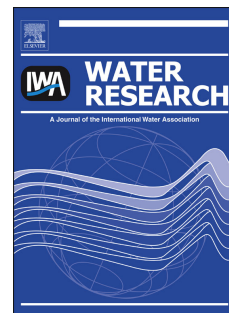


Accepted Manuscript

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

Authors: Ewan J. McAdam, Mark Pawlett, Simon J. Judd



PII: S0043-1354(09)00564-8

DOI: [10.1016/j.watres.2009.08.048](https://doi.org/10.1016/j.watres.2009.08.048)

Reference: WR 7610

To appear in: *Water Research*

Received Date: 18 March 2009

Revised Date: 17 August 2009

Accepted Date: 30 August 2009

Please cite this article as: McAdam, E.J., Pawlett, M., Judd, S.J. Fate and impact of organics in an immersed membrane bioreactor applied to brine denitrification and ion exchange regeneration, *Water Research* (2009), doi: 10.1016/j.watres.2009.08.048

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

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

Ewan J. McAdam¹, Mark Pawlett², Simon J. Judd¹

¹*Centre for Water Science, Cranfield University, Bedfordshire, MK43 0AL*

²*Natural Resources Department, Cranfield University, Bedfordshire, MK43 0AL*

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.

Keywords: *Ion-exchange; brine; biological denitrification; salt; nitrate*

1. INTRODUCTION

Anion-exchange (aIEX) is the most frequently adopted technology for nitrate (NO_3^-) 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 to 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 ($>30\text{gNaCl.l}^{-1}$). 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.

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 reuse); 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 (Figure 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°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 hours 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/ downshocking 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 hours.

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., 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 0-50 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 to 2.5 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, Llantrisant, UK) was loaded into a 50mm diameter x 1m glass

chromatography column and retained using 25 μm -rated frits at either end; the bed comprised 120g 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 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. The exhaustion flow rate was set to 20 Bv.h⁻¹ and the IEX feed contained 30 mgSO₄²⁻.l⁻¹, 115 mgCl⁻.l⁻¹, 150 mgCaCO₃.l⁻¹ and 22.6 mg.l⁻¹ NO₃⁻-N. 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.

111

112 **2.3 Chemical analysis**

113 *2.3.1 General analysis*

Mixed liquor suspended solids (MLSS) and bicarbonate were determined by standard methods. Oxyanion (NO₃⁻, NO₂⁻) 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 UV_{480nm} and UV_{750nm} respectively with D-glucose and bovine serum albumin (BSA) as standards. Particle

size distribution was measured with an integrated laser diffractor (Malvern Mastersizer 2000).

128

2.3.2 *Molecular weight fractionation*

Serial fractionation was undertaken using an Amicon 8400 series stirred cell, pressurised with N₂ (1 barg), and standard UF (Millipore) membranes, size range 10, 30, 50, 100 and 300kDa. Sample supernatant was pre-filtered using a 1.2µm 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 operate at a constant 100 rpm; the adopted filtrate/ retentate ratio was 0.4.

136

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).

146

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 (Figure 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 NO_2^- -N and NO_3^- -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 maybe 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 ($0.1 \text{ }\mu\text{m}$) MBR. In this study, SMP exhibited a principal protein peak of 55.1% between $<1.2 \text{ }\mu\text{m}$ and 300 kDa and a principal polysaccharide peak of 48.3% below 10 kDa (Figure 3). Organics between $1.2 \text{ }\mu\text{m}$ 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} (Figure 4). At steady state, DOC transmission was recorded between 54%

175 and 80% and was attributed to accumulation of low molecular weight (MW) organics
176 (below the membrane MWCO).

177

178 Critical flux analysis (J_c) was conducted using the flux step method before
179 recirculation and after reaching steady state (Figure 5). In both cases, J_c was between
180 12 and 15 $\text{l.m}^{-2}.\text{h}^{-1}$. Interestingly, similar exponential dP/dt trends were obtained for
181 both sets of conditions, evidenced by similar gradients $((dP/dt)/J)$ of between 0.23 and
182 0.27, however, dP/dt measured post-recirculation exhibited lower overall fouling
183 potential. This appears counter-intuitive, based on the presence of accumulated
184 organics and challenges previous reports which link fouling propensity to elevated
185 concentrations of biopolymers in the bulk phase (Judd, 2006; Reid et al., 2006).

186

187 **3.3 IEX Resin capacity**

188 To allow comparison with previous aIEX resin studies (Clifford and Liu, 1993; Bae et
189 al., 2002), NO_3^- -N breakthrough curves were determined using a 10 mgN.l^{-1} threshold
190 effluent concentration (US regulatory limit). Breakthrough curves (1 to 6) were run to
191 complete exhaustion initially using freshly produced regenerant (Brine_{fp} , 50gNaCl.l^{-1} ,
192 Figure 6(a)). The threshold was reached at c.400 bed volumes (BVs) in the second run
193 which corresponded to a resin capacity of 0.61 eq.l^{-1} or 88% of throughput obtained
194 with the virgin resin during the first run. Subsequent runs 3 to 6 indicated a near
195 identical trend demonstrating reproducible regeneration efficiency under these
196 conditions. A capacity of c. 0.46 eq.l^{-1} has been observed previously by Bae et al.
197 (2002) using the same commercially available resin (A520E); the lower capacity may
198 be explained by the authors' application of a lower strength regenerant (30gNaCl.l^{-1}).

199

Breakthrough curves (1-6) were subsequently generated with fresh resin using biologically treated brine (Brine_{bt} , 50gNaCl.l^{-1}) as the regenerant (Figure 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 $c.287\text{ mg.l}^{-1}$. Under these conditions, breakthrough occurred at $c.390\text{ BVs}$ 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(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 (Figure 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 120g resin bed was estimated at 26.4 mg (0.22 mgDOC.gResin). During exhaustion/regeneration cycles (Figure 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 (Figure 8). A transition in floc structure also occurred; at steady state (50 gNaCl.l⁻¹), a floc size distribution ranging 60 to 800µm was measured, however, following upshocking to 75 gNaCl.l⁻¹, a bi-modal distribution was recorded with the dominant peak ranging 0.2 to 5µm, indicating floc breakage into primary particles (Wilén et al., 2003). After 7 days at 100gNaCl.l⁻¹, the system was downshocked to 50 gNaCl.l⁻¹; sampling 24 hours after downshocking demonstrated near complete denitrification recovery to 98.4%.

Although the volume of particulate and colloidal material had apparently increased, critical flux analysis conducted before and after each salt increment (Figure 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% 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 corresponding to salt concentration (Figure 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 kDa) and 93.6% low MW (5 to 250 kDa) biopolymer rejection when using a 0.2 μm flat sheet membrane in an MBR and cited 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 (Lapidou 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 hours. 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 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. 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, Figure 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.

- 373 5. Under halophilic conditions, addition of exogenous substrate must be
 374 controlled to minimise breakthrough and to support complete denitrification
 375 (limiting the preferential formation of nitrite).
- 376 6. The efficacy of the denitrification MBR process is closely related to
 377 membrane rejection and the structural and functional attributes of the resultant
 378 organics; both the process operational determinants and the bacterial
 379 community generated may influence performance.

381 **Acknowledgements**

382 The authors would like to thank the Engineering and Physical Sciences Research
 383 Council (EPSRC), Anglian Water, Severn Trent Water and Yorkshire Water for their
 384 financial support.

386 **REFERENCES**

- 387 Aston, J.E., Peyton, B.M. (2007). Response of *Halomonas campisalis* to saline stress:
 388 changes in growth kinetics, compatible solute production and membrane phospholipid
 389 fatty acid composition. *FEMS Microbiol. Lett.* 274, 196-203.
- 390 Bae, B.-U., Jung, Y.-H., Han, W.-W., Shin, H.-S. (2002). Improved brine recycling
 391 during nitrate removal using ion exchange. *Water Res.* 36, 3330-3340.
- 392 Barker, D.J., Salvi, S.M.L., Langenhoff, A.A.M., Stuckey, D.C. (2000). Soluble
 393 microbial products in ABR treating low-strength wastewater. *J. Environ. Eng.* 126,
 394 239-249.
- 395 Bligh, E. G., Dyer, W. J. (1959). A rapid method of total lipid extraction and
 396 purification. *Can. J. Biochem. Physiol.* 37, 911-917.

- 397 Chiu, Y.-C., Chung, M.-S. (2003). Determination of optimal COD/nitrate ratio for
398 biological denitrification. *International biodeterioration biodegradation*. 51, 43-49.
- 399 Clifford, D., Liu, X. (1993). Ion exchange for nitrate removal. *J. Am. Water Works*
400 *Assoc.* 85, 135-143.
- 401 Cornelissen, E.R., Moreau, N., Siegers, W.G., Abrahamse, A.J., Rietveld, L.C.,
402 Grefte, A., Dignum, M., Amy, G., Wessels, L.P. (2008). Selection of anionic
403 exchange resins for removal of natural organic matter (NOM) fractions. *Water Res.*
404 42, 413-423.
- 405 Cyplik, P., Grajek, W., Marecik, R., Króliczak, P., Dembczyński, R. (2007).
406 Application of a membrane bioreactor to denitrification of brine. *Desalination*. 207,
407 134-143.
- 408 Dowling, N. J. E., Widdel, F., White, D. C. (1986). Phospholipid ester-linked fatty
409 acid biomarkers of acetate-oxidising sulphate-reducers and other sulphide-forming
410 bacteria. *J. Gen. Microbiol.* 132, 1815-1825.
- 411 Fawehinmi, F. (2006). Anaerobic MBR treatment of a low strength municipal
412 wastewater. PhD Thesis, Cranfield University, UK.
- 413 Forney, L.J., Liu, W.-T., Guckert, J.B., Kumagai, Y., Namkung, E., Nishihara, T.,
414 Larson, R.J. (2001). Structure of microbial communities in activated sludge: Potential
415 implications for assessing the biodegradability of chemicals. *Ecotoxicol. Environ. Saf.*
416 49, 40-53.
- 417 Frank, B.P., Belfort, G. (2003). Polysaccharides and sticky membrane surfaces:
418 critical ionic effects. *J. Membr. Sci.* 212, 205-212.
- 419 Frølund, B., Griebe, T., Nielsen, P.H. (1995). Enzymatic activity in the activated-
420 sludge floc matrix. *Appl. Microbiol. Biotechnol.* 43, 755–761.

- 421 Frostegård, Å., Tunlid, A., Bååth, E. (1991). Microbial biomass measured as total
422 lipid phosphate in soils of different organic content. *J. Microbiol. Methods* 14, 151-
423 163.
- 424 Judd, S.J. (2006). *The MBR book: Principles and applications in water and*
425 *wastewater Treatment*. Elsevier Science, Amsterdam.
- 426 Kim, P.H.-S., Symons J.M. (1991). Using anion exchange resins to remove THM
427 precursors. *J. Am. Water Works Assoc.* 83, 61-68.
- 428 Lapidou, C.S., Rittmann, B.E. (2002). A unified theory for extracellular polymeric
429 substances, soluble microbial products, and active and inert biomass. *Water Res.* 36,
430 2711-2720.
- 431 McAdam, E.J., Judd, S.J., Cartmell, E., Jefferson, B. (2007). Influence of substrate on
432 fouling in anoxic immersed membrane bioreactors. *Water Res.* 41, 3859-3867.
- 433 McAdam, E.J., Judd, S.J. (2008). Biological treatment of ion-exchange brine
434 regenerant for re-use: A review. *Sep. Purif. Technol.* 62, 264-272.
- 435 Petrovic, U., Gunde-Cimerman, N., Plemenitas, A. (1999). Salt stress affects sterol
436 biosynthesis in the halophilic black yeast *Hortaea werneckii*. *FEMS Microbiol. Lett.*
437 180, 325-330.
- 438 Peyton, B.M., Mormile, M.R., Peterson, J.N. (2001). Nitrate reduction with
439 *Halomonas Campisalis*: Kinetics of denitrification at pH9 and 12.5% NaCl. *Water*
440 *Res.* 35, 4237-4242.
- 441 Pflüger, K., Müller, V. (2004). Transport of compatible solutes in extremophiles. *J.*
442 *Bioenerg. Biomembr.* 36, 17-24.
- 443 Reid, E., Liu, X., Judd, S.J. (2006). Effect of high salinity on activated sludge
444 characteristics and membrane permeability in an immersed membrane bioreactor. *J.*
445 *Membr. Sci.* 283, 164-171.

- 446 Russell, N.J. (1989). Adaptive modifications in membranes of halotolerant and
447 halophilic microorganisms. *J. Bioenerg. Biomembr.* 21, 93-113.
- 448 Sutherland, I.W. (2001). Biofilm exopolysaccharides: a strong and sticky framework.
449 *Microbiology* 147, 3-9.
- 450 Wilén, B.-M., Jin, B., Lant, P. (2003). The influence of key chemical constituents in
451 activated sludge on surface and flocculating properties. *Water Res.* 37, 2127–2139.
- 452 Yakimov, M.M., Giuliano, L., Chernikova, T.N., Gentile, G., Abraham, W.-R.,
453 Lünsdorf, H., Timmis, K.N., Golyshin, P.N. (2001). *Alcalilimnicola halodurans* gen.
454 nov., sp. nov., an alkaliphilic, moderately halophilic and extremely halotolerant
455 bacterium, isolated from sediments of soda depositing Lake Natron, East Africa Rift
456 Valley. *Int. J. Syst. Evol. Microbiol.* 51, 2133-2143.
- 457 Yoshie, S., Ogawa, T., Makino, H., Hirosawa, H., Tsuneda, S., Hirata, A. (2006).
458 Characteristics of bacteria showing high denitrification activity in saline wastewater.
459 *Lett. Applied Microbiol.* 42, 277-283.
- 460 Zhang, X., Bishop, P.L., Kinkle, B.K. (1999). Comparison of extraction methods for
461 quantifying extracellular polymers in biofilms. *Water Sci. Technol.* 39, 211–218.
- 462 Zhang, J., Chua, H.C., Zhou, J., Fane, A.G. (2006). Factors affecting the membrane
463 performance in submerged membrane bioreactors. *J. Membr. Sci.* 284, 54-66.

464

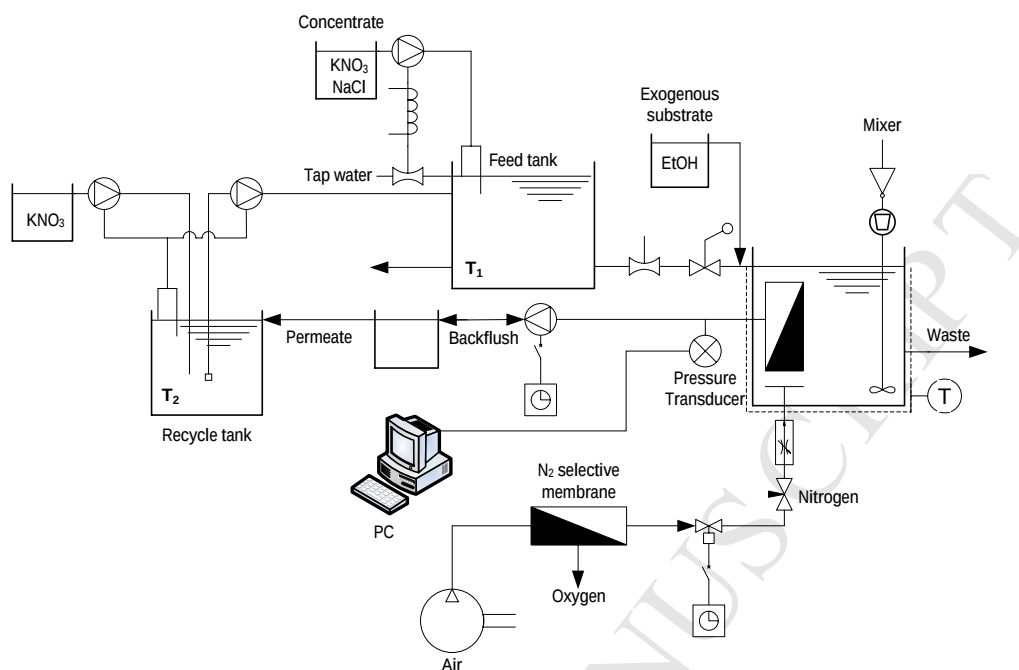


Figure 1. *Experimental set-up.*

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

Figure 3. *Molecular weight SMP and permeate fractionation for protein and polysaccharide at steady state.*

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

Figure 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), $0.39 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.*

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

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

Figure 8. *Impact of salt upshock on biologically derived organics measured in the SMP.*

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

Figure 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.

Table 1. Treatment performance during salt spiking.

NaCl (g.L ⁻¹)	Recovery Time	C:N	NO ₃ ⁻ -N	Ethanol ^a
			Reml. (%)	(mg.L ⁻¹)
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

^aPermeate concentration. ^bSalt downshock.

Table 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

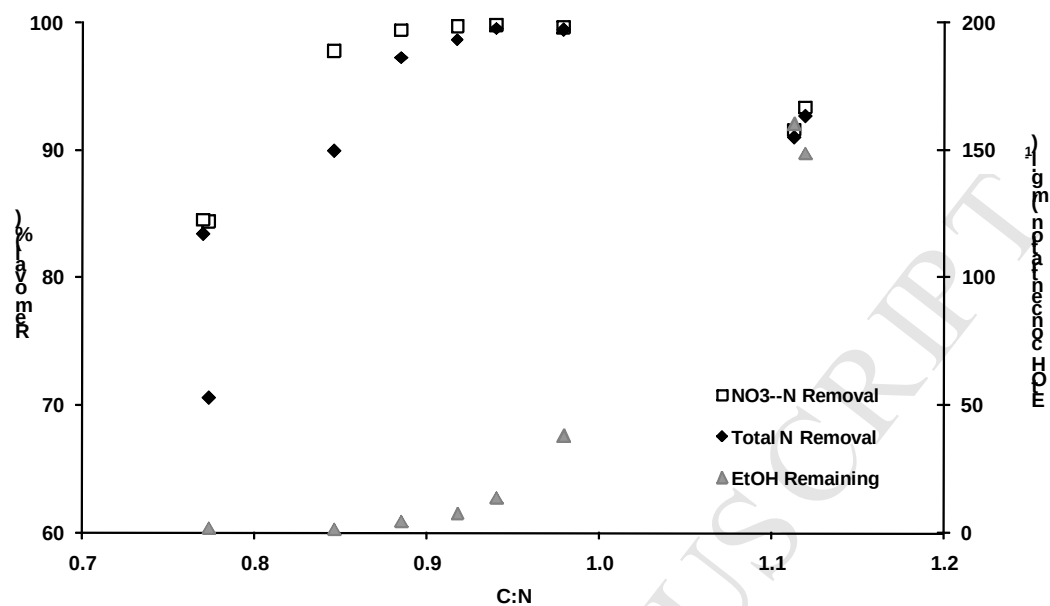


Figure 2. Optimising C:N ratio during steady state operation. Influent: 500 $\text{mgNO}_3^- \cdot \text{N} \cdot \text{L}^{-1}$, 50 $\text{gNaCl} \cdot \text{L}^{-1}$.

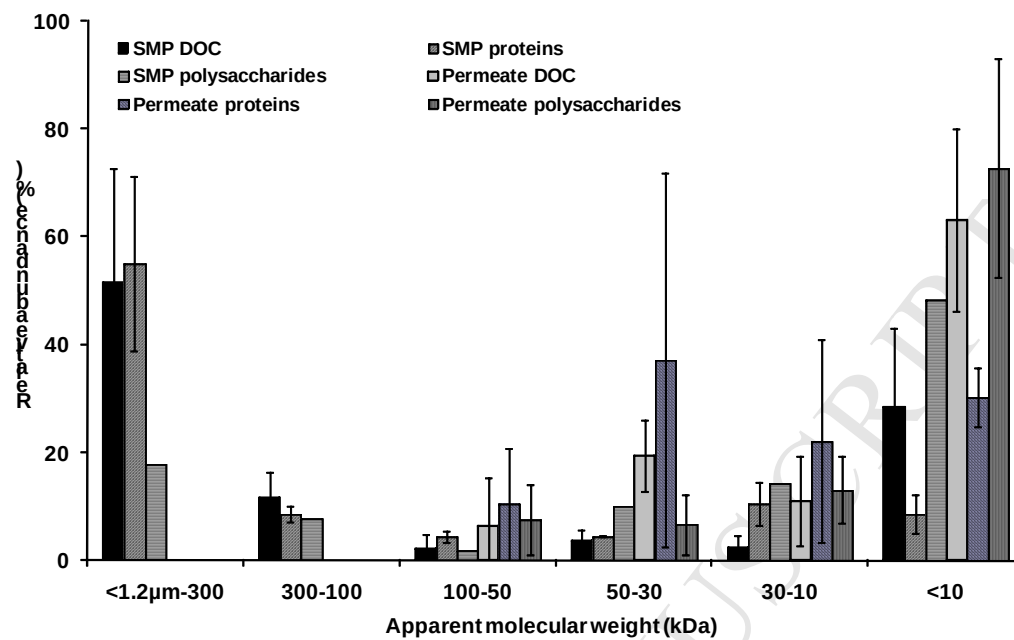


Figure 3. Serial fractionation of the SMP and permeate at steady state.

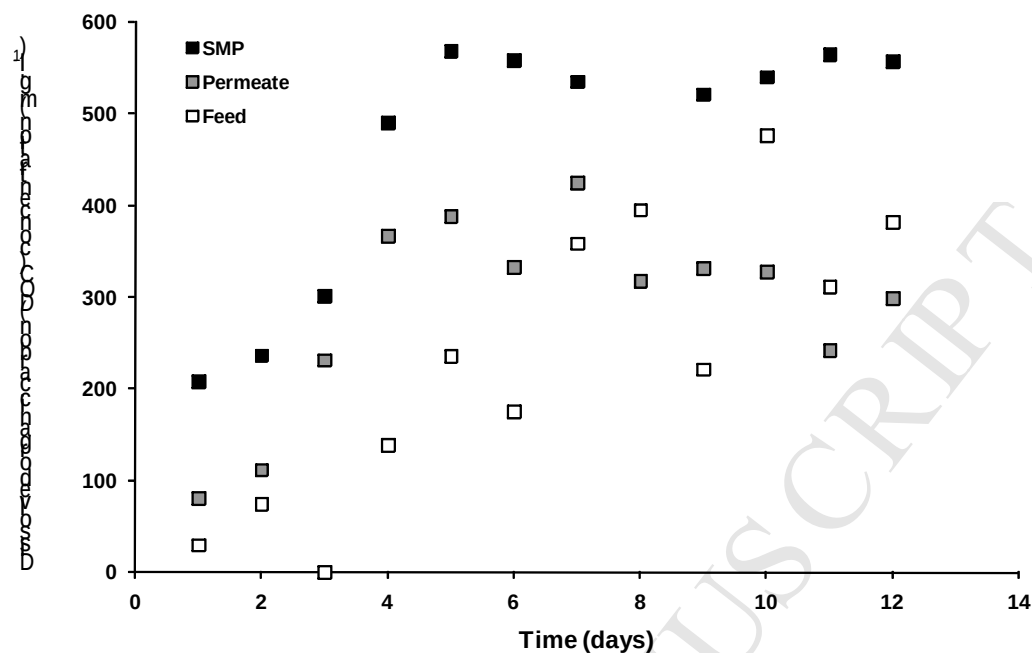


Figure 4. Impact of permeate recirculation to the main feed tank on dissolved organic carbon concentration (DOC) of the feed, permeate and SMP. salinities. Mean and standard deviation plotted. Percentage variation accounted for by PC shown in parenthesis on each axis.

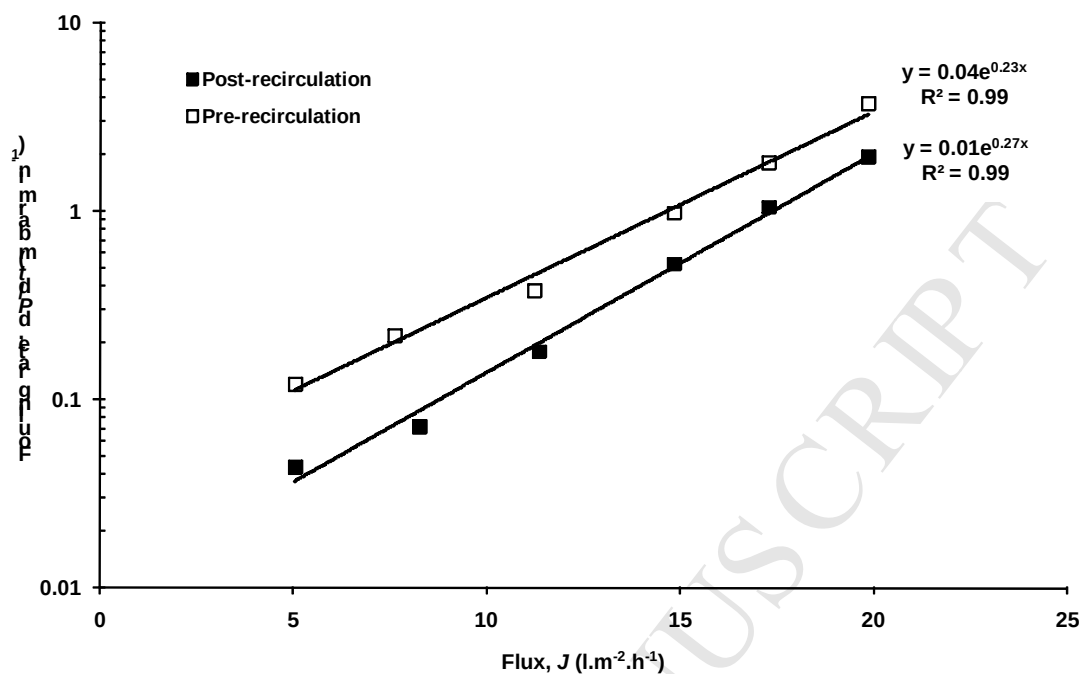
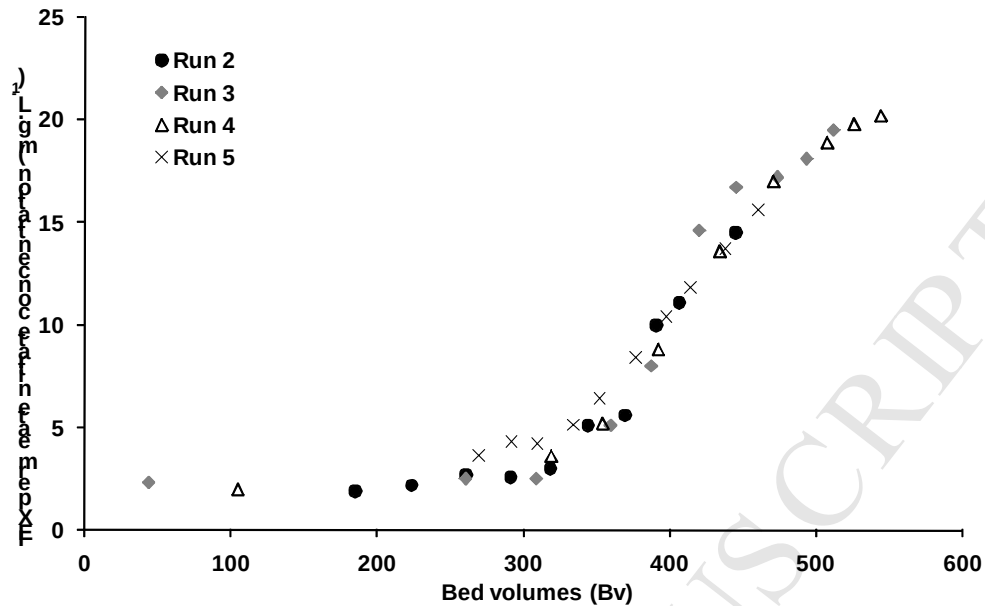
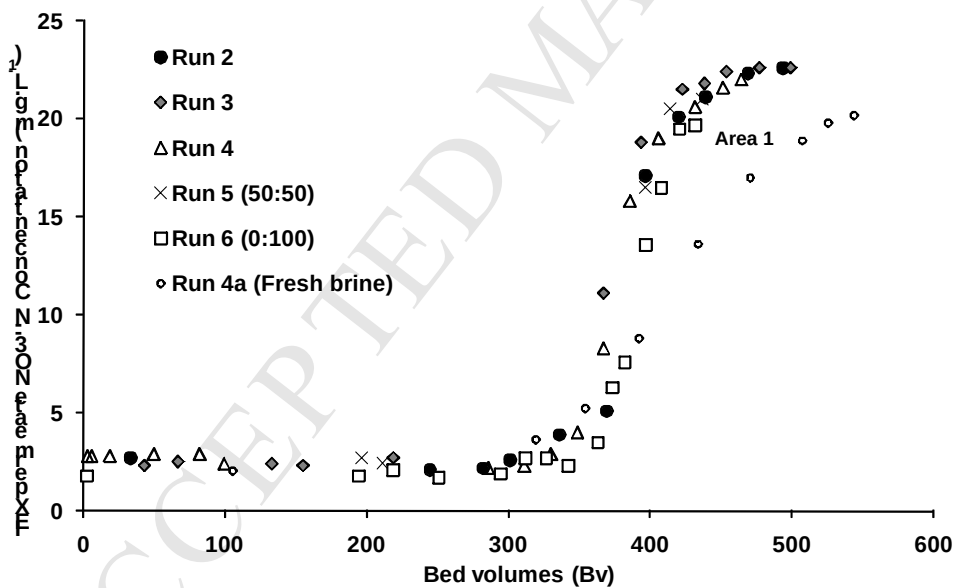


Figure 5. Critical flux analysis (J_c) before, during and after permeate recirculation to the main feed tank. SGD_m $0.39 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$.



(a)



(b)

Figure 6. Breakthrough curves observed from runs 2-6 using: (a) freshly produced brine; and (b) biologically treated brine. Influent concentration: NO_3^- -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} .

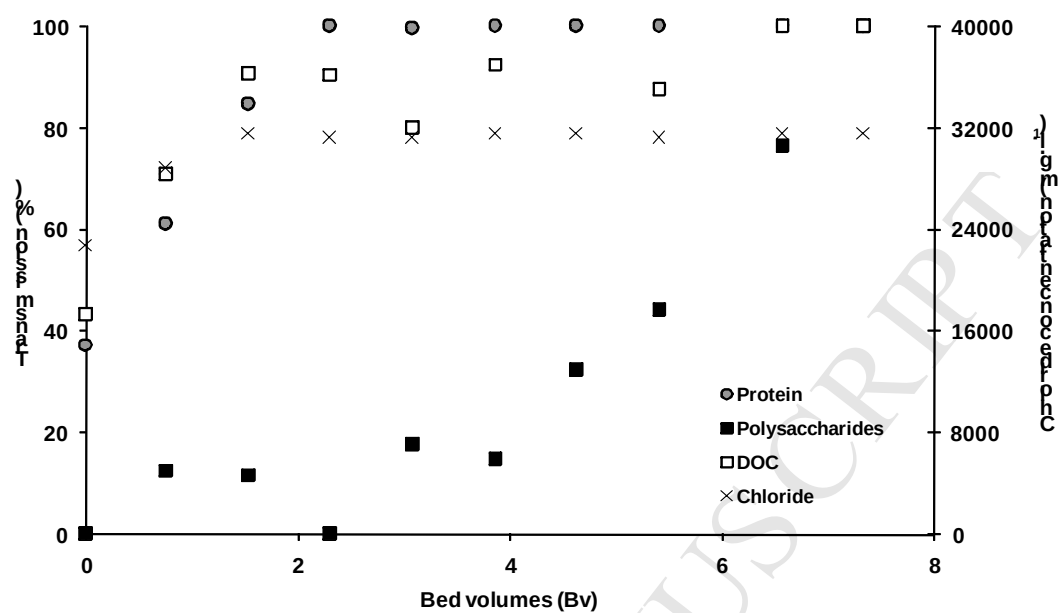


Figure 7. Adsorption of regenerant organics (protein, polysaccharide and DOC) by anion exchange resin.

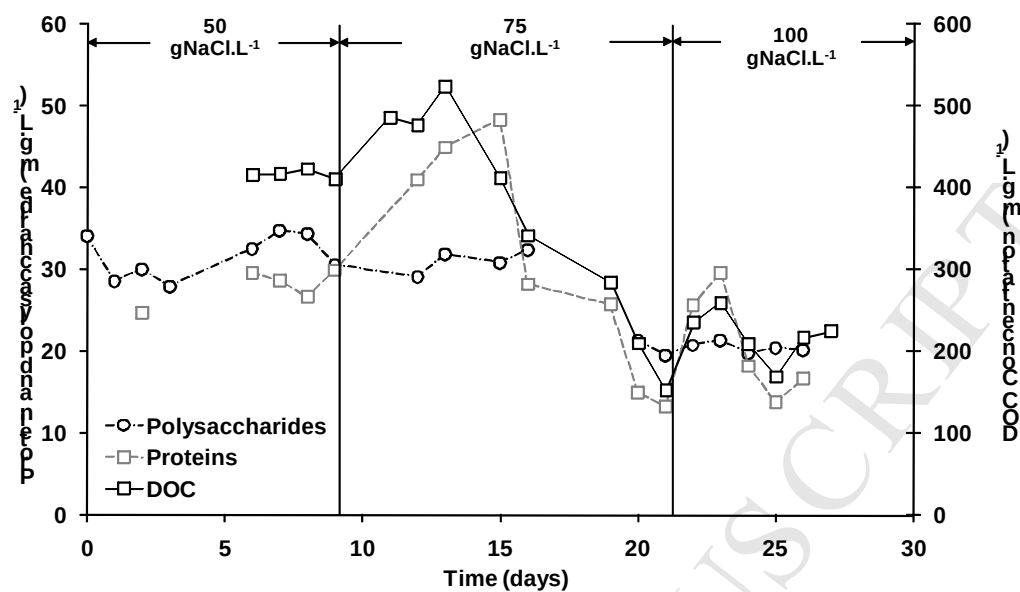


Figure 8. Impact of salt upshock on biologically derived organics measured in the SMP.

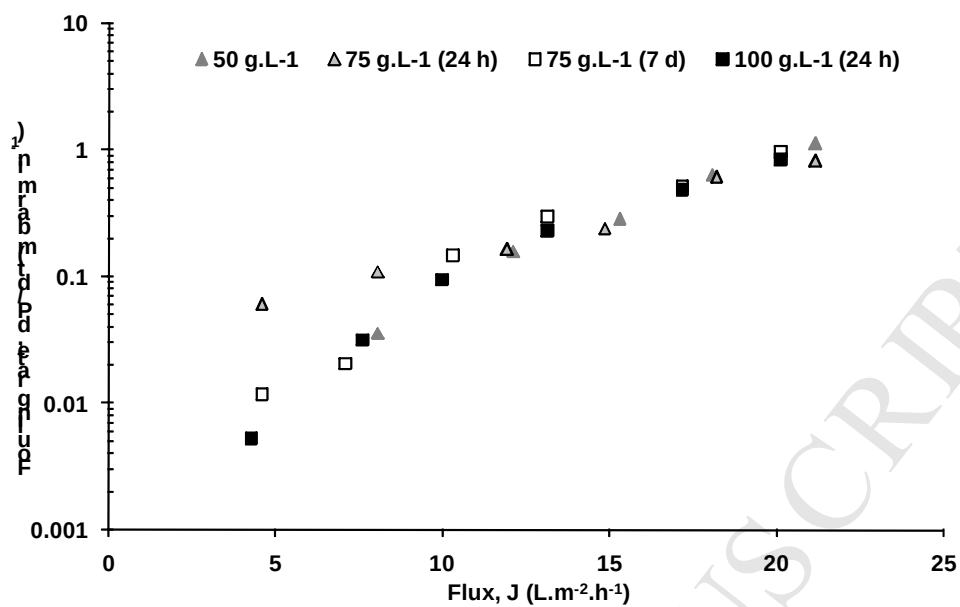


Figure 9. Critical flux analysis (J_c) before and after each increase in salt concentration. SGD_m $0.39 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

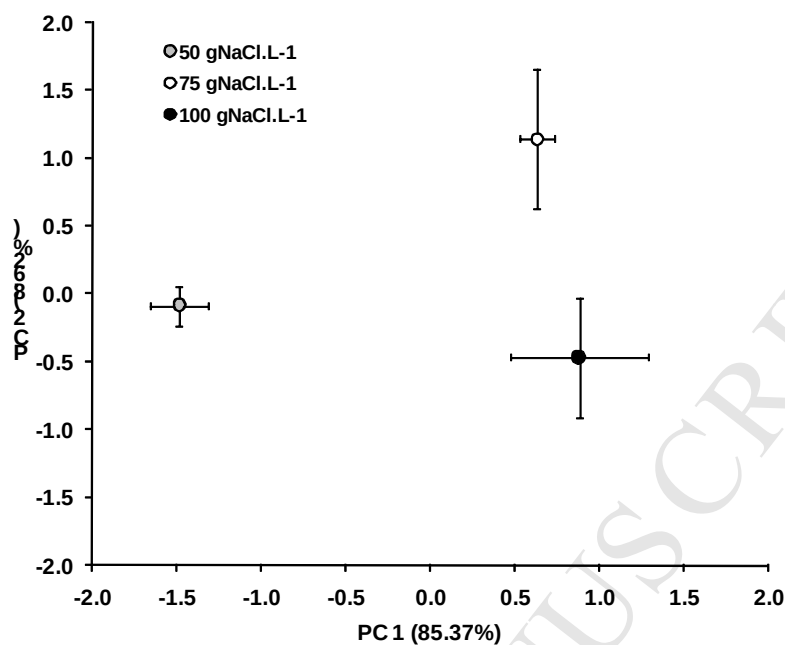


Figure 10. First and second principal components (PCs) derived from phospholipid fatty-acid profiles originating from biomass samples at the three salinities. Mean and standard deviation plotted. Percentage variation accounted for by PC shown in parenthesis on each axis.



DSPACE

<https://dspace.org/>

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

McAdam, Ewan J.; Pawlett, Mark; Judd, Simon J.

2010-01-31T00:00:00Z

Elsevier Science B.V., Amsterdam.

<http://dx.doi.org/10.1016/j.watres.2009.08.048>

Ewan J. McAdam, Mark Pawlett, Simon J. Judd, Fate and impact of organics in an immersed membrane bioreactor applied to brine denitrification and ion exchange regeneration, Water Research, Volume 44, Issue 1, January 2010, Pages 69-76