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Review

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.

Keywords: Brine; Salinity; Ion exchange; Biotreatment; Membrane

Contents

1. 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 (μg/L range) interfere with the uptake of iodine by the thyroid which inhibits both the synthesis and secretion of thyroid hormones [1]. Though specific regulations are not currently available, target perchlorate concentrations ranging 2–6 $\mu g\,L^{-1}$

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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 10–11.3 mg NO_3^-–N L^{-1} for treated potable water.

Sources of perchlorate include industries associated with rocket, missile and firework manufacture amongst others [2]. Highly concentrated nitrate wastes are produced from various industries including nuclear fuel processing, cellophane, pharmaceutical and fertiliser manufacture and metal finishing [3–5]. Both NO_3^- and ClO_4^- are readily soluble and bind poorly to soil, simplifying their transportation to ground and surface waters when discharged [3,6].

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 [7,8]. There is a reluctance to permit direct brine disposal to sewer, as it can cause problems in conventional municipal sewage systems [9]. 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 [10], 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 [9]. Ion exchange brine disposal now often entails tankering, representing a considerable process cost and carbon footprint as brine waste can constitute up to 0.8–2.4% of treated product flow [11].

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 [12]. The first combined IEX/bio-process for oxyanion removal, and nitrate specifically, was reported 9 years later [13]. The authors suggested a brine volume reduction of 95% was possible. Clifford and Liu [7] 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 [1]. Various IEX regenerants have been used including sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$) and ammonium hydroxide (NH_4OH) [1,14]. NaCl is the more commonly used regenerant. Though researchers are currently attempting to decrease NaCl concentrations required for regeneration (~0.5–1%) [15], regenerants remain highly concentrated: generally 6–12% [1] and 3–12% [7] for perchlorate and nitrate respectively and up to 15% in some instances [16]. Cang et al. [2] suggested that spent IEX regenerant from treating raw water with 50–100 μg ClO_4^- L^{-1} and 3–20 mg NO_3^-–N L^{-1} would contain 2.5–10 mg ClO_4^- L^{-1} and 150–500 mg NO_3^-–N L^{-1}. It has been recognised that certain regenerant constituents impede biological performance [11]. On this basis Lahav and Green [17] 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.

2. Biotreatment

2.1. Salinity and microbial community

The effect of salinity on traditional wastewater treatment is well known [18,19], and has been reported as impacting deleteriously on biological floc stability [20], BOD removal [21], anaerobic wastewater treatment [19,22], and generally a greater inhibition of denitrification [7,13] than nitrification [23] at very high salinities (>20 g NaCl L^{-1}). Inhibition of denitrification within this salinity range (and up to 70 g L^{-1}) has ranged from 10% [7] to 100% [3,24] depending largely on feedwater quality, microbial concentration and community structure. Inhibition of perchlorate and sulphate reduction has similarly been reported at salinities of 20–30 g NaCl L^{-1} [2,25], with substantial (>90%) reduction in perchlorate degradation rates reported when salinity was increased from 0 to 10–15% [1].

Inhibition has been variously attributed to osmotic pressure effects across the cell wall [25] as well as impacts on reaction pathways in substrate degradation [20]. Variations in salinity tolerance (halotolerance) have been linked to loading conditions [18] and the growth phase of the microorganisms, the very young or very old cultures being more susceptible to salinity variation [26], as well as community diversity and origin [27]. 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 g NaCl L^{-1}, i.e. seawater salinities [13,28]. This implies that IEX regenerants would generally require dilution for effective bioprocessing.

Table 1
Characteristics of real and synthetic waste brines

Process/App	Influent ($g\,L^{-1}$)											Reference
	NO_3^--N	$ClO_4^{-(a)}$	Na^+	Cl^-	SO_4^{2-}	$Ca^{2+(a)}$	$Mg^{2+(a)}$	TDS	Bicarb.	pH	Cond.[(b)]	
iMBR (Syn.) Sulphate	N/a	N/a	50[c]	N/a	2–11.8	N/a	120	N/a	N/a	N/a	60–70	[25]
extMBR (Real) ED Brine[d]	0.13	N/a	0.034	0.47	0.2	788	30	N/a	1.08[e]	7.11	3.49	[52]
SBR (Real) IEX ISEP® Brine[f]	0.35	3.5	N/a	N/a	1.6	22	2.5	68.3	N/a	N/a	91.6	[6]
SBR (Syn.) IEX Brine[f]	0.09–0.9	4.3	53–100[c]	N/a	0.6–6	N/a	N/a	N/a	11.0	5–10	N/a	[6]
SBR (Syn.) IEX Brine[d]	0.61–0.84	N/a	29.25[c]	8.4–11.2	1.7–2.1	N/a	N/a	N/a	5.8–9.1[e]	N/a	N/a	[7]
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[g]	7.2	N/a	[3]
HF-MBfR (Syn.) IEX Brine[h]	1.0	500	10–40[c]	N/a	0.08	0.0003	0.02	N/a	N/a	N/a	N/a	[16]
SBR (Syn) IEX Brine[h]	0.112	500	8–60[c]	N/a	N/a	380	1320	N/a	0.2[g]	N/a	N/a	[2]
Spent Brine (Real) IEX[i,d]	0.48	N/a	18.6	12.1	2.6	39.4	N/a	N/a	0.11[j]	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[j]	7.4	124.5	Site 1
Spent Brine (Real) IEX[i,d]	1.99	N/a	42.1	50.9	4.4	171.7	N/a	N/a	0.43[j]	7.4	108.3	Site 2
Raw water Borehole	7.99[a]	N/a	12.4[a]	30.5[a]	26.2[a]	34.5	N/a	0.4[a,k]	0.02[j]	6.2	0.26	Site 1

N/a, Not applicable. Syn, Synthetic.
[a] $mg\,L^{-1}$.
[b] $mS\,cm^{-1}$.
[c] NaCl concentration.
[d] NO_3^-.
[e] Alkalinity as HCO_3^-.
[f] ClO_4^-
[g] Alkalinity as $NaHCO_3$.
[h] NO_3^- & ClO_4^-.
[i] Mean values.
[j] Alkalinity as $g\,CaCO_3\,L^{-1}$.
[k] Organic carbon.

As an alternative, some authors have developed either mixed [2,15,29] or single *halophilic* cultures [5,30] capable of withstanding higher salinities. Halophiles can be separated into three broad ranges: mild (10–60 g NaCl L^{-1}), moderate (60–150 g NaCl L^{-1}) and extreme or *extremophiles* (150–300 g NaCl L^{-1}) [31].

Halophilic communities have been isolated from various sites, including salt evaporation facilities/salterns, sub-tidal sediments and salt marshes [15,29,32]. Logan et al. [29] found that not all locations yielded communities capable of perchlorate reduction at 30 g NaCl L^{-1}. *Citrobacter sp.* has been identified as an effective halotolerant ClO_4^- reducer [15] at concentrations up to 50 g NaCl L^{-1}, and *Halomonas denitrificans* and *Halomonas Campisalis* have been shown to reduce nitrate at salinities up to 180 g NaCl L^{-1} [30,5] at rates comparable to those measured in non-halophilic studies [33] (Table 2).

2.2. Acclimatisation and shocking

Successful acclimation of inocula depends on type and growth phase of micro-organisms and the rate of increase in salt concentration [19]. Increasing salinity rapidly to 60–70 g NaCl L^{-1} in non-halophilic communities has been shown to inhibit denitrification by between 60% [13] and 100% [3]; van der Hoek et al. [13] 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 [3], whilst other studies have demonstrated no impact [27]. Some authors have also shown that if the salinity drops, acclimation to NaCl is rapidly lost [34]. In another case, specifically inoculum from marine sediment acclimatised to high salinities of 30 g NaCl L^{-1}, shock loads between 53 and 80 g NaCl L^{-1} were found not to impair reduction of either perchlorate or nitrate [6].

2.3. Reduction mechanism

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

$$\underset{\text{Perchlorate}}{ClO_4^-} \rightarrow \underset{\text{Chlorate}}{ClO_3^-} \rightarrow \underset{\text{Chlorite}}{ClO_2^-} \rightarrow \underset{\text{Chloride}}{Cl^-} + O_2 \quad (1)$$

$$\underset{\text{Nitrate}}{NO_3^-} \rightarrow \underset{\text{Nitrite}}{NO_2^-} \rightarrow \underset{\text{NitricOxide}}{NO} \rightarrow \underset{\text{NitrousOxide}}{N_2O} \rightarrow \underset{\text{DinitrogenGas}}{N_2} \quad (2)$$

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 [1] and at least two denitrifying Halophilic bacteria *Paracoccus halodenitrificans* and *Haloferax denitrificans* have been identified as reducing perchlorate [15]. However, it appears perchlorate reduction is not maximised by adapting denitrifying cultures [29] and furthermore not all denitrifiers can reduce chlorate [35]. Similarly, only some perchlorate-reducing bacteria use nitrate [36], 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 [6,37]. 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 [6] and vice versa [2]. 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 [15,38] that it is beneficial to the reduction rate to develop mixed communities (halophiles, such as *Citrobacter sp.* with non-halophiles [15]) 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 [38].

2.4. pH

The pH of IEX brine is expected to be basic (pH 8–9) due to the accumulation of bicarbonate [6]. Although maximum denitrification capacity is typically observed in the neutral range [33,39], several authors [3,5,13,40] have reported increased efficacy of halotolerant dentrifying communities at higher pH levels, with rapid dentrification reported at pH 9–9.5 by saline-acclimated activated sludge compared with none for the same saline-acclimated community at pH 7.5 [3]. Similar efficiencies have been observed for halophilic communities at pH 9 [5,40]. Glass and Silverstein [3] 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.

2.5. 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 [41], 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 [5] 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. [2] 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. [6] also recommended nutrient addition, finding magnesium was required at a molar ratio 0.11 (Mg^{2+}/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
Specific denitrification rates from high salt and zero salt processes

NaCl Affinity/Reactor type	NaCl Concn. (g NaCl L^{-1})	Community origin	Specific rate (mg NO_3^-–N gVSS h^{-1})	Reference
Non-halotolerant CSTR	0	ASP	2–50	[55]
Non-halotolerant MBR	0	ASP	6.7[a,b]	[39]
Non-halotolerant MBR	0	ASP	11.3[a]	[56]
Halophilic Batch kinetic	125	*Halomonas Campisalis*	12.5–27.1	[5]
Halophilic MBR	180	*Halomonas Denitrificans*	54.2[a,b]	[30]

CSTR—Continuous stirred tank reactor. ASP—Activated sludge process. MBR—Membrane bioreactor.
[a] mg NO_3^-–N.gSS.h^{-1}.
[b] Max. rate observed.

2.6. 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 [13,14], and has also been noted as suppressing nitrite accumulation [13]. Highly concentrated sulphate has been found to have no effect on perchlorate reduction [6,28]. However, several cases [7,42] 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 [43] leading to sulphide production (Eq. 4), which is undesirable.

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 7H_2O + 5CO_2 + 2N_2$$
$$\Delta G_0(w) = -476.5\,\text{kj.mol}^{-1} \quad (3)$$

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow 2H_2O + 2CO_2 + HS^-$$
$$\Delta G_0(w) = -104.5\,\text{kj.mol}^{-1} \quad (4)$$

2.7. 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 [7] and treated water contamination. Yang et al. [14] 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 [19,20] due to poor settleability. Some authors advocated post-treatment by granular activated carbon (GAC) to address this [44] which extended IEX operation by ~70 bed volumes versus untreated effluent. Clifford and Liu [7] 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 [30,45,46] providing a valid argument for its assessment for this duty. Such studies were all based on activated sludge, however; the impact of halophilic processes

Table 3
Substrate adaptation by halophilic bacteria

Oxyanion	Community derivation	pH	Salinity (g $.L^{-1}$)	Substrate	Reactivity		Reference
					Growth	Reduction	
NO_3^-	*Halomonas campisalis*	9	125	Acetate	√	√[a]	[5]
				Ethanol	×	×	
				Glycerol	√	√	
				Lactate	√	√	
				Methanol	×	×	
ClO_4^-	*Citrobacter sp.*	7.5	25	Acetate	√	√	[15]
				Citrate	√	×	
				Ethanol	√	×	
				Formate	√	√	
				Fumerate	√	√	
				Glucose	√	√	
				Molasses	√	√	
				Yeast extract	√	√[a,b]	
SO_4^{2-}	*Desulfobacter halotolerans*	7.2	50	Acetate	√	√	[25]
				Ethanol	√	√[a,c]	

[a] Highest reduction rate observed.
[b] Combining yeast extract with sodium acetate yielded optimum reduction.
[c] biotin and 4-aminobenzoate also added.

Table 4
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 ($g.L^{-1}$)	Reference
					In	Out			Temp.(°C)	pH	HRT (h)	SRT (d)	C:N ($g.g^{-1}$)		
MBR Sulphate	0.006	Acetate Ethanol	*Desulfobacter halotolerans*	50	–	–	5.5[a]	6.6[a]	33	7.2	8–36	N/a	0.5[b]	0.85[c]	[25]
MBR ED-Concentrate[d]	0.013	Ethanol	Adapted AS	34[e] 476[f]	106–534	0.6–1.7	0.29	0.48–0.72[g]	20	6.3–9	5	7	1.3	0.5–2.5	[52]
MBR IEX-Brine[d]	0.005	Methanol	*Halomonas denitrificans*	180	500–1000	N/a	0.7–1.3	12–48[g]	N/a	7	1.25–5	7	1.3	10	[30]
SBR IEX-Brine[d]	0.0015	Methanol	Adapted AS	14.6–29.2	610–835	95%	N/a	0.65–0.89[g]	22	9.1	10.5–22.5[h]	N/a	0.9–1.3	3.2–4.4	[7]
SBR High salinity[d]	0.03	Acetate	Adapted AS	35–71	2700–8200	0	0.46–1.2	2.7–8.2[g]	N/a	9	24[i]	12	1.5	12–38	[3]
USBR[d]	0.005	Methanol	N/a	5–25	N/a	N/a	0.38	12[g,j]	N/a	8.8–9.2	0.3–0.55	N/a	0.8	32	[11]
MBfR IEX-Brine[k]	11.7 mL	Hydrogen	Salt pond Inoculum	10–40	200–1000[g] 500[l]	57–692[g] 184–499[l]	N/a	0.032–0.087[m]	N/a	N/a	108.6	N/a	3–5[n]	N/a	[16]
IEX-Brine[d]	Batch Kinetic	Lactate Glycerol Acetate	*Halomonas campisalis*	125 (88[o])	113	0	0.3–0.65	N/a	4–45	9	N/a	N/a	In excess	25–43[p]	[5]
MBR High salinity	0.021	N/a	Mixed yeast/Mixed bacteria	32	5000[q]	N/a	0.93[r]	N/a	N/a	3.5–4	4.5–16.1	15	N/a	4500	[20]

[a] SO_4^{2-}.
[b] COD/SO_4^{2-}.
[c] $VSS.L^{-1}$.
[d] NO_3^-.
[e] Na^+ concentration $mg\,L^{-1}$
[f] Cl^- concentration $mg\,L^{-1}$.
[g] NO_3^--N.
[h] Fill 10 min, reaction 8–20 h, settle 2.5 h, draw 10 mins.
[i] Batch cycle: 22 h reaction, 0.25 h fill, 1.25 h settle, 0.5 h withdraw.
[j] Maximum concentration.
[k] NO_3^- & ClO_4^-.
[l] ClO_4^-.
[m] nitrate flux $g\,m^{-2}\,d^{-1}$.
[n] H_2 pressure (PSI).
[o] Optimum growth occurring at $88\,g\,L^{-1}$.
[p] $mg\,L^{-1}$.
[q] COD.
[r] $gCOD.g\,MLSS\,d^{-1}$.

on permeate quality and IEX regeneration efficiency is uncertain.

Conventional anion IEX resin selectivity is hierarchical: $SO_4^{2-} > NO_3^- > Cl^- > HCO_3^-$, 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} [11,13]. 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 [7]. Though not significantly inhibitory to the reduction process, its use as a co-regenerant as suggested by Bae et al. [44] also requires further investigation.

3. Process

3.1. 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 [47]. van der Hoek et al. [11,13] 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 mg NO_3^-–N L^{-1} [41,48]. The USBR was operated at an upflow rate 11 m^3 h^{-1} and achieved 90% NO_3^-–N removal, resulting in a brine volume reduction of 40–80% [41,48]. However, steady-state was difficult to achieve due to a considerable chloride concentration and a varying nitrate load resulting in nitrite accumulation [41]. Vallero et al. [27] also reported difficulties in acclimating biomass to NaCl concentrations >7.5 g 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 [27].

In an attempt to avoid sulphate accumulation, Bae et al. [44] 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 g NaCl L^{-1}, 0.6–1.7 g NO_3^-–N L^{-1} and 0.5–2.5 g SO_4^{2-} L^{-1}) 96% removal was observed in the denitrifying reactor at a loading rate 5.4 g NO_3^-–N L^{-1} d^{-1} whereas sulphate reduction efficiency remained at ~62% at a loading rate of 1.8 g SO_4^{2-} L^{-1} d^{-1} [44]. More recently, the same authors [49] 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 [50]. This method has been trialled for nitrate removal from drinking water [51] and more recently for perchlorate and nitrate reduction in brine [16] (Table 2). Following inoculation from a salt pond, low reduction rates were observed for commercial (150 g NaCl L^{-1} *Purolite*) brine. Subsequent dilution by 50% increased reduction significantly. Studies with

Table 5
Membrane operating parameters

Process/Feed	Membrane			Reactor vol. (m^3)	Flux, J ($l\,m^{-2}\,h^{-1}$)		Membrane parameters				Cleaning		Reference
	Configuration/type/material	Pore size (μm)	Area (m^2)		Op.	Crit.	TMP (bar)	dP/dt (mbar min^{-1})	K ($l\,bar^{-1}$)	CFV ($m\,s^{-1}$)	Gas flow ($l\,min^{-1}$)	Phys.	Chem.	
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[b] 1.2[c]	Backflush [d]/Relaxation	NaOCl Citric acid[e]	[25]
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.[f]	[52]
MBR-PD IEX Brine	Ext./tubular/Ceramic	0.22	0.26	0.005	24.6–73	N/a	0.5–3	0.0014[g]	21.5–55.4[h]	2	N/a	N/a	1 M NaOH 0.1 M HCl	[30]
MBR-Df IEX Brine	Imm./HF/Polyethylene	0.4	0.53	11.7[i]	N/a	N/a	N/a	N/a	N/a	150[j] 570–766[k]	3–5[l]	N/a	N/a	[16]

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

[a] Approximate Initial permeability.
[b] N_2 gas sparge.
[c] Specific gas demand per unit membrane area (SGD_m), $m^3\,m^{-2}\,h^{-1}$.
[d] Backflush instigated when TMP > 0.15 bar. When TMP < 0.15 bar, relaxation was used.
[e] Chemical clean initiated when TMP > 0.4 bar (1 g NaOCl L^{-1} for 1 h, 3 g citric acid L^{-1} for 1 h).
[f] Membrane chemically regenerated until within 10% of its initial water K.
[g] J min^{-1}.
[h] K recorded at 2.5 bar for biomass concentrations ranging 5–15 g L^{-1}.
[i] mL.
[j] Recirculation rate, mL min^{-1}.
[k] Liquid velocity, cm min^{-1}.
[l] Hydrogen gas pressure, psi.

synthetic brine (20 g NaCl 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 [16]. 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 (Table 4).

Externally configured pressure driven membrane bioreactors have also been studied for brine produced from electrodialysis [52] and IEX [30]. 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. [27]. Cyplik et al. [30] reported a maximum denitrification rate 1.3 g NO_3^-–N. g SS d^{-1} at an HRT 1.66 h (solids retention time (SRT) 10 days) from a feed comprising 180 g NaCl L^{-1} and 500–1000 mg NO_3^-–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 gNO_3^-–N. gVSS^{-1} d^{-1} was also observed by Wisniewski et al. [52] treating ED brine, though the ionic concentrations of the concentrate flow were comparatively low.

3.2. Membrane fouling

In non-halophilic communities, it is commonly acknowledged that salinity induces cell dehydration [25] or plasmolysis [53], manifested as an increase in the soluble COD [34]. Subsequently cell lysis or decay can result in release of carbohydrates, proteins and nucleic acids which are recognised membrane foulants [54] and can also affect surface charge, hydrophobicity and the flocculation process [20,54]. Reid et al. [53] 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 [25] and fouling can be controlled by physical means, rather than the use of aggressive chemicals to maintain membrane permeability [30] (Table 5).

4. 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 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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