followed to reduce NPOC <1.5 mg.L⁻¹. LS – laboratory scale; PS – pilot scale; FS – full scale.

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CHAPTER 4

THE INFLUENCE OF SUBSTRATE ON FOULING IN ANOXIC IMMERSED MEMBRANE BIOREACTORS

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4 THE INFLUENCE OF SUBSTRATE ON FOULING IN ANOXIC IMMERSSED MEMBRANE BIOREACTORS

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ABSTRACT

The influence of carbon substrate chemistry on membrane bioreactor (MBR) fouling in anoxic conditions has been evaluated. The use of a weak carboxylic acid (acetic acid) resulted in the production of large open floc structures (up to 508 μm) that were susceptible to breakage. Primary particles (d_{10} and d_{20} particle sizes, 5.5 ± 1.3 and $15.3\pm8.2\mu\text{m}$ respectively) and macromolecular soluble microbial product (SMP) were generated, directly impacting on membrane fouling. The use of a primary alcohol (ethanol), on the other hand, encouraged the growth of flocs similar to activated sludge. These flocs produced low concentrations of primary particles (d_{10} and d_{20} particle sizes, 120.6 ± 36.1 and $185.2\pm62.7\mu\text{m}$ respectively) and high molecular weight SMP, and the particles had sufficient mechanical integrity to withstand shear. Consequently, the use of ethanol resulted in sufficient suppression of fouling to extend the filtration time by a factor of three. An increase in MLSS concentration did not directly impact upon fouling when operating with ethanol, primarily because of the low concentration of particulate matter produced.

4.1 INTRODUCTION

Fouling in aerobic membrane bioreactors (MBR) is now a relatively well researched area and, coupled with falling membrane costs, has aided the commercial development of MBR as a viable alternative to conventional wastewater processes. In contrast, research on anoxic/ anaerobic membrane bioreactor fouling has been limited, though significant commercial potential exists.

Kang et al. (2003) investigated the effect of dissolved oxygen (DO) concentration on immersed membrane fouling by applying various air/nitrogen mixtures to set an identical shear pattern at the membrane surface. The authors surmised that during anaerobic conditions (0.3 mg.L^{-1}) the mean particle size reduced from $30 \text{ }\mu\text{m}$ (DO 7.0 mg.L^{-1}) to $13 \text{ }\mu\text{m}$ resulting in an increased specific cake resistance (Kang et al., 2003). Jin et al (2006) investigated biofilm formation in aerobic and anaerobic conditions and reported that t_{crit} (critical filtration time) was arrived at 7.5 times earlier when operating at a DO equal to 0.1 mg.L^{-1} compared to 3.0 mg.L^{-1} and similar to Kang et al. (2003), concluded that this was due to an increased fine particle concentration ranging from $2\text{--}5 \text{ }\mu\text{m}$, in the biofilm as well as in bulk solution, when operating in anaerobic conditions (Jin et al., 2006).

Coinciding with a reduction in mean particle size, Kang et al. (2003) also reported that at lower dissolved oxygen concentrations more soluble microbial products (SMP) were generated, which supports the findings of other anaerobic fouling studies and as with aerobic MBR fouling, this colloidal organic material is considered to be the primary foulant in anoxic/ anaerobic conditions (Judd, 2006). Jang et al. (2006)

surmised that the high concentration of colloidal material present in anoxic conditions was due to a decline of exocellular polymeric substances (EPS) which resulted in floc deterioration and the subsequent release of high molecular weight SMP which caused increased pore blocking and higher cake resistance. This is consistent with the findings of Wilén et al. (2000) who found that activated sludge flocs deflocculated under anoxic and anaerobic conditions and reflocculated under aerobic conditions.

Anoxic and many anaerobic processes require a supplementary organic substrate to yield satisfactory removal of target contaminants. Grabińska-Łoniewska (1991) found that different substrates influenced both size and structural changes in flocs produced in anoxic conditions, reporting large and branched flocs when using acids, gelatinous flocs when using glycerol and flocs similar to activated sludge when fed with alcohols. Kuo et al. (1996) reported that SMP generation was significantly higher when aerobic biological growth was supported by glucose and was conversely much lower when acetate was used which consolidates the idea that functional and structural substrate composition can influence both floc structure and SMP generation. This paper therefore examines whether selecting an appropriate carbon substrate can enhance floc properties in anoxic conditions (applied to denitrification) and thus limit fouling. To this end, two structurally different substrates were selected for comparison, a weak acid (acetic acid) and a primary alcohol (ethanol).

4.2 MATERIAL AND METHODS

4.2.1 Experimental design

Two sealed 5 L bioreactors were fitted with submerged hollow fibre (HF) PVDF membrane modules (Zenon Env., ZW-1) rated 0.04 μm pore size (Figure 4.1). Permeate and waste sludge was extracted via a peristaltic pump (Watson Marlow, 313). Ethanol and acetic acid were delivered via an ultra low flow ($0.002 \mu\text{L}.\text{min}^{-1}$) peristaltic pump (Masterflex, C/L). Nitrogen enriched air (>99%) was introduced from a nitrogen selective hollow fibre membrane (N_2 Gen Ltd., TN-210) which was operated under 8 barg air pressure on the retentate side. The nitrogen flow rate was controlled via a needle gauge (Key Instruments, 0-5 L). Membrane gasification intensity equalled $0.007 \text{ m}^3.\text{m}^{-2}.\text{s}^{-1}$. Liquid level controllers (Broyce Control, B8LCR) were coupled to solenoid valves (Zoedale Plc, L120/B02) to provide constant head conditions (Variation in working volume $\pm 0.5\%$). The influent nitrate concentration was maintained with a dosing loop which introduced nitrate concentrate linearly against influent volume. Off-gas was released via a non-return valve. Temperature was maintained using a temperature-controlled water bath (Grant, VFP; $25 \pm 0.3^\circ\text{C}$) and pH was maintained using a phosphate buffer pair (pH 8 ± 0.1). Pressure was monitored with a pressure transducer (Endress and Hauser, Cerabar M (PMP41)) sited on the permeate line and data was subsequently recorded via a data logger (Pico Technology, ADC-16). Biomass was derived from a pilot scale plant operated with real sewage and was acclimatised on a feed comprising solely ethanol or acetic acid, nitrate and nutrients for 45 days (SRT, 10 days) prior to seeding the two reactors with mains water and biomass at a 10:1 ratio. Both reactors were operated for greater than 3 SRT prior to analysis.

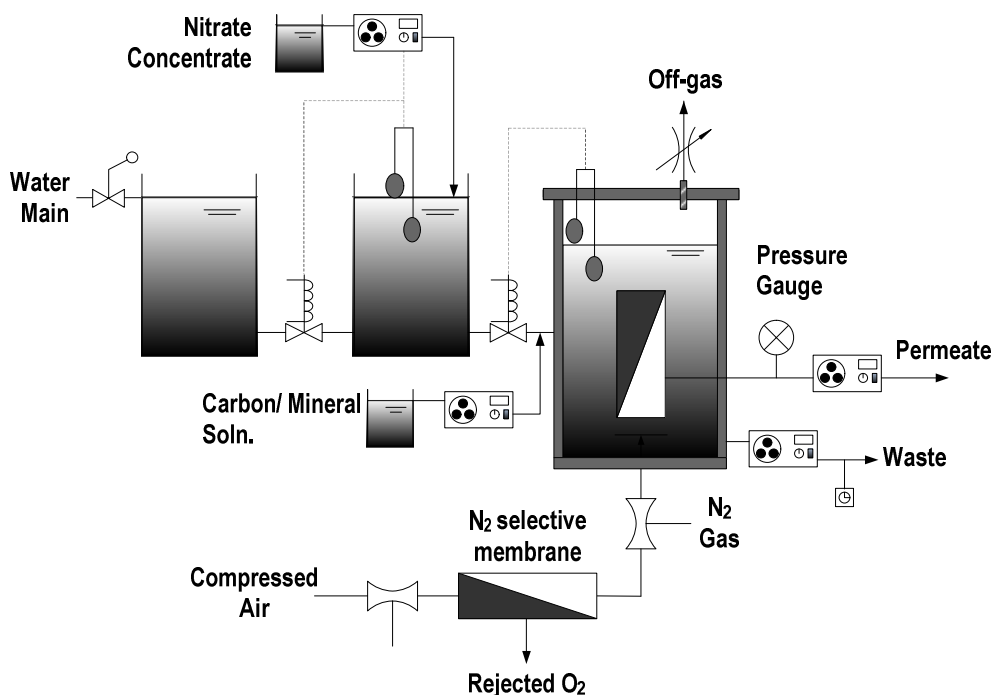


Figure 4.1 *Experimental set-up.*

4.2.2 Analysis

MLSS was determined by standard methods (APHA, 1998). Dissolved organic carbon (DOC) was analysed using a total organic carbon analyser (Shimadzu, TOC-5000). SMP and EPS were extracted according to the method provided in Judd (2006). Size exclusion chromatography (SEC) was undertaken with a Shimadzu *LC-10AD* liquid chromatograph fitted with a Phenomenex BiosepTM Sec-S column with subsequent UV_{254nm} detection. A Varian Cary Eclipse was used for fluorescence excitation-emission matrix (EEM) spectrophotometry, using a xenon lamp as the excitation source to produce spectra with emission from 280 to 500nm at 5nm increments and excitation wavelength from 200 to 400 nm.

4.2.3 Floc Breakage

A variable speed jar tester (Philipps and Bird, APB-900) was used to suspend the biomass in solution. Impeller speed (flat paddle, 76x25 mm) was varied and shear calculated using Eq. (1) and (2):

$$G_{imp} = \sqrt{\frac{P}{V_T \mu_w}} \quad (1)$$

$$P = k \rho n^3 D^5 \quad (2)$$

Where P is the power dissipated, μ is dynamic viscosity ($\text{N.s}^{-1}.\text{m}^{-2}$), V is reactor volume (m^3), ρ is density of water (kg.m^{-3}), n is the impeller speed (revolutions per second) and D is the diameter of the impeller. The completely mixed suspension was recirculated through the optical unit of a Malvern Mastersizer 2000 using a peristaltic pump (Watson Marlow). Floc size was subsequently measured at set intervals (typically 1 minute) using an integrated laser diffractor. Floc sizes were reported as d_{10} , d_{20} (the size of particle below which 10 or 20% of the sample lies) and d_{50} (the size at which 50% of particles are smaller and 50% are larger).

4.2.4 Fractionation and subsequent analytical methods

An Amicon 8400 dead-end stirred cell (Millipore, USA) was used for serial fractionation in combination with Biomax 76mm diameter polyethersulphone UF membranes having a nominal molecular weight limit (NMWL) of 5kDa, 10kDa, 30kDa, 50kDa, 100kDa and 300kDa. All experiments were conducted at $20 \pm 1^\circ\text{C}$ and 1 bar pressure applied using the pure nitrogen gas supply. Shear was imparted within

the cell to limit the effects of concentration polarisation. Following a period of validation, the external magnetic stirrer (Drehzahl, IKAMEG® REO) speed was set at 100 RPM.

4.3 RESULTS AND DISCUSSION

4.3.1 Fouling analysis

During normal operating conditions flux was maintained at $9 \text{ L.m}^{-2}.\text{h}^{-1}$ in both reactors, substantially below the critical flux (J_c , weak form) previously identified as $15 \text{ L.m}^{-2}.\text{h}^{-1}$ by flux step analysis. Both reactors were maintained operationally and hydrodynamically identical (Table 1). The recorded linear rates of pressure increase (dP/dt , the fouling rate) for both acetic acid (A_{Bio}) and ethanol (E_{Bio}) biomass during standard filtration were similar (0.11 and $0.13 \text{ mbar.min}^{-1}$ respectively). However, a pseudo-steady state filtration period (t_{crit}) of less than 16 hours was recorded for A_{Bio} compared to a time in excess of 48 hours for E_{Bio} , suggesting that the acetic-derived biomass was more highly fouling at the same (conservative) loading of $0.06 \text{ kg N.m}^{-3}.\text{d}^{-1}$.

Table 4.1 *Operating parameters.*

Parameter	
HRT (hours)	6
SRT (days)	10
Temp (°C)	25 ± 0.3
pH	8 ± 0.1
$\text{SAD}_m (\text{m}^3.\text{m}^{-2}.\text{h}^{-1})$	0.645
$\text{SAD}_p (\text{m}^3.\text{m}^{-3})$	72.3
Aeration Intensity ($\text{m}^3.\text{m}^{-2}.\text{s}^{-1}$)	0.007

Loading was increased from 0.06 to 0.10 and $0.15 \text{ kg N.m}^{-3}.\text{d}^{-1}$. As a consequence the MLSS increased from 0.09 to 0.35 g.L^{-1} and from 0.31 to 0.55 g.L^{-1} for A_{Bio} and E_{Bio}

respectively. Critical flux analysis was conducted using the flux step method at each loading. As loading increased, an increase in the fouling propensity of A_{Bio} (Figure 4.2) could be visibly observed as an increase in P_{ave} (average transmembrane pressure), and critical flux decreased from 15 to 12 $L.m^{-2}.h^{-1}$.

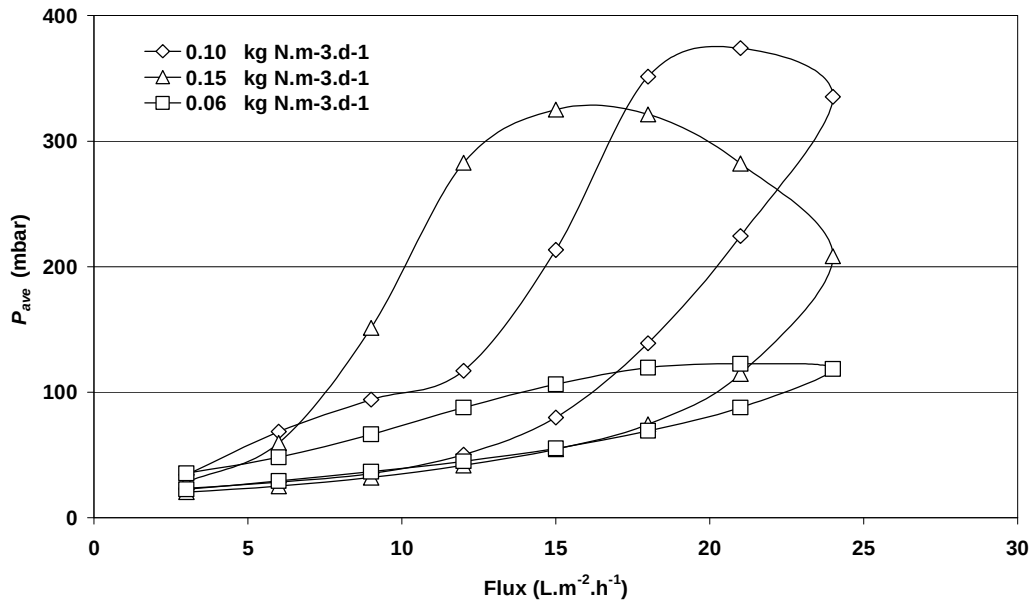


Figure 4.2 Comparison of P_{ave} data for acetic acid fed biomass (A_{Bio}) critical flux tests. Conducted at three loading rates 0.06, 0.10 and 0.15 $kg N.m^{-3}.d^{-1}$.

Statistical analysis using analysis of variance (ANOVA) verified that the difference in P_{ave} (P_{ave} was compared across loadings at each flux step) was statistically significant ($p < 0.1$) at fluxes above 9 $L.m^{-2}.h^{-1}$ on increasing flux stepwise implying that the fouling propensity of acetic derived biomass increased with increasing MLSS concentration. Several studies have shown that an increase in MLSS concentration, generally at low concentrations, can have a direct impact upon fouling (Schwarz et al., 2006; Defrance et al., 2000; Le Clech et al, 2003), particularly for a number of different anaerobic feed matrices (Judd, 2006).

At each loading the P_{ave} plot for E_{Bio} (Figure 4.3) produced a classical hysteresis curve, where P_{ave} increased with flux up to a maximum P_{ave} 96.4-119 mbar at the peak flux of $24 \text{ L.m}^{-2}.\text{h}^{-1}$. On reducing the flux step-wise from the maximum value, P_{ave} correspondingly decreased with each flux step but attained values slightly higher than those recorded for the upward step, indicating residual fouling. Contrary to acetic acid, analysis of variance revealed that fouling with ethanol derived biomass was not significantly different ($p<0.05$) upon increased loading and MLSS concentration, indicating in this case, that solids concentration is not the sole contributor to fouling even when operating at lower concentrations.

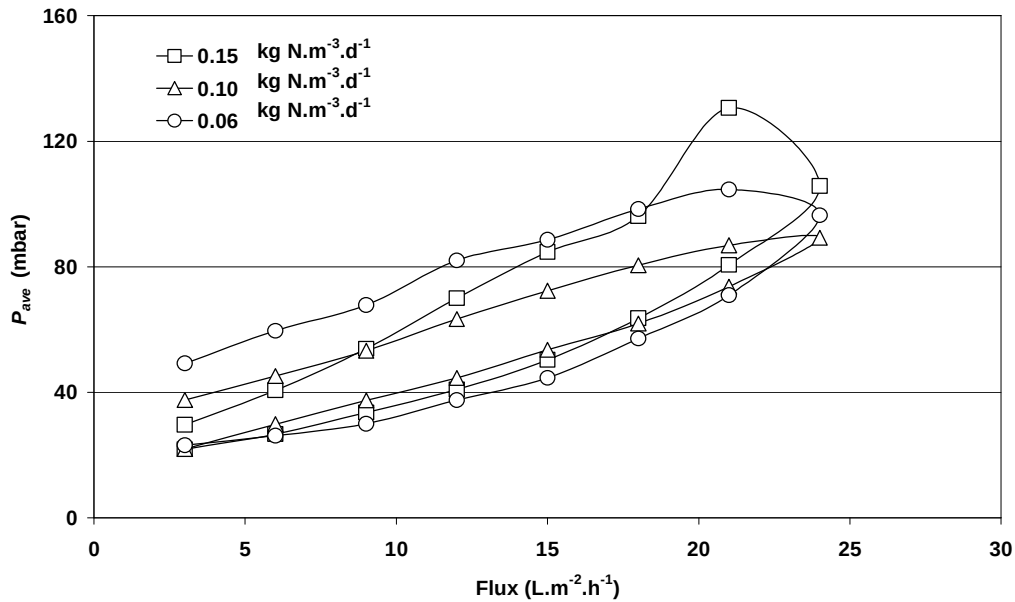


Figure 4.3 Comparison of P_{ave} data for ethanol fed biomass (E_{Bio}) critical flux tests. Conducted at three loading rates 0.06, 0.10 and $0.15 \text{ kg N.m}^{-3}.\text{d}^{-1}$.

At the peak flux setting ($24 \text{ L.m}^{-2}.\text{h}^{-1}$) for acetic derived biomass the highest P_{ave} recorded during J_c analysis was 335 mbar and was recorded at a loading of $0.10 \text{ kg N.m}^{-3}.\text{d}^{-1}$ (Figure 4.2). However, the highest P_{ave} value of 374 mbar was recorded at the same loading but at the first downward flux step of $21 \text{ L.m}^{-2}.\text{h}^{-1}$, indicating significant residual fouling due to a loss of open membrane area and a corresponding

increase in local flux which elevates the TMP. The P_{ave} peak was not exceeded when loading increased from 0.10 to 0.15 kg N.m⁻³.d⁻¹. However, the post-maximum (J decreased from 24 L.m⁻².h⁻¹) P_{ave} trend showed greater hysteresis at higher loadings, with P_{ave} increasing with decreasing flux step between 24 and 15 L.m⁻².h⁻¹.

Loading increased MLSS concentration in both reactors. Given the difference in fouling propensity of the two sludges, it can be concluded that MLSS concentration is not the principal cause of fouling even at low concentration. Nagaoka et al. (2000) correlated increased fouling at higher loading to the increased generation of extracellular polymeric substances (EPS). In the current study, normalised (against MLSS) SMP for A_{Bio} and E_{Bio} was 9.9 ± 4.5 and 2.3 ± 0.5 mgDOC.gMLSS⁻¹ respectively. This suggests that substrate may indeed influence SMP generation, as reported by other authors in aerobic (Boero et al., 1991) and anaerobic conditions (Kuo et al., 1996), and to some extent explains the difference in fouling potential of the two biomasses (Jang et al., 2006).

4.3.2 Particle Size Analysis

Grabińska-Łoniewska (1991) suggested that an increase in nitrate load generally promotes greater floc dispersion. However, at each loading in the current study a quasi-normal size distribution (Figure 4.4) was consistently observed for E_{Bio} flocs. As loading increased, the d_{50} median particle size also increased up to a maximum 1032 µm and the distribution became more leptokurtic, implying a reduction in particles of lower size. Median (d_{50}) floc size also increased with increased loading for A_{Bio} , although a bi-modal distribution (Figure 4.4) was observed at each loading

(tri-modally distributed at $0.06 \text{ kg N.m}^{-3}.\text{d}^{-1}$). Wilén et al. (2003) suggested that activated sludge can be divided into two basic fractions: flocs (typically $25\text{--}1000\mu\text{m}$ in diameter), and primary particles, such as bacteria and other floc components ($<0.5\text{--}5 \mu\text{m}$ in diameter). In the current study median d_{10} and d_{20} values for A_{Bio} averaged 5.5 ± 1.3 and $15.3\pm8.2 \mu\text{m}$ respectively across the three loadings compared to d_{10} and d_{20} values for E_{Bio} of 120.6 ± 36.1 and $185.2\pm62.7 \mu\text{m}$ respectively, indicating that the bi-modal distribution observed was due to the presence of primary particles in the A_{Bio} reactor. These were probably produced from either floc erosion or poor flocculation (Wilén et al., 2003) and it was the presence of primary particles in bulk solution that Jin et al. (2006) correlated to increased resistance and fouling in anoxic conditions.

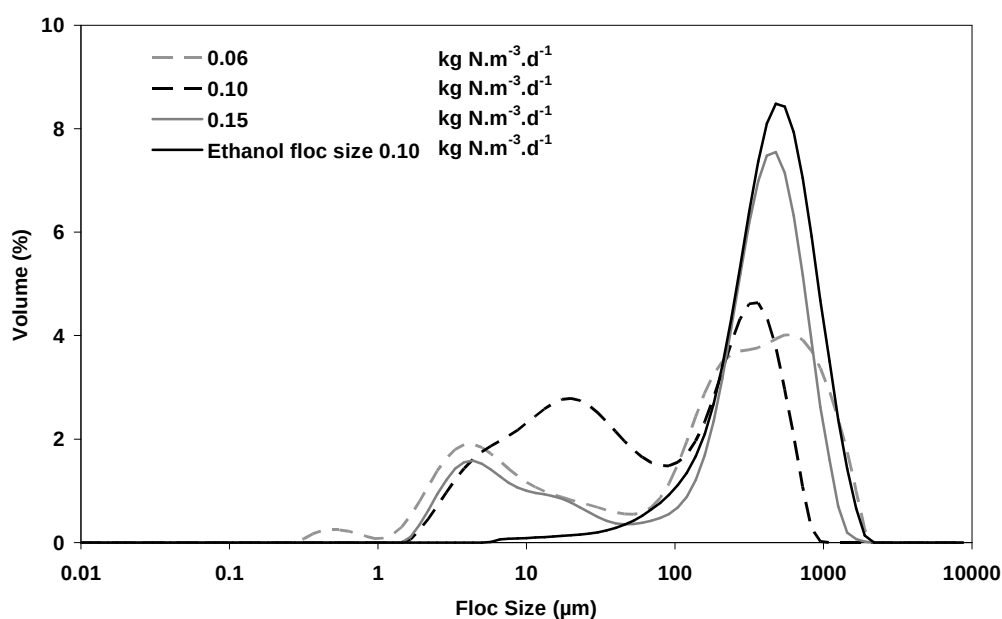


Figure 4.4 Bimodal particle size distribution was noted for A_{Bio} at each loading (0.06 to $0.15 \text{ kg N.m}^{-3}.\text{d}^{-1}$). A normal distribution was consistently observed with E_{Bio} ($0.10 \text{ kg N.m}^{-3}.\text{d}^{-1}$ presented here).

Samples of both biomasses (sampled at loading $0.15 \text{ kg N.m}^{-3}.\text{d}^{-1}$) were subject to a 25 minute period of low shear ($G = 14.0 \text{ s}^{-1}$) in a jar tester to promote floc growth

(Figure 4.5). After 25 minutes E_{Bio} flocs had reached a steady-state d_{50} floc size of 722 μm , more than double their initial median size. In contrast, A_{Bio} flocs yielded little growth with initial and final median floc sizes of 417 and 508 μm respectively. Following an increase in shear ($G = 239.9 \text{ s}^{-1}$), E_{Bio} flocs immediately decreased in size. After a 15 minute period at high shear, the d_{50} particle size was 424 μm . Similarly, following the increase in shear, A_{Bio} flocs immediately reduced in size to 396 μm , equivalent to their initial size at low shear. Shear was subsequently reduced again ($G = 14.0 \text{ s}^{-1}$) to promote re-growth. E_{Bio} flocs demonstrated similar re-growth behaviour to activated sludge flocs at low shear (Jarvis et al., 2005), agglomerating to produce flocs of $\sim 700 \mu\text{m}$ within the first minute. However, growth continued beyond the previous maxima (722 μm) to produce flocs of approximately 1030 μm . This suggests that shear stress destructured the flocs producing both a modification of the size distribution (Wisniewski and Grasmick, 1998) and the release of bacterial polymers (namely EPS) which increased microbial floc formation potential (Urbain et al., 1993) and resulted in the subsequent leptokurtic shift in size distribution (Figure 4.6) and increased median floc size.

By the end of the second low shear period, A_{Bio} median (d_{50}) floc size was similar to that observed in the high shear period, indicating a low re-growth potential. This low potential for growth was also demonstrated in the initial growth phase and implies that the low shear imposed already exceeded that corresponding to the dynamic equilibrium between aggregation and breakage (Wilén et al., 2003) for A_{Bio} flocs. This was again corroborated by the limited impact shear augmentation had on A_{Bio} floc size and supports the findings of Grabińska-Loniewska (1991) where flocs

produced with acetic acid are open structures which are susceptible to breakage and result in increased numbers of small particles (Jarvis et al., 2005).

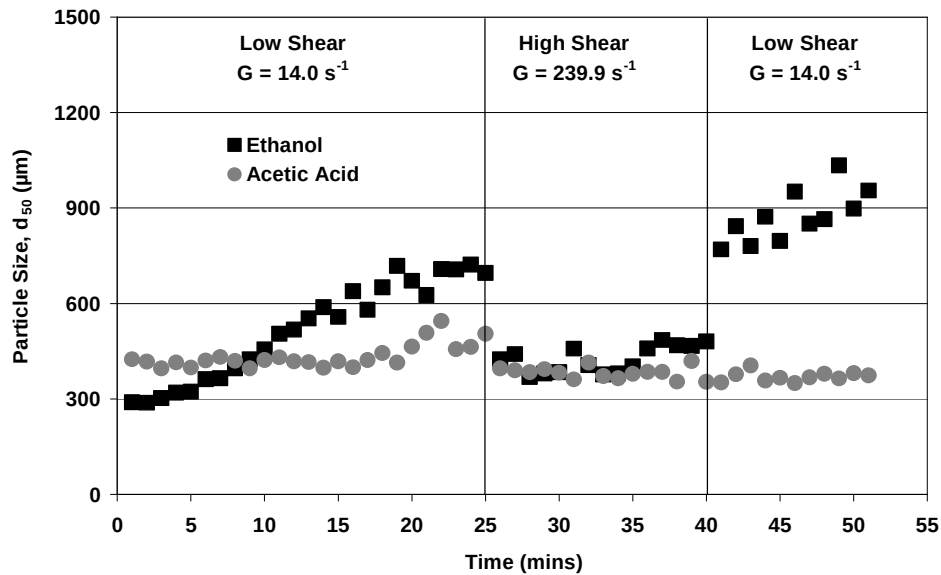


Figure 4.5 Floc strength test over three periods: Low shear ($G = 14.0 \text{ s}^{-1}$) for 25 minutes, followed by high shear ($G = 239.9 \text{ s}^{-1}$) for 15 minutes and finally a second subsequent low shear ($G = 14.0 \text{ s}^{-1}$) period.

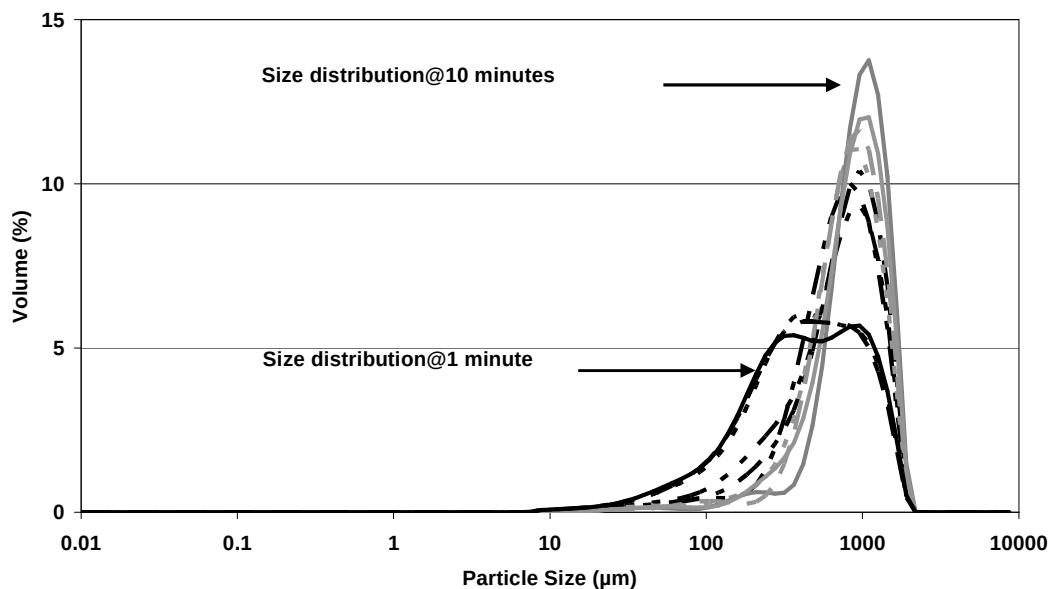


Figure 4.6 Particle size distributions at 1-minute intervals during the re-growth phase. Small flocs and fragments connect and grow into larger flocs, resulting in a final $d_{50} = 1032 \text{ μm}$, shifting the size distribution right (from solid black to solid grey).

Typical velocity gradients associated with aeration in conventional activated sludge are 88-220 s⁻¹ (Logan, 1999). Shear imparted within the reactor by gasification was calculated using Eq. (3) and (4) (Logan, 1999):

$$G_b = \sqrt{\frac{P}{V_T \mu_w \rho_w}} \quad (3)$$

$$P = \frac{\pi}{8} b_{d,b} d_b^2 \rho_w U_b^3 \quad (4)$$

Where $b_{d,b}$ is the bubble drag coefficient, d_b is the bubble diameter (m) and U_b is the bubble rise velocity (m.s⁻¹). At an applied specific aeration demand with respect to membrane area (SAD_m) of 0.65 m³.m⁻².h⁻¹, the shear (G_b) induced by coarse bubble gasification was equal to 175.6 s⁻¹ signifying a relatively high shear in the system. Though this cannot be directly compared to shear calculated for floc breakage analysis, it can be implied that the shear promoted within the MBR is sufficient to break flocs, particularly those more susceptible to breakage.

4.3.3 Fractionation

4.3.3.1 DOC analysis

Fractionation of acetic derived SMP produced a bi-modal distribution of >100 kDa and <10 kDa molecular weight (MW, Figure 4.7). Kuo and Parkin (1996) also found that SMP was bi-modally distributed for both aerobic and anaerobic conditions with MW either less than 1 kDa or greater than 10 kDa, although MW exceeding 10 kDa were not fractionated further in their investigation. Acetic derived SMP with MW >100 kDa comprised 43.1±33.7% of the total DOC concentration. Holakoo et al.

(2006) also observed SMP to be dominated by high MW organics (>100 kDa, 27.9-91.4% by DOC) which have been linked to cell fragments (Laabs et al., 2004), endogenous decay (Boero et al., 1996) and cell lysis (Jarusutthirak and Amy, 2006). Ethanol derived SMP was similarly bi-modally distributed, however the DOC distribution was more consistent (lower standard deviation observed) and SMP principally comprised high MW material with $68.5 \pm 2.9\%$ of the total DOC concentration >100 kDa. Though acetic acid derived SMP comprised a lower fraction of high MW material, the mean DOC concentration >100 kDa was higher than ethanol SMP (DOC ratio 1.8:1 (A_{Bio} : E_{Bio})) and its presence in bulk solution can be attributed to release from the weak floc structure observed.

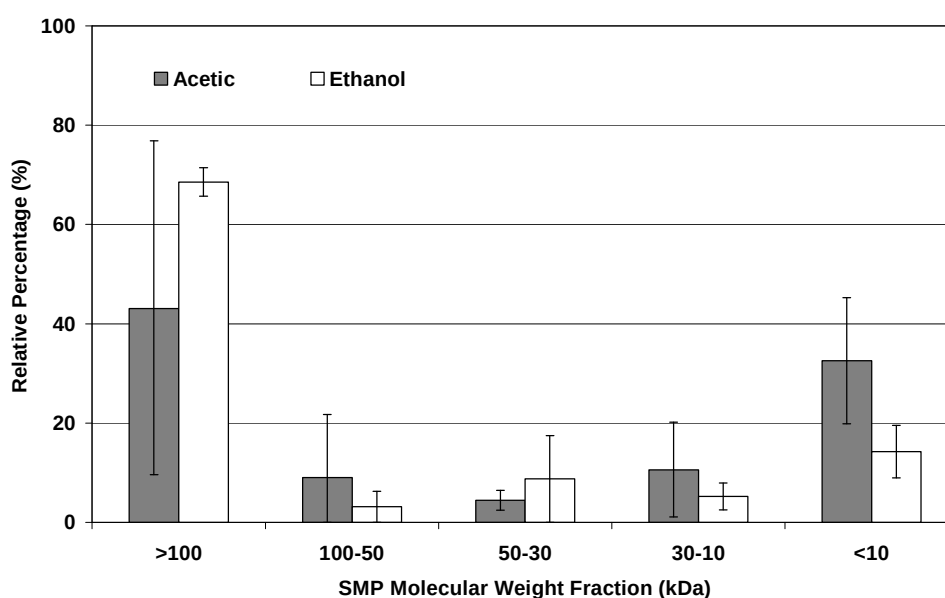


Figure 4.7 SMP molecular weight fractionation recorded as DOC and presented as a relative %.

The lower MW DOC peak (<10 kDa) constituted $32.5 \pm 12.7\%$ and $14.2 \pm 5.3\%$ of the total DOC concentration for A_{Bio} and E_{Bio} SMP respectively. This MW region has previously been related to the direct transformation of the influent substrate (Boero et

al., 1996). However, this cannot account for the difference observed between the two biomasses. When optimising the stirred cell in the current study, it was noted that high shear (above that finally adopted) can transform high MW SMP into low MW SMP. The influence of shear on SMP generation could also explain the considerable standard deviation observed with A_{Bio} .

4.3.3.2 HP-SEC Analysis and Fluorescence EEM

The most prominent feature of the A_{Bio} SMP HPSEC chromatogram was a broad peak eluting at 5.3-6.5 minutes (Figure 4.8(a)). Maximum peak absorbance was recorded for the high MW fraction (>100 kDa). Comparison with lower MW fractions indicated that approximately 65% of the absorbance was attributable to MW ranging 100-300 kDa. There was no peak below <30 kDa. This broad peak is typically associated with the elution of polysaccharides, proteins and colloids. Since detection was limited to the $UV_{254\text{nm}}$ range, this peak was assumed to correspond to proteins and colloids (detected by light scattering) rather than weakly absorbing polysaccharides. Fluorescence (EEM) detection (Figure 4.9) within this MW range produced a pair of peak maxima at excitation emission co-ordinates: Ex: 231 Em: 342 nm and Ex: 282 nm; Em: 339 nm, indicative of a protein like signature (Her et al., 2003). As with the HPSEC analysis, fluorescence detection confirmed that 65% of the intensity was attributable to the high MW components (>100 kDa). Absorbance was poor in the macromolecular range of the SEC chromatogram for E_{Bio} SMP (Figure 4.8(b)), suggesting that the DOC recorded in the high MW fraction comprised weakly UV absorbing components such as polysaccharides.

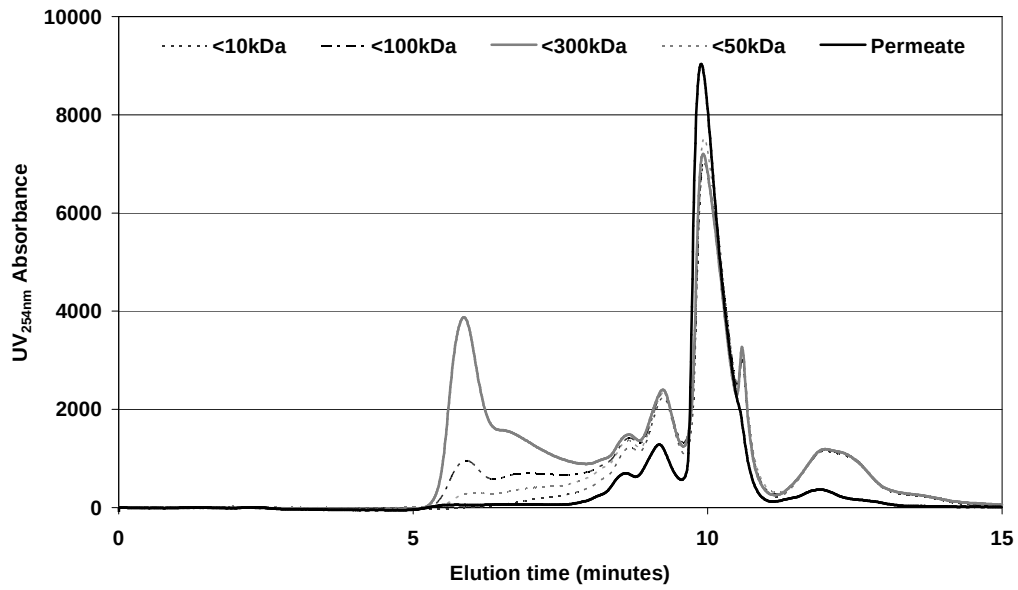


Figure 4.8a. HPSEC chromatograms of each A_{Bio} SMP fraction compared to A_{Bio} reactor permeate.

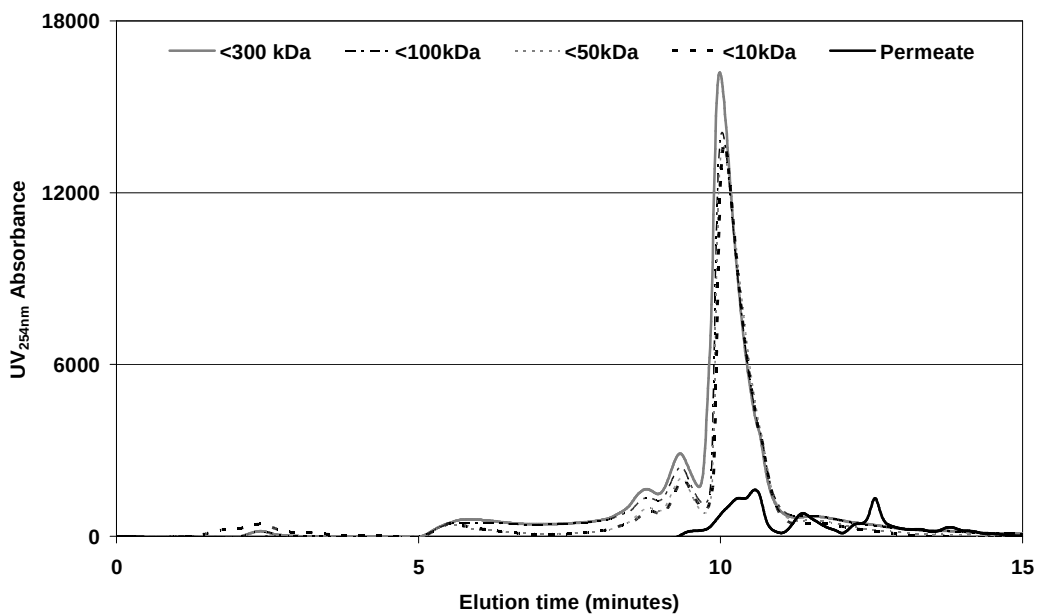


Figure 4.8b. HPSEC chromatograms of each E_{Bio} SMP fraction compared to E_{Bio} reactor permeate.

Comparison with MBR permeate demonstrated that macromolecular components were completely retained by the UF membrane (0.04 μm) in both reactors. Ho and

Zydney (2006) observed a similar trend, suggesting that tighter UF (0.01-0.08 μm pore size) retained much of the colloidal material. It is implied that it is these macromolecules, which constitute the primary foulants. Laabs et al. (2006) also reported this peak to be the primary source of UF membrane fouling for a membrane pore size of 0.014 μm , MWCO 100 kDa. A comparison of heat extracted EPS (eEPS) from A_{Bio} and E_{Bio} (Figure 4.10) indicated the origin of the $\text{UV}_{254\text{nm}}$ peak to be ‘tightly’ bound polymeric substances present in both extractions. The absence of this peak in the E_{Bio} SMP (Peak ratio SMP/EPS: A_{Bio} , 1.3; E_{Bio} , 0.1) further corroborates the relative stability of the flocs derived from ethanol. The presence of an SMP protein peak in A_{Bio} could explain the difference in floc structure observed, as an increased concentration of available protein can destabilise the floc structure, as observed by Jang et al. (2006), by increasing the negative surface charge and, in turn, lower the floc mechanical strength (Reid et al., 2006). The presence of this protein peak is thus indicative of a weak floc and the concomitant release of colloidal foulant material; protein substances may not necessarily be primary foulants themselves.

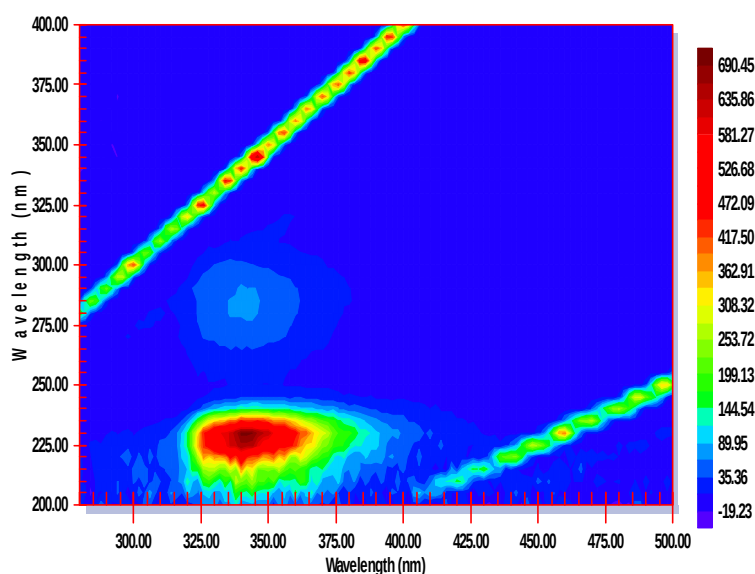


Figure 4.9 FS-EEM image of Acetic biomass fraction <300 kDa. Excitation-emission at co-ordinates Ex: 231 Em: 342 is indicative of protein like components.

Lower MW constituents (<5 kDa) are eluted beyond the polysaccharide peak. Comparison of low MW A_{Bio} SMP and permeate demonstrates that this material passes through the membrane and gel layer to form permeate DOC (1.6 ± 0.8 mgDOC.L⁻¹). Conversely, the lower MW region was retained within the E_{Bio} MBR either by rejection by the gel layer or, more likely, retention within the floc structure (permeate 0.4 ± 0.7 mgDOC.L⁻¹). Various investigations have attributed significant fouling potential to the lower molecular weight fraction (MWCO characteristically varies between studies) by assessment as an isolated component (Judd, 2006; Laabs et al., 2004). However, results from the current study suggest that the contribution of this fraction to fouling is limited when within a heterogeneous matrix, especially one which promotes the formation of stable flocs.

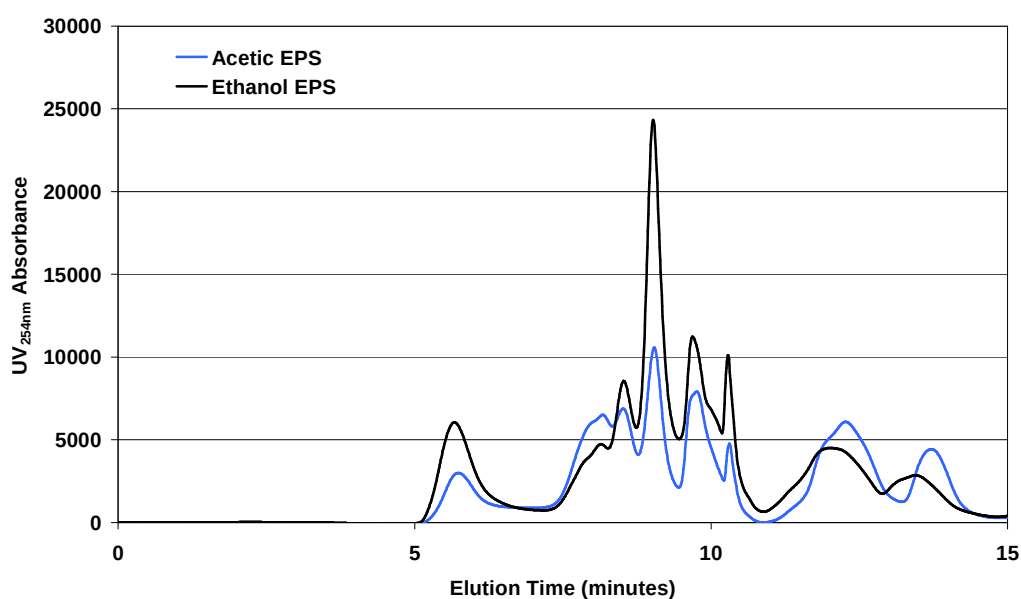


Figure 4.10 Comparison of eEPS extracted from A_{Bio} and E_{Bio} . Significant peak formation at 5.3 – 6.5 minutes indicates the source of the A_{Bio} SMP peak.

4.3.4 Blocking law analysis

Regression analysis of a single filtration cycle was undertaken using the linearised form of the constant flowrate blocking laws proposed by Hlavacek and Bouchet (1993) (Eq. (5)):

$$\frac{d^2t}{d(\Delta P)^2} = K \left[\frac{dt}{d(\Delta P)} \right]^n \quad (5)$$

Pore blocking was defined as the dominant fouling mechanism ($R^2 = 0.9918$) for fouling by acetic derived biomass (Figure 4.11).

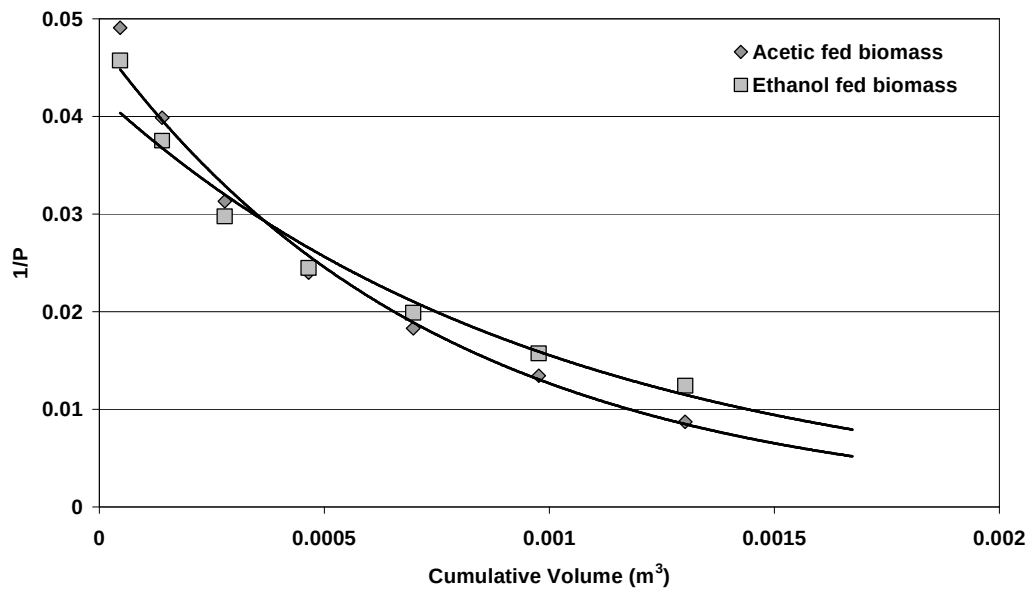


Figure 4.11 Pressure transients at $9 \text{ L.m}^{-2}.\text{h}^{-1}$ and $\text{SAD}_m 0.65 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$ for a 30 minute filtration cycle. Data plotted for pore blocking. This model provided the strongest correlation to fouling by acetic acid ($R^2 = 0.9918$).

This can be attributed to the generation of high concentrations of fine and colloidal particulates which are more readily convected towards the membrane surface (Zhang et al., 2006) than the larger particles within suspension, and are either deposited directly within the pores or onto the surface to form a biofilm with a very low porosity (Jin et al., 2006). This is consistent with visual observation, the biofilm apparently comprising a thin, relatively homogenous layer with few areas of gross solids (Figure

4.12(a)). Cake filtration was determined as the dominant fouling mechanism ($R^2 = 0.9979$) associated with ethanol biomass. This permits the extension of filtration time due to the low concentration of macromolecules and the generation of a highly porous cake (Figure 4.12(b)).

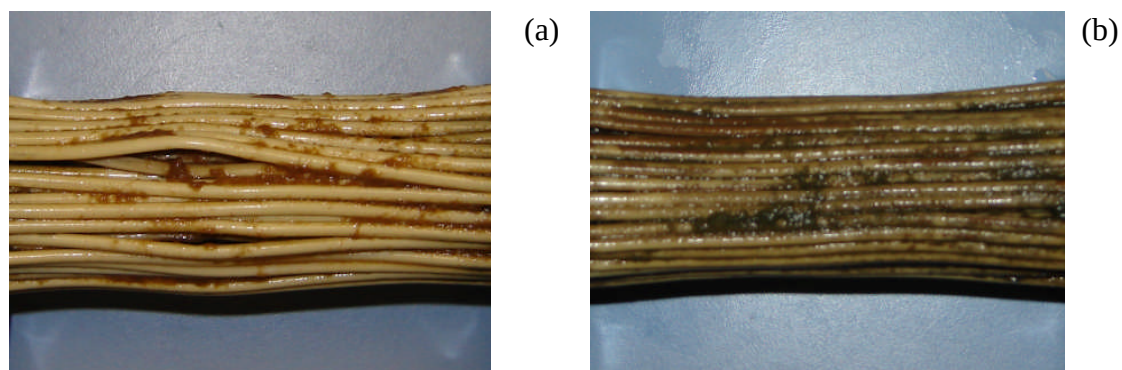


Figure 4.12 Foulant layer formed in the presence of: (a) A_{Bio} (Loading $0.15 \text{ kg N.m}^{-3}.\text{d}^{-1}$); and (b) E_{Bio} (Loading $0.15 \text{ kg N.m}^{-3}.\text{d}^{-1}$) sufficient to raise TMP >450 mbar.

4.4 CONCLUSIONS

Previous research has provided a generic explanation for fouling in anoxic conditions where increased fouling propensity is observed (over aerobic conditions) due to an increase in concentrations of small particles arising from floc instability. This mechanism was consistent with the fouling observed when employing acetic acid as the sole substrate, since high concentrations of small particles were generated from weakly formed flocs. However, ethanol supported the formation of strong flocs that were capable of withstanding shear and consequently significantly extended the available process time. An increase in MLSS concentration did not directly impact upon fouling when using ethanol because of the low particulate concentrations generated. The quantity of SMP generated may be directly related to the substrate employed, though indirectly the quantity of SMP available is also a function of floc strength. Furthermore, floc breakage is related both to the shear applied at the

membrane and the mechanical strength of the floc. As observed in previous studies, it is the high MW organics that constitute primary foulants during filtration. However, the 'polysaccharide peak' should not be thought of as the foulant in isolation but rather an indicator of foulant potential as larger particles such as cell fragments can equally contribute to the development of biofilms with low porosity. Low MW organics apparently had a limited influence upon fouling when retained in a reactor promoting a stable floc structure.

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CHAPTER 5(a)

OPTIMISATION OF DEAD-END FILTRATION CONDITIONS FOR AN IMMERSED ANOXIC MEMBRANE BIOREACTOR

SUBMITTED TO: *Journal of Membrane Science*

5(a) OPTIMISATION OF DEAD-END FILTRATION CONDITIONS FOR AN IMMERSED ANOXIC MEMBRANE BIOREACTOR

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ABSTRACT

The optimisation of the energy demand in the application of dead-end filtration in an immersed membrane bioreactor applied to groundwater denitrification has been studied. Filtration cycle length was varied at a set flux to control the amount of foulant deposited at the membrane surface. Physical cleans comprising a simultaneous backflush and gas injection were subsequently instigated and the reversibility of the deposit determined by the residual resistance, R_{res} . Examination of R_{res} versus flux and cycle length variation indicated an operational envelope where limited fouling occurred. The transition from limited fouling to extensive fouling was indicated by a parameter based on the critical accumulated mass, indicating incipient deposit consolidation. The transition between regions became less severe when the solids retention time was increased from 10 to 25 and 40 days. This was apparently related to a shift in bulk physical characteristics. Nevertheless, low residual fouling was observed during long-term filtration when operating below the critical mass, resulting in a 20x reduction in energy demand over that of constant gas injection.

5.1 INTRODUCTION

Groundwater nitrate levels in many areas now exceed regulatory limits (Urbain et al., 1996). Treatment is commonly by ion exchange which selectively extracts nitrate from the source water and subsequently produces a concentrated brine waste stream of up to 2% of the influent flow. Biological denitrification using membrane bioreactors (MBRs) represents a technically attractive alternative treatment, since an inert product (nitrogen gas) is produced whilst the process also provides a physical barrier for separating the biomass from the product water.

To maintain biochemical reduction, dissolved oxygen (DO) should remain below 0.1 mg.L^{-1} . Consequently, nearly all previous pressure driven membrane bioreactor research has focused on external (Urbain et al., 1996; Delanghe et al., 1994; Chang et al., 1993) (or sidestream) rather than immersed configured MBRs. This circumvents the requirement for air scouring of the membrane, which otherwise greatly improves the energetic efficiency of the configuration over that of the sidestream (Judd, 2004). Reducing air scour (to ~5 seconds every 10 minutes) so as to sufficiently reduce DO levels ($<0.1 \text{ mg.L}^{-1}$) to maintain anaerobic conditions has been shown to provide insufficient shear to control fouling in an immersed anaerobic MBR (Lee et al., 2001). The use of recycled nitrogen gas for membrane scouring has been successfully demonstrated (Rezania et al., 2007), but in this study gasification was on a 10s on/10s off basis. Since gas pumping makes up 30-40% of the overall energy demand (Judd, 2008), and the use of recycled nitrogen from the reactor headspace presents a significant process modification challenge, it is of interest to seek other means of maintaining membrane permeability.

The current paper explores hydrodynamic optimisation of immersed hollow fibre membranes for the groundwater denitrification of by an immersed MBR employing intermittent dead-end filtration. The study specifically addresses:

- a) minimisation of the energy demand required for gas scouring by limiting its application,
- b) deposit reversibility (and thus permeability recovery),
- c) the deposit formation mechanism, and
- d) operational stability with respect to solids retention time (SRT) variation.

5.2 MATERIAL AND METHODS

5.2.1 Filtration rig

Biomass was initially adapted to anoxic conditions in batch mode. The 75 L reactor (Figure 5.1) was subsequently seeded at a ratio 10:1. The influent nitrate concentration was set at $22.6 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{L}^{-1}$, approximately equivalent to mid-way between the mean and peak nitrate loads experienced in full-scale applications (Urbain et al., 1996). Ethanol was supplied as the exogenous substrate and dosed at a previously defined optimum C:N ratio of 1.45 (McAdam et al., 2007). Reactor temperature was maintained around 20°C using a thermostatically controlled heating jacket. Biomass distribution was ensured through impeller mixing below the membrane module at a speed of 30 rpm creating a root mean square velocity gradient (G) of 12.8 s^{-1} , and the shear imparted to the membrane from this mixing was demonstrated as being negligible. The hydraulic residence time (HRT) was c.6 hours. The SRT in successive tests was set at 10, 25 and 40 days. The process was allowed 3 SRTs to arrive at steady state prior to testing.

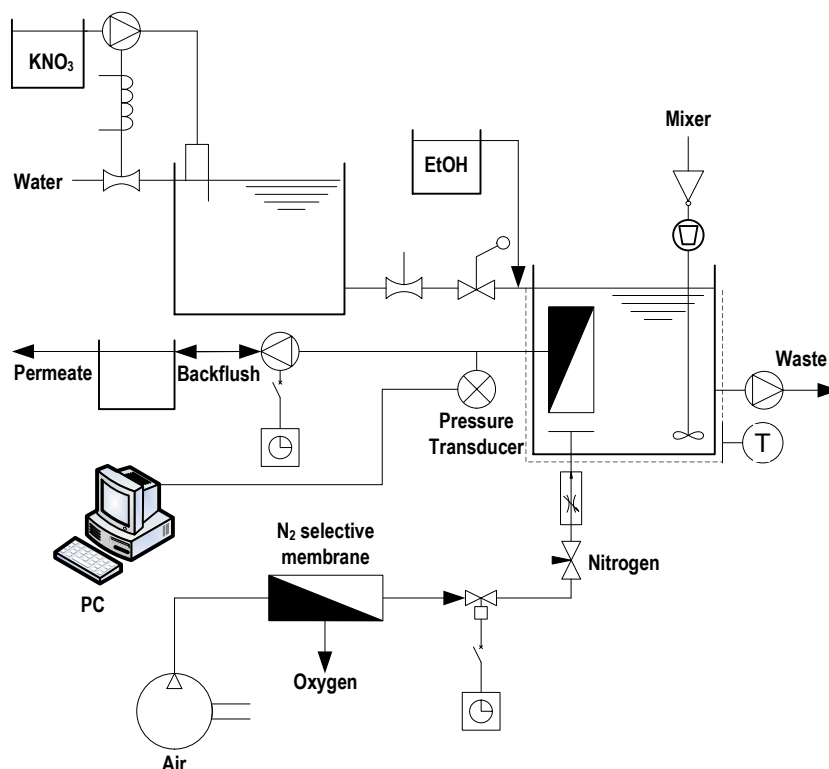


Figure 5.1 *Experimental set-up.*

A 0.93 m² out-to-in immersed PVDF hollow-fibre membrane with 0.04 µm nominal pore size was used. Permeate was withdrawn under suction from the membrane using a piston pump (FMI Inc.) operated in both forward and reverse motion in accordance with a digital programmable relay (Allen and Bradley, 700-HX). To avoid the entrainment of air Nitrogen enriched air (>99%) was used to scour the membrane, produced from compressed air (8 barg) using a nitrogen selective hollow-fibre membrane (N₂ Gen Ltd, 5-M). Gas was introduced using a solenoid valve (Zoedale Plc) controlled with a programmable digital relay (Kübler GmbH) and its flow rate controlled with a needle valve. Pressure was monitored using a pressure transducer (Gem Sensors, UK) whose signal was recorded with a data logger (Pico technology, ADC-16).

5.2.2 Analysis

Mixed liquor suspended solids (MLSS) were determined by standard methods. DOC was measured using a Shimadzu TOC-5000A analyser. Particle size was measured with a Malvern Mastersizer 2000, and a Malvern Zetasizer (Malvern, UK) used to perform zeta potential measurements. Since the zeta potential of biomass flocs could not be measured directly the flocs were agitated and the charge of the supernatant determined (Meng et al., 2006). Soluble microbial products (SMP) were extracted according to the method described in Judd (2006), and carbohydrate and protein content respectively determined using the phenol–sulphuric acid method (Zhang et al., 1999) and modified Lowry method (Frølund et al., 1995). Absorbance was measured using a Jenway 6505 UV/Vis spectrophotometer at UV_{480nm} and UV_{750nm} absorbance, respectively using D-glucose and bovine serum albumin (BSA) as standards for protein and carbohydrate.

5.2.3 Sampling protocol

Cyclic filtration was conducted in dead-end mode. The quantity of solids deposited on the membrane was varied by varying cycle duration (5, 10, 20, 30, 45, 60 and 90 minutes). To characterise residual (irreversible) fouling, cyclic filtration was continued for c.24 hours up to a set filtered volume (equivalent to 350 L.m^{-2} membrane area). Between cycles, a low energy physical clean was applied to remove the reversible layer comprising a simultaneous 30 second backflush at the same rate as the operating flux and gas injection at a specific gas demand (SGD_m) of 0.39

$\text{Nm}^3 \cdot \text{h}^{-1}$ per unit membrane area. The remaining resistance was considered to be the irreversible layer (Bessiere et al., 2005). Following each run, the membrane module was removed, rinsed and soaked in NaOCl (500mgL^{-1}) for 5h. During this period, a spare module was inserted to maintain stable operation. After chemical soaking, the module was rinsed with clean water and the permeability assessed to assure recovery.

5.2.4 Data Analysis

Residual fouling for the overall filtration period up to $350 \text{ L} \cdot \text{m}^{-2}$ was calculated from the initial pressure at the start of each cycle (Figure 5.2). Residual resistance, R_{res} , from the same filtration period can be calculated using (Bessiere et al., 2005):

$$(R_{res})_{n+1} = \frac{(\Delta P_i)_{n+1} - (\Delta P_i)_n}{\mu J} \quad (1)$$

where $(\Delta P_i)_n$ and $(\Delta P_i)_{n+1}$ are the initial pressures from cycle n and $n+1$ respectively.

Fouling within individual filtration cycles is characterised by a change in pressure with time (dP/dt) taken from the two linear parts of the curve, phase 1 (ph1) and phase 2 (ph2). A critical volume (V_{crit}) is denoted by the intersection of the regression from these two sections. Blocking law analysis of individual filtration cycles was undertaken using the combined blocking law analysis proposed by Bolton et al. (2006). The models were optimised by adjusting the fitted parameter (K , representing resistance) to minimise the sum of squared residuals (SSR):

$$SSR = \sum_{j=1}^N (TMP_{j,meas.} - TMP_{j,calc.})^2 \quad (2)$$

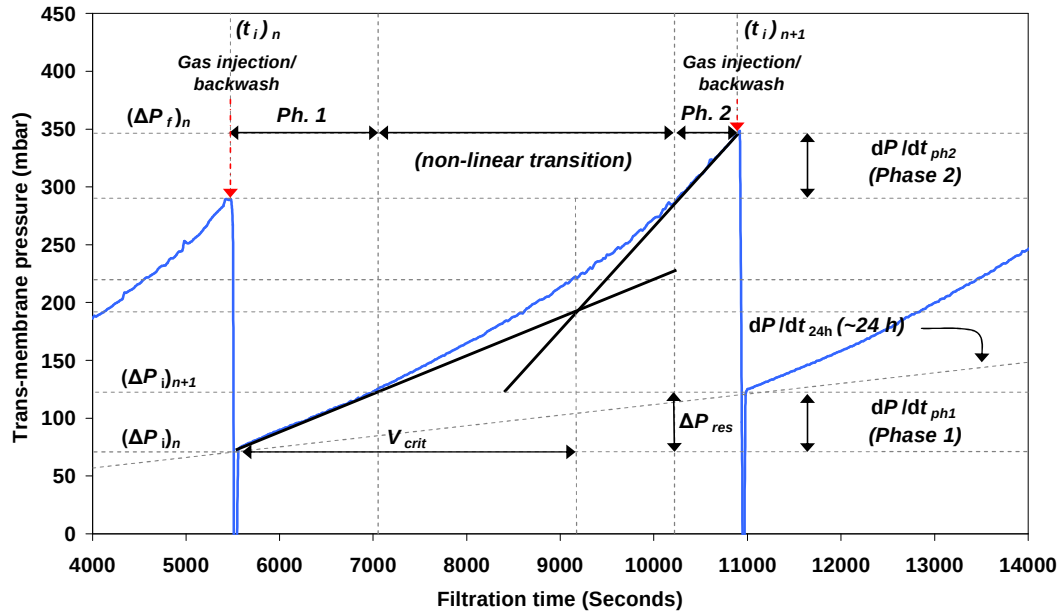


Figure 5.2 Manipulated pressure trend to illustrate how the pressure and volume parameters are derived.

5.3 RESULTS

5.3.1 Residual resistance and filtered volume

For experiments performed at a flux (J) of $15 \text{ L.m}^{-2}.\text{h}^{-1}$ and a filtration cycle duration of <30 minutes (MLSS $0.55 \pm 0.1 \text{ g.L}^{-1}$), the fouling rate over 24 hours operation (dP/dt_{24h}) remained in the range $0.2\text{-}0.7 \text{ }\mu\text{bar.min}^{-1}$ (Figure 5.3). However, on increasing cycle duration to 60 minutes, dP/dt_{24h} increased significantly to $10.4 \text{ }\mu\text{bar.min}^{-1}$. Harmant and Aimar (1996) also observed a cycle length duration below which low residual resistance arose during the filtration of a mono-disperse latex suspension. Elevated dP/dt_{24h} can be attributed to increased particle accumulation at the membrane wall that was generated by the extension of the cycle length.

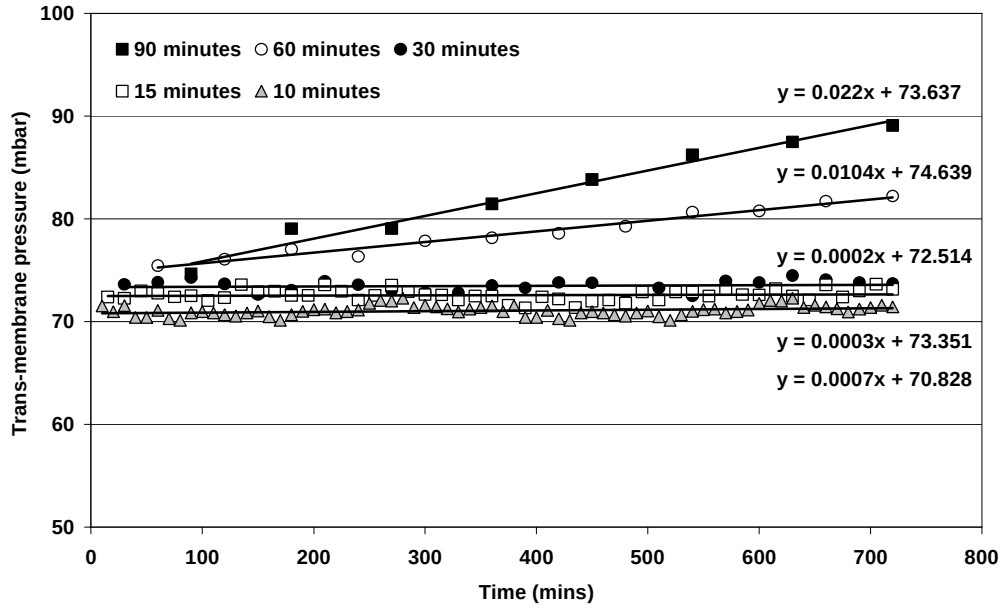


Figure 5.3 Pressure trends observed over 24 hours (dP/dt_{24h}) for operation at various cycle lengths (10, 15, 30, 60 and 90 minutes). J $15 \text{ L.m}^{-2}.\text{h}^{-1}$, SRT 10 days, MLSS $0.55 \pm 0.1 \text{ g.L}^{-1}$.

In Figure 5.4, residual resistances are plotted as the mean and standard deviation of three data sets repeated at each filtration cycle duration. As observed in Figure 5.3, two periods are clearly identifiable: an initial period of low resistance from 10 to 30 minutes; and a second period >30 minutes of increasing resistance. Bessiere et al. (2005) extrapolated these two regions to identify a critical filtered volume (V_{crit}) of c.55 and c.81 L.m^{-2} for clay and latex dispersions respectively, indicating the volume filtered prior to highly fouling conditions. Using the same technique, a V_{crit} of c.12.5 L.m^{-2} is identified for this study.

Two regions were also identified by analysis of a single 90 minute duration filtration cycle (Figure 5.4): an initial (Phase 1) linear rise in TMP, dP/dt_{ph1} $1.8 \text{ mbar.min}^{-1}$ which lasted c.0-1700 seconds, and a second linear phase (Phase 2) commencing c.4400 seconds corresponding to a sharp rise in TMP, dP/dt_{ph2} $5.3 \text{ mbar.min}^{-1}$. Both

linear intervals were regressed using 300-500 seconds of data recorded at 5-20 second intervals (Equations 3 and 4), the regressions bisecting at V_{crit} c.14.8 L.m⁻².

$$\text{Phase 1} \quad Y = 1.82x + 76.72 \quad (R^2 = 0.99) \quad (3)$$

$$\text{Phase 2} \quad Y = 5.29x - 124.72 \quad (R^2 = 0.99) \quad (4)$$

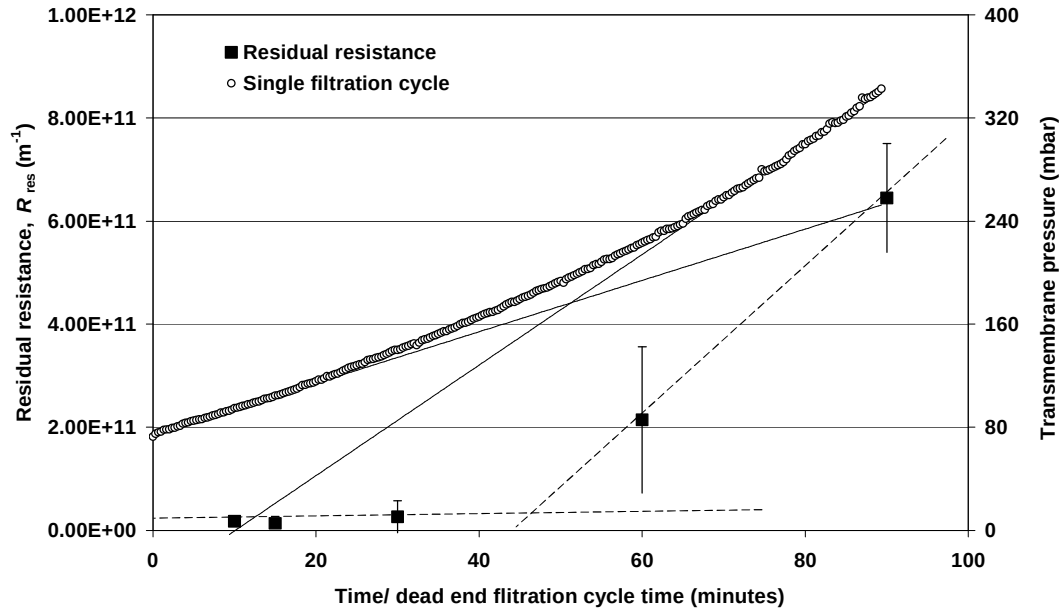


Figure 5.4 Residual resistance (R_{res}) calculated from 24 hour filtration runs at various cycle lengths. Intersection of dotted lines indicates approximate location of V_{crit} . Also plotted: Single 90 minutes filtration cycle. Intersection of the regressions also designate V_{crit} approximately. J 15 L.m⁻².h⁻¹, SRT 10 days, MLSS 0.55±0.1g.L⁻¹.

Subsequent 24 hour replicates demonstrated that the intersection was reproducible, with a mean filtered volume 13.6±2.4 L.m⁻² correlating closely with that identified by residual resistance. Ho and Zydney (1996) recorded a similar two phase transition within a dead-end filtration cycle during the microfiltration of BSA. Two of the classical blocking laws proposed by Hermia (1982) were applied in combination to describe initial fouling (phase 1) by pore blocking and subsequent (phase 2) fouling by cake filtration formed over the blocked areas. To elucidate the blocking mechanism in this study, the combined models proposed by Bolton et al. (2006) were applied (Figure 5.5). The models employ two fitted parameters and reduce to an

individual model when one mechanism dominates (Table 5.1). The combined cake-intermediate model (Equation 5) presented the best-fit to experimental data, yielding a slightly better fit (lower SSR) than the classical cake filtration model.

$$\frac{P}{P_0} = \exp(K_i J_0 t) \left(1 + \frac{K_c J_0}{K_i} (\exp(K_i J_0 t) - 1) \right) \quad (5)$$

Although the difference was not decisive, ratio analysis of the fitted parameters using $K_c J_0^2 / K_b$, $K_c J_0 / K_i$ and $K_c J_0 / K_s$ were 2.5, 13.1 and 21 respectively, emphasising the importance of cake filtration regardless of the chosen model (Bolton et al., 2006).

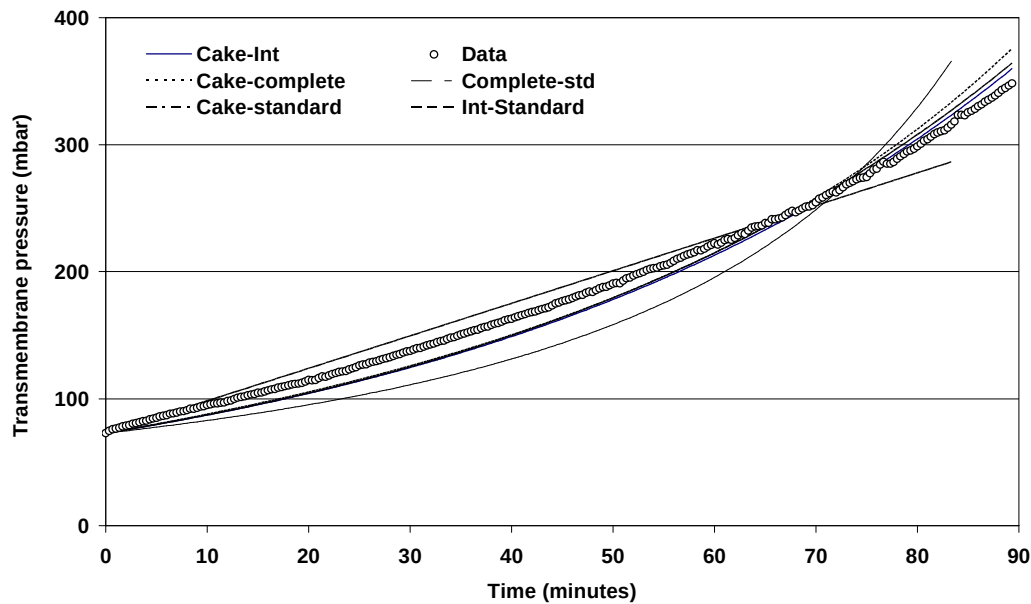


Figure 5.5 Combined blocking laws proposed by Bolton [14] applied to a 90 dead-end filtration cycle. J 15 $L.m^{-2}.h^{-1}$, SRT 10 days, MLSS $0.55 \pm 0.1 g.L^{-1}$.

Table 5.1 Summary of model data based on Bolton et al. (2006).

Model	Error, SSR	Parameters
Cake-intermediate	2.53×10^2	$K_i = 71.5 m^{-1}$ $K_c = 2.2 \times 10^8 s.m^{-2}$
Cake-complete	3.16×10^2	$K_b = 9 \times 10^{-5} s^{-1}$ $K_c = 1.3 \times 10^7 s.m^{-2}$
Cake-standard	2.72×10^2	$K_s = 6.3 m^{-1}$ $K_c = 3.2 \times 10^7 s.m^{-2}$
Cake	3.98×10^3	$K_c = 3.6 \times 10^7 s.m^{-2}$

K fitted parameters: K_i - Intermediate, K_c - Cake, K_b - Complete, K_s - Standard

5.3.2 Imposed flux

As J increased from $12 \text{ L.m}^{-2}.\text{h}^{-1}$ to $24 \text{ L.m}^{-2}.\text{h}^{-1}$ (MLSS $0.55 \pm 0.1 \text{ g.L}^{-1}$), V_{crit} decreased from c. 18.2 L.m^{-2} to c. 7.8 L.m^{-2} (Figure 5.6). This compares with previously reported data where for a set permeate flux, a specific V_{crit} can be determined (Bessiere et al., 2005; Harmant and Aimar, 1996; Jönsson and Jönsson, 1996). To describe this relationship, previous authors have used the product of the two components (J and V_{crit}) (Bessiere et al., 2005). Analysis of flux data from Figure 5.4 ($12, 15, 18$ and $24 \text{ L.m}^{-2}.\text{h}^{-1}$) yielded a JV_{crit} of 196.6 ± 17.2 (9%) $\text{L}^2.\text{m}^{-4}.\text{h}^{-1}$. Although the literature recognises SMP as a principal foulant in traditional cross-flow MBR (Judd, 2006), in an MBR operated in dead-end, the dominant component (by mass) deposited at the membrane surface can be best described by the MLSS concentration. Since particle accumulation at the membrane surface can be assumed to be proportional to filtered volume in dead-end operation, a critical accumulated mass (Harmant and Aimar, 1996) can be derived by the product JV_{crit} and C_b , where C_b is the MLSS concentration. Thus data from Figure 5.6 can be described by $JV_{\text{crit}}C_b$ or 102.3 ± 7.5 (7.4%) $\text{L g h}^{-1} \text{ m}^{-4}$. This parameter is indicative of the maximum volume throughput available for a given flux to provide sustainable conditions (MLSS $0.55 \pm 0.1 \text{ g.L}^{-1}$).

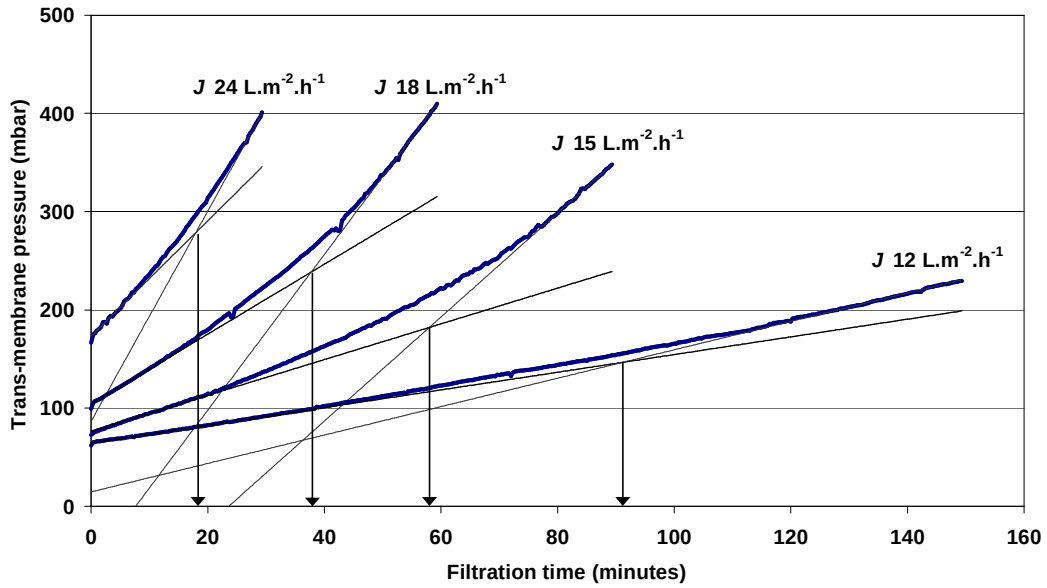


Figure 5.6 Single dead-end filtration cycles at various fluxes ($12\text{--}24 \text{ L.m}^{-2}.\text{h}^{-1}$). SRT 10 days, MLSS $0.55 \pm 0.1 \text{ g.L}^{-1}$.

5.3.3 Increased SRT

SRT was increased from 10 to 25 days which subsequently increased steady-state MLSS concentration to $1.1 \pm 0.2 \text{ g.L}^{-1}$. In Figure 5.7, residual resistances for a J value of $24 \text{ L.m}^{-2}.\text{h}^{-1}$ were plotted as mean and standard deviation of three data sets (Section 3.1). Two periods are again clearly identifiable: an initial period of low resistance from 0 to 10 minutes; and a second period >10 minutes of increasing resistance. Extrapolation of these two regions identified a V_{crit} of $\sim 6 \text{ L.m}^{-2}$. Regression of a single 40 minute dead-end filtration cycle (also presented in Figure 5.7), produced a V_{crit} value of $\text{c.}5.2 \text{ L.m}^{-2}$. Comparison with data at $J 24 \text{ L.m}^{-2}.\text{h}^{-1}$ and MLSS 0.55 g.L^{-1} (Figure 5.6) demonstrates a reduction in V_{crit} from $\text{c.}7.8 \text{ L.m}^{-2}$, due to the increased particulate concentration at the higher SRT.

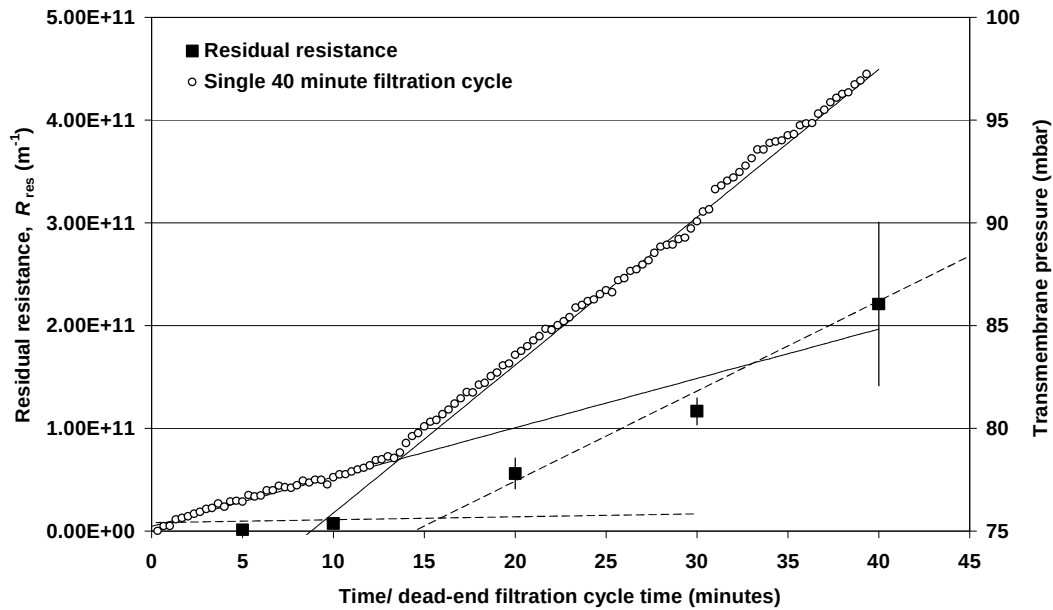


Figure 5.7 Residual resistance (R_{res}) calculated from 24 hour filtration runs at various cycle lengths. Intersection of dotted lines indicates approximate location of V_{crit} . Also plotted: Single 40 minute filtration cycle. Intersection of the regressions also designate V_{crit} approximately. J 24 $L.m^{-2}.h^{-1}$, SRT 25 days, MLSS 1.1 ± 0.2 $g.L^{-1}$.

The transition between non-fouling and fouling conditions remains clearly identifiable even though SRT has been increased and the principal components of the biomass (Table 5.2) have changed. Comparison of the ‘critical mass’ ($M_{crit} = V_{crit}C_b$) observed at the two SRT (Figure 5.6 and 5.7) produced values of 4.6 $g.m^{-2}$ and 4.8 $g.m^{-2}$ (J 24 $L.m^{-2}.h^{-1}$) for 10 and 25 day SRT respectively.

Table 5.2 Summary of biomass parameters.

Parameter		SRT (days)		
		10	25	40
MLSS	($g.L^{-1}$)	0.55 (0.1)	1.1 (0.2)	1.6 (0.2)
PSD, d_{50}	(μm)	239	182	69
SMP (DOC)	($mg.L^{-1}$)	14.3	10.9	4.8
SMP	P/C ¹	0.76	2.09	0.62
Zeta potential	(mV)	-18.6 (0.6)	-19.1 (1.2)	-16.8 (1.1)

¹P/C = Ratio of protein to carbohydrate

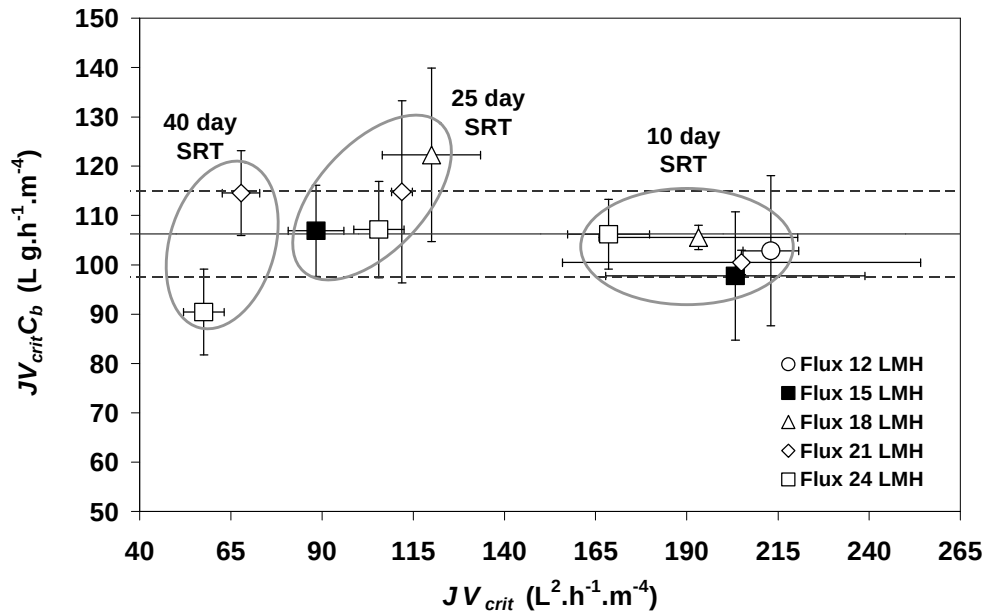


Figure 5.8 Approximate mass accumulated on the surface (C_b) incorporated to normalise data sets from three SRT ($JV_{crit}C_b$). Solid horizontal line = total data set mean; Broken horizontal lines = total data set standard deviation.

The SRT was further increased to 40 days, yielding an MLSS concentration 1.6 ± 0.2 $g \cdot L^{-1}$. The regressive technique (Section 3.1) was used to define V_{crit} for flux data at each of the three SRT values. Data was subsequently plotted against critical accumulated mass ($JV_{crit}C_b$) (Figure 5.8), the value of the latter being consistently 106 ± 8.3 $L \cdot g \cdot h^{-1} \cdot m^{-4}$ across the entire data set independent of flux and SRT. Bessiere et al. (2005) determined critical accumulated masses of 88 $L \cdot g \cdot h^{-1} \cdot m^{-4}$ and 1312 $L \cdot g \cdot h^{-1} \cdot m^{-4}$ at 80 $L \cdot m^{-2} \cdot h^{-1}$ for clay (0.02 $g \cdot L^{-1}$) and latex (0.02 wt.%) respectively, indicating that critical accumulated mass is directly linked to suspension characteristics. The suspensions studied by the authors were classic mono-disperse colloidal systems with controlled ionic environments and narrow size distributions. According to the current study, the same principles seem apply to an ostensibly heterogeneous suspension, yielding a similar absolute critical accumulated mass value as that measured for clay.

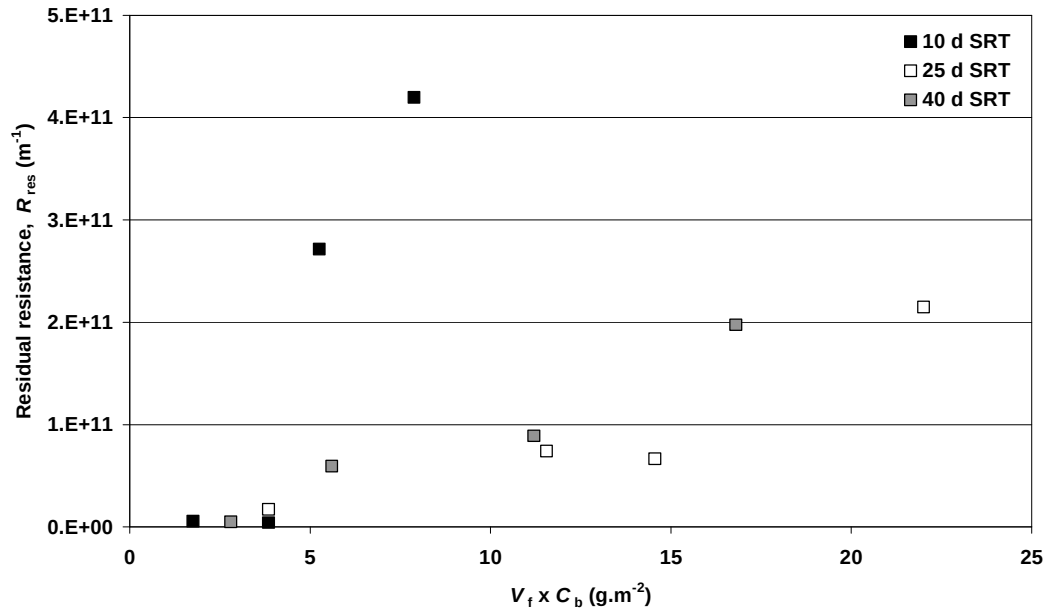


Figure 5.9 Residual resistance (R_{res}) calculated from 24 hour filtration runs plotted versus the approximate mass accumulated within a single filtration run. J 21 $L.m^{-2}.h^{-1}$.

5.3.4 Impact of system change and long term operation

Residual resistance data computed from varying filtration cycle length runs for 10, 25 and 40 day SRT were correlated with the estimated mass deposited during each filtration cycle ($V_{filt} \times C_b$) (Figure 5.9). When SRT was increased from 10 to 25 and 40 days, the increase in R_{res} was significantly less. Bessiere et al. (2005) observed a similar low increase in resistance during filtration of a clay suspension (cf. latex), indicative of a less clear transition from non-fouling to fouling conditions. This change in transitional behaviour is also clear from the change in dP/dt behaviour observed in phase 1 of the dead-end filtration cycle (Figure 5.10), i.e. during particle deposition. As SRT was increased, dP/dt_{ph1} decreased from 5.8 $mbar.min^{-1}$ at 10 days SRT to 1.4 and 2.5 $mbar.min^{-1}$ at 25 and 40 days SRT respectively. The relationship between hydraulic resistance and deposited MLSS concentration can be calculated from (1996):

$$\alpha = \frac{R}{D_{mlss}} \quad (6)$$

Where α is the specific resistance of the deposited layer (m.kg^{-1}), R the resistance from deposition in phase 1 (m^{-1}) and D_{mlss} the density of the deposit at the membrane wall, using MLSS as an approximation (kg MLSS.m^{-2}).

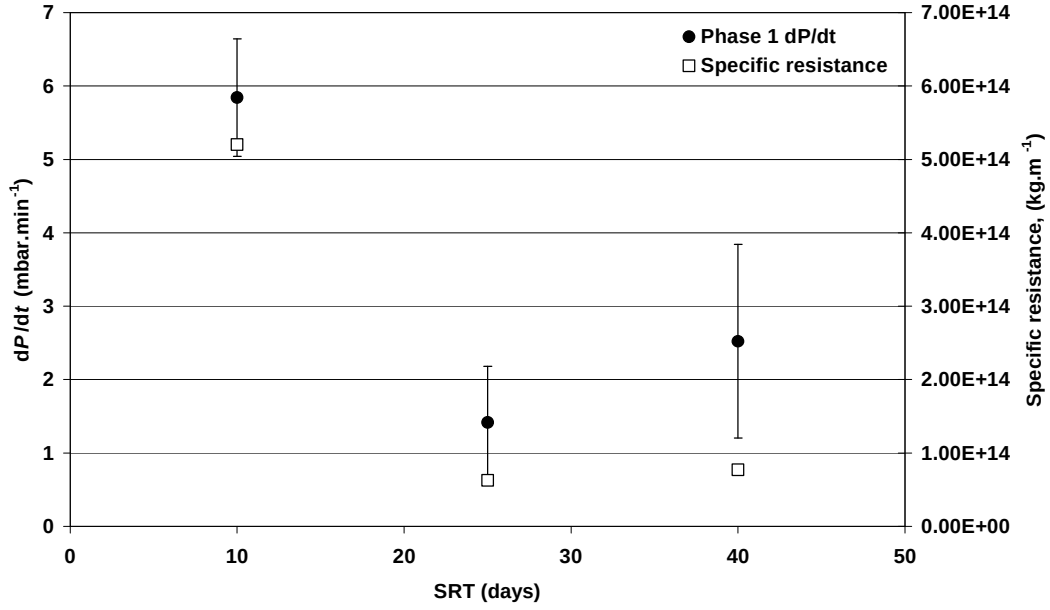


Figure 5.10 Fouling rate observed within the first phase (dP/dt_{ph1}) of the filtration cycle during the three SRT periods. Specific resistance (α) calculated from the average of this data. J 21 $\text{L.m}^{-2}.\text{h}^{-1}$.

Although the transition between non-fouling and fouling conditions were less clear at extended SRTs, V_{crit} remained identifiable from regression analysis of the filtration cycle and the change in R_{res} . The MBR was operated for periods up to 2 weeks $< JV_{crit}C_b$. Permeability (K) typically remained stable with no evidence of fouling. For example, while operating at 21 $\text{L.m}^{-2}.\text{h}^{-1}$ and 40 days SRT (MLSS 1.6 g.L^{-1}), K was stable at 130 $\text{L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1} \pm 5 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ (Figure 5.11). Physical cleaning during this period comprised a 30 second gas scour every 10 minutes at a flow rate equivalent to a SGD_m value of 0.39 $\text{m}^3.\text{m}^2.\text{h}^{-1}$, decreasing to a time-averaged SGD_{mnet}

of $0.019 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, in conjunction with a 30 second backflush at c.1.15x forward flux (yielding 5.7% product flow loss).

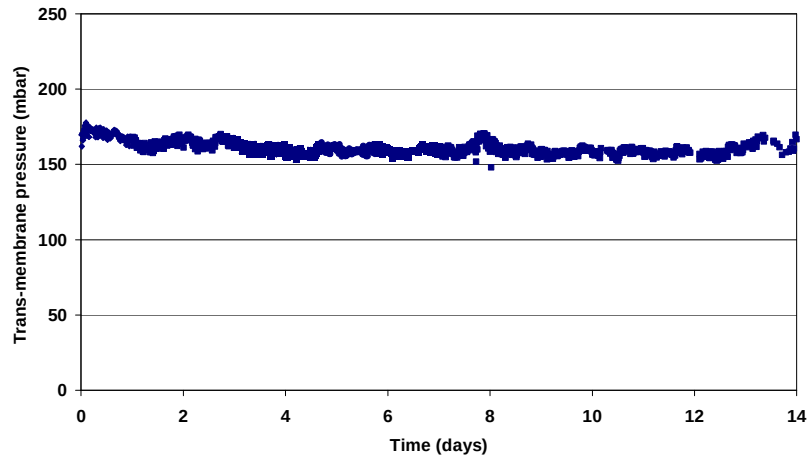


Figure 5.11. 14 day transient during operation at $J \ 21 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, and SRT 40 d ($1.6 \pm 0.2 \text{ g} \cdot \text{L}^{-1}$). Physical cleaning comprised gas ($\text{SGD}_m \ 0.39 \text{ m}^3 \cdot \text{m}^2 \cdot \text{h}^{-1}$) and backflush ($24 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) for 30 seconds in between filtration cycles.

5.4 DISCUSSION

5.4.1 Critical accumulated mass

In standard MBR operation, cross-flow of liquid or gas generates a tangential shear to balance the convective force of permeate withdrawal. The influence of particle radius (a^2) on shear-induced diffusivity (D_s) has been demonstrated (Equation 6) (Leightone and Acrivos, 1987). This explains the preferential transport of small particles (e.g. SMP) to the membrane wall in polydisperse suspensions (Kromkamp et al., 2006); colloidal SMP is dominantly controlled by Brownian motion thus shear is relatively ineffective in controlling deposition (Jiang et al., 2007).

$$D_s = 0.33\gamma a^2 \phi^2 (1 + 0.5e^{8.8\phi}) \quad (7)$$

Conversely, in dead-end MBR operation, aggregates (flocs), primary particles and colloids are convected toward the membrane during permeate withdrawal. The key finding of this study was that a critical deposited mass density (mass per unit membrane area), corresponding to the maximum specific mass of particles that can be reversibly deposited for a given flux (Harmant and Aimar, 1996), exists for the denitrification MBR. Harmant and Aimar (1996) explained the critical mass concept using a force balance where drag force within the first layer of the loose cake increases as layer number increases until a critical value is reached which induces coagulation or 'collapse' into a consolidated layer. In this study, once consolidation had occurred (phase 2 of the filtration cycle), the low energy physical clean was unable to re-disperse the deposit effectively and a growth in residual resistance was observed.

Critical specific mass has principally only been observed previously in colloidal dispersions with fixed particle size and ionic environments (Bessiere et al., 2005; Jönsson and Jönsson, 1996), thus it is of interest that a similar pattern is presented in this study comprising such a heterogeneous matrix. Electrostatic forces are responsible for the deposition boundary observed for colloids; if convective forces exceed repulsion, physical adsorption takes place, if convection balances repulsion, deposit reversal is possible (Harmant and Aimar, 1996). In this study, particle-particle relationships (between aggregated and non-aggregated bacterial cells and SMP) are potentially too complex to be solely described using discrete surface forces. However, the physical interaction between the accumulated particles and membrane wall is of significance. This was demonstrated by Li et al. (2003) during cross-flow micro-filtration (MF) where the re-suspension of sub-micron bacteria (c.0.8 μm) was

dependent on the time the cake had remained at the surface and the ionic composition of the feed. The authors subsequently related this to interactions within the cake but also to interactions between the bacteria and membrane surface.

5.4.2 Filtration cycle analysis

In this study, average α ranged from 10^{13} to 10^{14} m.kg⁻¹ during the initial stages of deposit formation (phase 1 of the filtration cycle). Although α from this study cannot be compared directly to cross-flow operation from other studies due to filtration and suspension variations, α values reported for cross-flow operation have ranged between 10^{15} and 10^{17} m.kg⁻¹ (Nagaoka et al., 1996; Metzger et al., 2007) - several orders of magnitude higher than that observed in this study. The distinction between the two operations can be linked to deposition kinetics and particle radius (Equation 6); in cross-flow, particles of lower radius preferentially migrate toward the membrane wall generating a closely packed, high resistance cake whereas dead-end operation permits convection of particulate material with a broad size distribution creating a highly porous aggregate. The lower specific resistance apparently simplifies re-dispersion of the bacterial aggregate and reduces the specific energy demand.

The transition from phase 1 to phase 2 during a single filtration cycle was less sharp than that observed by other authors when filtering colloidal and macromolecular suspensions (Ho and Zydney, 2002; Chen et al., 1997). Ho and Zydney (2002) described the significance of the initial phase of filtration within a filtration cycle on dP/dt during dead-end filtration of BSA using a 0.2 μm polycarbonate membrane. The sharpness of this transition is dependent on membrane pore size (Ho and Zydney,

2002) and dispersion characteristics (size, charge (Harmant and Aimar, 1996) and shape (Bessiere et al., 2005)), subsequently dictating the mechanism by which the initial deposit is formed. Blocking law analysis indicates cake dominant filtration which may explain the less sharp transition observed in this study and further explain the simplicity with which it is reversed.

During initial deposition (phase 1), the specific resistance of the deposit was most significant at the lowest MLSS concentration (10 days SRT). At higher MLSS concentrations (25 and 40 days SRT), α decreased to approximately one-third. Kwon et al. (2000) suggested that higher TMP values recorded at low suspension concentrations reflect more ordered and tightly packed deposits which could explain the higher α value observed at the lowest SRT. The concentration of SMP was also most significant at 10 days SRT (c.14 mg DOC.L⁻¹), which may have also influenced the deposit structure. Although α varies with SRT, the critical accumulated mass is none-the-less indicative of incipient residual resistance growth. The magnitude of the specific resistance observed within filtration cycle analysis correlated to the extent of residual resistance growth observed over longer periods of filtration. The transition from low to high fouling conditions was far more significant at 10 days SRT than at 25 and 40 days respectively. Bessiere et al. (2005) observed similar discontinuity during ultrafiltration of suspended bentonite suggesting that the reduction in criticality between non-fouling and fouling conditions may be due to particle shape and a broad particle size distribution (compared to latex).

5.5 CONCLUSIONS

Previous studies have demonstrated that using concepts of critical specific mass (deposited mass per unit membrane area), sustainable dead-end colloidal filtration can be maintained provided cake formation kinetics are understood (Harmant and Aimar, 1996). The work in this paper presents the first application of these concepts to a complex polydisperse matrix, specifically a denitrification MBR. The key parameter of critical accumulated specific mass apparently indicated incipient deposit consolidation, and critical conditions were identified at three SRT values. When optimum conditions were adopted for longer term trials low residual fouling rates ($dP/dt < 1.2 \times 10^{-3} \text{ mbar.h}^{-1}$) were recorded, implying long term sustainable operation of MBR is possible in dead-end mode with an associated 20x reduction in energy demand over that for constant gas scouring.

As SRT increased, the specific resistance of the deposit decreased resulting in a more diffuse transition from low to high fouling. At the dilute feed waters associated with this application (i.e. potable water denitrification) it is unlikely that the MLSS concentration will increase significantly above that studied. For conventional wastewater applications this may not be the case, though the critical accumulated specific mass parameter may still be used to determine limiting conditions for cyclic aeration and the dependency of R_{res} on the hydrodynamics of the physical clean.

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CHAPTER 5(b)

**A COMPARISON OF CONSTANT AND INTERMITTENT
(DEAD END) GAS SCOURING FOR ANOXIC
IMMERSED MEMBRANE BIOREACTOR OPERATION**

IN PREPARATION FOR SUBMISSION TO: *Separation Science
and Technology*

5(b) A COMPARISON OF CONSTANT AND INTERMITTENT (DEAD END) GAS SCOURING FOR ANOXIC IMMERSED MEMBRANE BIOREACTOR OPERATION

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ABSTRACT

This paper presents a comparison of cross-flow and dead-end filtration in an immersed membrane bioreactor applied to groundwater denitrification. Long term filtration in dead-end mode presented a significantly lower fouling rate (dP/dt) than in cross-flow. Backflush in combination with gas scour presented no inherent benefit over using gas scour in isolation during dead-end filtration but reduced dP/dt from $0.011 \text{ mbar.min}^{-1}$ to $0.004 \text{ mbar.min}^{-1}$ during cross-flow filtration. An experimental hollow fibre was used to monitor local pressure variations. The pressure drop during DE filtration was fairly stable whereas pressure distribution during CF exhibited greater variability. Resistance in series analysis demonstrated irreversible and cake resistance to be most strongly associated with cross-flow and dead-end filtration respectively and is indicative of the variation in deposition kinetics associated with the two operations. Although cross-flow conditions have not been excessively optimised in this study, it is apparent that immersed MBR operated in dead-end mode can compare at low suspended solids concentration. This is significant when considering the energy demand associated with constant gas scour and backflushing.

5.7 INTRODUCTION

Immersed membrane bioreactors (iMBR) are commonly exploited for aerobic wastewater treatment. However, great opportunities also exist for anoxic redox conditions (McAdam and Judd, 2007; McAdam and Judd, 2008a). The iMBR configuration is superficially limited for this application as air cannot be applied for scour if dissolved oxygen (DO) concentration is to be maintained below 0.1 mg L^{-1} . To overcome this limitation, two options intuitively exist: (a) applying two-stages and (b) using headspace gas recirculation. The two-stage MBR incorporates an initial anoxic tank for denitrification and a subsequent aerobic stage for excess carbon removal and permeate withdrawal under air scour (Buttiglieri et al., 2005). However, elevated DO concentration in the recycle can impact on denitrification (Buttiglieri et al., 2005). Rezania et al. (2007) instead recirculated accumulated head space nitrogen gas (N_2) for membrane scour thereby providing a single stage process. Both headspace recirculation and air scour constitute a cost penalty when operated in continuous or cross-flow (CF) mode. As such many researchers have sought to optimise hydrodynamics for this application. Lee et al. (2001) opted for an air backwash to create intermittent shear in anaerobic conditions. However, scouring >5 seconds every 10 minutes increased the DO residual and, as a consequence, sustainable operating conditions were not attained. In previous work, this Centre has shown that under well defined operating conditions, dead-end (DE) conditions can be applied constituting an energy saving of c.20 times over continuous scour (McAdam and Judd, 2008b). The aim of this paper is therefore to: (i) more comprehensively study the hydrodynamics of DE MBR operation; and (ii) compare operation to CF hydrodynamics in identical reactor and biomass conditions.

5.8 MATERIAL AND METHODS

5.8.1 Experimental set-up and analysis

The pilot scale rig comprised a 75 L bioreactor with an immersed hollow fibre (HF) PVDF 0.93m² (0.04 µm) module. The rig was designed for potable water denitrification. Anoxic conditions were maintained by using N₂ for gas scour. Further rig details are reported in McAdam and Judd, 2008b. This study was completed having reached steady state (>3 SRT) at 25 days SRT (1.1±0.2g.L⁻¹).

DE experiments were initially conducted in the MBR. Dead-end operation involved permeate withdrawal for a set period (up to 40 minutes) in the absence of scour. Permeate withdrawal was then ceased for either 30 or 120 seconds and a combination of gas scour and backflush introduced for physical cleaning. CF operation involved applying continuous gas scour during permeate withdrawal. Backflush, when employed, was incorporated every 10 minutes for 30 seconds. Finally, DE conditions were continued to maintain the reactor at steady state. In this phase the hollow fibre section (Section 2.2) was also placed inside the reactor.

Mixed liquor suspended solids (MLSS) were determined by standard methods. Particle size was measured with a Malvern Mastersizer 2000. Soluble microbial products (SMP) and extractable extracellular polymeric substances (eEPS) were extracted according to the method described in Judd (2006), and carbohydrate and

protein content were determined using the phenol–sulphuric acid method (UV_{480nm}) (Zhang et al., 1999) and Lowry method (UV_{750nm}) (Frølund et al., 1995) respectively. As with Zhang et al. (2006), total EPS (EPS_{tot.}) was considered to be the sum of SMP and EPS. Absorbance was measured using a Jenway 6505 UV/Vis spectrophotometer using D-glucose and bovine serum albumin (BSA) as standards for carbohydrate and protein respectively.

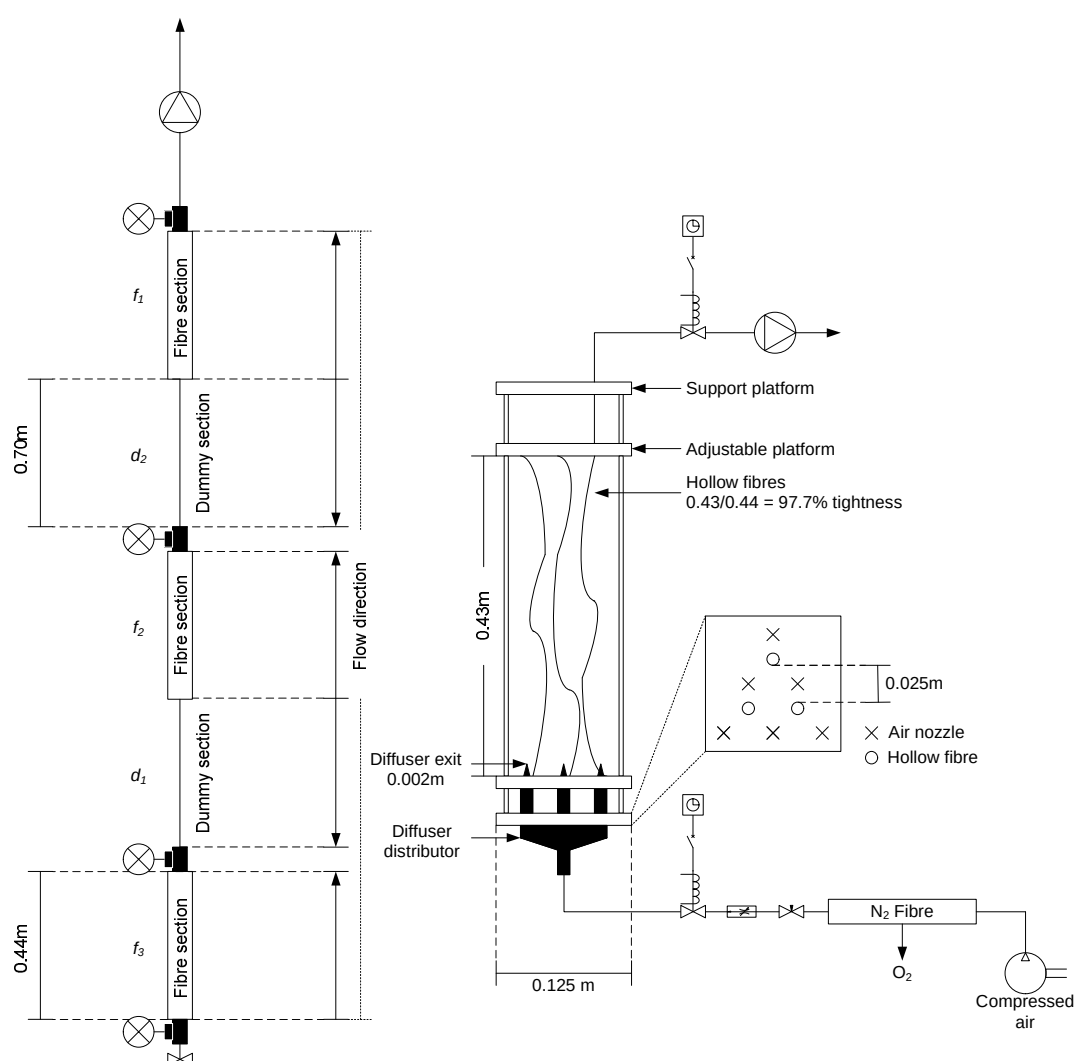


Figure 5.11 *Fibre section experimental set-up.*

5.8.2 Hollow fibre section

HF sections (using the same material as above) were used to study variations in local pressure distribution (Figure 5.11). Internal and external diameters were assumed as 0.9 mm and 1.9 mm respectively, the latter measurement being used to compute flux. Fibre ends were affixed into epoxy resin. The clean water permeability of each fibre was then tested to assure similarity (Table 5.6). Fibres were secured into T-connectors (internal space c.10mm). Three fibres (f_1 to f_3) were connected in series with an individual active fibre length of 0.44 m. To ensure exact hydrodynamic similarities, fibres were vertically oriented between two adjustable platforms and each fibre sited in the centre of three diffuser tips. Dummy sections were used to extend path length. Platforms were adjusted to provide a fibre tightness of 97.7%. Gas flow rate (N_2) and flux (J) were 4 L.min⁻¹ ($G = 262.5 \text{ s}^{-1}$) and 7.6 L.m⁻².h⁻¹ respectively. DE operation comprised 10 minutes dead-end filtration/30 seconds gas scour. The lumen-side hollow fibre pressure profile was measured in clean water and validated according to Hagen-Poiseuille (Eq. 1):

$$\frac{dp}{dx} = -\frac{32\mu v}{D_i^2} \quad (1)$$

where p is lumen side pressure, D_i is the effective internal diameter, v is flow velocity and μ is viscosity. Resistance caused by caking (R_c) and by pore plugging and irreversible adsorption (R_f) were calculated using (Bae and Tak, 2005):

$$R_c = \frac{\Delta P_T}{\mu J_{AS}} - R_m - R_f \quad (2)$$

$$R_f = \frac{\Delta P_T}{\mu J_w} - R_m \quad (3)$$

where J_{AS} is the flux during sludge filtration at set process volume and J_w is the initial water flux after removing the cake layer with a DI water rinse. Shear intensity (G) developed through gas sparging was calculated using (Delgado et al., 2008):

$$G = \left(\frac{\rho_s g Q_a}{A \mu_a} \right)^{0.5} \quad (4)$$

where Q_a is gas flow-rate, ρ_s is density, g is gravitational acceleration, μ_a is apparent viscosity and A is the cross-sectional air sparging area which can be calculated from:

$$A = \frac{\pi}{4} d_s^2 - n_f \frac{\pi}{4} d_f^2 \quad (5)$$

where d_s is module diameter, d_f is outer fibre diameter and n_f is fibre number.

5.9 RESULTS

5.9.1 Cross-flow versus dead-end

The HF membrane was operated at various fluxes and an SRT of 25 days to discern sustainable conditions (Figure 5.12). The transition between a slow rise in dP/dt (Stage 2) and a rapid rise in dP/dt (Stage 3), t_{crit} , was observed at 60 h and 132 h for 29 and 24 $L.m^{-2}.h^{-1}$ respectively.

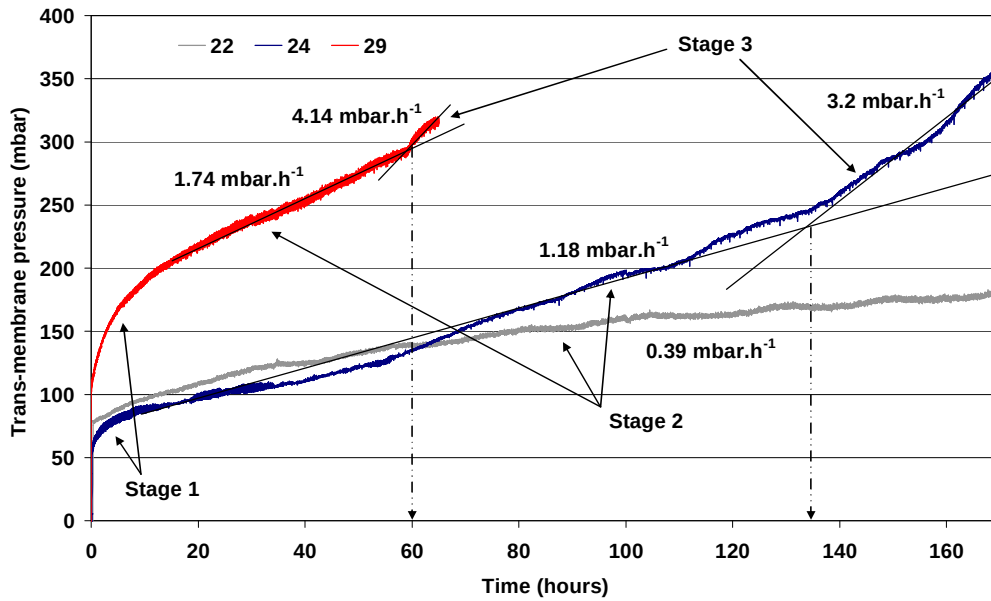


Figure 5.12 Definition of sustainable flux (J). SGD_m $0.39 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ($G = 259 \text{ s}^{-1}$). $MLSS$ $1.1 \text{ g} \cdot \text{L}^{-1} \pm 0.2 \text{ g} \cdot \text{L}^{-1}$. SRT 25 days.

When compared to other studies (Table 5.3), the transition from Stage 2 to Stage 3 fouling, denoted by $St_{2dP/dt} / St_{3dP/dt}$, does not appear to be as significant. Zhang et al. (2006) suggested that conditioning (St_1) was due to pore closure or blockage and Stage 2 (St_2) was the result of pore blocking and biopolymer deposition. It is therefore rational to conclude that pore size, hydrodynamic and biomass characteristics will influence the extent of the sharp rise in TMP, or jump (Judd, 2006). At $22 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, t_{crit} (and stage 3) was not observed over a 7 day period indicating that conditions were not sufficiently critical to induce local flux effects (Zhang et al., 2006).

Table 5.3 Comparison of critical conditions.

Config./ Feed	J ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	MLSS ($\text{g} \cdot \text{L}^{-1}$)	t_{crit} (h)	dP/dt		$St_{2dP/dt} / St_{3dP/dt}$	Ref.
				Stage 2	Stage 3		
SS HF $0.22 \mu\text{m}$ 50L/ Syn. Mun.	30	5-6	N/a	0.012	0.03	2.5	[Wen]
Imm. Tub. $0.03 \mu\text{m}$ 40L/ Syn. Ind.	6	6	137	0.0051	0.031	6.1	[Brookes]
Imm. HF $0.04 \mu\text{m}$	24	1.1	138	0.02	0.053	2.7	[This stu]

In contrast, critical conditions in dead-end filtration are defined by the volume filtered (V_f) within a single filtration cycle (a run comprises a series of cycles) as this can describe the mass deposited at the membrane surface (Figure 5.13). For example, in this study, provided the mass deposited at the membrane surface remained below 4.8 g.m^{-2} when operating at $24 \text{ L.m}^{-2}.\text{h}^{-1}$ and 25 days SRT (MLSS $1.1 \pm 0.2 \text{ g.L}^{-1}$) (McAdam and Judd, 2006), dP/dt was low at <0.01 to 0.06 mbar.d^{-1} (Table 5.4).

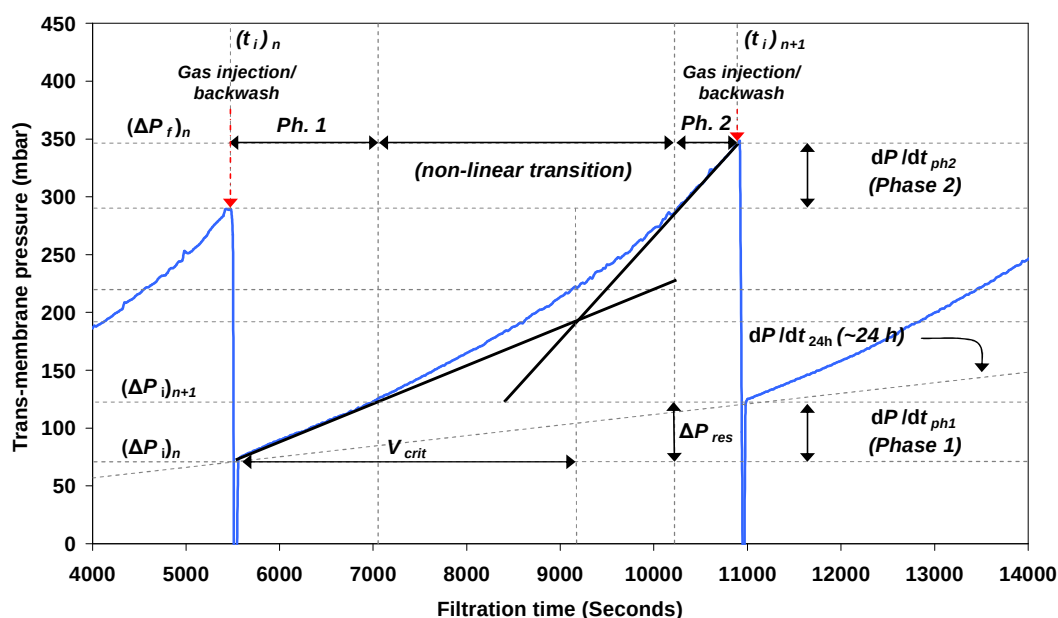


Figure 5.13 Example of the dead-end curve (adapted from Chapter 5a).

Table 5.4 Fouling rates for various filtration modes.

Filtration mode	J ($\text{L.m}^{-2}.\text{h}^{-1}$)	SRT (d)	SS (g.L^{-1})	dP/dt (mbar.d^{-1})	SGD_{mnet}^4 ($\text{m}^3.\text{m}^2.\text{h}^{-1}$)
CF (no b/wash)	22.4	25	1	16 (0.011) ³	¹ 0.387
CF (with b/wash)	23.5	25	1	5.8 (0.004) ³	¹ 0.387
DE	21.3	40	1.5	<0.01 - 0.06	² 0.018

¹Nitrogen. ²Air. ³ mbar.min^{-1} . ⁴ SGD_{mnet} – time averaged SGD_m .

Under cross-flow conditions at the same J and SGD_m ($0.39 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$), dP/dt increased by two orders of magnitude to 16 and $5.8 \text{ mbar} \cdot \text{d}^{-1}$ (or $0.011 \text{ mbar} \cdot \text{min}^{-1}$ and $0.004 \text{ mbar} \cdot \text{min}^{-1}$ respectively) corresponding to operation with and without backwash respectively. Filtration mode variation in MBR has been previously demonstrated to influence cake structure and composition (Metzger et al, 2007). The SMP component within the fouling layer (determined as a global cake, Table 5.5) increased from $15\% \pm 6\%$ to $41\% \pm 11\%$ when operation was modified from DE to CF filtration and can be attributed to the preferential migration of the finer particles toward the membrane during CF filtration creating a more tightly packed irreversible fouling layer. When conditions were changed to CF, there was also a decrease in floc size (d_{50}) from $182 \text{ }\mu\text{m}$ to $52 \text{ }\mu\text{m}$ due to the augmented shear intensity, which apparently impacted upon bulk composition (Table 5.5) and may have subsequently impacted upon the composition of the deposit formed at the membrane wall.

Table 5.5 *Global cake components. SRT 25 days, MLSS $1.1 \text{ g} \cdot \text{L}^{-1} \pm 0.2 \text{ g} \cdot \text{L}^{-1}$.*

	Cross-flow		Dead-end	
	Bulk	Biofilm	Bulk	Biofilm
$\text{EPS}_{\text{tot.}}$		1.4 (0.2)		3.5 (0.6)
SMP	0.9 (0.6)	0.9 (0.1)	2.1 (0.5)	2.2 (1.6)
$\text{SMP}/\text{EPS}_{\text{tot.}} (\%)$		41 (10.9)		15 (5.8)
eEPS	1.8 (0.3)		3.7 (0.4)	

Standard deviation in parenthesis.

5.9.2 Dead-end hydrodynamics

The effect of specific gas demand (SGD_m , $0.3\text{-}1.6 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) or shear intensity (G , $236\text{-}529 \text{ s}^{-1}$) on dP/dt over 24 hours operation for V_f from 3.5 to $14 \text{ L} \cdot \text{m}^{-2}$ was investigated (Figure 5.14). When V_f was $3.5 \text{ L} \cdot \text{m}^{-2}$, dP/dt was limited to $<0.0005 \text{ mbar} \cdot \text{min}^{-1}$ provided $\text{SGD}_m > 0.65 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. The optimum SGD_m existed between

0.32 and 0.65 $\text{m}^3.\text{m}^{-2}.\text{h}^{-1}$. Typically dP/dt decreased with increasing SGD_m until a plateau was reached, beyond which no further suppression of dP/dt was attained. This is a well reported phenomenon in CF operation (Ueda et al., 1997). In this study, commencement of the plateau was dictated by the imposed V_f ; with the value increasing with increased gas demand. However, the same dP/dt observed at 3.5 $\text{L}.\text{m}^{-2}$ was not attained for $V_f > 3.5 \text{ L}.\text{m}^{-2}$ even when the optimum SGD_m was adopted. In our previous study, exceeding a critical filtered volume (V_{crit}) of c.4.6 $\text{L}.\text{m}^{-2}$ (for these conditions) indicated where deposit consolidation occurred.

The significance of SGD_m and backflush were further examined by operating the MBR using either gas or backflush to control deposition. When operating at 3.5 $\text{L}.\text{m}^{-2}$ and using only gas scour, increasing SGD_m from 0.32 to 1.29 $\text{m}^3.\text{m}^{-2}.\text{h}^{-1}$ exerted a limited influence on dP/dt indicating that the hydrodynamic limit was reached at around 0.32 $\text{m}^3.\text{m}^{-2}.\text{h}^{-1}$ (Figure 5.15). This corresponded to a dP/dt of 0.00054 $\text{mbar}.\text{min}^{-1}$, which is comparable to performance attained in combination with backflush (Figure 5.14). Conversely, when backflushing was used in isolation (Figure 5.16), dP/dt for the same applied J and V_f was 0.022 $\text{mbar}.\text{min}^{-1}$ - two orders of magnitude higher than when applied in combination with gas implying scour may be necessary to promote back transport. Extending backflush length improved efficiency which is qualitatively similar to Kennedy et al. (1998) who identified that backflushing efficiency is more dependent on backflush time than pressure (or flux). Increasing backflush flux from 1.3x to 2.7x forward J actually increased dP/dt dramatically possibly due to the increased disturbance of the cake layer.

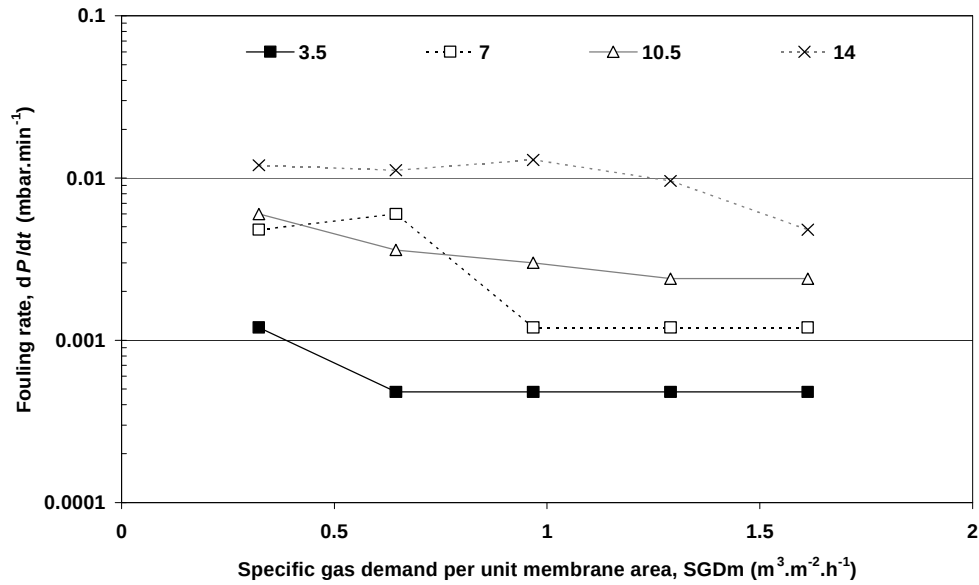


Figure 5.14 Impact of SGD_m on fouling rate (dP/dt) over 24 hours for J 21 $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and filtered volumes (V_f) ranging from 3.5 to 14 $\text{L} \cdot \text{m}^{-2}$. Backflush J set at x2 forward J .

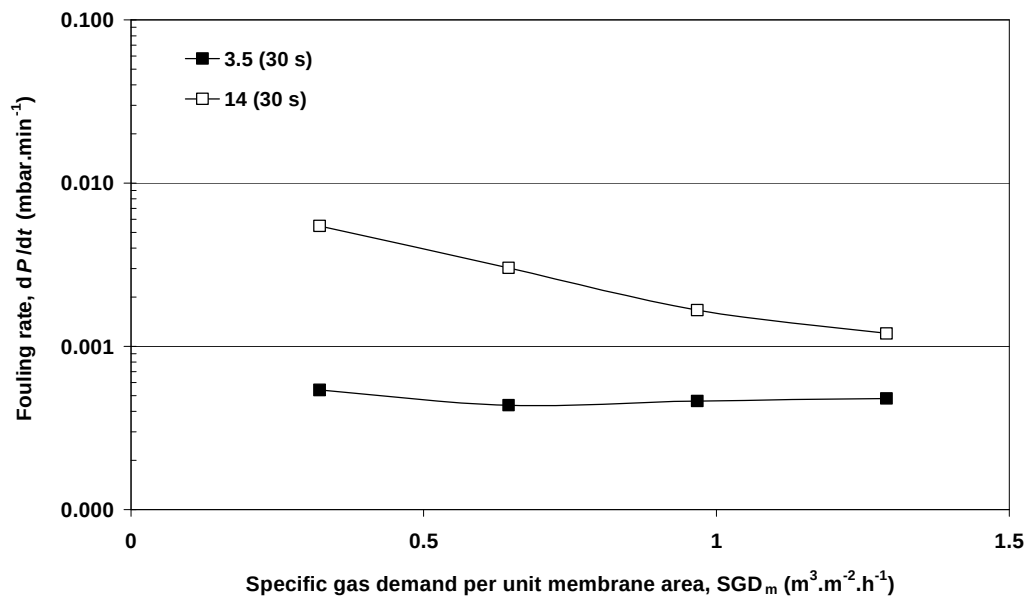


Figure 5.15 Impact of SGD_m on fouling rate (dP/dt) over 24 hours without backflush. J 21 $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and filtered volumes (V_f) 3.5 and 14 $\text{L} \cdot \text{m}^{-2}$.

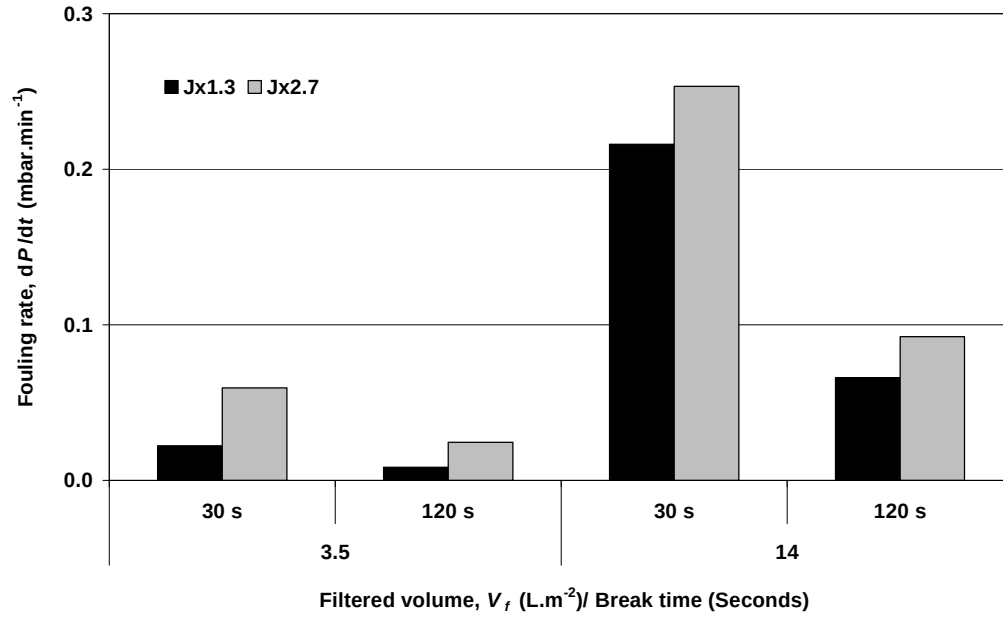


Figure 5.16 Impact of backflush flux (J) at 1.3x and 2.7x forward flux on fouling rate (dP/dt) over 24 hours without gas scour. Filtered volumes (V_f) 3.5 and 14 L.m⁻². J 21 L.m⁻².h⁻¹. Break time (backflush length) 30s and 120s.

5.9.3 Pressure drop characterisation

From visual observations made of the cake formed at the membrane wall during DE (operated $>V_{crit}$) and CF operation (Figure 5.17), variations in spatial deposition were apparent. To probe this variation, pressure distribution was monitored using a sectional HF approach (Figure 5.11).

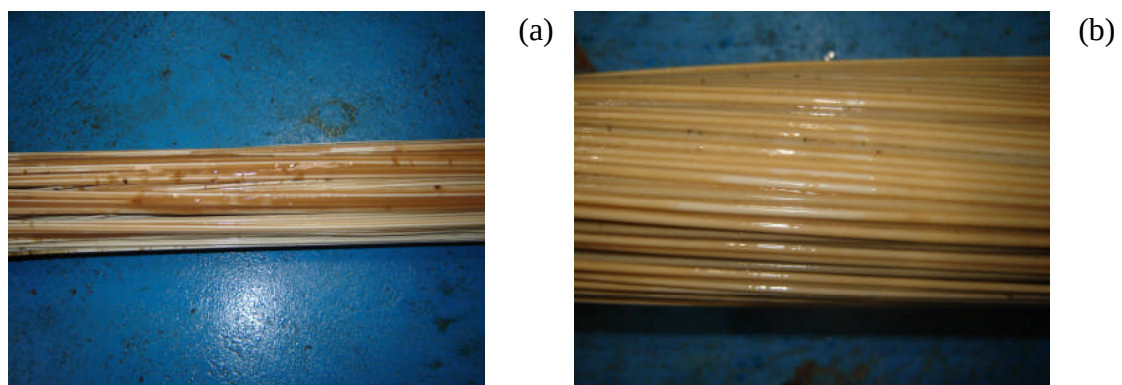


Figure 5.17 Visual biofilm observation of: (a) Typical cake formed during CF filtration. J 22 L.m⁻².h⁻¹. SGD_m 0.39 m³.m².h⁻¹; and (b) Typical cake formed during DE filtration ($>V_{crit}$). J 15 L.m⁻².h⁻¹. SGD_m 0.39 m³.m².h⁻¹.

A HF D_i of 0.94mm was found to most closely correlate theoretical and experimental data in clean water conditions (Figure 5.18), constituting c.4.4% deviation from the manufacturers' specification.

Pressure drop increased along the total fibre due to the commensurate increase in flow. Pressure drop across each fibre was given by $\Delta P_{n+1} - \Delta P_n$. During MBR filtration, pressure drop increased rapidly in all fibres upon start-up from 0 to c.30 minutes. A response lag observed for fibre sections 2 and 3 was probably due to the extended path length provided by the dummy sections. At steady state, the highest pressure drop was observed across the exit fibre (f_1) (Figure 5.19); regular spacing between fibre section pressure drops indicated normal flux distribution (Yoon et al., 2008).

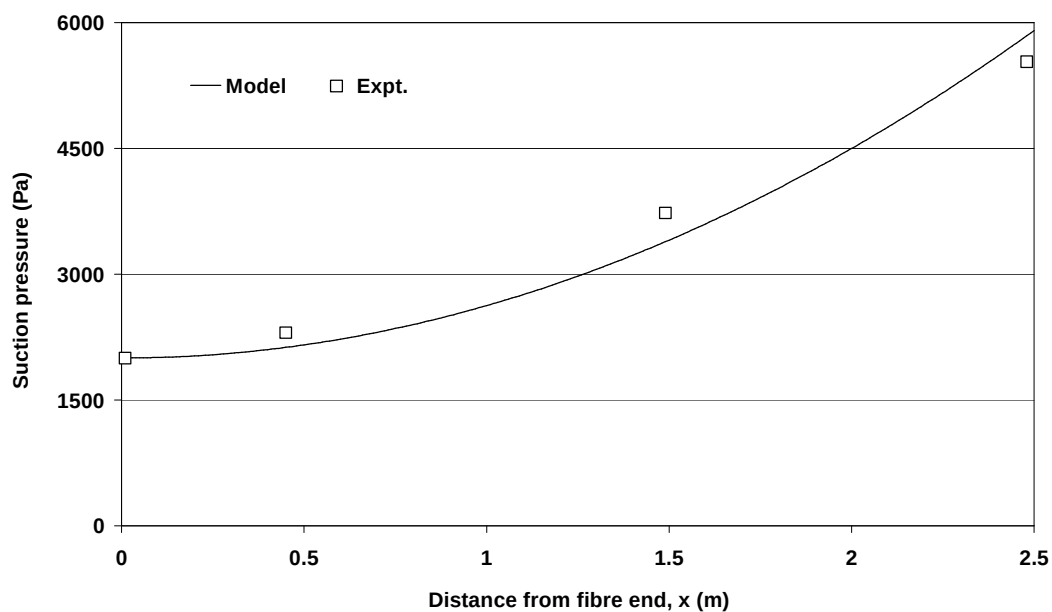


Figure 5.18 Experimental and theoretical (Hagen-Poiseuille) pressure drop data in clean water conditions. J 7.55 $L.m^{-2}.h^{-1}$. Optimum D_i 0.94 mm.

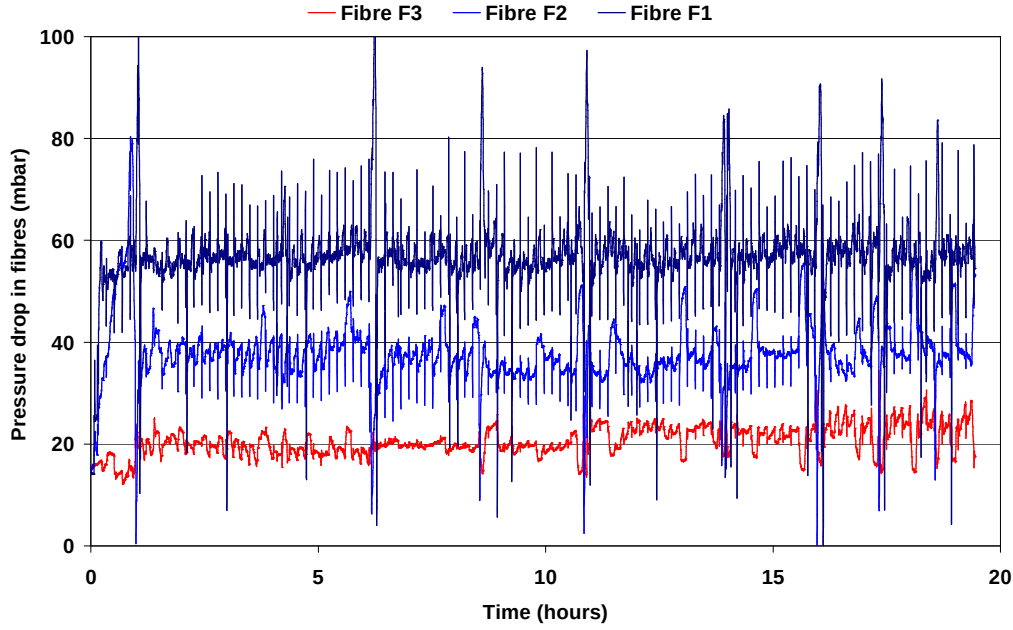


Figure 5.19 DE steady-state filtration through sectional HF. J $7.55 \text{ L.m}^{-2}.\text{h}^{-1}$; V_f 1.3 L.m^{-2} ; SGD_m $30.5 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$ ($G = 231 \text{ s}^{-1}$). Gas scour period 30 seconds.

Inspection of the pressure drop data indicated that fine pressure compensations continually arose across f_1 to f_3 during steady-state filtration. However, significant pressure drop re-distribution occurred at around 15.3 and 20.5 hours for CF and DE conditions respectively. At 20.5 hours DE filtration, f_3 increased from ~ 23.5 to ~ 38.5 mbar in 0.5 hours (Fig. 5.20). Prior to this, f_3 exhibited the lowest dP/dt of $\sim 0.084 \text{ mbar.h}^{-1}$. At 15.3 hours (CF filtration), a rapid increase in pressure drop across f_1 of $\sim 8.2 \text{ mbar.h}^{-1}$ occurred in conjunction with decreased and increased pressure drop across f_2 and f_3 respectively. As the pressure drop increased across the farthest fibres (from the exit), f_1 stabilised. At ~ 35 hours, pressure drop increased in both f_2 and f_3 . Yoon et al. (2008) observed pressure redistribution across fibre sections within the first 40 minutes of operation, suggesting cake collapse took place on the exit fibre resulting in low local fluxes, which then promoted flux compensation (or an increased pressure drop) across subsequent fibre sections. Data from both CF and DE conditions corroborate this, although differences within the two profiles were evident. Resistance

in series analysis during the sectional HF experiments corroborated the dissimilarity in deposition; DE filtration was dominated by cake resistance whereas CF filtration was dominated by irreversible fouling (Table 5.6).

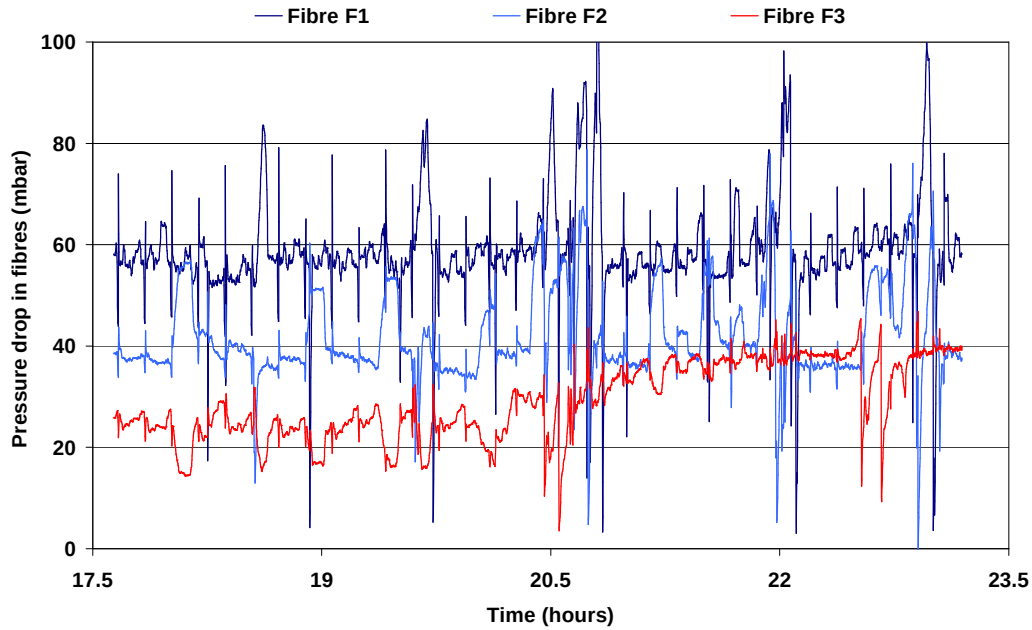


Figure 5.20 Example of pressure drop increase across fibre 3 at 20.5 hours. J 7.55 $L.m^{-2}.h^{-1}$; V_f 1.3 $L.m^{-2}$; SGD_m 30.5 $m^3.m^{-2}.h^{-1}$ ($G = 231 s^{-1}$). Gas scour period 30 seconds.

Table 5.6 Individual fibre parameters.

	Dead-end ³			Cross-flow ⁴		
	f_1	f_2	f_3	f_1	f_2	f_3
$K_i (L.m^{-2}.h^{-1}.bar^{-1})^{1,2}$	254	252	265	279	267	265
$K_t (L.m^{-2}.h^{-1}.bar^{-1})$		253.8			248.5	
$R_c (m^{-1})$		1.69×10^{12}			1×10^{11}	
$R_f (m^{-1})$		2.59×10^{11}			1.95×10^{12}	

K_i – Initial clean water permeability. K_t – Total module permeability. ¹Measured from top side connection (other end dead-ended). Bottom side end checked for K: SD between top and bottom end below $\pm 3\%$. ²K based on HF outer D 1.9mm. ³DE K_i ave. 257 ± 7 (SD $\pm 2.7\%$). ⁴CF K_i ave. 270 ± 6.2 (SD $\pm 2.3\%$).

5.10 DISCUSSION

5.10.1 Biofilm developed in DE and CF conditions

Previous CF MBR studies have identified polysaccharide as the dominant biofilm component, even though protein dominated the bulk suspension EPS (Zhang et al., 2006). The authors postulated that the supernatant components principally fouled the membrane since the cross-flow would be expected to suppress floc deposition, and the supernatant (SMP) had high polysaccharide content. In this study, during CF filtration $41\% \pm 10.9\%$ of the biofilm was composed of SMP biopolymers; this finding is in agreement with Zhang et al. (2006) and is intuitively linked to the limited influence shear induced diffusivity can exert upon colloidal ($<1 \mu\text{m}$ diameter) biopolymers (McAdam and Judd, 2008b). In contrast, the biofilm formed during DE filtration was low in SMP, and the similarity of the EPS_{tot} biopolymer ratio to the eEPS fraction of the bulk solution suggests direct floc deposition.

Protein dominated in the bulk and biofilm components during steady-state DE operation. Ethanol was intentionally under-dosed to ensure substrate breakthrough did not occur (McAdam and Judd, 2007). As nitrogen was not limiting, the production of nitrogen-containing proteins could proceed whereas the carbon limitation may have inhibited synthesis of the carbon-rich long-chain polysaccharides which promote cake stability (Leslie et al., 1993), and can explain the low adhesive potential of the bulk sludge at the membrane surface during DE filtration. The high P/C ratio could also improve sludge repulsion at the hydrophilic membrane interface due to the

hydrophobic character exhibited by high MW proteins as observed in a previous study (Ji and Zhou, 2006).

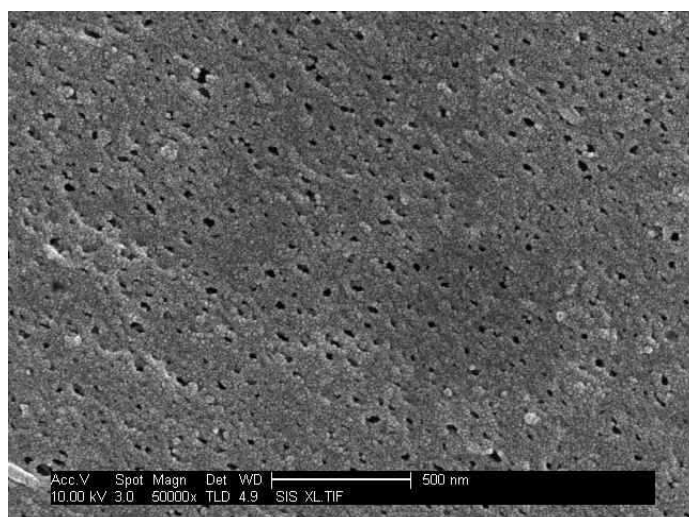
During CF filtration, protein and polysaccharide concentrations in the SMP were comparable at $P/C\ 0.9\pm0.8$ which was presumably due to modification by floc breakage affected by augmented shear stress. Migration and concentration of these components at the membrane surface during CF produced a visibly thick and resistive hydrogel (Figure 5.17a) as observed previously with alginate (Ye et al., 2005). This physiologically modified the membrane surface and created a polymer ‘footprint’ which is recognised to enhance bacterial adhesion (Marshall, 1988).

5.10.2 Hydrodynamics and pressure drop

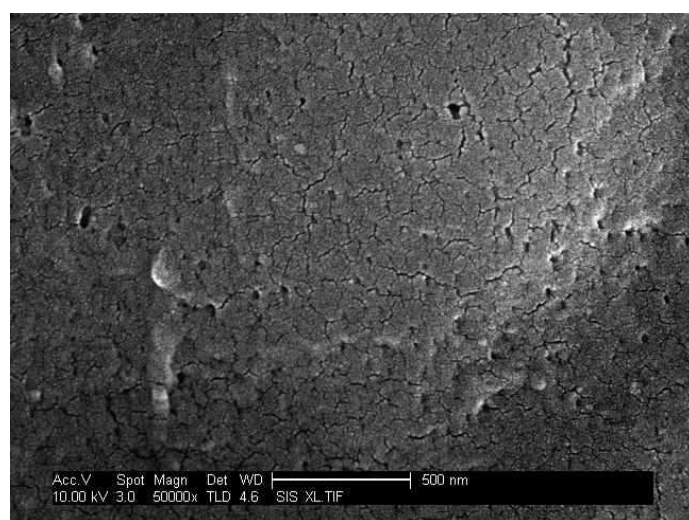
Operating below V_{crit} during DE filtration resulted in low long term dP/dt due to the high deposit reversibility observed (Table 5.4) (McAdam and Judd, 2008b). For static surfaces, Marshall (1988) defined reversible microbial adhesion as an instantaneous attraction where cells could still exhibit Brownian motion and were readily removed by a moderate shear force; irreversible adhesion was time dependent. This appears to be the case for surfaces in this study exposed to convective flow. Application of increased intermittent tangential shear forces (Figure 5.14) allowed cycle volumes above V_{crit} to be hydrodynamically optimised (by reaching a plateau). However, an equivalent dP/dt to that observed $<V_{crit}$ (at $3.5\ L.m^{-2}$) could not be attained indicating that shear was controlling cake height (Leslie et al., 1993) rather than providing for deposit reversibility. This dependency on volume (or more specifically mass) may be similar to bacterial microfiltration, where compressing of bacteria into a cake has

been observed, the cumulative attractive forces (weak van der Waal's) increase and cake adhesion proceeds (Leslie et al., 1993).

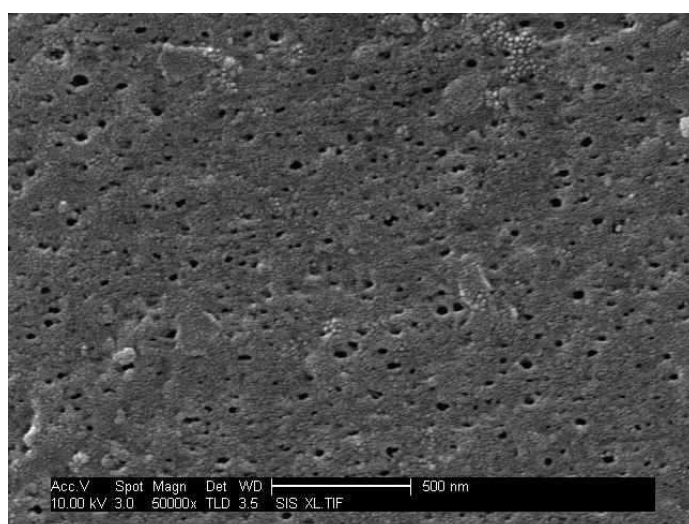
Application of gas scour without backflush (Figure 5.15) during DE filtration provided comparable dP/dt values to those from gas scour combined with backflush. Conversely, when backflush was applied in isolation, dP/dt could not be stabilised (Figure 5.16). Fibre vibration may therefore be as important as gas induced shear for controlling deposition in DE (Wicaksana et al., 2005). During CF operation, backflush promoted sustained operation (Table 5.4) and can therefore be considered advantageous once higher resistance deposits have formed. It is also clear that for effective use (Figure 5.16), CF must accompany backflushing to provide back-transport of particulates to the bulk phase. Resistance in series analysis emphasised that under CF conditions, a greater degree of irreversible fouling is formed. This was further elucidated with SFEG images (Figure 5.21) indicating a cleaner membrane surface following DE filtration. The sectional HF indicated local pressure redistribution in both CF and DE operation, consolidating the local flux distribution hypothesis as described elsewhere (Zhanget al., 2006). Pressure redistribution was considerably more erratic under CF conditions. During direct observation experiments, Li et al. (2003) observed that cake was removed during cross-flow in the form of rolling floc and large aggregated groups. This in conjunction with axial distribution effects (Gourgues et al., 1992) could explain why the pressure distribution in CF was so erratic and why CF biofilms were visually different from that observed during DE filtration (Figure 5.17).



(a)



(b)



(c)

Figure 5.21 SFEG membrane surface images. Typical surface images (a) Chemically cleaned membrane. (b) Membrane surface from CF filtration post DI rinse. (c) Membrane surface from DE filtration post DI rinse. Note the difference in visible pores between (b) and (c). Acc. V. 10.0 kV. Magnification 50000x.

5.11 Conclusions

1. Lower fouling rates (dP/dt) were observed during DE filtration compared to CF filtration at identical flux and shear rate (Table 5.4).
2. During DE filtration, a low resistance deposit was produced that could be practically completely reversed using only intermittent gas scour. This further improves process efficiency over that already reported (McAdam and Judd, 2008b) as permeate is not applied for backflush.
3. CF operation impacted on floc size and apparently on SMP composition. Analysis of the P/C ratio indicated protein dominance during DE operation. This may influence bacteria-bacteria and bacteria-membrane interactions however, it should be observed that P/C ratios were 0.76 and 0.62 for 10 and 40 days SRT respectively and their influence on attachment in DE operation appeared limited. The distinction between DE and CF is considered to be more closely correlated to hydrodynamic variances imposing contradictory deposition kinetics.
4. During DE filtration, low dP/dt operation could not be attained when operating above V_{crit} , even when higher shear rates were adopted. Pressure redistribution in the sectional fibre was observed and was more erratic during CF operation. This may be explained by the displacement of discrete aggregates from the membrane surface during continuous shear. The sectional fibre provided insight into fouling deposition, though it must be conceded that the specific hydrodynamics and mass transfer may not correlate particularly well to fibres in practice.

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CHAPTER 6

FATE AND IMPACT OF ORGANICS IN AN IMMERSED MEMBRANE BIOREACTOR FOR BRINE DENITRIFICATION AND ION EXCHANGE REGENERATION

IN PREPARATION FOR SUBMISSION TO: *Water Research*

6 FATE AND IMPACT OF ORGANICS IN AN IMMERSSED MEMBRANE BIOREACTOR FOR BRINE DENITRIFICATION AND ION EXCHANGE REGENERATION

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ABSTRACT

The application of membrane bioreactors to brine denitrification for ion exchange regeneration was studied. The developed culture was capable of complete brine denitrification at 50 gNaCl.L⁻¹. Denitrification reduced to c.60 and c.70% when salinity was increased to 75 and 100 g.L⁻¹, presumably due to reduced growth rate and low imposed solids retention time (10 days). Polysaccharide secretion was not induced following salinity shocking, implying that cell lysis did not occur. Fouling propensity, monitored by critical flux, was steady at 12-15 L.m⁻².h⁻¹ during salinity shocking and after brine recirculation, indicating that the system was stable following perturbation. Polysaccharides physically adsorbed onto the anion exchange resin during regeneration resulting in a capacity loss of c.6.5% when operating up to complete exhaustion. However, when compared to anion exchange resin regenerated with freshly produced brine over a number of exhaustion runs and up to a set threshold (10 mgN.L⁻¹), the resin capacity was similar. It was concluded that a denitrification MBR was an appropriate technology for IEX spent brine recovery and reuse.

6.1 INTRODUCTION

Anion-exchange (aIEX) is typically applied to nitrate (NO_3^-) removal during potable water processing due to its low cost and operational simplicity. The aIEX resin adsorbs the nitrate, and a strong salt (NaCl) solution is used to regenerate the resin. However, a highly concentrated brine (waste regenerant) is produced containing the target anion, chloride and other oxyanions (McAdam and Judd, 2008). This waste stream can comprise 0.8-2.4% of treated product flow (McAdam and Judd, 2008); its disposal is usually by tankering, constituting a significant proportion of the process cost. Operation of aIEX in combination with biological nitrate reduction of the waste brine to recover the regenerant presents a more sustainable alternative, reducing the waste volume, salt (NaCl) consumption and treated product losses.

Previous investigators have sought to examine microbial communities from standard activated sludge for this application. However, elevated salt concentrations ($>30\text{gNaCl.L}^{-1}$) inhibited denitrification and, in some cases, caused plasmolysis due to the osmotic gradient created across the cell membrane. More recently, monocultures *Halomonas denitrificans* (Cyplik et al., 2007) and *Halomonas campisalis* (Peyton et al., 2001) have been successfully adapted for denitrification at high salt concentrations from 30 to 180 g.L^{-1} , obviating dilution prior to biotreatment. However, adaptation of halophiles to brine processing is yet to be examined in detail.

Other restrictions to this application include the concentration of bicarbonate and sulphate due to recirculation, and the impact of organics and microbial carryover from the bioreactor on downstream resin regeneration. High sulphate levels have not been

reported to impact upon either resin or biological performance where nitrate selective resins have been used (Clifford and Liu, 1993). Bicarbonate has limited impact upon reduction capacity of non-halophiles (McAdam and Judd, 2008) and has been suggested as a co-regenerant by Bae et al. (2002). The same authors reported that microbial associated particulates and organics foul the resin, observing that sand filtration and GAC post-treatment were required to nullify the impact. Though little information exists on the impact of residual organics on resin capacity, the application of “classical” biomass separation membrane bioreactor (MBR) technology to this duty has been mooted to provide absolute bacterial rejection and high MW biopolymer retention, promoting a consistent permeate quality (McAdam and Judd, 2008).

The current paper assesses the viability of a denitrification MBR for waste aIEX brine recovery and reuse in the regeneration of ion exchange resins. Specifically, the aims are to determine a) fate of organics during permeate (brine) recirculation (to simulate re-use); b) impact of organics on resin capacity; c) influence of salt variation on halophilic treatment performance; and d) impact on fouling propensity.

6.2 MATERIAL AND METHODS

6.2.1 Experimental rig

A bacterial seed was initially developed from the anaerobic layer of a coastal sediment. Following acclimation in batch conditions (50 gNaCl.L^{-1} , $500 \text{ mgNO}_3^- \text{-N.L}^{-1}$), a 75 L reactor (Figure 6.1) was seeded at a ratio 15:1. The influent nitrate concentration was set at $500 \text{ mg NO}_3^- \text{-N.L}^{-1}$. Ethanol was supplied as the exogenous

substrate and dosed at a C:N ratio of 0.85:1 (g.g⁻¹). Reactor temperature was maintained around 20°C using a thermostatically controlled heating jacket. Biomass distribution was ensured through impeller mixing below the membrane module. The hydraulic and solids residence times (HRT and SRT respectively) were 17.5 hours and 10 days respectively. The process was allowed 3 SRTs to reach steady state prior to testing. During recirculation experiments, MBR permeate was collected in a holding tank (T₂), supplemented with NO₃⁻ and pumped back to the feed tank (T₁).

A 0.93 m² out-to-in immersed PVDF hollow-fibre membrane with 0.04 µm nominal pore size was used. Permeate was withdrawn under suction from the membrane using a piston pump (FMI Inc.). To avoid the entrainment of air, nitrogen-enriched air (>99%) was used to scour the membrane, produced from compressed air (8 barg) using a nitrogen selective hollow-fibre membrane (N₂ Gen Ltd, 5-M). Gas was introduced using a solenoid valve (Zoedale Plc) controlled with a programmable digital relay (Kübler GmbH) and its flow rate controlled with a needle valve. Pressure was monitored using a pressure transducer (Gem Sensors, UK) whose signal was recorded with a data logger (Pico technology, ADC-16).

6.2.2 Anion exchange resin

120g of commercially available nitrate selective macroporous styrene based anion exchange resin (Purolite A520E) with a size range of 0.28 to 1.26 mm (d₅₀ 0.61 mm) was loaded into a 50mm diameter x 1m glass chromatography column (Omnifit). 25 µm-rated glass frits at the column ends retained the resin. Prior to use, DI water was pumped through the resin bed at 20 bed volumes (BV).h⁻¹ for 30 minutes, followed by

a 30 minute 50gNaCl.L^{-1} flush (to ensure saturation) at 5 Bv.h^{-1} and a subsequent DI rinse for 60 minutes at 5 Bv.h^{-1} . Exhaustion flow rate was set to 20 Bv.h^{-1} . IEX feed contained $30\text{ mgSO}_4^{2-}.\text{L}^{-1}$, $115\text{ mgCl}^{-}.\text{L}^{-1}$ and $150\text{ mgCaCO}_3.\text{L}^{-1}$. Influent $\text{NO}_3^{-}\text{-N}$ was set at c. 22.6 mg.L^{-1} . Regeneration comprised a 60 minute cycle at 5 Bv.h^{-1} , followed by slow and fast rinses of 5 Bv.h^{-1} for 30 minutes and 20 Bv.h^{-1} for 10 minutes respectively.

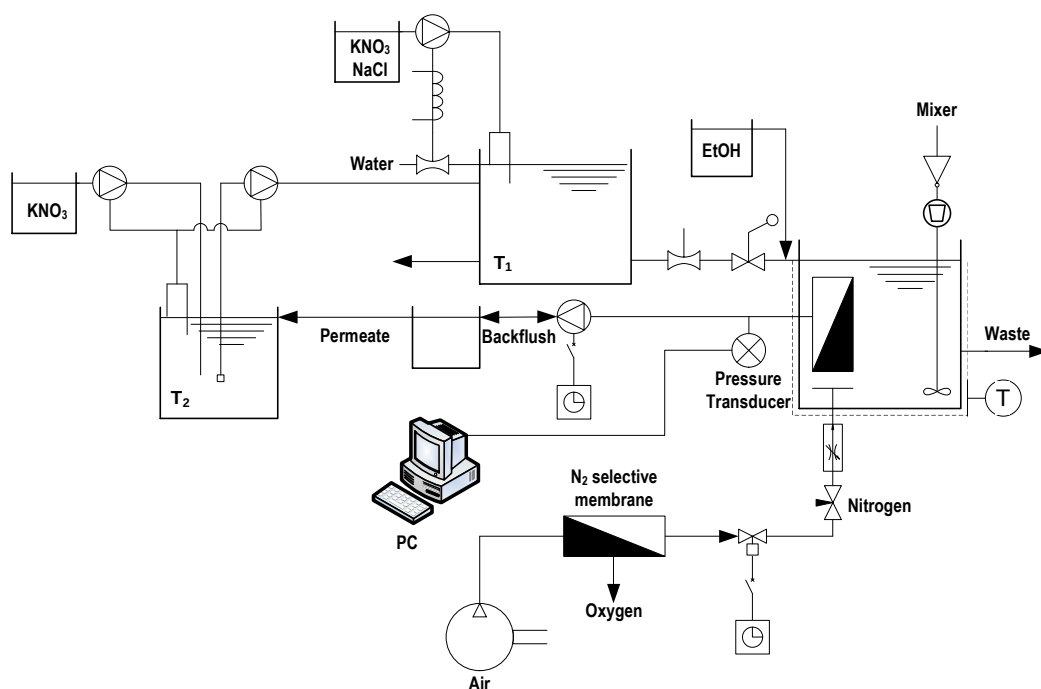


Figure 6.1 *Experimental set-up.*

6.2.3 Chemical analysis

Mixed liquor suspended solids (MLSS) and bicarbonate were determined by standard methods. DOC was measured using a Shimadzu TOC-5000A analyser. Particle size was measured with a Malvern Mastersizer 2000. Soluble microbial products (SMP) were extracted according to the method described in Judd (2006), and carbohydrate and protein content respectively determined using the phenol–sulphuric acid method

(Zhang et al., 1999) and modified Lowry method (Frølund et al., 1995). Absorbance was measured using a Jenway 6505 UV/Vis spectrophotometer at UV_{480nm} and UV_{750nm} absorbance, respectively using D-glucose and bovine serum albumin (BSA) as standards for protein and carbohydrate. UV absorbance was conducted using the same spectrophotometer set at UV_{254nm} . Oxyanion (NO_3^- , NO_2^-) and chloride concentrations were measured using UV spectrophotometry (Merck Spectroquant). Ethanol concentration was determined using a commercially available enzymatic method (Boehringer-Mannheim). Serial fractionation was undertaken using an Amicon 8400 series stirred cell, pressurised with N_2 (1 barg), and standard UF (Millipore) membranes, size range 10, 30, 50, 100 and 300kDa. Sample supernatant was pre-filtered using a $1\mu m$ glass micro-fibre filter and the subsequent sample split between two 300 kDa membranes to limit concentration polarisation. The filtrate/retentate ratio adopted was 0.4. Size exclusion chromatography (SEC) was performed with a Shimadzu LC-10AD liquid chromatograph fitted with a Phenomenex BiosepTM Sec-S column and subsequent UV_{254nm} detection. Phospholipid fatty acid (PLFA) analysis was used to assess the community structure using the method of Frostegård et al. (1991). Samples were freeze dried prior to analysis. Lipids were extracted from the freeze dried sample using the Bligh and Dyer (1959) ratio of 1:2:0.8 (v/v/v) of chloroform, methanol and citrate buffer. Lipids were then fractionated by solid phase extraction. The phospholipid fraction was derivatised by mild alkaline methanolysis (Dowling et al., 1986). The resultant fatty-acid methyl esters (FAMES) were analyzed by GC-FID (Agilent). Peak identification was undertaken using GC-MS (Agilent).

6.3 RESULTS

6.3.1 Exogenous and endogenous organics transmission at steady state

Nitrate removal efficiency increased from 84.6% to a maximum 99.8% as the carbon to nitrogen ratio (C:N) increased from 0.77 to 0.94 (Figure 6.2). Increasing C:N beyond 0.89, generated ethanol in the permeate. The existence of an optimum C:N has been reported previously (McAdam et al., 2007). However, other investigators have reported a low residual total N (sum of NO_2^- -N and NO_3^- -N removed) ion concentration, as the optimum C:N is passed (Chiu and Chung, 2003). In this study, on increasing C:N >0.98 inhibition was observed resulting in between 71.4% and 97.1% of the available NO_3^- being converted to NO_2^- for C:N values up to 8.5. The enzymatic activity of anoxic halophiles has to date received little attention (Aston and Peyton, 2007), though Yoshie et al. (2006) also reported nitrite accumulation in both continuous and batch denitrification indicating reductase activity maybe very different at high salinity.

Protein and carbohydrate transmission through the membrane at steady state were $27.3\% \pm 8.0\%$ and $81.5\% \pm 10.5\%$ respectively. Fawehinmi (2006) observed similar transmission rates for proteins and carbohydrates, recording 49% and 80% respectively during the operation of an anaerobic immersed hollow fibre (0.1 μm) membrane bioreactor. The SMP exhibited a principal protein peak of 55.1% between <1 μm and 300 kDa and a principal carbohydrate peak of 48.3% below 10 kDa (Figure 6.3). Organics between 1 μm and 100 kDa were absent in the permeate

indicating the molecular weight cut off (MWCO) of the hollow-fibre (and any associated biofilm) was around 50 to 100 kDa.

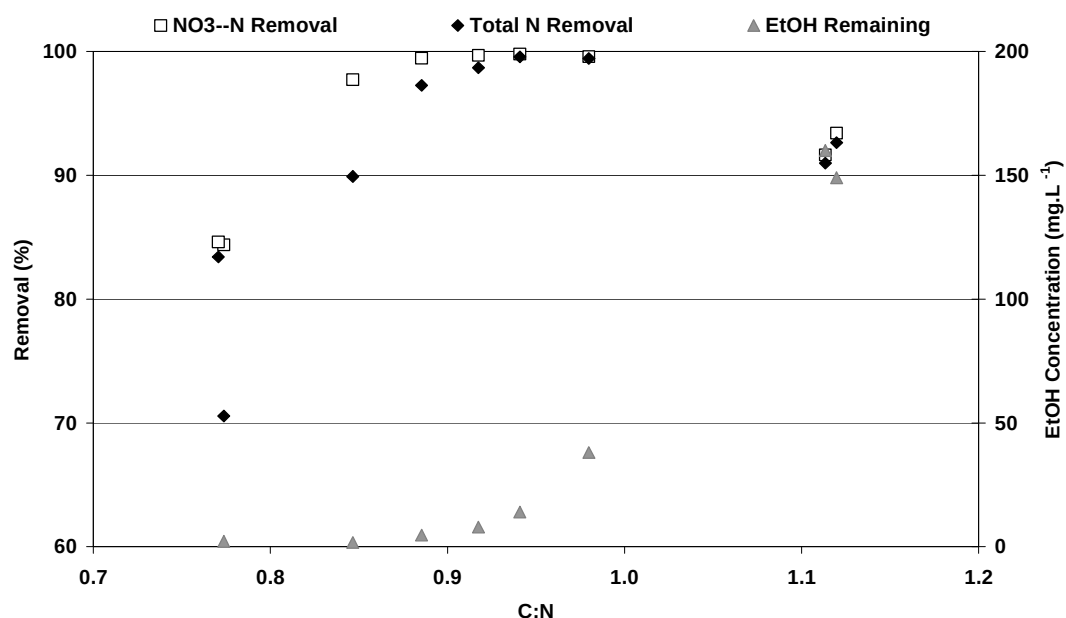


Figure 6.2 Optimising C:N ratio during steady state operation. Influent: 500 mgNO₃⁻-N.L⁻¹, 50 gNaCl.L⁻¹.

6.3.2 Accumulation of organics during recirculation

After 7 days recirculation, the SMP DOC concentration had increased from 160 to 180 mg.L⁻¹ (32 to 36 mgDOC.gMLSS⁻¹) up to a maximum concentration of 545 to 569 mgDOC.L⁻¹ (Figure 6.4). At steady state, DOC transmission between 54% and 80% was recorded, attributed to accumulation of low molecular weight organics (below the membrane MWCO).

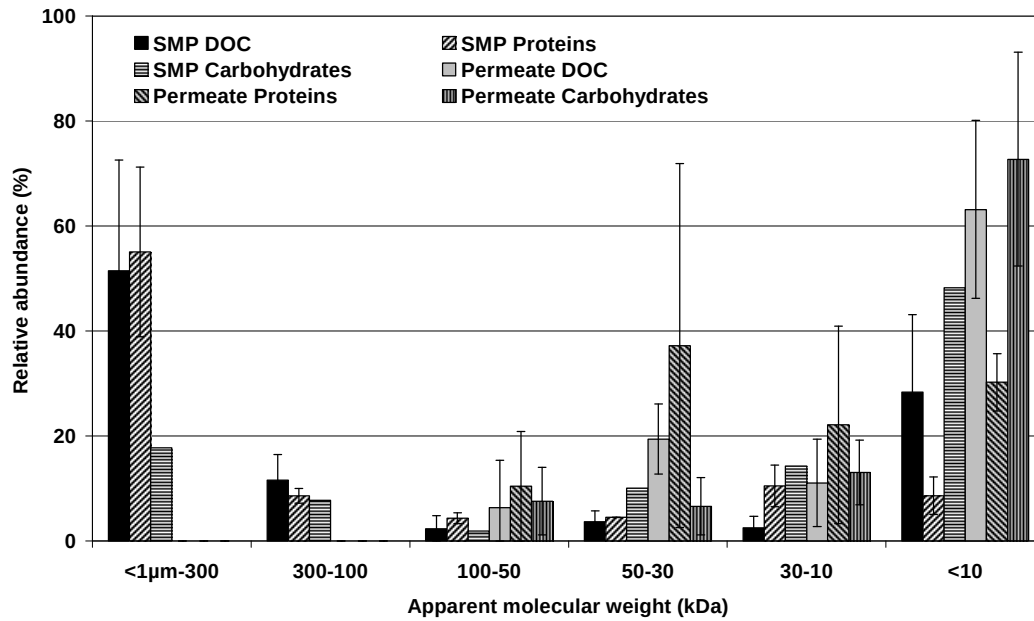


Figure 6.3 Serial fractionation of the SMP and permeate at steady state.

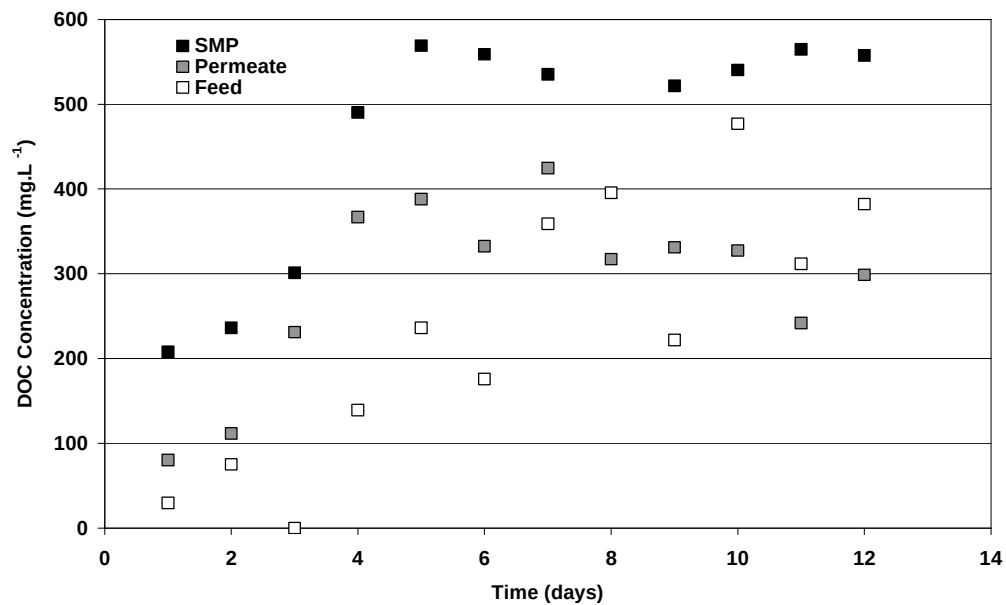


Figure 6.4 Impact of permeate recirculation to the main feed tank on dissolved organic carbon concentration (DOC) of the feed, permeate and SMP.

Critical flux analysis (J_c) was conducted using the flux step method before recirculation and after reaching steady state (Figure 6.5). In both cases, J_c was between 12 and 15 L.m⁻².h⁻¹. Similar exponential dP/dt trends were obtained for both sets of conditions, evidenced by similar slopes $(dP/dt)/J$. This challenges previous

reports which link fouling propensity to elevated concentrations of biopolymers in the bulk phase (Judd, 2006; Reid et al., 2006).

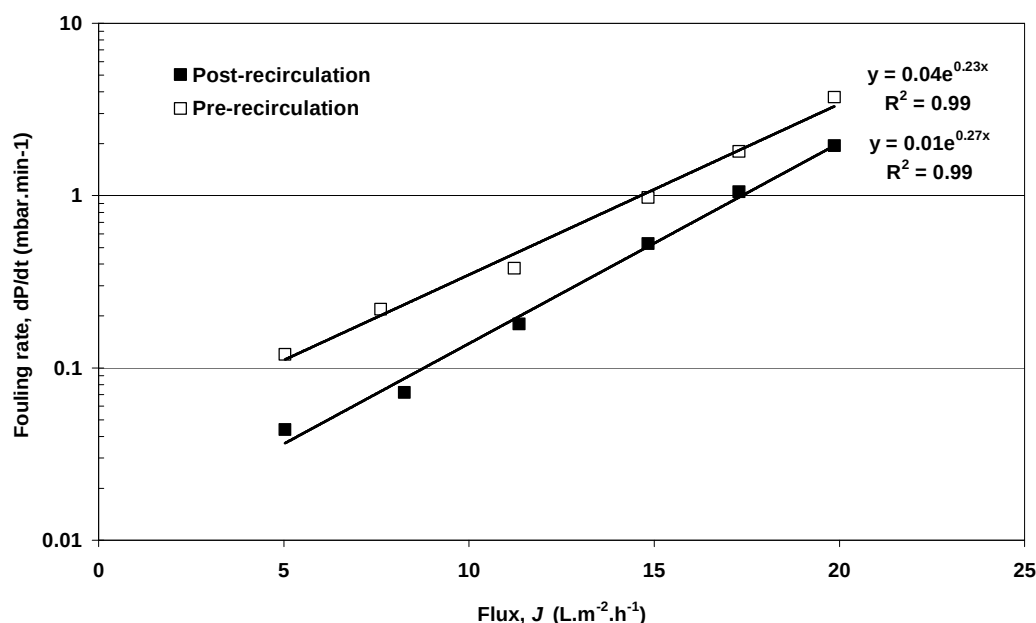
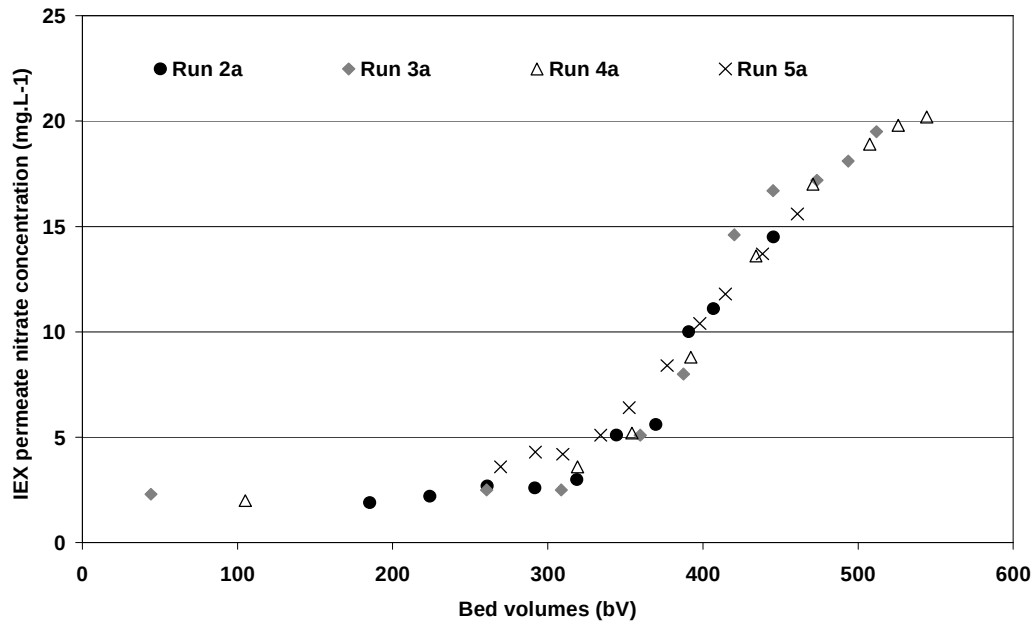


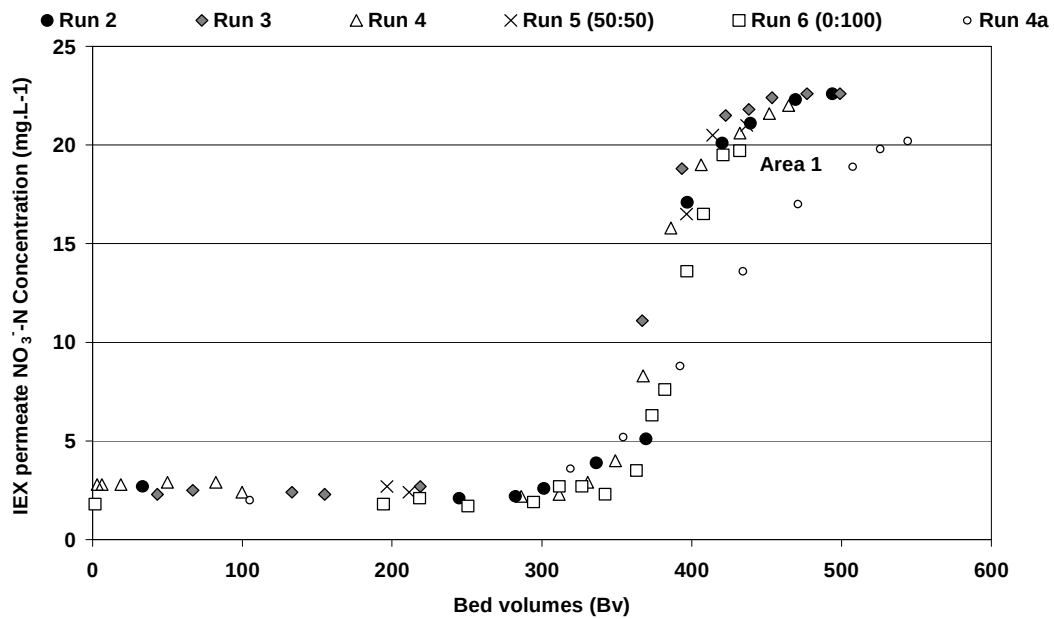
Figure 6.5 Critical flux analysis (J_c) before, during and after permeate recirculation to the main feed tank. SGD_m $0.39 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

6.3.3 IEX Resin capacity

To allow comparison with previous studies (Clifford and Liu, 1993; Bae et al., 2002), breakthrough curves were determined using a $10 \text{ mgN} \cdot \text{L}^{-1}$ threshold concentration—the US regulatory limit. Breakthrough curves (1-6) were run to complete exhaustion using freshly produced regenerant (Brine_{fp} , $50 \text{ gNaCl} \cdot \text{L}^{-1}$) (Figure 6.6(a)). Breakthrough occurred at c.400 bed volumes (BVs) in the second run, corresponding to $0.61 \text{ eq} \cdot \text{L}^{-1}$ or 88% of throughput obtained with the virgin resin during the first run. Subsequent runs indicated a near identical trend demonstrating reproducible regeneration efficiency. A slightly lower capacity of c. $0.46 \text{ eq} \cdot \text{L}^{-1}$ has been observed previously (Bae et al., 2002) using the same resin (A520E); the difference may be explained by the authors' application of a lower strength ($30 \text{ gNaCl} \cdot \text{L}^{-1}$) regenerant.



(a)



(b)

Figure 6.6 Breakthrough curves observed from runs 2-6 using: (a) freshly produced brine; and (b) biologically treated brine. Influent concentration: $\text{NO}_3^- \text{-N}$ 22.6 mg.L^{-1} ; SO_4^{2-} 30 mg.L^{-1} ; Cl^- 115 mg.L^{-1} and HCO_3^- 150 mg.L^{-1} .

Breakthrough curves (1-6) were generated with a fresh resin using biologically treated brine (Brine_{bt} , 50gNaCl.L^{-1}) as the regenerant (Figure 6.6(b)). Brine_{bt} was sampled from the MBR permeate once steady state had been reached during permeate

recirculation. At steady state, the DOC concentration of the brine_{bt} was c.287 mg.L⁻¹. Breakthrough occurred at c.390 BVs in the second run, corresponding to 0.58 eq.L⁻¹ or 87% of throughput obtained with the virgin resin during the first run. Comparison with run 4 (a) using brine_{fp} (Figure 6.6(b)) demonstrated a loss in capacity (Area 1), implying biologically derived organics had deposited on the resin in the first regeneration. Integration of the area between the brine_{fp} and brine_{bt} exhaustion curves estimated the capacity loss at 59 meq.L⁻¹ or c.6.5% of the estimated exhaustive capacity. Bae et al. (2002) observed significant capacity losses using permeate from an upflow sludge blanket reactor (USBR) for regeneration unless subsequent treatment steps were incorporated. However, in this study subsequent regenerations displayed a similar reproducibility indicating that the resin had reached a maximum capacity for organics at the end of the first regeneration.

The resins capacity for brine_{bt} organics within the regenerant was quantified using a virgin salt saturated resin (Figure 6.7). Brine regenerant was assumed to exit the column once chloride transmission reached 100% (assuming chloride uptake to be zero at saturation). Chloride and protein transmission reached 100% between 1 and 1.5 BVs, indicating protein adsorption to be negligible. Polysaccharide and DOC transmission were recorded at c.15% and c.90% respectively up to 4 BVs, where a rapid increase in transmission between 4 and 7 BVs was observed. At 7 BVs, polysaccharide and DOC transmission reached 100% indicating that the resin was saturated with polysaccharide. Adsorbed DOC was estimated at 26.4 mg. During exhaustion/regeneration cycles (Figure 6.6(b)), the adsorptive mechanism of the polysaccharides was evaluated by regenerating the resin with a 50/50 fresh brine/biological regenerant (Run 5) and 100% fresh brine (Run 6). The reproducibility

(i.e. low reversibility) of the following curves suggested physical adsorption rather than ion exchange to be the predominant mechanism.

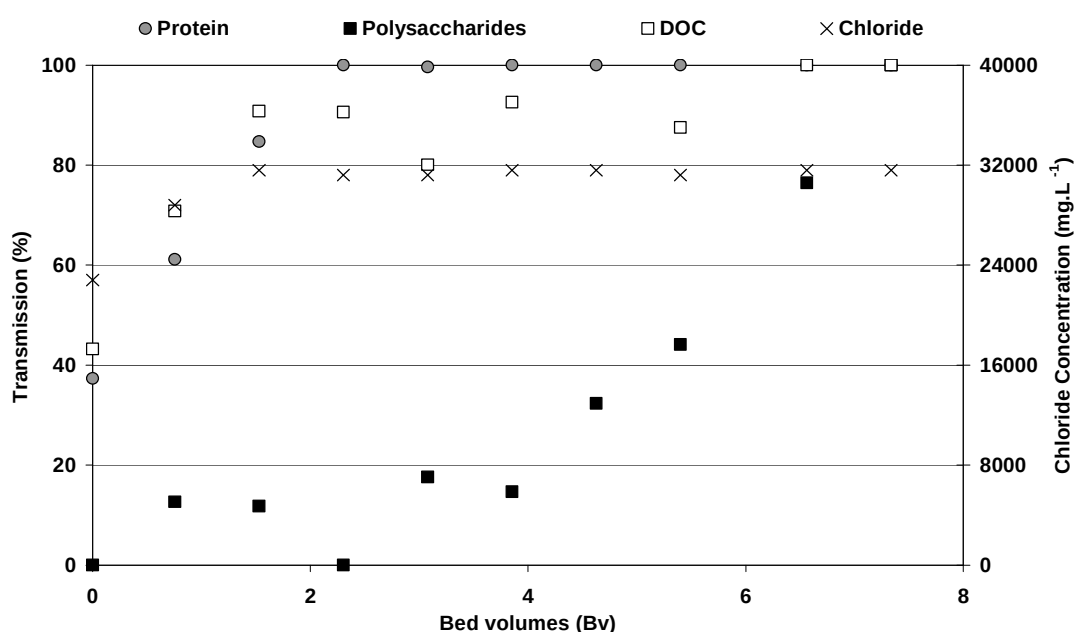


Figure 6.7 Adsorption of regenerant organics (protein, polysaccharide and DOC) by anion exchange resin.

6.3.4 Salt shocking

To reflect the significant salt variations occurring in brine regenerant waste, the feed was initially upshocked with 75 gNaCl.L⁻¹ and 7 days later was increased to 100 gNaCl.L⁻¹. Nitrate removal reduced from 95% to 70% following salt shock (Table 6.1) indicating a direct impact on biomass specific denitrification capacity. Spikes in the SMP protein concentration from c.30 mg.L⁻¹ to c.50 mg.L⁻¹ and c.15 mg.L⁻¹ to c.30 mg.L⁻¹ were observed following salt concentration increases to 75 g.L⁻¹ and 100 g.L⁻¹ respectively (Figure 6.8). In addition, bimodal floc size distribution changed (Figure 6.9), particularly during the transition from 50 g.L⁻¹ to 75 g.L⁻¹; the dominant volume fraction shifted from the 60-800 µm band to the 0.2-5 µm band, indicating the

breakage of flocs into primary particles (Wilén et al., 2003) and was possibly the source of the increased protein concentration.

Table 6.1 *Treatment performance during salt spiking.*

NaCl (g.L ⁻¹)	Recovery Time	C:N	NO ₃ ⁻ -N Reml. (%)	NO ₂ ⁻ -N ^a (mg.L ⁻¹)	Ethanol ^a (mg.L ⁻¹)
50	N/a	0.92	99.7	5.2	4.1
75	24 h	0.87	60.1	18.8	75.1
	7 d	0.91	58.6	9.6	113
100	24 h	0.97	73.6	7.7	176.7
	7 d	0.99	73.3	6.0	209
50 ^b	24 h	0.94	98.4	1.6	10.7

^aPermeate concentration. ^bSalt downshock.

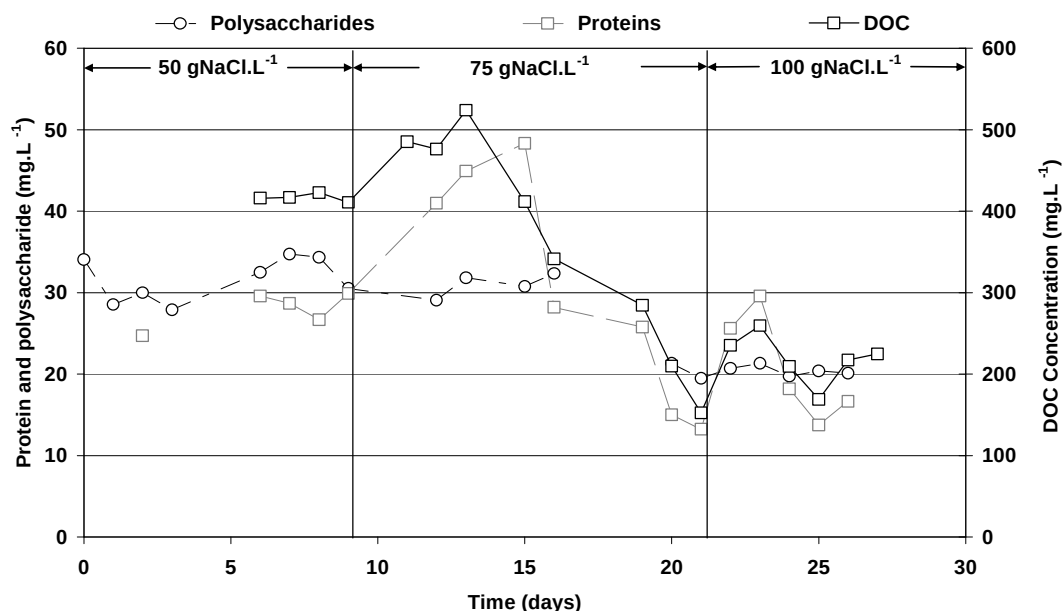


Figure 6.8 *Impact of salt upshock on biologically derived organics measured in the SMP.*

Although the volume of particulate and colloidal material had apparently increased, critical flux analysis conducted before and after each salt increment (Figure 6.10) indicated that fouling propensity remained stable as demonstrated by the similar dP/dt trends obtained. In addition, J_c was consistently recorded at c.12 L.m⁻².h⁻¹ and is comparable to that recorded during steady-state recirculation. This contradicts a previous study in a non-halophilic MBR when a 5 g.L⁻¹ chloride residual induced both

protein and polysaccharide release; permeability decline (flat sheet, 0.4 μm) was strongly correlated to SMP polysaccharide (Reid et al., 2006). The disparity may arise from the difference in microbiology (halophile versus non-halophile), the absence of secreted polysaccharide and the physical characteristics of the membrane (Zhang et al., 2006).

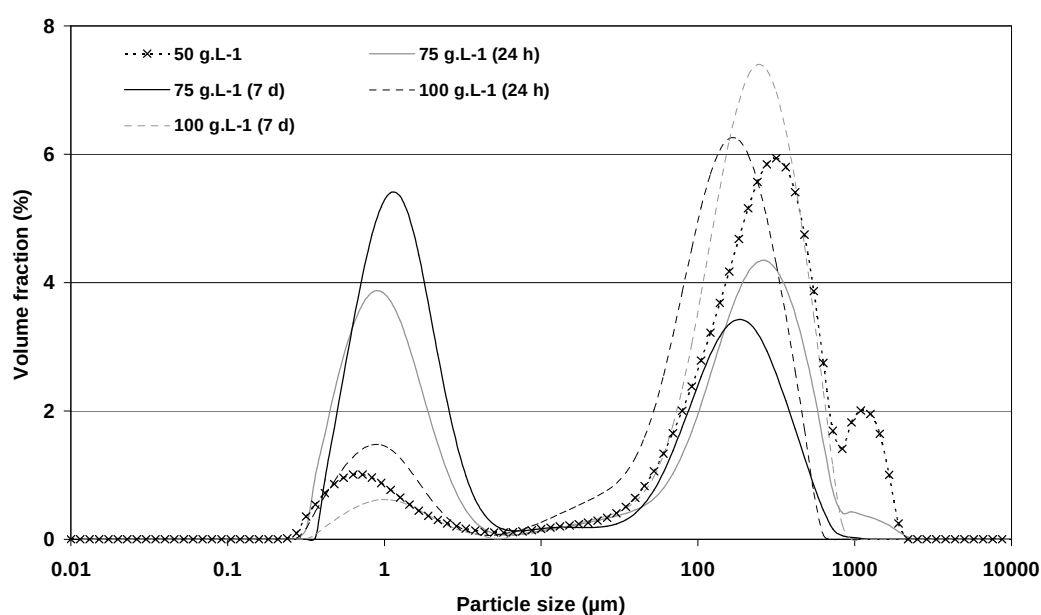


Figure 6.9 Particle size distributions before and after salt upshock from 50 g.L^{-1} to 75 g.L^{-1} and 75 g.L^{-1} to 100 g.L^{-1} . Samples are reported from 24 hours and 7 days after upshock.

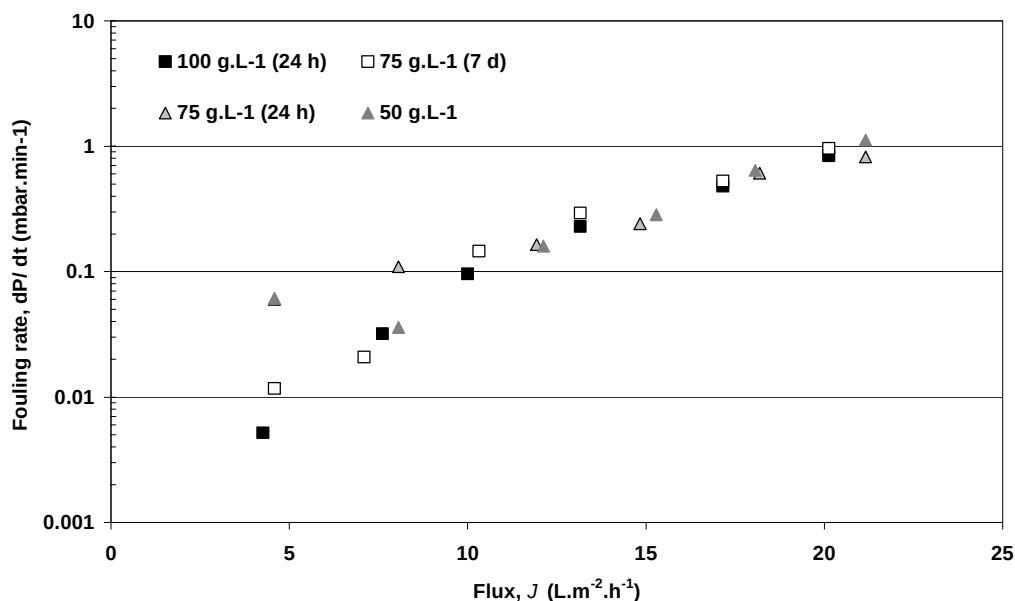


Figure 6.10 Critical flux analysis (J_c) before and after each increase in salt concentration. SGD_m $0.39 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

Twenty PLFA fatty acid methyl esters (FAMES) were identified by MS and principally comprised normal saturates and terminally branched saturates. Trans-monoenoic fatty acids concentrations were less than the limit of detection. Dominant FAMES were C16:0, C16:1, C17:0, C18, C18:1 ω 9c and C19:0cy over all salinities tested and accounted for c.95% of PLFAs detected (Table 6.2).

Similar elution profiles (and the absence of trans-monoenoic fatty acids) were observed previously for a range of moderately and extremely halophilic bacterium (Aston and Peyton, 2007; Yakimov et al., 2001). Principal component analysis (PCA) showed three discrete data groupings corresponding to salt concentration (Figure 6.11). Analysis of variance of the principal components (PC) confirmed significant differences of $P < 0.001$ and $P < 0.01$ for principal components PC1 and PC2 respectively. This distinction indicates abrupt changes in phenotypic profile between step changes in salinity.

Table 6.2 Major constituents of PLFA analysis (%).

	NaCl Concentration		
	50	75	100
C16:0	13.87	13.04	13.62
C16:1	24.95	27.12	26.06
C17:0	2.45	1.76	1.73
Exhibit 1 ^a	48.9	50.47	51.2
C19:0cy	7.07	5.24	4.77
Total (%)	97.2	97.6	97.4
Cyc/ cis	0.145	0.110	0.093

^aExhibit 1 – Comprises C18:0 and C18:1ω9c

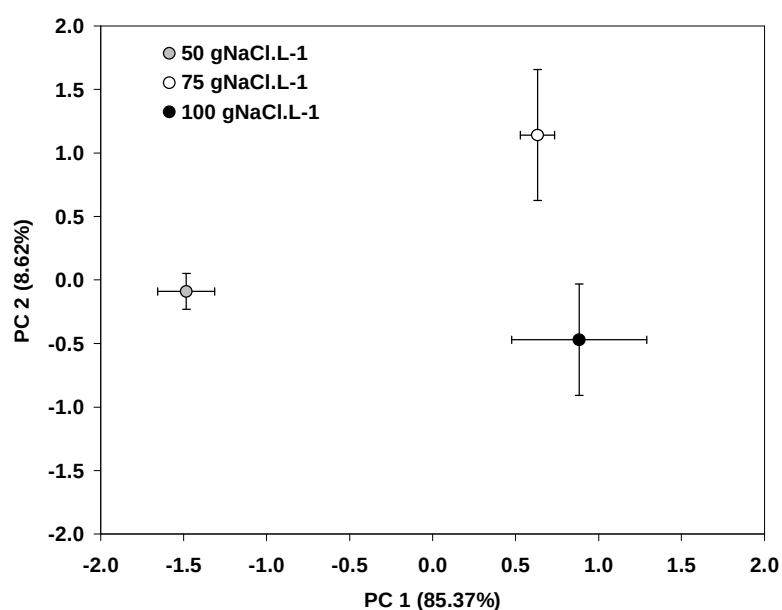


Figure 6.11 First and second principal components (PCs) derived from phospholipid fatty-acid profiles originating from biomass samples at the three salinities. Mean and standard deviation plotted. Percentage variation accounted for by PC shown in parenthesis on each axis.

6.4 DISCUSSION

6.4.1 MBR Fouling

High polysaccharide transmission of c.81.5% was observed during steady state due to the production of low MW biopolymers and corresponded to a mean DOC removal c.44%. Low MW biopolymers are generally associated with substrate metabolism and

biomass growth (Barker et al., 2000) and are produced in all MBR applications. Using LC-OCD, Zhang et al. (2006) observed 99.8% high MW (c.250 kDa) and 93.6% low MW (5 to 250 kDa) biopolymer rejection with a 0.2 μm flat sheet membrane and cited polysaccharides as the major foulant. The authors suggested this behaviour to be a common trait of fouled MF membranes; improved retention of low MW biopolymers (and higher dP/dt) in their investigation may arise from more significant internal deposition created by the wider pore size. In this study, concentration of low MW biopolymers in the bulk phase by permeate recirculation did not increase fouling propensity. This indicates that: (1) low MW biopolymers asserted poor aggregation potential upon recirculation and thus were not filtered; and (2) biopolymers exhibited limited binding potential to the membrane surface and any biofilm present. This contradicts previous experiences with polysaccharides (Zhang et al., 2006; Frank and Belfort, 2003), though research has typically focused on high MW polysaccharides (100- 1600 kDa) which assert more structural and functional complexity than those of lower MW (48.3% below 10 kDa) as in this study and may thus concentrate at the membrane surface by both size exclusion and surface adhesion (Frank and Belfort, 2003).

Fouling propensity was not greatly increased by salt shocking. The characteristic response of non-halophilic micro-organisms exposed to salt upshock is to undergo plasmolysis due to a loss in turgor pressure (Reid et al., 2006). This induces the release of soluble cellular components through the cell membrane (Laspidou and Rittmann, 2002) and in some instances the subsequent release of cell wall components such as acid mucopolysaccharides, resulting in high concentrations of proteins and polysaccharides in the bulk phase (Reid et al., 2006, Zhang et al., 2006). In this study,

only protein was released implying that the cells did not lyse. Halophilic bacteria possess modified highly negatively charged proteins on the external cell wall to mediate osmotic shifts (Petrovic et al., 1999); the protein release observed may therefore have been an adjustment in cell wall composition (Russell, 1989) producing either release or increased negative surface charge (Reid et al., 2006). This may have caused floc destabilisation as observed at the transition between 50 and 75 gNaCl.L⁻¹ (Figure 6.9).

6.4.2 Microbial community

PLFA profiles were dominated by a small range of fatty acids that are common amongst halophiles (Aston and Peyton, 2007; Yakimov et al., 2001) but identification at the species level is not possible. The trans/cis ratio was consistently <0.15 across all three salinities indicating that the cell membrane remained stable (>0.25 indicates instability) (Aston and Peyton, 2007). This substantiates previous observations that plasmolysis did not occur. All moderate and extreme halophiles are capable of offsetting transient turgor pressure (Pflüger and Muller, 2004). Most achieve this by accumulation of compatible solutes (soluble organic molecules) within the cell (Pflüger and Muller, 2004) in sufficient concentration to offset the external osmotic pressure. Differences observed between PLFA profiles indicated a reordering of the membrane lipid composition for osmoregulation (Russell, 1989) and potential restructuring of the microbial community structure (Forney et al., 2001) as has been described previously upon saline upshock during halophilic denitrification (Yoshier et al., 2006). This shift may be due to specific growth rate variations amongst the bacterial community. For example, although *Halomonas campisalis* has been

previously shown to denitrify at 180 gNaCl.L^{-1} (Peyton et al., 2001), maximum specific growth rate has been identified at $c.30 \text{ gNaCl.L}^{-1}$ (Aston and Peyton, 2007). In this study, upon shocking down to 50 gNaCl.L^{-1} , denitrification capacity immediately recovered; extension of the SRT should offset the lower growth rate.

6.4.3 Resin operation

It has been suggested that polysaccharides do not normally deposit easily onto aIEX resin due to impeded diffusion (by size exclusion) and low contact times (Cornelissen et al., 2008). In this study, polysaccharides contacted the resin during regeneration rather than exhaustion, thus increasing contact time by a factor of four. It is intuitive that exopolysaccharide adsorption occurs as they are principally polyanionic due to the number of uronic acid or ketal linked pyruvate groups exhibited on the long chain structures ($c.500$ to 2000 kDa) (Sutherland, 2001). However, due to the low affinity shown for desorption in this study, it can be speculated that the lower MW polysaccharides present in the brine_{bt} exhibit a charge closer to neutrality. DOC uptake could not be quantified during exhaustion runs due to competition effects with the influent DOC. However, the charge density (approximated by normalising lost resin capacity with DOC uptake, Figure 6.8) was $c.3.9 \times 10^{-4} \text{ meq.gDOC}^{-1}$ further indicating that adsorption was not exchange based. Kim and Symons (1991) postulated that physical adsorption was more likely to occur at the resin skeleton. After the first regeneration with brine_{bt} , physical adsorption reached a maximum presumably due to the limited number of adsorption sites available.

6.5 CONCLUSIONS

In this study, high salinity denitrification and the impact of organic accumulation on process performance was demonstrated and the following conclusions drawn:

1. Recirculation generated high concentrations of low molecular weight organics though their impact on mass transfer was negligible.
2. Although salt upshock induced protein release from the external cell wall, the impact on mass transfer was again minimal. This contrasts previous reported investigations with non-halophilic communities.
3. Treatment performance was impeded. Whilst polysaccharide secretion was negligible, PLFA analysis indicated that salt shocking modified the community. Adoption of a higher SRT should recover performance; however, fouling and organics transmission may be very different.
4. Due to the low molecular weight of the organics and an increased contact time, diffusion within the pores and physical adsorption to the resin structure occurred. However, the loss in capacity was minimal and implies long term operation using brine_{bt} is possible.
5. The efficacy of the denitrification MBR process is closely related to molecular weight, membrane rejection and the structural and functional attributes of the resultant organics, thus the impact of bacterial community and process operation modification (HRT, SRT, loading) may bias performance.

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CHAPTER 7

STANDARDISATION IN THE MUNICIPAL MEMBRANE

MARKET: CURRENT INFLUENCE AND FUTURE

IMPACT

7 STANDARDISATION IN THE MUNICIPAL MEMBRANE MARKET: CURRENT INFLUENCE AND FUTURE IMPACT

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ABSTRACT

The impact of standards on segments within the municipal membrane market has been studied. Standards within these segments relate to characterisation methods, membrane design and safety assessment. Reverse osmosis membrane design has evolved by a de facto standardisation process. Subsequent market forces also supported the development of de jure characterisation methods to promote segmental transparency. A standard membrane design for the membrane bioreactor segment has also been considered, however, the market may have evolved too far for this to be implemented. Rather than design standardisation, a bureaucratic approval process (quality standard) has hindered competition within the potable water segment (microfiltration and ultrafiltration) creating a significant barrier to entry. Reverse osmosis is apparently the only segment where standards have created social welfare, however, new characterisation and approval standards for the membrane bioreactor and potable segments respectively are currently being considered.

7.1 INTRODUCTION

Membrane technology has seen steady growth of c.5% to 10 % per annum over the past 15 years (Krukowski, 2001; BCC, 2006a; BCC, 2006b; Filtration Industry Analyst, 2007). Drivers for growth across the market include a reduction in membrane material cost and an improvement in user satisfaction, which is partially fuelled by

product innovation in the areas of fouling and reliability but also through a greater understanding of specific end uses (Krukowski, 2001; Laine et al., 2001). A new generation of legislation is also driving growth. This is particularly pertinent to the potable and membrane bioreactor (MBR) segments where traditional processes can be ineffective for meeting new water quality targets. Future product price growth will be restrained by further improvements in membrane material production, resulting from an increased number of new entrants and a shift toward economies of scale (Freedonia Group Inc., 2004). However, two facets threaten to restrain market growth.

Product validation is a necessary requirement as water providers are legally restricted to use only products that have been validated for consumer protection. Validation is a lengthy process, in the region of months to years (Hegarty, 1997), and is slowing market penetration (Business Wire, 2005). Approval costs can range into the hundreds of thousands (Wilcock and Finnan, 1994; Hegarty, 1997) creating a barrier to entry. These procedures mandated by regulatory authorities are a major hindrance in a number of membrane market segments (Frost and Sullivan, 2004).

As well as legislative pressure, issues surrounding water scarcity and the addition of chemicals for treatment (Frost and Sullivan, 2004) are forcing decision makers to consider membrane technologies for varying applications. Decision makers remain cautious about investment as there is a perception that high levels of technical skill and operation and maintenance are required (Judd, 2006). This outlook is based on the negative operating experiences reported that can be attributed to inexperience or lack of process knowledge. However, lack of sufficient information (or information asymmetry) also represents a significant barrier to trade (Black, 1998).

Standards can be applied as a tool to positively influence market conduct and performance and improve social welfare. Standards arise in various forms, often dependent upon the originator and subsequent legitimacy but also on the market type and structure. This paper reviews the core municipal membrane segments (potable, MBR and RO) and considers the impact and relevance of current standards whilst also contemplating future developments.

7.2 LITERATURE REVIEW

7.2.1 Market entry and barriers

New market entrants exert a noticeable pressure on price and productivity creating a positive welfare effect. The anticipation of entry alone can induce incumbents to lower prices (Geroski et al., 1989). In practice, it is rare that a potential entrant can enter and exit a market without capital loss; any entry will incur some sunk cost which in itself can constitute a barrier to entry (Baumol et al., 1982). Even if entry cost is small, the potential for aggressive pricing by an incumbent makes entry unattractive (Geroski et al., 1989). Key barrier theory is summarised in Table 7.1.

Strategic barriers are those which restrict market conduct by imposed government sanction. Historically, these have often been tariff barriers (e.g. to export trade, such as custom duties) but more recently non-tariff barriers to trade (Matutes and Regibeau, 1996) are common and can materialise in national (or regional) policy or standards to control or restrict imports (protectionism).

Table 7.1 *Definition of mobility barriers (data adapted from Geroski, 1989).*

Barrier theory	Definition	Effect	Ref
Structural barrier	Condition of entry is determined by the advantages of established sellers in an industry over potential entrant sellers.	An entrant cannot achieve the profit levels that the incumbent enjoyed prior to arrival.	Bain (1956)
Stigler and Chicago School	A cost of producing (at some or every rate of output) which must be borne by firms which seek to enter an industry - not borne by incumbents ^a .	An agent must incur a cost to enter an industry.	Stigler (1968)
A normative definition	Socially undesirable limitations to entry of resources which are due to protection of resource owners already in the market.	Too little entry due to excessive protection/ too much entry due to too little protection.	von Weizsacker (1980)
The value of incumbency	Focus on the advantages that accrue to established firms, i.e. a barrier exists if the firm earns rents as a consequence of incumbency.	Historic consequences; firm earns premium due to establishment in an industry.	Gilbert (1989)

^aThis includes whatever costs an entrant must incur to overcome a product differentiation advantage of an incumbent firm.

7.2.2 Standardisation

Standards can lower market barriers and support export led growth (Table 7.2). In contrast, standards can also disadvantage free-trade by creating relatively high compliance costs (Chen et al., 2006). Compatibility standards (mix and match) allow consumers to create systems by combining horizontally differentiated products providing greater variety in quality and cost (horizontal product differentiation remaining unchanged) (Matutes and Regibeau, 1996). This lowers switching costs which is crucial for decision makers. Quality standards specify acceptable product or service performance reducing the risk of adverse selection by providing the distinction between high and low quality (Tassey, 2001). Information standards are often applied in technologically advanced industries where universally accepted measurement and test method standards provide information which greatly reduces transaction costs between buyer and seller by nullifying disparities between validation and claimed performance (Tassey, 2000). Variety reducing standards aim to reduce the number of variables in a product (e.g. size) thereby limiting product range which

encourages economies of scale and lowers unit costs. However, welfare can be reduced through the subsequent decline in innovation when the diversity effect outweighs the competition effect (Veall, 1985).

Table 7.2 *Theoretical approaches to standards (data adapted from Blind and Jungmittag, 2005).*

Theoretical approach	Type of standards		Economic effects	Impact	
				Imports	Exports
Competitive advantage	International	✓	Improve quality and/ or reduce cost of ntl. prod.	✓	✗
	National	✓		✓	✗
Trade distortion/ Competitive disadvantage	National prod. Std.		Reduce openness of ntl. mkt./ chances on foreign mkt.	✗	✗✗
	National proc. Std.		Increase prod. cost for domestic consumer	✗	✓
Intraindustry trade	International	✓			
	National	?			
	Compatibility Std.		Increase openness of ntl. mkt.	✓✓	✓
	Quality Std.		Increase openness of ntl. mkt.	✓✓	✓
	Variety-reducing Std.		Reduce product diversity	✗	✗

Prod. – Product. Proc. – Process. Mkt. – Market. Std. – Standard. Ntl. – National. ? – Possible.

Standards can be developed through standards-writing organisations (*de jure*) or through an informal (*de facto*) market process which is sponsored (identified originator with a proprietary interest) or unsponsored. The former are of superior quality and legitimacy. However, development of *de jure* standards is slow and there is an increasing shift toward *de facto* standardisation due to the fragmentation of standards setting organisations (Belleflamme, 2002).

Market structure and consumer welfare (in terms of innovation and variety) can be dependent on the extent of standardisation (Blind and Jungmittag, 2005). In some markets, national or international standards can be opted for. If domestic standards are adhered to, products are unlikely to meet export market standards and vice versa, creating compliance costs (Blind and Jungmittag, 2005). Delay in obtaining

information related to varying standards has also been cited as a barrier (Chen et al., 2006).

7.3 MEMBRANE SEGMENTS

7.3.1 Potable Ultrafiltration/ Microfiltration (UF/MF) membranes

7.3.1.1 Introduction of potable membrane technology in the UK

Following several *Cryptosporidium* outbreaks, a risk assessment programme (Section 29, Water Supply Regulations 2000) correlated outbreak with inadequate treatment (Dezuane, 1997). The DWI subsequently agreed that if treatment plant was capable of continuous retention of particles $>1\mu\text{m}$ diameter, continuous monitoring was not required (DWI, 1999). This became the principal driver for membrane uptake in the UK potable segment. Membrane technology uptake was rapid with c.90 plants installed between 1997 and 2003, providing a total treated volume of c.1000000 $\text{m}^3.\text{d}^{-1}$ (Hall, 2003). Operational experiences in this period were varied. Many water providers (and operators) assumed filtration systems were ‘plug and play’. A DWI review in 2002 (DWI, 2002) revealed the extent of the problem. Not only did water providers and operators not understand the purpose of, for example, integrity testing (used to identify breaches in membrane elements), neither were they aware of who was responsible for its implementation. Guidance was subsequently administered by the DWI to clarify ownership however, water providers remained passive toward system development as guidance was non-specific. In addition, monitoring processes to meet DWI standards were not available; membrane manufacturers considered

integrity monitoring to be beyond the remit of the instructions for use (IFU) document (DWI, 2002) required for product approval thus no protocol was available. Johnson and MacCormick (2003) reported similar findings in the US, hypothesising that conflicting views reflected differing vested interests.

7.3.1.2 The approval process to date

The potable membrane market, as with several other sectors, is also currently constrained by the product approval process (Frost and Sullivan, 2004). All membrane elements selected for drinking water production must be validated for use by the Committee on Products and Processes (CPP) (a DWI select committee) which can take years.

In 2000, EU members integrated the EC drinking water directive ((EC DWD) (98/83/EC)) into national regulations to provide a more transparent approval scheme (Fielding et al., 2001). However, translation resulted in a lack of commonality. Consequently independent countries would not accept products directly with approval from other countries (Fielding et al., 2001). This was the case in the UK until 2004 (Reg. 31 Water Supply Regs. 2000) when the CPP became obliged to at least consider test results already acquired in other EU member states. European countries with their own approval process use a combination of national and international standards, toxicological assessment and expert bodies to assess individual products. Testing requirements also vary by country, the UK having one of the more advanced approval systems (Table 7.3). Many European countries provide ‘positive lists’ specifying chemicals (e.g. monomers) which may be used in manufacture without the applicant

having to provide any further toxicological data (Genderen and Hegarty, 1999); manufacturers then have a better knowledge of chemicals that are likely to be accepted by the regulator and because toxicological knowledge has already been ascertained, cost and application period can be significantly reduced (Table 7.4). Germany has developed its approval process toward the positive list to such an extent that a product cannot be approved unless all chemicals used in its manufacture are present on their positive list (Fielding et al., 2001).

Central to the approval process is the migration test used to evaluate leaching. Until recently, this varied significantly between countries and was primarily based on systems to test generic products. In the Netherlands, the element was separated into individual components and tested individually, dynamic tests were used in the US and France and in the UK static testing was employed. Method evaluation indicated disadvantages with all three protocol and leaching rate variations of up to 40 times were observed. An agreed protocol has since been developed (CEN Workshop Agreement, 14247 (2001)), comprising an agreed, internationally focused approach to leachate/ migration testing.

Table 7.3 *Current differences between NAS in Europe (adapted from Fielding et al., 2001).*

Country	Group	Approval		Positive list	Foreign Approvals			Testing Requirements		
		Type	Scope		Accepted	Considered	Organoleptic	Microbial	TOC	Specific
Austria	EU	Std	Dist.	✓	✗	Variable	✓	N/a	✓	✓
Belgium	EU	Std + EB	Public	✓	✗	✓	✓	✓	✓	✓
Cyprus	EU	No System		✗	✓	N/a	N/a	N/a	N/a	N/a
Czech Republic	EU	Regs.	Public, Private	✓	✗	✓	✓	N/a	N/a	✓
Denmark	EU	Std + Tox.	Dist., Bldg.	✗	Variable	✓	✓	N/a	✓	✓
Estonia	EU	N/a	Public, Private	✗	N/a	✓	N/a	N/a	N/a	N/a
Finland	EU	Std + EB	Bldg.	✗		✓	✓	N/a	✓	✓
France	EU	Std + EB	Public, Dist.	✓	✗	N/a	✓	N/a	✓	✓
Germany	EU	Std	Public, Private, Dist.	✓	✗	N/a	✓	✓	✓	✓
Greece	EU	No System		✗	✓	N/a	N/a	N/a	N/a	N/a
Hungary	EU	Std + EB	Public, Private, Dist.	✓	✗	✓	✓	N/a	✓	✓
Iceland	EFTA	No System		✗	Variable	N/a	N/a	N/a	N/a	N/a
Ireland	EU	No System		✗	Variable	N/a	N/a	N/a	N/a	N/a
Italy	EU	No System		✓	Variable	✓	N/a	N/a	N/a	N/a
Lichtenstein	EFTA	N/a		✗	Variable	N/a	N/a	N/a	N/a	N/a
Luxemburg	EU	No System		✗	Variable	N/a	N/a	N/a	N/a	N/a
Netherlands	EU	Std + EB	Public, Private, Dist.	✓	✗	✓	✓	N/a	✓	✓
Norway	EFTA	Std + Tox.	Public, Bldg.	✗	Variable	Variable	✓	✓	✓	✓
Poland	EU	Tox.	Public, Private	✗	✗	✓	N/a	N/a	N/a	N/a
Portugal	EU	No System		✗		✓	N/a	N/a	N/a	N/a
Slovenia	EU	Tox.	Public, Private	✓	✗	✓	✓	N/a	✓	✓
Spain	EU	No System		✓	✗	✓	N/a	N/a	N/a	N/a
Sweden	EU	Std	Public	✗	Variable	✓	✓	✓	✓	✓
Switzerland	EFTA	Std + EB	Dist., Bldg.	✓	✗	Variable	✓	✓	✓	✓
United Kingdom	EU	Std + Tox.	Public, Bldg.	✗	✗	✓	✓	✓	✓	✓

N/a-Not available, EB-Expert body, Std-Standards, Regs.-National regulations, Tox.-Toxicological assessment, Dist.-Distribution, Public.-Public Water Supply, Private. Private Water Supply. Bldg.-Building.

Table 7.4 *A summary of bottlenecks faced in the approval process in the UK.*

Application stage	Typical reason for lengthening of application/ Issue	Regulator shortfall
Instructions for use	Insufficient detail: Address specifically for water type/ proposed use	No consultation available in preparation or upon failure
Testing	Insufficient leaching/ tox. data	Case by case (No positive list). Regardless of how many times the same chemical is reviewed, must be re-tested.
Product formulation	Only 4 accredited laboratories: backlog/lead time?? Supplier disclosure: willingness to disclose commercially sensitive documentation.	Supplier can submit sensitive documents directly to CPP (chemical formulation/manufacturing process), however, CPP not authorised to enter into confidentiality agreement
Review stage	Complexity of chemical formulation. Cost/ extent of leaching tests. Meet only every 3 months	Failure of application leads to re-application in 3 months (without consultation)
Post approval: Audit/ product alteration	Any change to: process, source of raw material, manufacturing location, company ownership	Lead-time. Can require complete re-testing/ re-approval. Cost.
Post approval: Change to toxicological status/ approval process		For change to approval process, regulator is unclear on impact of status of already approved products
Post approval: Impact on water provider	Operation outside IFU without DWI notification can result in prosecution	How strictly can the IFU be adhered to in practice when water chemistry is so variable? Flexibility given?
Post Approval: Impact of water provider	Monitoring technology currently insufficiently sensitive to detect breakthrough	No guidance on monitoring techniques. However, guidance/ advice is in development

7.3.1.3 Future prospects

Working groups within the CEN have attempted to implement harmonised European standards through the European Acceptance Scheme (EAS) for over a decade with limited success (DWI, 2005b). Under the proposed standard, products tested and accepted under the EAS will be eligible for use in any EU (and EFTA) member state. Previous bottlenecks have been addressed (e.g. confidentiality, applicant guidance, inclusion of a positive list and a composition List). Due to implementation problems, a revision to the Mandate was made in September 2005 excluding water conditioning equipment thus it is currently unclear whether these products will even be included in the EAS. Until this time, national regulations of Member States remain in effect (NSF International, 2006).

7.3.2 Standardisation in the reverse osmosis (RO) membrane segment

Filmtec Corp. patented the FT-30 reverse osmosis element design in 1970 (Membrane Technology, 2005) and dominated the RO market for the duration of the patent. When first introduced, membrane element cost was c.\$1500 yielding low volume sales in niche (high-value) applications; high energy demand was possibly another factor for low uptake. The FT-30 patent allowed exclusivity until c.1992. after which element costs reduced by c.20% almost immediately to c.\$1300 (8-inch diameter module) due to new market entrants. New entrant designs were broadly based on the FT-30 (spiral wound form) and this remains the core market product (Anon, 2008). Element cost continued to fall c.5% to 10% per year until c.2000 where costs stabilised at c.\$450. Market size has subsequently increased at c.15% per year since (BCC Report GB-255R). In addition to cost reductions, newer elements can now produce twice as much water as a result of manufacturing improvements (Filtration and Separation, 2005) and further R&D investment.

As the market evolved from early '90's on the basis of a single design, a de facto market standard was created. Each module though varying in exact composition (i.e. material formulation, hydrodynamic design, manufacturing process etc.) had identical dimensions; 8-inch diameter, 1 m length. The same standards apply today (4 and 8 inch modules are available) and remain dictated by market forces. A consortium of manufacturers has now recommended 16-inch diameter elements to continue to push water production costs down (Filtration and Separation, 2005). Element standardisation significantly lowers switching costs as the pressure vessels (within which the elements are fitted) and all other peripheral engineering can be retained when changing products. Although the impact of this change

cannot be quantitatively expressed (not least because standardisation occurred simultaneously with IP expiration), it is anecdotally suggested that standardisation was a strong driving force behind the rapid uptake of RO membrane technology. De jure information standards have also been developed by the American National Standards Institute to clarify and normalise operation promoting industry transparency for manufacturers, operators and regulators. Although the number of element manufacturers has increased, Dow-FilmTec (formerly FilmTec) remain market leaders with c.43% market share. Finally, whilst standardisation aided market growth, welfare through innovation may have been lost: e.g. when spiral-wound modules became de-rigueur, hollow-fibre RO module development ceased before realising commercial viability (Fane, 2007).

7.3.3 Standardisation in the Membrane Bioreactor (MBR) segment

The following text provides a précis of a white paper (De Wilde et al., 2005) written as part of an EC framework program (AMEDEUS) in liaison with the CEN (and Deutsches Institut für Normung).

Significant growth has been observed in the sector in recent years (annual growth 11%, value c.€65M in 2005) (Frost & Sullivan, 2006) and the products offered are considerably diverse. In the white paper, 60% of respondents agreed that module standardisation could further market development by lowering the switching cost for decision makers investing in MBR. Although many participatory groups (operators, plant constructors and academic experts) believed standardisation would be beneficial, >50% of module suppliers suggested standardisation now is too early; 85% of module suppliers also believed it would hinder innovation.

Immersed modules have dominated this segment and two module designs have evolved: flat sheet (FS) and hollow fibre (HF). The white paper considered standardisation primarily to provide interchangeability between all module designs. The review concluded that to produce a standard for both FS and HF modules would be difficult with >30 factors impeding progress (Table 7.5), particularly those related to geometry and dimensions. Standardisation of HF and FS as separate products was therefore suggested. Brief analysis implied that similar obstacles are faced; this is further complicated as some products are in the early stage of their life cycle and therefore subject to significant R&D spend/ development.

Standardisation of characterisation methods was also considered, namely: membrane acceptance tests, fouling characterisation, integrity and ageing (standardisation towards uniform quality assessment methods). Nearly all respondents (c.80%) agreed standardisation was apposite and would aid segmental transparency and the development of trust amongst consumers. Many of the protocols are underdeveloped; e.g. only 27% of end-users received a procedure for membrane acceptance at module delivery.

Table 7.5 *Summary of advantages/ disadvantages as a result of MBR filtration module standardisation (adapted from De Wilde et al., 2005).*

	End-user	Module supplier/ constructor
Opportunities	<ul style="list-style-type: none"> ✓ Avoids vendor lock-in - No dead-ends - Security of supply - Competitive market price ✓ Price decrease ✓ Increased trust and acceptance ✓ Improved comparability of modules ✓ Easier/ standardised training of operators 	<ul style="list-style-type: none"> ✓ Bigger market ✓ Applying standardisation in design and construction – cost savings ✓ Reduction of introduction times for new products ✓ SMEs may be able to compete (fairly) with large enterprises
Threats	<ul style="list-style-type: none"> ✗ Civil constructions may be over dimensioned ✗ Extra cost and works to the peripherals ✗ Process+plant performance might be affected (smaller reliability) ✗ Perhaps more complex legal/ guarantee matters 	<ul style="list-style-type: none"> ✗ Higher competition ✗ Lower profit margins ✗ Limitation for innovative module producers to enter the market ✗ Can restrict innovation or affect internal R&D efforts – makes differentiation more difficult

7.4 DISCUSSION

Standards (or consideration there of) are present in all three core municipal membrane applications albeit in different forms. In the potable segment, incompatibility amongst NAS's has created a barrier to free-trade within the EU and EFTA. Following the development of the new migration testing protocol by European consensus, the approval process now appears an adequate safety standard for membrane technology.

However, barrier height remains dictated by the transparency of the national system or the extent of the intra-regional trade agreements (e.g. Sweden, Denmark, Finland and Norway) that have developed to liberalise trade. As well as the anti-competition effect, time to market also reduces the impact innovation or new entrants can make. The introduction of the EAS will lower these barriers (cost, length and number of approval processes required to trade in Europe). However, by this time, market penetration costs for product/ brand establishment to compete against the incumbents may constitute too significant a barrier for smaller manufacturers (Geroski, 1989). Considerable confusion has arisen around the implementation of this system and although protectionism cannot be considered directly, various industry groups are becoming increasingly wary of developments within the process (Nury and Meijerung, 2004).

Over estimation of process autonomy, lack of operator training and regulatory guidance created a poor public perception on the inception of potable membrane technology, but whether this has hindered implementation since is uncertain. Some information standards are evolving in this segment and cover both operational issues (e.g. ASTM Integrity test method) and the

approval process (NSF International, 2006) which will deliver some transparency for stakeholders.

At first glance, a technical standard for MBR looks unlikely to arise. Module suppliers are correct to consider the impact of standardisation on innovation; early adoption causes inadequate standards and inferior product quality whereas late adoption results in users locked into proprietary products raising switching costs for manufacturers/ water companies (Tassey, 2000). Standardisation in the RO segment may have been too early and impacted upon innovation (Fane, 2007) however, subsequent innovations in manufacturing process at an efficient scale have reduced unit costs and improved product reliability and capacity (Filtration and Separation, 2005).

Unsponsored de facto standardisation has aided RO segment economic growth; this has been observed in other sectors. Although the market has been competitive for >15 years, FilmTec have remained the dominant incumbent, which agrees with the literature that new entrants rarely achieve significant market share (Geroski, 1989). Implementation of a de jure standard for MBR is more complex as legitimacy protracts the process. Additionally more than one element design has been established in the market place. Therefore unlike in RO where the standard element design is dictated by a consortium comprising the dominant incumbents, for the MBR segment, an appropriate design to standardise against is both a legal and political decision. There are historic examples of standardisation processes where the proximity of incumbents to the regulator has been questioned (Nellis and Parker, 2004); the CEN have procedures to deal with such a scenario (CEN: Guide 8).

Standardisation of characterisation methods for the MBR segment is valid and has already been undertaken for the RO segment thus development is entirely possible. Early adopters of membrane technology were exposed to significant risk as membrane technology was an experience good and limited process and product knowledge (e.g. membrane life) were available. Decision makers have retained a negative perception of MBR technology (Judd, 2006). Whilst information standards are perhaps less conducive to economic growth than product standards, they are important for developing tacit knowledge and comparability thereby simplifying evaluation in the future decision making process (Tassey, 2000).

7.5 CONCLUSIONS

A review of the literature demonstrated that a mixture of de facto and de jure standards have been or are being considered for implementation across various segments of the membrane market. Competition is currently constrained in the potable MF/UF segment due to the adoption of a de jure umbrella approval system. Although, this will have limited the number of manufacturers operating in the segment, it is uncertain whether this lack of competition has impeded segment growth. Reverse osmosis is apparently less constrained by de jure standards and has instead evolved into a classic lead-follow paradigm where the dominant incumbent dictates market response. RO is the only segment in which an increase in social welfare has been observed through standardisation. Membrane design for the MBR segment was not conceived from the expiration of intellectual property rights and consequently several competing membrane designs have evolved; it is unlikely that a standardised design will be reached. However, standardisation of characterisation methods holds real potential for assisting segmental transparency and its success has been observed elsewhere.

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CHAPTER 8

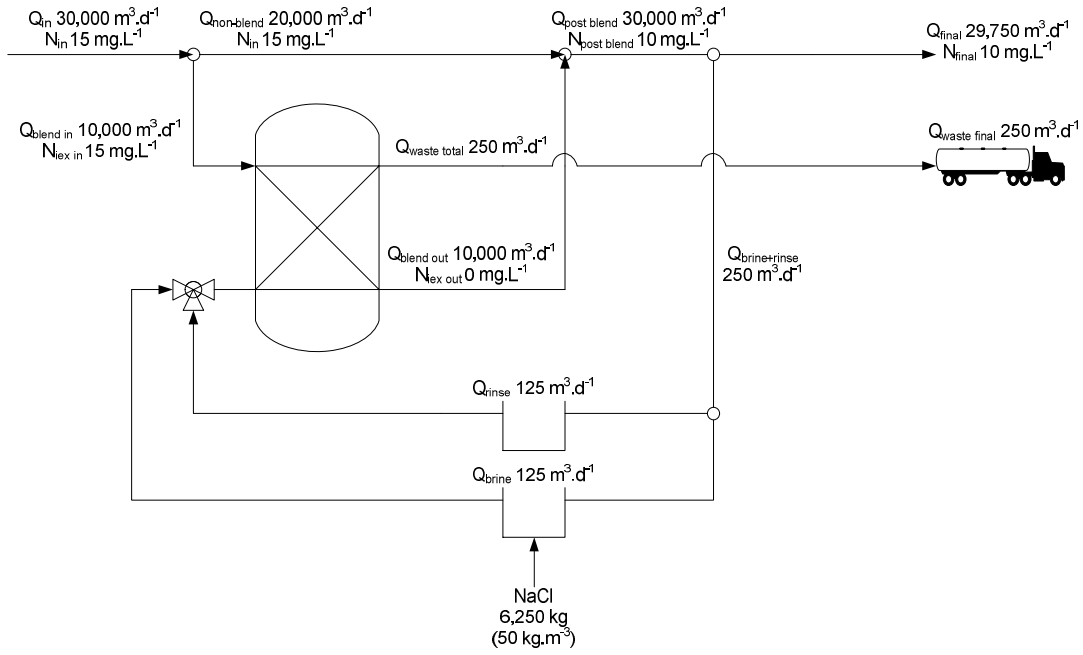
DISCUSSION – PROCESS DESIGN CONSIDERATIONS

8 DESIGN CONSIDERATIONS

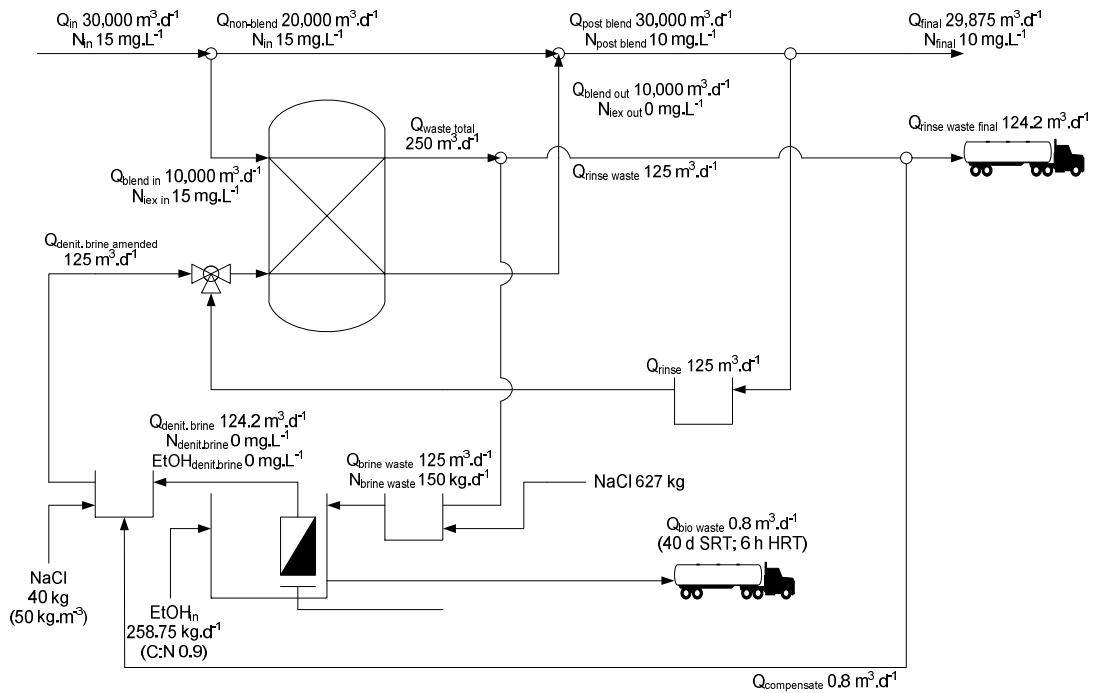
In this thesis, the application of immersed pressure driven MBR to potable water denitrification has been studied. The preceding literature reviews and technical papers have all contributed towards this aim. Here, the implications of these findings are considered with respect to full scale application. Based on a preliminary cost evaluation (Appendix A), the ion exchange replacement MBR option was established to be uneconomic due to the capital cost associated with the large quantity of membrane surface area required. This section therefore focuses on the MBR for brine regenerant treatment and re-use.

8.1 PROCESS DESIGN AND COST

A basic process mass balance of the two ion exchange processes (linked to either disposal or re-use), is demonstrated in Figure 8.1. The balance is based on using a standard regenerant concentration of 50 g NaCl.L^{-1} , flow rate of 5 bed volumes per hour (bV.h^{-1}) and regeneration time of 60 minutes (van der Hoek and Klapwijk, 1989; Chapter 6). This volume can potentially be reduced by optimising the regeneration time, increasing the salt concentration or by operating the resin in partial regeneration to recover a lower proportion of c.40-60% of the resin capacity (Liu and Clifford, 1996; van der Hoek, 1987). The regeneration volume used will dictate the closed loop volume (van der Hoek and Klapwijk, 1989) and therefore the MBR capacity. However, it is considered that the cost benefit of $\text{c.£}0.07.\text{m}^{-3}$ of treated flow (Table 8.1) is a reasonable projection on the basis of the principal operating costs involved (tankering, salt and ethanol).



(a)



(b)

Figure 8.1 Idealised mass balances of proposed works (a) Ion exchange with complete disposal to tanker; and (b) Ion exchange with brine treatment and re-use. Assumed protocol: Exhaustion flow 20 bV.h^{-1} ; regenerant flow 5 bV.h^{-1} (60 minutes); regenerant concentration 50 gNaCl.L^{-1} ; slow rinse 5 bV.h^{-1} (30 minutes); and fast rinse 20 bV.h^{-1} (10 minutes).

Table 8.1 Comparison of operating costs associated with the two process options outlined in Figure 8.1. Plant flow – 30000 m³.d⁻¹ (Costs provided from full scale ops.).

	Tankering ¹		Salt ²		Ethanol ³		Cost	Cost ⁴
	Vol. (m ³ .d ⁻¹)	Cost (£.d ⁻¹)	Mass (kg.d ⁻¹)	Cost (£.d ⁻¹)	Mass (kg.d ⁻¹)	Cost (£.d ⁻¹)	(£.d ⁻¹)	(£.m ⁻³)
Tanker	250	3250	6250	687.5	N/a	N/a	3937.5	0.132
MBR	124.2	1615	667	73.4	258.75	137.1	1825.5	0.061
Difference	125.8	1635	5583	614.1	258.75	-137.1	2112	0.070

¹Tankering £13.m⁻³. ²Salt £0.11.kg⁻¹. ³Ethanol £0.53.kg⁻¹. ⁴Based on full flow of plant.

Rinse volume (sum of fast and slow rinse) cannot be added to the regenerant loop as it must comprise freshly produced water to flush the bed before use. The rinse water will still contain salt, nitrate and other oxyanions, albeit in lower concentrations, and must therefore be wasted (Clifford and Liu, 1993). The rinse in this study was in accordance with the manufacturers' recommendation (Purolite) and comprised c.50% of the total water volume. Clifford and Liu (1993) used only 2bV for rinse water compared to 5bV in this investigation implying that further optimisation is possible.

The above costing (Figure 8.1) is based on considering the resin globally rather than as individual resin beds (or lines): although this facet is unlikely to influence operating cost, the impact on capital cost is potentially significant. The simplest layout is that proposed by van der Hoek et al. (1987) which comprises 2 lines to provide for operation and standby, and is used in most small scale designs (Dow, 2008). Larger plants >c.400 m³.h⁻¹ are more frequently designed to reduce redundancy and vessel size. The number of lines can be calculated using (Dow, 2008):

$$No.oflines = \frac{Runlength(h) + Regen.time(h)}{Regen.time(h)} \quad (Eq. 1)$$

On this basis, the number of vessels in the above design could be as many as 10. If the MBR is designed to only denitrify sufficient regenerant volume for the standby vessel (van der Hoek et al., 1987), the quantity of membrane surface area required could be reduced from c.1000 m²

(based on $5 \text{ L.m}^{-2}\text{h}^{-1}$ and one vessel) to as little as $c.100\text{m}^2$ (based on 10 vessels). Considering a membrane cost of $c.£50.\text{m}^{-2}$ (Fletcher et al., 2007), payback for membrane material is in the order of days rather than years (cf. the potable full-flow MBR design). Furthermore, if the closed loop volume can be reduced to this extent, it may be more pertinent to regenerate at higher salt concentrations and operate the resin closer to complete (rather than partial) regeneration.

8.2 DESIGN ISSUES FOR THE BRINE REGENERANT MBR

8.2.1 Intermittent filtration for the brine regenerant MBR

Analysis of the ion exchange replacement MBR provided insight into the potential for deposit reversibility using intermittent gas scouring. This strategy was also considered for the brine regenerant MBR. During brine treatment, flux (J) was approximately $4.6 \text{ L.m}^{-2}.\text{h}^{-1}$ and filtration time was arbitrarily set at 10 minutes with a subsequent 30 second gas injection (no backwash). Permeability was sustained over several days' operation demonstrating that the dead-end strategy in Chapter 5 (A) is transferable to this application, at least at low J . In this thesis, nitrogen gas (N_2) was generated from a nitrogen selective hollow fibre module (>99%) for sparging to ensure that no dissolved oxygen (DO) was entrained however, due to a high capital cost of $c.£1000$ for a maximum SGD_m of $c.0.54 \text{ Nm}^3.\text{m}^{-2}.\text{h}^{-1}$, the process is not economic. Headspace N_2 recirculation has been recently successfully demonstrated in a sealed lab scale MBR (Rezania et al., 2007) and could be an option at full scale. Alternatively to maintain design simplicity, experiments that have not been reported thus far in this thesis, have demonstrated that air can be applied effectively, due to the intermittency of scour and the use of a coarse bubble aerator with a poor mass transfer characteristic ($c.1\%$) (Figure 8.2).

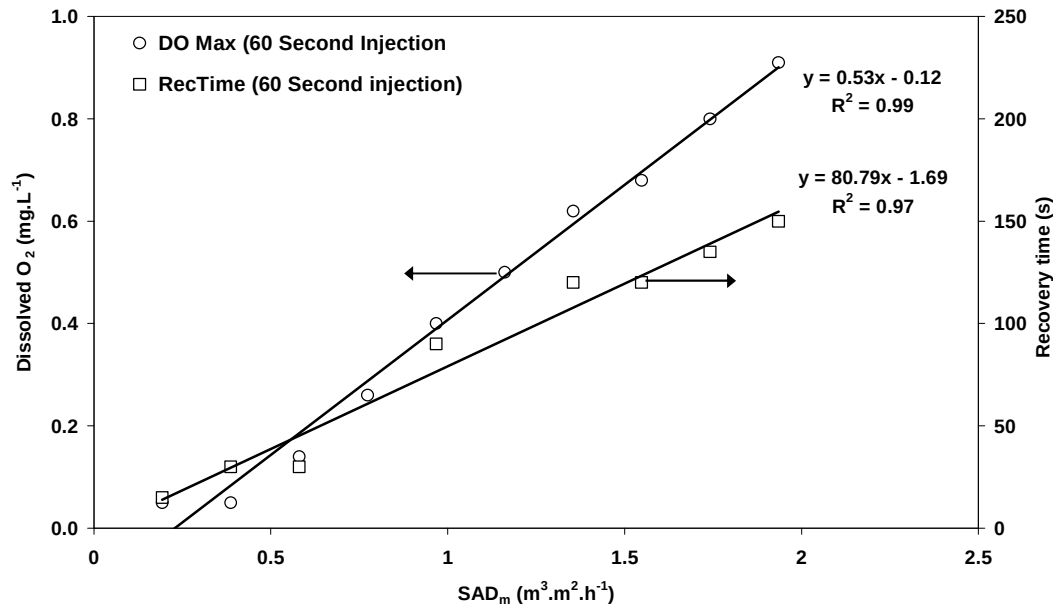


Figure 8.2 Dissolved oxygen (DO) experiments. Conducted in situ (MBR, MLSS $1.1\text{g.L}^{-1} \pm 0.2\text{g.L}^{-1}$). Recovery time is equal to the time required to recover to initial reactor DO concentration. DO concentration is equal to the reactor DO concentration after a 60 second gas scour. Reported measurements were taken at 0.30m below the liquid surface using a calibrated DO meter (WTW Oxi340i).

DO residual was observed to be dependent upon injection time and the SAD_m applied. The recovery time approximated to the oxygen uptake rate of the biomass which was recorded at $17.7 \pm 1.7 \text{ mgO}_2.\text{gMLSS.h}^{-1}$ using batch respirometry. By operating within the confines outlined in Chapter 5A (lower SAD_m and injection time than in Figure 8.2) it was possible to avoid a DO residual indicating that standard (non-sealed) MBR design can be implemented for this application. It should be noted that due to the smaller scale of the brine MBR, the process is less sensitive to power costs associated with the air blower.

8.2.2 Brine regenerant quality

A review of the literature and experimental analysis on brine treatment provided insight into the impact salt variation can have on process performance. Large salt upshocks are consistently observed in brine waste at full scale (Figures 8.3) and can significantly impede denitrification

capacity in both halophilic and non-halophilic communities (Aston and Peyton, 2007; Kargi and Dincer, 1999).

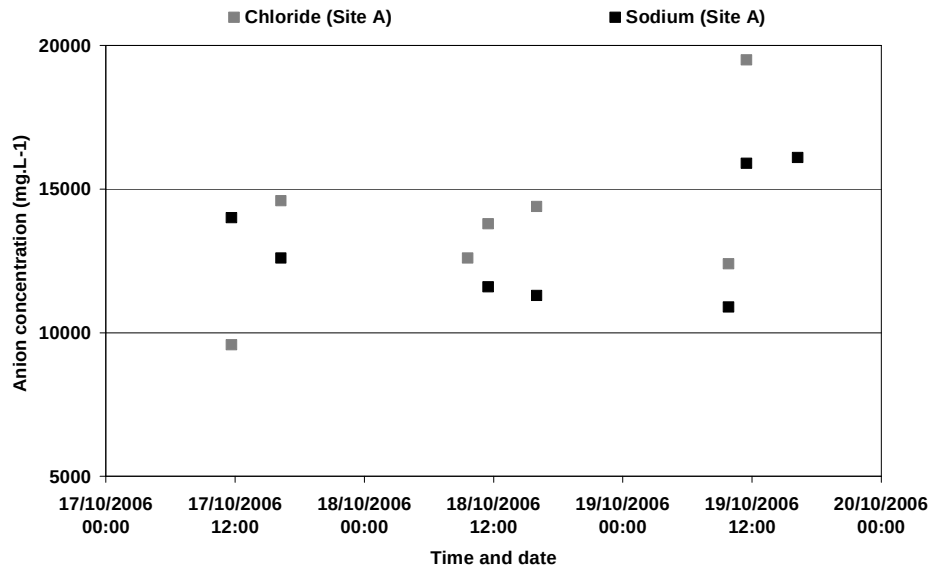


Figure 8.3 Waste brine sodium and chloride concentration variations observed over 2 days full scale operation.

For example, in Chapter 6 of this thesis, a reduction in denitrification capacity was observed when salt concentration was upshocked from 50g.L⁻¹ to 75 g.L⁻¹. Extension of the solids retention time can compensate for the reduction in growth rate. Yoshie et al. (2006) have also shown that specific denitrification rates at high salinity can be augmented by acclimatising cultures initially (from seed) at higher salt concentrations. Acclimatisation at full scale should therefore be carried out at the highest salt concentration that it is envisaged will be reached. The degree of salt variation may also be smoothed due to: the incorporation of a balancing tank; and the exclusion of rinse water from the closed loop cycle.

8.3 OTHER CONSIDERATIONS

Other considerations for brine regenerant re-use include the necessity for residual disinfection, polysaccharide stability in the resin matrix and the seasonal usage of the plant. As the

denitrified brine regenerant will be subject to storage prior to use, there may exist a potential for re-growth. Chlorine will react with organics in the brine to form disinfection by-products as indicated in Chapter 3 of this thesis. Although the brine regenerant does not come into direct contact with the product water, regulators may be cautious; in addition the subsequent by-product structure and conformation may improve adsorption of these organics during regeneration. This is analogous to the issue of polysaccharide stability within the resin; regulators may demand evidence that leaching of organics will not occur during exhaustion.

Nitrate peaks can be seasonal and are often correlated to periods of increased rainfall. This can result in long standby periods. For extended periods, this may require feeding the biomass a nitrate supplement to ensure bacterial survival as used for the early packed bed processes (Richard, 1989). This conveys several issues regarding process robustness, supplemental cost, process complexity and bacterial adaptation during standby.

8.4 MARKET PENETRATION AND BARRIERS TO ENTRY

In addition to the outstanding technical issues detailed in sections 8.1-8.3, there is also a perception barrier to overcome. As described in Chapter 7 of this thesis, decision makers in the wastewater industry remain cautious about investing in MBR technology due to concerns over hidden operation and maintenance costs (Judd, 2006). In comparison, there is no knowledge of MBR technology in the potable sector indicating that there is an even greater need for data transparency to support decision makers (Figure 8.4).

External environment		Technological	
		Strengths	Weaknesses
		<ul style="list-style-type: none"> - Established tech. in w/water - Positive result at bench - Low scale - Low capex/ opex - No direct product contact - Low energy - Low flux – simple operation - Standard MBR design (8.2.1) 	<ul style="list-style-type: none"> - No full scale data - Real brine yet to be tested - Long term stability of polysaccharide unknown - Impact of influent variation - Alcohol as a substrate - Standby/ seasonal operation - Impact of chlorination
Threats	Opportunities	<ul style="list-style-type: none"> - Use a scaled up process to demonstrate cost competitiveness on real waste. - Assess process for the destruction of other oxyanions in brine (e.g. perchlorate). - Evaluate transferability of intermittent strategy to other MBR (e.g. anaerobic) 	<ul style="list-style-type: none"> - Use scaled up process to address technical unknowns: - Carbon retention - Polysaccharide stability - Re-growth potential - Chlorination impact - Process standby - Involve end-users to drive development: use their sites; feeds etc.
	<ul style="list-style-type: none"> - Many sites - Several different oxyanions - Transference of intermittent strategy to other MBR apps. - Current technology expensive - Oil price rising - Road haulage cost rising - Legislative drivers - End-users interested - Both groundwater and surface water issues 	<ul style="list-style-type: none"> - Unknown technol. in segment - Cautious decision makers - Future legislation - Technology approval: Time to market? - Operator inexperience - Alternative simple technology - Control of nitrate vulnerable zone sufficient to control nitrate below standard? Now/ future? - Adopt simplified process design (8.2.1) to allow standard MBR technology to be adopted. This may alleviate the pressure on decision makers over uptake of bespoke technology - Demonstrate cost, low energy consumption and reduction in carbon footprint - Demonstrate simplicity of low flux operation in terms of fouling/ cleaning/ maintenance 	<ul style="list-style-type: none"> - Encourage data sharing from demonstration plant to improve understanding of the concept - Review competitive technology to disseminate competition and inherent advantages/ disadvantages - Create a dialogue with the regulator to determine what they consider are the critical factors before implementation

Figure 8.4 *SWOT analysis based on brine regenerant MBR treatment.*

The potable industry may still be hesitant to invest in new membrane technology processes following the turbulent transition of MF/UF for cryptosporidium (DWI, 2002). In this application, the investment risk may be considered low as the process is small scale (low cost) and does not directly treat the product water.

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CHAPTER 9

CONCLUSIONS AND FURTHER WORK

9 CONCLUSIONS AND FURTHER WORK

9.1 CONCLUSIONS

The present thesis has extended understanding of the application of membrane bioreactors to the denitrification of potable water. The following conclusions can be drawn from this work:

1. A review of the literature identified that some membrane bioreactor configurations cannot control substrate breakthrough and that all pressure driven membrane bioreactors are configured in pumped sidestream to avoid using air scour (Objective 1).
2. Complete retention of the exogenous substrate was determined by maximising the C:N dose. Intermediate compounds were controlled by chlorination. Any substrate breakthrough increased the concentration of disinfection by-products post chlorination (Objective 2).
3. When applied as a substrate, ethanol allowed for the formation of large flocs which were sufficient to withstand process shear. An improvement in permeability over the use of acetic acid was closely linked to particle size. Even at low suspended solids concentrations, an increase in suspended solids concentration did not necessarily correlate to an increase in fouling propensity (Objectives 3 and 4).
4. Optimised intermittent gas injection in an immersed MBR sustained permeability in anoxic conditions and reduced cost over continuous gas scour by c.20 times. The relationship between flux, filtered volume and mass was a good indicator of the

transition between fouling and non-fouling conditions. This transition became less apparent at higher solids retention times (Objective 4).

5. The deposit formed during intermittent gas operation was different to that formed during constant gas scour; greater irreversible fouling was formed under constant gas scour and was closely linked to a lower mean particle size due to the increased shear intensity and preferential migration of smaller particles under a continuous gas stream (Objective 4).
6. Denitrification efficiency was strongly inhibited by the upshock of salt concentration during brine regenerant treatment. Salt upshock induced protein release and a phenotypic profile shift of the microbial community however, no effect on permeability was observed (Objective 5).
7. The high concentration of organic material contained within the brine regenerant did not significantly impact upon resin capacity. Resin performance was comparable to operation with freshly produced brine (Objective 5).

9.2 FURTHER WORK

A number of areas where further research would be beneficial have been identified during the course of this research. These are detailed below:

1. Ethanol effectively supported denitrification and improved permeability. Assessing the fouling potential of other non-contentious substrates to support denitrification might improve technological acceptance with regulators.
2. This research identified a hydrodynamic protocol that provided for deposit reversibility. It is not known whether this effect can be attributed to characteristics of the biomass and organics, the operational parameters (e.g. substrate limitation) set in this investigation or the membrane type used. Further work could include different feed matrices, biomass and membrane configurations to determine potential knowledge transfer.
3. Larger scale on-site testing of real brine regenerant would provide more detail of the stability of biological treatment and the fouling potential of the biomass. In these circumstances, it would provide the ideal opportunity to challenge the intermittent filtration strategy with a more complex feed.
4. Ion exchange resin was shown to adsorb onto the resin during regeneration. Assessment of the long term stability of polysaccharides on the resin would be beneficial to allay concerns over their leaching potential.
5. Chlorination is often required for water storage to prevent re-growth. It may be pertinent to assess the impact of chlorination as this may influence the conformation of the residual organics increasing their binding potential toward the resin.
6. The rinse water was shown to contribute to a significant volume of the waste. It would be beneficial to identify whether any alternative treatment or disposal routes are available for a waste stream with lower ionic and organic content than that of the regenerant.

APPENDIX A

IMMERSED MEMBRANE BIOREACTORS FOR NITRATE REMOVAL FROM DRINKING WATER: COST AND FEASIBILITY

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A IMMERSSED MEMBRANE BIOREACTORS FOR NITRATE REMOVAL FROM DRINKING WATER

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ABSTRACT

Brine disposal remains a key consideration when employing ion exchange (IEX) for nitrate removal. To circumvent this issue, research was conducted into developing an immersed membrane bioreactor (MBR) as a replacement for ion-exchange. This paper compares the economics of the two process options whilst also considering MBR for brine treatment. At a blend flow rate of $3000 \text{ m}^3 \cdot \text{d}^{-1}$, total life cycle costs were £0.095, 0.128 and $0.064 \cdot \text{m}^{-3}$ for IEX, MBR and IEX with brine recycle MBR respectively. Capital and O&M costs associated with MBR were extremely sensitive to membrane price variation. For blend flows $>700 \text{ m}^3 \cdot \text{d}^{-1}$, IEX with brine recycle MBR proved the most cost effective option (total life cycle cost £0.044- $0.087 \cdot \text{m}^{-3}$, $1500\text{-}30000 \text{ m}^3 \cdot \text{d}^{-1}$) when assuming similar hydrodynamic efficiencies to the IEX replacement MBR. Further cost reductions ($\leq 17\%$) can be found by operating Brine recycle MBR at higher salinity ($\sim 100 \text{ gNaCl} \cdot \text{L}^{-1}$), provided an appropriate halo-tolerant community can be established.

A.1 INTRODUCTION

Several technologies are commercially available to treat nitrate contaminated raw water to meet drinking water standards including reverse osmosis, electro dialysis, biological denitrification and ion exchange (IEX). IEX is typically selected due to its low cost and simplicity. However,

costs primarily associated with brine disposal (and secondarily with salt consumption) have significantly increased process cost as restrictions on disposal options have increased (Figure A.1).

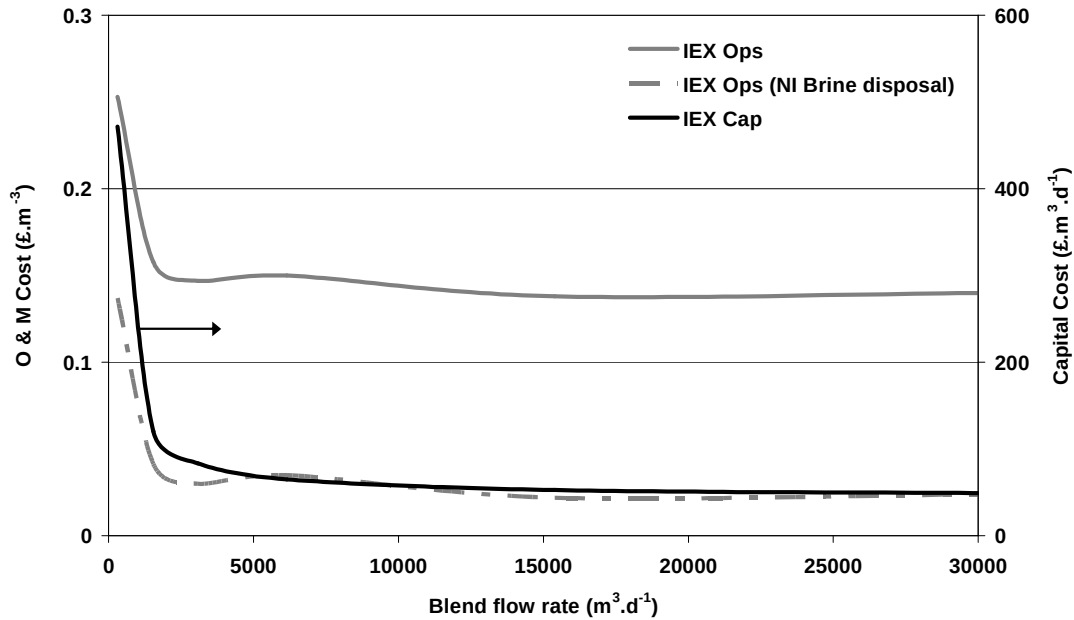


Figure A.1 IEX capital and O&M costs (With brine disposal and without).

Biological nitrate removal presents a viable alternative to ion-exchange as it facilitates the complete destruction of the nitrate ion. Biological denitrification was first trialled at full-scale for drinking water in 1982 (Matějů et al., 1992) however, when compared economically to ion exchange, construction could be 2.5-3 times that of a resin plant (Richard et al., 1989) and to assure compliance, extensive post-treatment was required to remove micro-organisms, turbidity and nitrites (Clifford and Liu, 1993a). Membrane bioreactors (MBR) offer several advantages over traditional biological processes including separation of micro-organisms from the product water, greater process control and limited channelling effects (thus low nitrite accumulation). Urbain et al. (1996) reported on successful full-scale operation of a pressure driven (externally configured) membrane bioreactor for groundwater nitrate removal in France. Various authors (Clifford and Liu, 1993b; Chung et al, 2007) have also considered biological processing of the

brine regenerant in conjunction with IEX, significantly reducing waste volumes and salt costs. Following a technical study into immersed MBRs as a replacement for ion exchange, this paper uses the data obtained to evaluate whether cost reduction is maximised by replacing IEX completely or, combining MBR with IEX to omit (or at least significantly reduce) brine disposal.

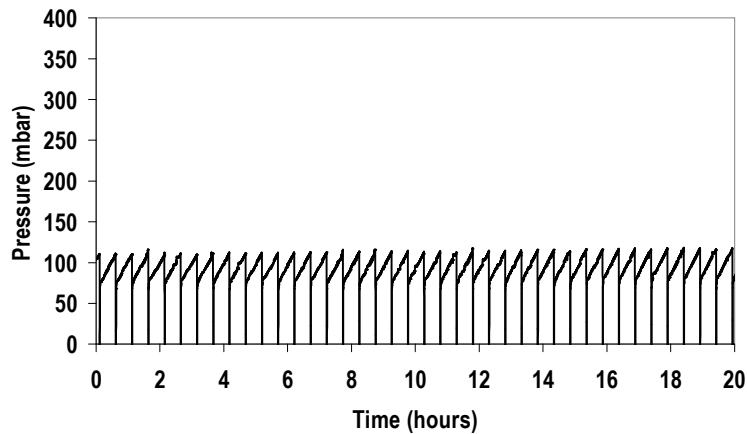


Figure A.2 *Pressure transient at set flux $15 \text{ L.m}^{-2}.\text{h}^{-1}$, gas sparged in combination with backflush every 30 minutes for 30 seconds.*

A.2 METHODS

A.2.1 Ion Exchange – IEX Blend

Nitrate selective resin with a maximum specific exchange capacity 0.9 Eq.L^{-1} and a $\text{Cl}^-/\text{NO}_3^-$ equivalent ratio 3.5 was assumed. Optimum nitrate selectivity was assumed to be 0.89. Exhaustion was determined on the basis of influent NO_3^- -N concentration and flow. Brine regenerant concentration was 100gNaCl.L^{-1} . Partial regeneration was not considered. Brine disposal volume was calculated using the regenerant concentration and equivalent ratio. Life expectancy of the resin was 7 years. Influent nitrate concentration was set as $14.67 \text{ mgNO}_3^- \text{ N.L}^{-1}$ with a target N set to $10 \text{ mgNO}_3^- \text{ N.L}^{-1}$ (Blended).

A.2.2 Membrane Bioreactor – MBR Blend

Immersed membranes were used in this investigation (Table A.1) for their low specific energy demand (Cornel and Kraus, 2006) and operational flexibility. In this current study, the authors have found that at relatively low suspended solids concentrations, it is possible to operate immersed hollow fibres sustainably with limited air injections (Figure 2, 30 seconds every 30 minutes). Due to the brevity of the gas injection, low air flow and limited oxygen mass transfer associated with coarse bubble aerators, dissolved oxygen concentration recovered to $<0.1 \text{ mg.L}^{-1}$ quickly and no noticeable impact on biological activity was observed. Specific biomass activity ($\text{mg N.g MLSS.h}^{-1}$) was calculated according to predicted average temperature and operating pH using data from this current investigation and the relationship proposed by Timmermans and van Haute (1983):

$$SA = SA_{\max,20} \left(\frac{10^{0.052(t-20)}}{1 + 0.0502(10^{(8.3-pH)-1})} \right) \quad (1)$$

Hydraulic residence time (hence tank size) is based upon specific activity, influent N concentration and assumed mixed liquor suspended solids (MLSS) concentration at the set solids residence time (SRT, 40 days). Power for mixing (Eq. 2), blowers (Eq. 3) and pumps (Eq. 4) were determined according to the design equations below (Metcalf and Eddy, 2003):

$$P = G^2 \mu V \quad (2)$$

$$P_w = \frac{wRT_1}{29.7ne} \left[\left(\frac{p_2}{p_1} \right)^{0.283} - 1 \right] \quad (3)$$

$$P_w = \frac{\rho g H}{1000\xi} \cdot \frac{Q_{\text{pump}}}{Q_p} \quad (4)$$

where G is (s^{-1}), μ is viscosity (N.s.m^{-2}), V is tank volume (m^3), w is air flow (kg.s^{-1}), R is air gas constant ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$), T is temperature (K), n is (0.283 for air), e is blower

efficiency, ρ is density (kg.m^{-3}), g is gravity (m.s^{-2}), H is pump head (m of water), ξ is pump efficiency. When MBR is configured to process brine regenerant, salt concentration is reduced to 30gNaCl.L^{-1} (3%) and consequently flow of brine regenerant to the brine MBR is increased. Under these conditions, biomass SA is assumed to fall to 90% of the MBR blend process (Clifford and Liu, 1993a).

Table A.1 *Membrane Bioreactor (MBR) operating conditions.*

Parameter	MBR	Brine MBR
Influent N (mg N.L^{-1})	14.67 (<i>mean</i>)	600-1400
Target N (mg N.L^{-1})	10 (<i>once blended</i>)	<60
Blend Ratio	0.31 (Based on the above)	N/a
NaCl Concentration (%)	N/a	3
Net flux ($\text{L.m}^{-2}.\text{h}^{-1}$)	17.1	17.1
SAD_m (SAD_m net) ($\text{m}^3.\text{m}^{-2}.\text{h}^{-1}$)	0.77 (0.01)	0.77 (0.01)
Permeability (LMH.bar^{-1})	150	150
Backflush: Frequency (mins)	30	30
Backflush: Duration (secs)	30	30
Clean-in-place: Frequency (d)	14	14
Complete Chemical Clean (d)	180	180
HRT (hours)	1.4	13.65 (Influent 586.3mgN.L^{-1})
SRT (d)	40	40

A2.3 Costs

All costs are given either as installed capital cost ($\text{£.m}^{-3}.\text{d}^{-1}$), operating cost (£.m^{-3}) or total life cycle cost (£.m^{-3}). All of these produced values refer to the blend stream product cost rather than the total site flow. Breakdown of costs and assumptions are listed below (Table 2). For further item specific costs refer to Fletcher et al. (2007). Membrane material cost is scaled down with increasing blend flow to $\text{£}40.\text{m}^{-2}$ (minimum). Labour (Hours) is scaled according to total treatment works flow (Adham, 2004).

Table A.2 *Summary of costing assumptions used.*

Capital Items		Design data	
Brine disposal	£11.m ⁻³	Power	£0.12 kWh
Membrane cost	£40-80.m ⁻²	Plant life expectancy	20 years
		Maintenance	0.5% Capital
		Interest + Inflation	8%
		Labour	Scaled ^a
		Conversion	\$/£0.51; €/£0.68 ^b

^aTaken from Adham, 2004. ^bAs of 12 March 2007.

A.3 RESULTS AND DISCUSSION

A.3.1 Capital cost

Calculated installed costs for the IEX replacement MBR are highly competitive (Figure 3) versus other MBR capital costs reported for more typical applications such as re-use and reclamation (Côté et al., 2004) and municipal wastewater (Hanft, 2006; Adham et al., 2000), ranging from £325.m⁻³.d⁻¹ (Q, 1709 m³.d⁻¹) to £156.7.m⁻³.d⁻¹ (Q, 34188 m³.d⁻¹). This can be attributed to smaller tank capacity per unit flow (i.e. no aeration or anaerobic basins) coupled with zero screening or biological aeration requirements. Furthermore, due to the aeration strategy adopted, cassettes are gassed sequentially and intermittently thus the number of blowers required for membrane gasification is limited yielding a capital saving ~7.3% (blend flow, 3400m³.d⁻¹). Civil structures were the dominant cost when constructing the early heterotrophic nitrate removal plants (Kapoor and Viraraghavan, 1997). Process intensification provided by MBR limits these costs. However, membrane material constitutes a significant fraction of the total capital (>50%), resulting in significant sensitivity (Table 3) to fluctuations in membrane cost and material requirements. Consequently, whilst the MBR design is cost competitive versus standard MBR designs, the total cost is between 1.2 and 3.6 times the cost for IEX plant (Figure 1) construction. Specific costs for the brine recycle MBR are high (£2923-£503.m³.d⁻¹ for brine recycle flows ranging 7.7-770 m³.d⁻¹) however, for plant sizes

$>500 \text{ m}^3.\text{d}^{-1}$, capital costs for IEX with MBR for brine recycling was significantly cheaper than MBR alone (Figure 4) and only slightly more expensive than IEX (1.3-1.03 times the cost), ranging from $\text{£}160.\text{m}^{-3}.\text{d}^{-1}$ ($Q, 1538.5 \text{ m}^3.\text{d}^{-1}$) to $\text{£}50.3.\text{m}^{-3}.\text{d}^{-1}$ ($Q, 30769 \text{ m}^3.\text{d}^{-1}$).

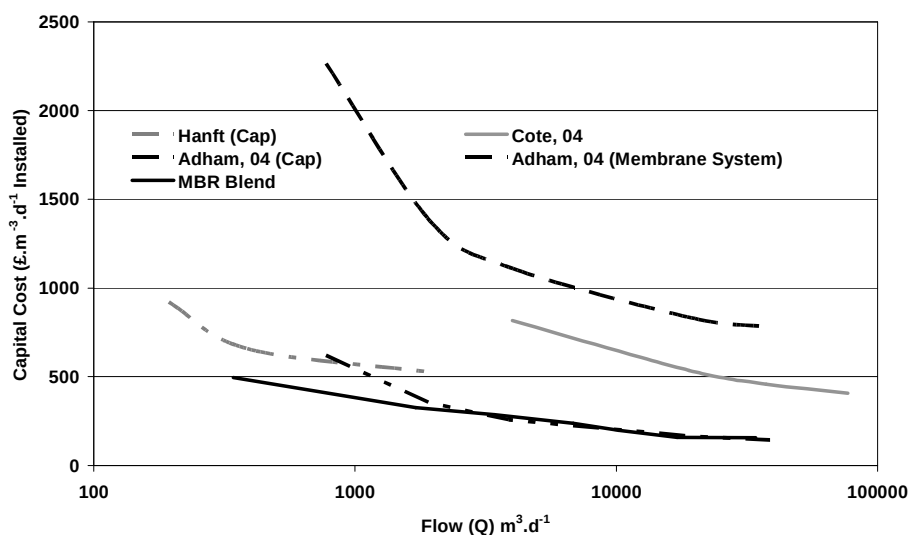


Figure A.3 MBR installed capital costs ($\text{£}.\text{m}^{-3}.\text{d}^{-1}$) from several authors compared to the MBR blend.

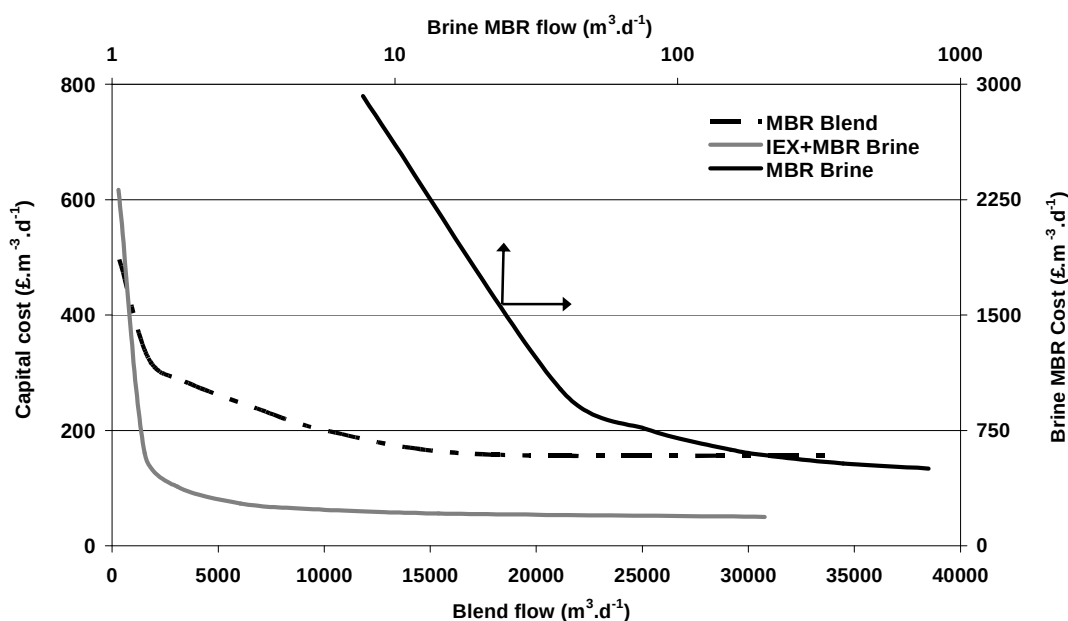


Figure A.4 Installed capital cost comparison between MBR blend and IEX combined with MBR brine (MBR Brine costs also shown independently).

Due to the scale of the brine MBR, capital cost for IEX and brine recycle combined is relatively insensitive to membrane cost variations compared to MBR alone. However, both

processes are sensitive to specific bacterial activity (SA, mgN.gMLVSS.h⁻¹). A factor of safety (fos 1.5) was therefore assigned to oversize the brine and replacement MBR tanks which should offset influent concentration variation. Limited research has been conducted on the influence of salinity on denitrifying communities. Clifford and Liu (1993a) reported that SA of denitrifiers derived from activated sludge declined by only 10% at 30gNaCl.L⁻¹ (3%) concentration however, significant effects have been reported at higher concentrations. Investigators have made use of Halo-type bacteria (e.g. *Halomonas campisalis*) typically derived from marine sediments which report similar SA at high NaCl concentrations (12.5%, 125gNaCl.L⁻¹) to common soil denitrifiers (e.g. *Pseudomonas denitrificans*) in non-saline environments (Peyton et al., 2001). In this costing, use of a low salinity bacterial community has been assumed. If operation was switched to highly saline conditions (100gNaCl.L⁻¹), flow in the MBR brine recycle loop would decrease from 231 to 97.5 m³.d⁻¹ (blend flow 9230 m³.d⁻¹) reducing capital and operating costs (IEX and brine MBR combined) by £4.54.m⁻³.d⁻¹ (~7%) and £0.015.m⁻³ (~22%) treated respectively.

Table A.3 Sensitivity analysis. Basis: total flow 30 MLD, influent NO₃⁻ 14.67mg NO₃⁻-N.L⁻¹.

Parameter	+/- (%)	MBR Blend		IEX Blend		IEX & MBR Brine	
		Cap ^a	Op. (£.m ⁻³)	Cap ^a	Op. (£.m ⁻³)	Cap ^a	Op. (£.m ⁻³)
Pre-analysis		198.36	0.087	58.97	0.144	64.06	0.067
SA ^b	20	4.24	0.005	N/a	N/a	1.15	0.0012
Resin ^d	20	N/a	N/a	3.32	0.0013	1.43	0.0004
Salt ^d	10	N/a	N/a	N/a	0.0014	N/a	0.0001
Brine ^d	10	N/a	N/a	N/a	0.0227	N/a	0.00247
Sludge ^d	10	N/a	0.002	N/a	N/a	N/a	0.00047
Ethanol ^d	10	N/a	0.002	N/a	N/a	N/a	0.00188
Membrane	10	16.44	0.003	N/a	N/a	0.64	0.00014
Flux ^e	10	19.63	0.004	N/a	N/a	0.87	0.00015
Resin Life	20	N/a	N/a	N/a	0.002	N/a	0.00069
Mem. Life	20	N/a	0.012	N/a	N/a	N/a	0.00046
SAD _m	50	0.4	0.0005	N/a	N/a	0.3125	0.00005

^a(£.m⁻³.d⁻¹). ^bSpecific activity. ^cCapacity. ^dConsumption/ disposal costs. ^eVariation (L.m⁻².h⁻¹).

^fBased on lifetime projection. N/a – Not applicable.

A.3.2 Operating and Maintenance

Nitrate selective resins have reduced waste brine generation by limiting sulphate and bicarbonate adsorption and reducing the chloride/ nitrate ($\text{Cl}^-/\text{NO}_3^-$) equivalency ratio required for regeneration (Clifford and Liu, 1993a). However, costs associated with tankering or alternative methods of disposal (literature range £4-13.m⁻³ brine disposal) remain cost intensive (Figure 6). Consequently both the replacement MBR and IEX with brine recycle MBR have significantly lower O&M cost (Figure 5). Salt replenishment and brine disposal are still required when operating the brine recycle MBR due to concentration amendment (NaCl) post bio-treatment, water losses over time and to avoid anionic (sulphate and bicarbonate) accumulation. A net loss of 7.5% brine regenerant volume was assumed based on a study by Clifford and Liu (1993a) which corresponds to a reduction in salt mass of ~93%. Although salt requirements are lower for the two alternative processes, chemical costs remain higher than for IEX primarily due to electron donor consumption (ethanol), owing to either process scale (throughput of product water relative to total flow (MBR Blend)) or influent strength (600-1400 mgNO₃⁻-N.L⁻¹ (MBR Brine)). However, both processes show similarly low to moderate operating cost sensitivity to ethanol bulk purchase price (Jonsson, 2004) variation.

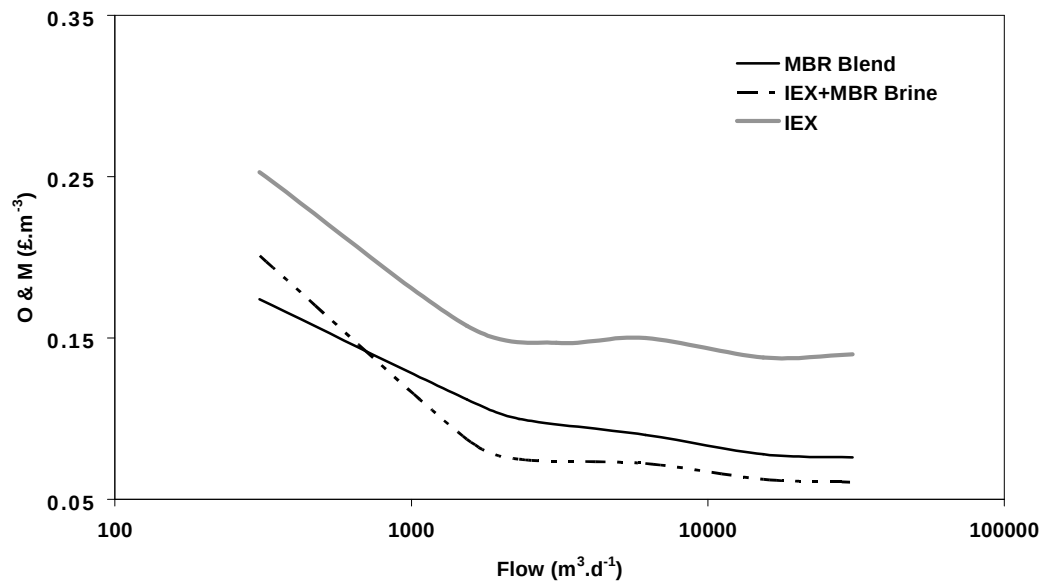


Figure A.5 *O&M Costs.*

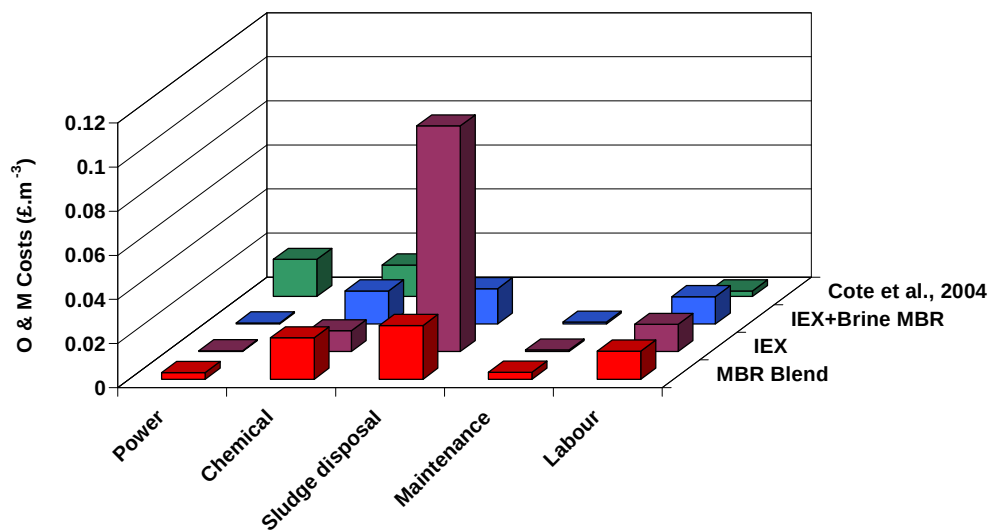


Figure A.6 *O&M Cost breakdown.*

Côté et al. (1997) reported low specific energy requirements for immersed (0.3 kWh.m⁻³) compared to externally configured MBR (1-4 kWh.m⁻³) (Cornel and Kraus, 2006). Due to the extended gassing intermittency (30 seconds/ 30minutes) adopted in this investigation, specific

energy requirements associated with near constant gassing (0.29 kWh.m^{-3} , $\text{SAD}_m 0.77 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$) were reduced to 0.025 kWh.m^{-3} ($\text{SAD}_m 0.01 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$) through experimental optimisation for the MBR blended process.

Replacement costs are dominated by the two principal process components, IEX resin and membrane material. Due to the scale of the replacement MBR, cost, flux and most notably life expectancy (Membrane 8 years; Resin 7 years), impact heavily upon O&M cost. Membrane replacement costs constituted 33% of the total O&M (Quite high due to the low specific energy demand), 93% of which is directly attributable to membrane replacement. In comparison, replacement costs constitute only 4.8% of the total O&M for IEX coupled with brine MBR even when operating with low salinity (30 gNaCl.L^{-1}) regenerant (hence higher brine MBR flows). Côté et al. (2004) assumed low labour costs in their MBR cost analysis on the basis of complete automation however, in this current study, low level automation has been assumed and labour 'contact time' has been scaled in accordance with plant scale (Adham, 2004) thus labour cost is equal when comparing processes at set flows (Figure 6).

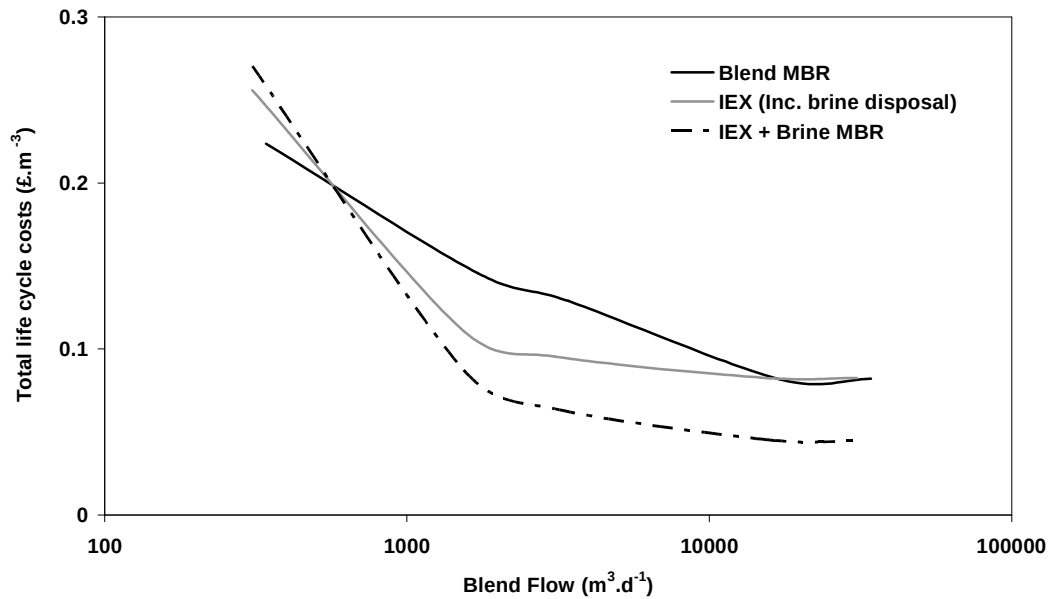


Figure A.7 Comparison of total life cycle costs for IEX, replacing IEX with MBR and combining MBR to treat brine. Project period 20 years. Interest rate 8%.

A.3.3 Total life cycle costs (TLCC)

Total costs were assessed based on a 20 year life expectancy and 8% combined interest ($PV=9.818$) and inflation rate (Figure 7.). Although the replacement MBR O&M costs were significantly below IEX with brine disposal, the saving was insufficient to off-set the significant capital cost. As such the replacement MBR was only cost competitive on total life cycle costs at flow rates $<700 \text{ m}^3.\text{d}^{-1}$, equating to $\sim£0.032.\text{m}^{-3}$ below IEX with brine disposal ($TLCC \text{ } £0.26\text{-}0.082.\text{m}^{-3}$). Therefore if membrane cost continues to fall for small-scale applications, the process could be competitive at low flow rates. For blending flow rates $>700 \text{ m}^3.\text{d}^{-1}$, $TLCC$ for IEX with brine recycle MBR ranged from $£0.087$ to $£0.044.\text{m}^{-3}$ (Blend flow, $1500\text{-}30000 \text{ m}^3.\text{d}^{-1}$) dependent upon scale which constitutes a saving of $£0.038\text{-}0.173.\text{m}^{-3}$ compared to IEX with brine disposal. Total life cycle costs could be further reduced by $\leq 17\%$ by optimising brine regeneration for high salinity processing.

A.4 CONCLUSIONS

MBR designed for IEX replacement exerts a very low specific energy demand compared to conventional MBR designs and a low specific O&M relative to conventional IEX however, membrane cost renders the process uncompetitive versus IEX with brine disposal at flows $>700 \text{ m}^3 \cdot \text{d}^{-1}$. IEX with brine recycle MBR was cost competitive with total life cycle cost savings of $\text{£}0.038\text{-}0.059 \cdot \text{m}^{-3}$ over IEX with brine disposal. The process was less sensitive to membrane costs and a further total life cycle cost reduction $\leq 17\%$ is possible by operating at considerably higher salinities. To validate process viability, further research is required to assess the impact of varying saline concentrations on nitrate removal. Furthermore, although the influence of salinity shocking on fouling propensity in municipal wastewater MBR has been documented (Reid et al., 2006), fouling within a permanently high saline environment is less well understood which also needs to be addressed.

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