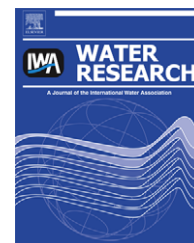


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Fate and impact of organics in an immersed membrane bioreactor applied to brine denitrification and ion exchange regeneration

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ABSTRACT

The application of membrane bioreactors (MBRs) to brine denitrification for ion exchange regeneration has been 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 respectively increased to 75 and 100 g.l⁻¹, presumed to be due to reduced growth rate and the low imposed solids retention time (10 days). Polysaccharide secretion was not induced by stressed cells following salt 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. Low molecular weight polysaccharide physically adsorbed onto the nitrate selective anion exchange resin during regeneration reducing exchange capacity by c.6.5% when operating up to complete exhaustion. However, based on a breakthrough threshold of 10 mgNO₃⁻.N.l⁻¹ the exchange capacity was comparative to that determined when using freshly produced brine for regeneration. It was concluded that a denitrification MBR was an appropriate technology for IEX spent brine recovery and reuse.

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1. Introduction

Anion-exchange (aIEX) is the most frequently adopted technology for nitrate (NO₃⁻) removal during potable water treatment due to its low cost and operational simplicity. A strong salt (NaCl) solution is used to regenerate the resin resulting in the production of concentrated waste brine containing the target anion, chloride and other oxyanions. This waste stream can comprise 0.8–2.4% of treated product flow (McAdam and Judd, 2008) and its disposal (usually by tankering) constitutes a significant proportion of the process cost. Operation of aIEX in combination with biological nitrate reduction of the waste brine for regenerant recovery presents a more sustainable

alternative by reducing the waste volume, salt (NaCl) consumption and treated product losses.

Studies adapting non-halophilic microbial communities from standard activated sludge processes for this application have reported inhibition of denitrification and, in some cases, plasmolysis to be promoted by the elevated salt concentrations (>30gNaCl.l⁻¹). More recently, halophilic monocultures *Halomonas denitrificans* (Cyplik et al., 2007) and *Halomonas campisalis* (Peyton et al., 2001) have been successfully adapted at laboratory scale 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.

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Other restrictions to this application include the accumulation of inorganic constituents (e.g. sulphate) due to recirculation, and the impact of organics and microbial carryover from the bioreactor on downstream resin regeneration. In brine re-use trials, elevated sulphate concentrations were not reported to impact upon either resin or biological performance when nitrate selective resins have been used (Clifford and Liu, 1993). However, Bae et al. (2002) reported that microbial associated particulates and organics present in the regenerant fouled anion exchange resins, thus the integration of both sand filtration and GAC were required downstream of the denitrification reactor 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 treatment and reuse in the regeneration of ion exchange resins, specifically this study will address: the fate of organics during permeate brine recirculation (to simulate re-use); the impact of organics on resin capacity; the influence of salt variation on halophilic treatment performance; and the impact of perturbation on fouling propensity.

2. Material and methods

2.1. Experimental rig

To establish a salt tolerant bacterial community, a seed culture was harvested from the anaerobic layer of a coastal sediment at low tide. Following acclimation in batch conditions (50 gNaCl.l^{-1} , $500 \text{ mgNO}_3^- \cdot \text{N.l}^{-1}$), a 75 l reactor (Fig. 1) was

seeded at a v/v ratio of 15:1. The influent nitrate concentration was set at $500 \text{ mg NO}_3^- \cdot \text{N.l}^{-1}$. During substrate optimisation, ethanol was supplied as the exogenous substrate and dosed at a C:N ratio of between 0.77:1 and 8.5:1 (g.g^{-1}); under normal conditions, a C:N of 0.85:1 was used. Reactor temperature was maintained at $c.20^\circ\text{C}$ using a thermostatically controlled heating jacket. An impeller mixer was used to ensure complete biomass distribution with the impeller blade sited below the membrane module. The hydraulic and solids residence times (HRT and SRT respectively) were 17.5 h and 10 days respectively. The process was allowed 3 SRTs to acclimatise prior to testing. During recirculation experiments, MBR permeate was collected in a holding tank (T_2), supplemented with NO_3^- and pumped back to the feed tank (T_1). During salt upshocking/down shocking experiments, the NaCl concentrate dosed into T_1 was changed to meet the required concentration providing an incremental spike; fluid residence time in T_1 was approximately 20 h.

A 0.93 m^2 out-to-in immersed PVDF hollow-fibre membrane with $0.04 \mu\text{m}$ nominal pore size was used. Permeate was withdrawn under suction from the membrane using a piston pump (FMI Inc., Syosset, US). To maintain anoxic conditions, nitrogen-enriched air ($>99\%$) was used to scour the membrane. Gas was introduced via a solenoid valve (Zoedale Plc, Bedford, UK) and controlled with a programmable digital relay (Kübler GmbH, Ludwigshafen, Germany); flow rate was controlled with a $0\text{--}50 \text{ l min}^{-1}$ needle valve (RS Ltd., Corby, UK). Pressure was monitored using a -0.5 to 0.5 barg calibrated pressure transducer (Gem Sensors, Basingstoke, UK) and data recorded using a 16-bit $0\text{--}2.5 \text{ V}$ data conversion unit (Pico technology, St. Neots, UK).

2.2. Anion exchange resin

A commercially available nitrate selective macroporous styrene based anion exchange resin (Purolite A520E,

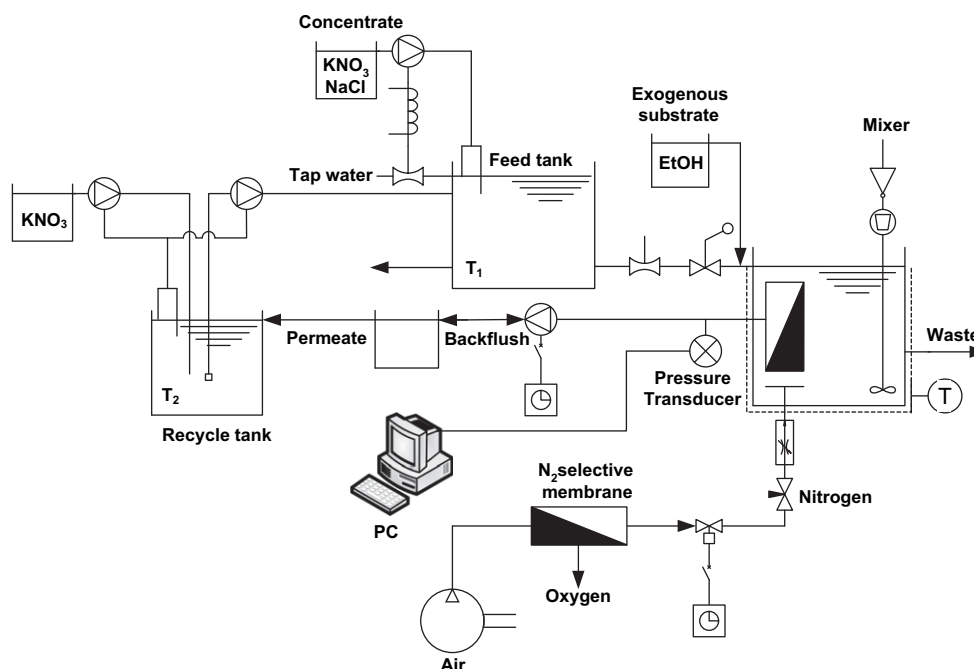


Fig. 1 – Experimental set-up.

Llantrisant, UK) was loaded into a 50 mm diameter \times 1 m glass chromatography column and retained using 25 μm -rated frits at either end; the bed comprised 120 g of resin. After initial rinsing, the A520E resin size ranged from 0.28 to 1.26 mm (d_{50} 0.61 mm). Prior to use, DI water was pumped through the resin bed at 20 bed volumes (Bv). h^{-1} for 30 min, followed by a 30 min 50gNaCl. l^{-1} flush (to ensure saturation) at 5 Bv. h^{-1} and a subsequent DI rinse for 60 min at 5 Bv. h^{-1} . The exhaustion flow rate was set to 20 Bv. h^{-1} and the IEX feed contained 30 $\text{mgSO}_4^{2-}.\text{l}^{-1}$, 115 $\text{mgCl}^{-}.\text{l}^{-1}$, 150 $\text{mgCaCO}_3.\text{l}^{-1}$ and 22.6 mg.l^{-1} $\text{NO}_3^{-}\text{-N}$. Regeneration comprised a 60 min 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 min respectively.

2.3. Chemical analysis

2.3.1. General analysis

Mixed liquor suspended solids (MLSS) and bicarbonate were determined by standard methods. Oxyanion (NO_3^{-} , NO_2^{-}) and chloride concentration was measured using proprietary cell tests (Merck Spectroquant) with spectrophotometric detection. Dissolved organic carbon (DOC) was measured using a Shimadzu TOC-5000A analyser. Ethanol concentration was determined using a commercially available enzymatic method (Boehringer-Mannheim, Roche). Soluble microbial products (SMP) were extracted according to the method described in Judd (2006) and polysaccharide and protein concentration quantified using the phenol-sulphuric acid method (Zhang et al., 1999) and modified Lowry method (Frølund et al., 1995) respectively. Absorbance for polysaccharide and protein determinations was measured using a Jenway 6505 UV/Vis spectrophotometer at $\text{UV}_{480\text{nm}}$ and $\text{UV}_{750\text{nm}}$ respectively with D-glucose and bovine serum albumin (BSA) as standards. Particle size distribution was measured with an integrated laser diffractor (Malvern Mastersizer 2000).

2.3.2. Molecular weight fractionation

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 300 kDa. Sample supernatant was pre-filtered using a 1.2 μm filter and the subsequent sample split between two 300 kDa membranes to limit concentration polarisation. Concentration polarisation was limited by application of an integrated bar stirrer operated at a constant 100 rpm; the adopted filtrate/retentate ratio was 0.4.

2.3.3. Phospholipid fatty acid analysis

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).

3. Results

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 (Fig. 2). Once a C:N ratio of 0.89 had been exceeded, ethanol was detected in the permeate above the limit of detection ($>0.5 \text{ mg.l}^{-1}$). Although the existence of an optimum C:N has been reported previously (McAdam et al., 2007), research studies typically observe low $\text{NO}_2^{-}\text{-N}$ and $\text{NO}_3^{-}\text{-N}$ effluent concentrations as the optimum C:N is exceeded due to the surplus of available carbon (Chiu and Chung, 2003; McAdam et al., 2007). In this study, on increasing C:N >0.98 inhibition was observed resulting in 71–97% of the available NO_3^{-} being converted to NO_2^{-} for C:N values up to 8.5. Yoshie et al. (2006) also reported nitrite accumulation in concentrated brines indicating reductase activity may be very different at high salinity.

Protein and polysaccharide 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 polysaccharides, recording 49% and 80% respectively, for operation of an anaerobic immersed hollow fibre (0.1 μm) MBR. In this study, SMP exhibited a principal protein peak of 55.1% between $<1.2 \mu\text{m}$ and 300 kDa and a principal polysaccharide peak of 48.3% below 10 kDa (Fig. 3). Organics between 1.2 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 c.50 to 100 kDa.

3.2. Impact of organics accumulation during recirculation

After 7 days recirculation, the SMP DOC had increased from an initial concentration of c.170 mgDOC.l^{-1} (c.34 mgDOC.gMLSS^{-1}) up to a maximum concentration of 557 mgDOC.l^{-1} (Fig. 4). At steady state, DOC transmission was recorded between 54% and 80% and was attributed to accumulation of low molecular weight (MW) organics (below the membrane MWCO).

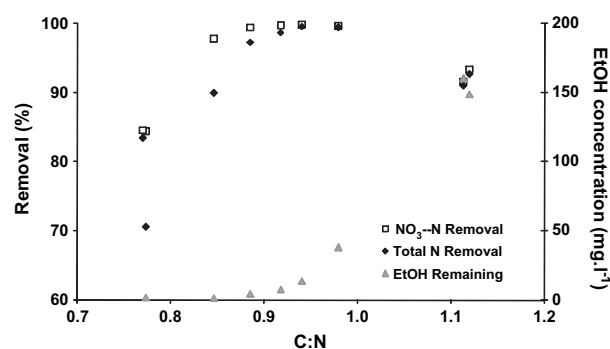


Fig. 2 – Optimising C:N ratio during steady state operation. Influent: 500 $\text{mgNO}_3^{-}\text{-N.l}^{-1}$; 50 gNaCl.l^{-1} .

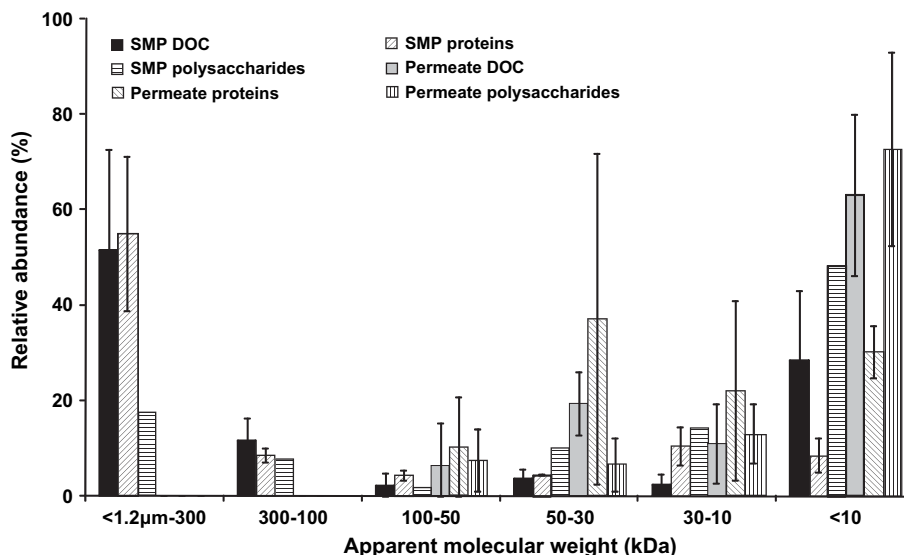


Fig. 3 – Molecular weight SMP and permeate fractionation for protein and polysaccharide at steady state.

Critical flux analysis (J_c) was conducted using the flux step method before recirculation and after reaching steady state (Fig. 5). In both cases, J_c was between 12 and 15 l.m⁻².h⁻¹. Interestingly, similar exponential dP/dt trends were obtained for both sets of conditions, evidenced by similar gradients ($(dP/dt)/J$) of between 0.23 and 0.27, however, dP/dt measured post-recirculation exhibited lower overall fouling potential. This appears counter-intuitive, based on the presence of accumulated organics and challenges previous reports which link fouling propensity to elevated concentrations of biopolymers in the bulk phase (Judd, 2006; Reid et al., 2006).

3.3. IEX Resin capacity

To allow comparison with previous aIEX resin studies (Clifford and Liu, 1993; Bae et al., 2002), NO₃⁻-N breakthrough curves were determined using a 10 mgN.l⁻¹ threshold effluent concentration (US regulatory limit). Breakthrough curves (1 to 6) were run to complete exhaustion initially using freshly

produced regenerant (Brine_{fp}, 50gNaCl.l⁻¹, Fig. 6(a)). The threshold was reached at c.400 bed volumes (BVs) in the second run which corresponded to a resin capacity of 0.61 eq.l⁻¹ or 88% of throughput obtained with the virgin resin during the first run. Subsequent runs 3–6 indicated a near identical trend demonstrating reproducible regeneration efficiency under these conditions. A capacity of c.0.46 eq.l⁻¹ has been observed previously by Bae et al. (2002) using the same commercially available resin (A520E); the lower capacity may be explained by the authors' application of a lower strength regenerant (30gNaCl.l⁻¹).

Breakthrough curves (1–6) were subsequently generated with fresh resin using biologically treated brine (Brine_{bt}, 50gNaCl.l⁻¹) as the regenerant (Fig. 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. Under these conditions, 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

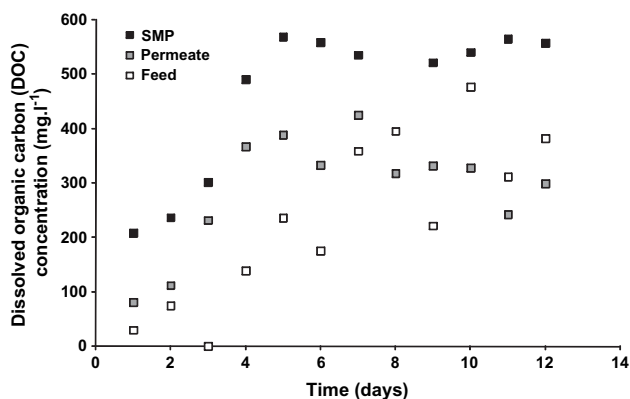


Fig. 4 – Impact of permeate recirculation to the main feed tank on dissolved organic carbon concentration (DOC) in the feed, permeate and SMP.

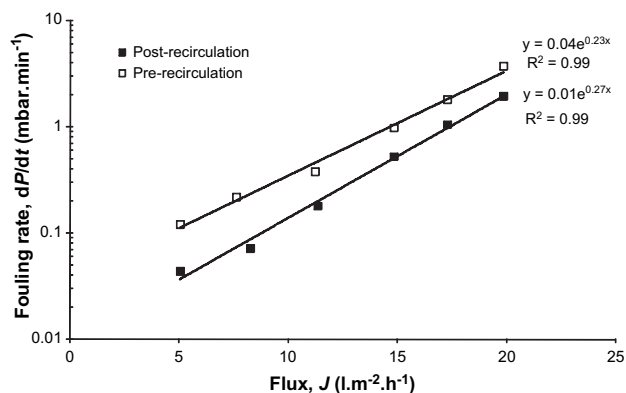


Fig. 5 – Critical flux analysis (J_c) before, during and after permeate recirculation to the main feed tank. Specific gas demand per unit membrane area (SGD_m), 0.39 m³.m⁻².h⁻¹.

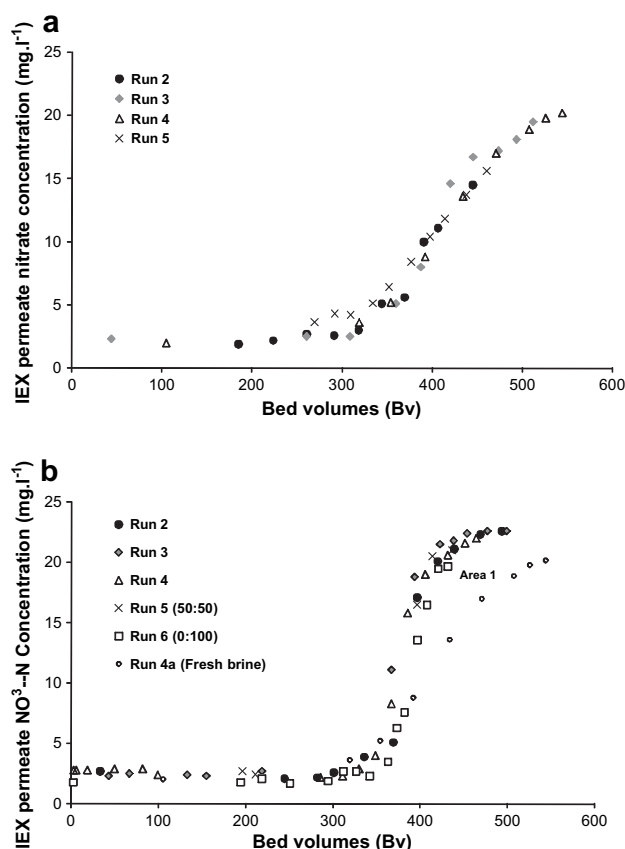


Fig. 6 – Breakthrough curves observed from runs 2–6 using: (a) freshly produced brine; and (b) biologically treated brine. Influent concentration: $\text{NO}_3\text{-N}$ 22.6 mg.l^{-1} ; SO_4^{2-} 30 mg.l^{-1} ; Cl^- 115 mg.l^{-1} and HCO_3^- 150 mg.l^{-1} .

with Run 4 (a) using brine_{fp} (Fig. 6(b)) demonstrated a loss in capacity (Area 1) indicating the extent of interference created by the biologically derived organics. Integration of the area between the brine_{fp} and brine_{bt} exhaustion curves recorded a capacity loss of 59 meq.l^{-1} or c.6.5% of the estimated exhaustive resin capacity. Bae et al. (2002) observed significant capacity losses when using permeate from an upflow sludge blanket reactor (USBR) for regeneration unless subsequent treatment steps were incorporated. However, in this study subsequent regenerations using brine_{bt} displayed a similar reproducibility indicating that the resin had reached a maximum organic capacity at the end of the first regeneration cycle.

The uptake of brine_{bt} organics by the resin was quantified using a virgin salt saturated resin (Fig. 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% simultaneously 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 in the interval between 4 and 7 BVs was observed. At 7 BVs, polysaccharide and DOC transmission reached 100%, indicating saturation of the resin with polysaccharide. Total adsorbed DOC on the

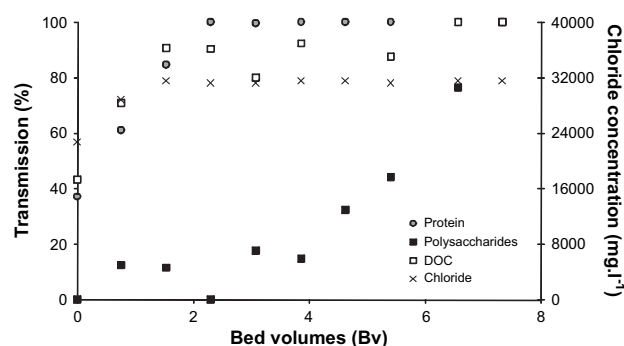


Fig. 7 – Adsorption of regenerant organics (protein, polysaccharide and DOC) by anion exchange resin.

120 g resin bed was estimated at 26.4 mg (0.22 mgDOC.gResin). During exhaustion/regeneration cycles (Fig. 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 similarity of the subsequent exhaustion curves suggested low polysaccharide exchange potential (i.e. reversibility).

3.4. Salt shocking

To reflect the significant salt variations occurring in brine regenerant waste, the regenerant was initially upshocked to 75 gNaCl.l^{-1} which was subsequently further increased to 100 gNaCl.l^{-1} after 7 days. Following the initial upshock (75 gNaCl.l^{-1}), nitrate removal decreased from 99.7 to 60.1% (Table 1) demonstrating a decrease in the specific biomass denitrification capacity. Protein release was also recorded with an increase in bulk phase concentration from c.30 to c.50 mg.l^{-1} and from c.15 to c.30 mg.l^{-1} following salt upshock to 75 and 100 gNaCl.l^{-1} respectively (Fig. 8). A transition in floc structure also occurred; at steady state (50 gNaCl.l^{-1}), a floc size distribution ranging 60–800 μm was measured, however, following upshocking to 75 gNaCl.l^{-1} , a bi-modal distribution was recorded with the dominant peak ranging 0.2–5 μm , indicating floc breakage into primary particles (Wilén et al., 2003). After 7 days at 100 gNaCl.l^{-1} , the system was downshocked to 50 gNaCl.l^{-1} ; sampling 24 h after downshocking demonstrated near complete denitrification recovery to 98.4%.

Table 1 – Treatment performance during salt spiking.

NaCl (g.l^{-1})	Recovery Time	C:N	$\text{NO}_3\text{-N}$	Ethanol ^a (mg.l^{-1})
			Reml. (%)	
50	N/a	0.92	99.7	4.1
75	24 h	0.87	60.1	75.1
	7 d	0.91	58.6	113
100	24 h	0.97	73.6	176.7
	7 d	0.99	73.3	209
50 ^b	24 h	0.94	98.4	10.7

a Permeate concentration.

b Salt downshock.

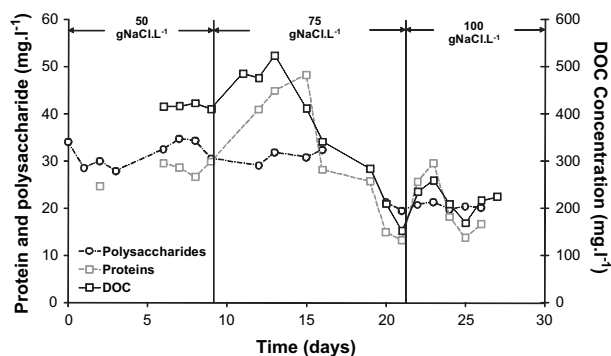


Fig. 8 – Impact of salt upshock on biologically derived organics measured in the SMP.

Although the volume of particulate and colloidal material had apparently increased, critical flux analysis conducted before and after each salt increment (Fig. 9) indicated that fouling propensity remained stable as demonstrated by the similar dP/dt trends obtained. In addition, J_c was consistently recorded at $c.12 \text{ l.m}^{-2}.\text{h}^{-1}$ and is comparable to that recorded during steady-state recirculation. This contradicts a previous non-halophilic MBR study where upon exposure to a 5 g.l^{-1} chloride residual ($0.83\% \text{ NaCl}$) both protein and polysaccharide were released causing permeability decline (flat sheet, $0.4 \mu\text{m}$) which was correlated to the elevated SMP polysaccharide concentration (Reid et al., 2006); the absence of elevated concentrations of secreted polysaccharide in this current study may in part explain this disparity.

Twenty PLFA fatty acid methyl esters (FAMES), identified by MS, principally comprised normal saturates and terminally branched saturates. Trans-monoenoic fatty acid concentrations were below the limit of detection. Dominant FAMES were C16:0, C16:1, C17:0, C18, C18:1 ω 9c and C19:0cy at 50, 75 and 100 gNaCl.l^{-1} and accounted for $c.95\%$ of PLFAs detected (Table 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

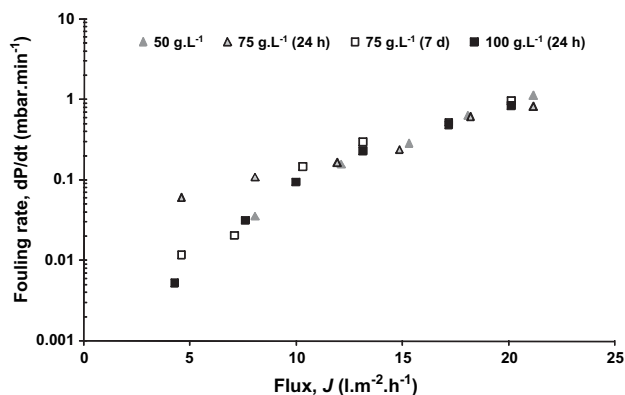


Fig. 9 – Critical flux analysis (J_c) before and after each increase in salt concentration. Specific gas demand per unit membrane area (SGD_m), $0.39 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$.

Table 2 – Major constituents of PLFA analysis (%).

	NaCl (g.l^{-1}) 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

^a Exhibit 1 – Comprises C18:0 and C18:1 ω 9c.

corresponding to salt concentration (Fig. 10). 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.

4. Discussion

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 of $c.44\%$. 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 ($c.250 \text{ kDa}$) and 93.6% low MW (5 to 250 kDa) biopolymer rejection when using a $0.2 \mu\text{m}$ flat sheet membrane in an MBR and cited

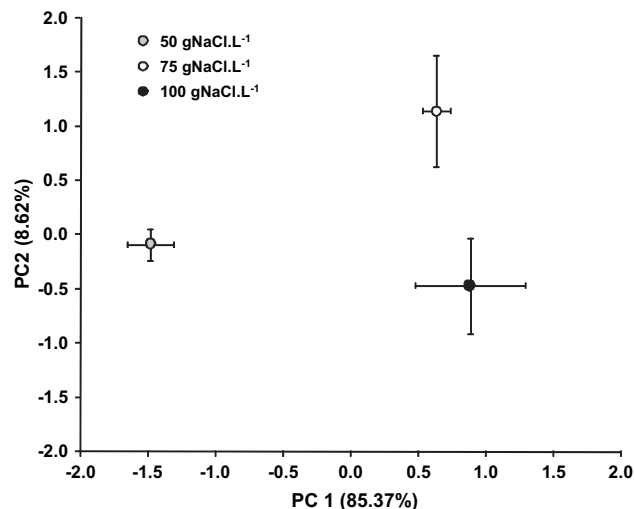


Fig. 10 – First and second principal components (PCs) derived from phospholipid fatty-acid profiles originating from biomass samples at the three salinities. Mean and standard deviation plotted. Percentage variation accounted for by PC shown in parenthesis on each axis.

polysaccharide 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 larger pore size. In this study, concentration (accumulation) 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), however, past research has typically focused on high MW polysaccharides (100 to 1600 kDa) which possess more structural and functional complexity than those of lower MW biopolymers (48.3% below 10 kDa) as in this study; higher MW structures 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 cell lysis did not occur. 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). In addition, cell wall modification may have initiated the floc destabilisation observed upon upshocking causing indirect release of extracellular protein from the floc matrix as postulated by Reid et al. (2006). The absence of secreted polysaccharide, structure and size distribution of the organics produced by halophilic bacteria and the lower membrane pore size adopted in this investigation (0.04 μm , potentially limiting internal deposition) may explain the disparity in organics rejection and fouling compared to previous literature findings (Reid et al., 2006; Zhang et al., 2006).

4.2. Microbial community and treatment performance

PLFA profiles were dominated by a small range of fatty acids that are common amongst halophiles (Aston and Peyton, 2007; Yakimov et al., 2001). The trans/cis ratio was consistently < 0.15 at all three salt concentrations indicating that the cell membrane remained stable – a ratio above 0.25 indicating instability (Aston and Peyton, 2007) – further suggesting that plasmolysis did not occur. Transition of PLFA profiles at each salt increment indicated reordering of the membrane lipid composition for osmoregulation (Russell, 1989; Pflüger and Muller, 2004) and microbial community restructuring (Forney et al., 2001) as described previously for salt upshocking of denitrifying halophiles (Yoshie et al., 2006). The

decrease in nitrate removal from 99.7% to between 58.6% and 73.6% may therefore be due to microbial restructuring, however, lower specific bacterial growth rates have been observed at high salt concentrations. Peyton et al. (2001) established that *Halomonas campisalis* could effectively denitrify at 180 gNaCl.l^{-1} (Peyton et al., 2001), though the maximum specific growth rate for the monoculture was identified at $c.30 \text{ gNaCl.l}^{-1}$ (Aston and Peyton, 2007). In this study, upon down shocking to 50 gNaCl.l^{-1} denitrification capacity recovered to 98.4% within 24 h. This demonstrates that whilst transition in community structure occurred following salt upshocking, an effective residual halotolerant denitrifying community remained following perturbation; extension of SRT (> 10 days) may be sufficient to offset the lower growth rates observed at high salt concentrations.

4.3. Resin operation

It has been suggested that polysaccharides do not normally deposit easily onto aEX 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. Adsorption of exopolysaccharides to anionic resins is intuitive as their structure is principally polyanionic due to the number of uronic acid or ketal linked pyruvate groups contained within the long chain high MW (500–2000 kDa) structures (Sutherland, 2001). However, based on the low affinity shown for desorption of polysaccharides in this study, it appears that the dominant adsorption mechanism associated with the lower MW polysaccharides present in the brine is physical rather than exchange based. DOC uptake could not be quantified during exhaustion runs due to competition effects with the influent DOC. Therefore, based on physical data, the theoretical charge density (approximated by normalising lost resin capacity with DOC uptake, Fig. 7) was $c.3.9 \times 10^{-4} \text{ meq.gDOC}^{-1}$; this negligible result further demonstrates that adsorption was not exchange based and indicates that the adsorbed organics exhibited a charge closer to neutrality. 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.

5. Conclusions

A study of the denitrification of high salinity ion exchange brine regenerant and the impact of accumulation on process performance has demonstrated recycling for ion exchange regeneration to be viable.

1. Whilst recirculation generated high concentrations of low MW organics, their impact on membrane permeability was negligible.
2. Although salt upshock induced protein release, the permeability decline was minimal, contrary to previous studies based on non-halophilic communities.

3. Nitrate removal of c.99.7% was observed at steady-state (50 gNaCl.l⁻¹); at salt concentrations above 50 gNaCl.l⁻¹ nitrate removal decreased and the community profile was modified, though this could be countered by adoption of a higher SRT to offset the lower growth rates.
4. Adsorption of the low MW organics generated during denitrification onto the resin structure resulted in minimal loss in resin capacity, implying long-term operation using recovered brine is possible.
5. Under halophilic conditions, addition of exogenous substrate must be controlled to minimise breakthrough and to support complete denitrification (limiting the preferential formation of nitrite).
6. The efficacy of the denitrification MBR process is closely related to membrane rejection and the structural and functional attributes of the resultant organics; both the process operational determinants and the bacterial community generated may influence performance.

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