Cost-effective bioregeneration of nitrate-laden ion exchange brine through deliberate bicarbonate incorporation

Qi Li a,b, Bin Huang a,b,* Xin Chen a,b, Yi Shi a,b

a Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China
b State Key Laboratory of Forest and Soil Ecology, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110164, China

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ABSTRACT
Bioregeneration of nitrate-laden ion exchange brine is desired to minimize its environmental impacts, but faces common challenges, i.e., enriching sufficient salt-tolerant denitrifying bacteria and stabilizing brine salinity and alkalinity for stable brine biotreatment and economically removing undesired organics derived in biotreatment. Incorporation of 0.25 M bicarbonate in 0.5 M chloride brine little affected resin regeneration but created a benign alkaline condition to favor bio-based brine regeneration. The first-quarter sulfate-mainly enriched spent brine (SB) was acidified with carbon source acetic acid for using CaCl₂ at an efficiency >80% to remove sulfate. Residual Ca²⁺ was limited below 2 mM by re-mixing the first-quarter and remained SB to favor denitrification. Under CO₂—HCO₃⁻ system buffered pH condition (8.3–8.8), nitrate was removed at 0.90 gN/L/d by hematite-enriched well-settled activated sludge (SVI 8.5 ml/g) and the biogenic alkalinity was retained as bicarbonate. The biogenic alkalinity met the need of alkalinity in removing residual Ca²⁺ after sulfate removal and in CaCl₂-induced CaCO₃ flocculation to remove 63% of soluble organic carbon (SOC) in biotreated brine. Carbon-limited denitrification was also operated after activated sludge acclimation with sulfide to cut SOC formation during denitrification. Overall, this bicarbonate-incorporation approach, stabilizing the brine salinity and alkalinity for stable denitrification and economical removal of undesired SOC, suits long-term cost-effective brine bioregeneration.

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1. Introduction

Nitrate pollution in groundwater is increasingly serious worldwide (Burow et al., 2010; Kaushal et al., 2011; Zhang et al., 1996). Proper treatment of nitrate-contaminated groundwater is in great need to minimize its health risks as drinking water (Fewtrell, 2004; Ginkel et al., 2008). A practical approach has been intensively explored for processing nitrate-contaminated groundwater, i.e., obtaining drinkable
water through ion exchange and then treating the nitrate-concentrated spent brine (SB) (Bae et al., 2002; Lehman et al., 2008; Yang et al., 2013). It is desirable to reuse SB after removal of nitrate and other undesired substances, especially in water-shortage inland areas, not to worsen soil and aquifer salinization. Direct bioregeneration of nitrate-exhausted resin has also been explored to bypass the need of SB biotreatment, but creates the needs of repeated resin unloading/reloading and intensive resin cleaning after bioregeneration.

Various chemical approaches, including photochemical, electrochemical and catalytic approaches, have been explored for nitrate removal in SB (Dortsiou et al., 2009; Yang et al., 2013), but generally face the difficulty in controlling the formation of byproducts nitrite and ammonium (Hirayama et al., 2012; Zhang et al., 2009). Highly concentrated nitrate in SB can also be removed at high efficiencies in downsized bioreactors (Ginkel et al., 2008; Lehman et al., 2008; McAdam and Judd, 2008), although three common challenges exist, i.e., enrichment and maintenance of sufficient salt-tolerant denitrifying bacteria and stabilization of brine salinity and alkalinity for long-term stable brine biotreatment, and economical removal of bacterially derived organics for reliable brine reuse.

Salt-tolerant denitrifying bacteria, typically in form of denitrifying activated sludge (DAS), are often enriched with inocula from saline and/or non-saline environments (Cang et al., 2004; Ginkel et al., 2008; Logan et al., 2001; Okeke et al., 2002). A good settling property is essential for DAS to be less likely lost but well maintained at suitable levels for long-term brine biotreatment (Dan et al., 2002; Lefebvre and Moletta, 2006). The use of chemically inert and reactive substances such as activated carbon and soluble iron may promote the enrichment of well-settled activated sludge (Vlyssides et al., 2009; Yu et al., 1999).

Stabilization of brine salinity and alkalinity also favors stable brine biotreatment (Ginkel et al., 2008). Nevertheless, both sulfate and bicarbonate typically accumulate to cause considerable variations of brine salinity and alkalinity in recycled brine. Even the sulfate level in recycled brine is finally stabilized when nitrate selective resins are used, the stabilized sulfate level may be more than 150 mM, considerably increasing the brine salinity (Lehman et al., 2008). When non-selective resins are used, sulfate continuously accumulates in recycled brine and needs to be lowered below certain levels (e.g., <100 mM) to not affect biotreated and resin regeneration. Sulfate removal via CaSO4 precipitation is less effective than via BaSO4 precipitation but cheaper and environmentally safer, and is applicable if the residual Ca2+ level can be well limited (e.g., <2 mM) to lower its negative effect on denitrifying bacteria (Bae et al., 2004; Ismail et al., 2010). Sulfate removal through bioreduction is also possible but increases the cost for electron donor and the need for malodor control (Bae et al., 2002; Cang et al., 2004).

Unlike sulfate, which is enriched from raw water, bicarbonate accumulated in recycled brine is primarily transformed from hydroxide alkalinity generated from denitrification. Since bicarbonate as resin regenerant is much less effective than chloride, very often when its level in recycled brine is already high enough (e.g., >50 mM), extra bicarbonate is typically neutralized so that pH may not continue to increase to affect the performance of denitrification (Bae et al., 2002). However, with the co-presence of a certain level of dissolved CO2 either internally derived from heterotrophic denitrification or externally supplemented, the CO2–HCO3− buffer system can maintain a suitable pH range during the process of denitrification (Huang et al., 2011), although the addition of Mg2+ is needed to compensate the limitation of Ca2+ to favor bacterial growth when bicarbonate is at a much higher level (e.g., >200 mM) (Lehman et al., 2008). When sulfate and bicarbonate levels in recycled brine are properly stabilized and chloride is supplemented to compensate its consumption during resin regeneration, then the brine salinity and alkalinity can be basically stabilized to favor long-term stable performance of brine biotreatment.

Cost-effective removal of bacterially derived undesired organics should be one of the biggest practical challenges for brine bioregeneration. A considerable portion of carbon source supports the growth of denitrifying bacteria and finally goes into the pool of undesired organics during brine biotreatment. Thus, without proper post treatment of biotreated brine before reuse, the performance of resins quickly deteriorates (Bae et al., 2002; Clifford and Liu, 1993). The use of activated carbon for removal of undesired organics in biotreated brine is relatively expensive. Isolating denitrifying bacteria from brine with ion exchange membrane during biotreatment may lower the need of post treatment (Ginkel et al., 2008; Shrimali and Singh, 2001). Since a low level of nitrate (e.g., up to 10 mM) in brine little affects practical (partial) regeneration of nitrate-exhausted resins, carbon-limited brine biotreatment may be an optional choice when perchlorate is not enriched in SB to reduce the formation of undesired organics. Nevertheless, nitrite reduction is normally slower than its formation to easily cause nitrite accumulation during denitrification even under carbon sufficient conditions (Chung et al., 2009; Peyton et al., 2001; Show et al., 2013; Tavares et al., 2006; Xiao et al., 2010). To conduct carbon-limited brine biotreatment, special acclimation is likely needed to synchronize bacterial nitrate and nitrite reduction to avoid accumulation of residual nitrite at the end of operation.

To jointly meet the three common challenges above-mentioned in SB bioregeneration, namely, enriching well-settled salt-tolerant DAS, stabilizing brine salinity and alkalinity and cost-effectively removing undesired organics from biotreated brine, bicarbonate incorporation in the range of 100–250 mM in brine is proposed to favor bio-based brine regeneration. In the first step for sulfate removal, the first-quarter sulfate-mainly enriched alkaline SB is acidified with acetic acid (also carbon source for denitrification) for using CaCl2 to partly remove sulfate, and re-alkalized with the remained alkaline SB to limit the level of residual Ca2+ to favor brine biotreatment. In the second step for nitrate bioreduction, hematite (α-Fe2O3) is used to enrich well-settled high-density DAS to denitrify nitrate and the biogenic alkalinity is retained in the benign form of bicarbonate under CO2–HCO3− system buffered pH condition. In the third step for removal of undesired organics produced in biotreatment, biogenic alkalinity and CaCl2-induced CaCO3 flocculation is used to save the cost of post treatment.
In this study, the limited role of bicarbonate in resin regeneration with chloride-based brine was briefly verified to ensure its low consumption in resin regeneration. Then, the bicarbonate incorporation approach to brine bioregeneration was evaluated with specific aims at the feasibility of i) CaCl\textsubscript{2}-induced sulfate removal with little residual Ca\textsuperscript{2+}; ii) high-rate nitrate reduction by hematite-enriched DAS under CO\textsubscript{2}−HCO\textsubscript{3}− system buffered pH condition; iii) synchronization of nitrate and nitrite reduction for carbon-limited denitrification; iv) removal of undesired organics through biogenic alkalinity and CaCl\textsubscript{2}-induced CaCO\textsubscript{3} flocculation.

2. Methods and materials

2.1. Nitrate-exhausted resin regeneration with bicarbonate-highly incorporated brine

A resin column, prepared by filling a Plexiglas column with a gel type strong base type I nonselective anion exchange resin, was initially regenerated at 4.3 BV/h for 4 h with brine composed of 0.5 M NaCl with or without 0.25 M NaHCO\textsubscript{3}, and washed with deionized water at 6 BV/h until the effluent conductivity was <200 \mu S/cm. Then, the resin column was downwardly fed with raw water (nitrate, chloride, sulfate and bicarbonate at 3.2, 0.8, 2.1 and 1.7 mM, respectively) at 14 BV/h until nitrate content in the produced water was above 0.7 mM, upwardly regenerated at 4.3 BV/h until nitrate content in SB was <10.0 mM. Changes in nitrate, sulfate, chloride and bicarbonate contents in produced water and SB were measured using an ion chromatography (DIONEX, ICS-900).

2.2. Partial sulfate removal from SB before biotreatment

Sulfate in SB produced from resin regeneration with the brine composed of 0.5 M NaCl and 0.25 M NaHCO\textsubscript{3} was partly removed before brine biotreatment. The first-quarter sulfate-highly enriched SB was separately collected. One volume of the first-quarter SB (250 ml) was acidified to pH below 5.5 with acetic acid (also as carbon source for denitrification), added with CaCl\textsubscript{2} to lower the sulfate level below 100 mM through CaSO\textsubscript{4} precipitation, and finally re-alkalinized with 3 volumes of the remained SB (750 ml) to precipitate residual Ca\textsuperscript{2+} below 2 mM through CaCO\textsubscript{3} precipitation to favor brine biotreatment.

2.3. Biotreatment of nitrate-concentrated SB after partial sulfate removal

2.3.1. Preparation of artificial SB

Based on the composition of anions in the SB after partial removal of sulfate (Section 2.2), bicarbonate-highly incorporated SB for biotreatment was prepared with NaCl, NaHCO\textsubscript{3}, KCl, MgSO\textsubscript{4} and CaCl\textsubscript{2} at 500, 250, 25, 25 and 1 mM, respectively. Minor nutritional substances were supplemented (Cang et al., 2004; Ginkel et al., 2008) to favor brine biotreatment. Concentrated nitrate and acetic acid solutions were added to reach desired final levels for brine biotreatment.

2.3.2. Enrichment of DAS with hematite addition for brine biotreatment

Using the artificial SB as the feed, and a marine sediment and activated sludge from a wastewater treatment plant as inocula, salt-tolerant DAS was enriched for 49 days in a SBR (inner diameter 9 cm, height 100 cm and effective volume 5.4 L) with addition of powdery hematite on the 14th, 28th and 35th day of enrichment (\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}, 3.0 g/L on each date). In each daily cycle of enrichment operation, the SBR was replaced with 2.2 L of brine (40% of exchange) in 5 min, and DAS was gas-suspended while the brine pH was maintained between 8.3 and 8.8 through the CO\textsubscript{2}−HCO\textsubscript{3}− buffer system by internal cycling of a mixture of N\textsubscript{2} and CO\textsubscript{2} (initial molar ratio 85:15) from a 10 L bag into the SBR bottom at 20 L/min for 0.3 min in every 10 min. Extra gases produced in denitrification were bubbled out from a water-sealed outlet of the gas bag. DAS was settled for 30 min at the end of operation and 2.2 L of the biotreated brine was then discharged in 5 min with the gas bag to buffer the SBR headspace pressure change. The enrichment of DAS was operated for 21, 14, 7 and 7 cycles with nitrate in the feed at 15, 30, 45 and 60 mM and sufficient carbon source (COD/NO\textsubscript{3}−N = 3.7), respectively. DAS was then sampled for determining SVI and MLSS and MLVVS contents. The performance of the SBR with well-enriched DAS was subsequently evaluated with 60 mM nitrate and sufficient carbon source in the feed by repeated measurement of temporal changes in nitrate and nitrite contents in 2 cycles of brine biotreatment.

2.3.3. Acclimation of hematite-enriched DAS with sulfide for carbon-limited brine biotreatment

The hematite-enriched DAS received further acclimation with sulfide for conducting carbon-limited brine biotreatment. In each daily cycle of acclimation, the SBR was replaced with 2.2 L brine containing 60 mM nitrate, operated under about 25% carbon shortage (COD/NO\textsubscript{3}− as 2.8 without consideration of residual nitrate left in the previous cycle of operation) while 20 ml of 50 mM sulfide (in form of Na\textsubscript{2}S) was dosed into the SBR once every 20 min for 15 times (15 mmol of sulfide addition in total) through a mini pump. The acclimation of DAS with sulfide under carbon limitation continued for 14 cycles when the residual nitrite level was below detection at the end of operation. Then, the SBR was fed with 2.2 L brine containing 60 mM nitrate, operated under about 20% carbon shortage (COD/NO\textsubscript{3}−N at 3.0, with consideration of residual nitrate left in the SBR after the previous cycle of operation) for 9 cycles, with an intended 7-day idling before the last 3 cycles, to evaluate the feasibility of carbon-limited brine biotreatment.

2.4. Post treatment of biotreated SB

The biotreated brine received sequential post treatment, including the use of biogenic alkalinity to support CaCl\textsubscript{2}-induced CaCO\textsubscript{3} flocculation, filtration through activated carbon column at 12 BV/h, and 15 min of ozone disinfection. Based on the amount of bicarbonate alkalinity generated from nitrate bioreduction and the small consumption of bicarbonate in resin regeneration, the biotreated brine was added with 20 mM CaCl\textsubscript{2}, mixed for 10 min at 90 rpm, and settled for 1
hour. The biotreated brine also received post treatment by filtration at 12 BV/h with activated carbon, CaCO₃ powder or fine sands (<0.1 mm) for demonstrating the advantage of biogenic alkalinity and CaCl₂-induced CaCO₃ flocculation in SOC removal. The biotreated SB samples before and after different post treatments were filtered through a 0.45 µm filter and analyzed by for determination of the changes in SOC content using a multi N/C® 3100 analyzer.

2.5. Reuse of bioregenerated brine for resin regeneration

After the sequential post treatment, the brine biotreated under carbon shortage was evaluated with comparison of fresh brine of the same composition of inorganic anions for regenerating resins exhausted in processing nitrate-polluted water for 10 cycles as described in Section 2.1. The diagram of this bicarbonate incorporation approach to bioregeneration of nitrate-laden ion exchange brine is shown in Fig. 1.

3. Results and discussion

3.1. Impacts of bicarbonate incorporation in brine on resin regeneration and exhaustion

The role of bicarbonate as regenerant has been mentioned in resin regeneration (Vanderhoek et al., 1988). Bicarbonate as regenerant is weaker than chloride, and its incorporation in chloride-based brine exerted small effects on resin regeneration and exhaustion as shown in Fig. 2. The incorporation of 0.25 M NaHCO₃ into 0.5 M NaCl only slightly accelerated the elution of sulfate and nitrate, and the duration of practical (partial) resin regeneration (with <10 mM nitrate in the SB at the end of resin regeneration) was only shortened from 3.5 h to 3.25 h. When using the resins regenerated with bicarbonate-incorporated brine for exhaustion, an increase in bicarbonate level in the produced water was only observed in the very early period of exhaustion (Fig. 2d). The net contribution of bicarbonate to ion exchange was only about 6.6% based on the average increase in bicarbonate level in the produced water, re-confirming its weak involvement in chloride-dominated resin regeneration. The slight increase in bicarbonate is generally beneficial for the produced water for drinking purpose. Overall, deliberate incorporation of 0.25 M bicarbonate in 0.5M chloride-based recycled brine did not bring about negative impacts on resin regeneration and exhaustion but created a bicarbonate-dominated benign alkaline condition to favor bio-based SB regeneration as presented in the followed sections.

3.2. Partial sulfate removal prior to spent brine biotreatment

Conventional sulfate removal via CaSO₄ precipitation leaves elevated residual Ca²⁺ to negatively impact brine biotreatment (Bae et al., 2004; Ismail et al., 2010). In this study, due to the faster sulfate elution relative to nitrate elution during resin regeneration (Figs. 2a, b), >90% of sulfate eluted was enriched in the first-quart SB. So, the first-quart SB was suitable to be separately collected for more efficient use of Ca²⁺ to induce CaSO₄ precipitation-based sulfate removal. Through a sequential use of acetic acid to adjust the pH to <5.5 and 55 mM CaCl₂ to induce CaSO₄ precipitation, the sulfate level was lowered from 138 mM to 92 mM with the residual Ca²⁺ level being between 9 and 10 mM. The overall efficiency of Ca²⁺ for sulfate removal was 83.6%. Moreover, subsequent re-mixing of the first-quart SB after partial sulfate removal with the remained SB further lowered the residual Ca²⁺ level below 2 mM, not only favoring brine biotreatment, but also retaining the brine alkalinity for adopting CaCl₂-induced CaCO₃ flocculation to remove undesired organics in post treatment of biotreated brine.

Fig. 1 – Diagram of bioregeneration of nitrate-laden spent brine through bicarbonate incorporation.
It should be noted, that the bicarbonate level maintained in SB is positively related to the nitrate level in SB, so that the amount of acetic acid added to acidify the first-quarter SB will not be more than that needed as carbon source for nitrate bioreduction. For example, to fit the need of acetic acid as carbon source for removal of a low level of nitrate around 40 mM in SB, and as acidifier for the first-quarter SB, the bicarbonate level needs to be around 100 mM in SB, so that it is still sufficient to limit Ca\(^{2+}\) < 2 mM after partial sulfate removal and to allow CaCO\(_3\) flocculation to co-remove extra biogenic alkalinity and undesired organics after brine biotreatment.

3.3. Enrichment of well-settled DAS with hematite for brine biotreatment

Maintaining a long-term stable performance of denitrifying bacteria during brine biotreatment is very challenging (Ginkel et al., 2008; Okeke et al., 2002), especially when the brine was recycled, gradually accumulating bicarbonate and sulfate to cause salinity and alkalinity variations (Clifford and Liu, 1993; Vanderhoek et al., 1988; Lehman et al., 2008). In this study, stabilizing sulfate and bicarbonate levels in brine and buffering the brine pH within a narrow range of 8.3 and 8.8 through the CO\(_2\)–HCO\(_3^-\) system both favored the enrichment and maintenance of DAS in brine condition, and inoculation of diverse denitrifying bacteria from a marine sediment and activated sludge of a wastewater treatment plant also benefited denitrification in brine environments (Cang et al., 2004; Ginkel et al., 2008).

In addition, instead of using activated carbon (Yu et al., 1999), we selected powdery hematite to enrich well-settled DAS, primarily due to that it has a higher density than activated carbon but is also basically chemically inert in a wide pH range from 5 to 10. After 49-day enrichment with hematite, well-settled high-density DAS was obtained (Fig. 3), with a low SVI value of 8.5 ml/g. The concentration of DAS was also high, with the MLSS value as 14.8 g/L and the MLVSS value as 4.5 g/L. As a result, hematite-enriched well-settled DAS could remove nitrate at a rate of 0.90 gN/L/d (Fig. 4), which was considerably high as compared with those reported by other researchers (Bae et al., 2004; Lehman et al., 2008).

A possible disadvantage associated with the use of hematite for DAS enrichment is iron dissolution to form reddish colloids with organics. However, the reddish colloids were little formed after DAS enrichment and easily removed by biogenic alkalinity and CaCl\(_2\)-induced CaCO\(_3\) flocculation during post treatment (Section 3.5).

**Fig. 2** – Nitrate, sulfate, bicarbonate and chloride levels during resin elution with 0.5 M NaCl without (a) and with 0.25 M NaHCO\(_3\) (b) and during exhaustion with nitrate-polluted water (c, d).
3.4. Acclimation of DAS with sulfide for carbon-limited brine biotreatment

Nitrite accumulated considerably even after the depletion of nitrate during the process of denitrification under carbon-sufficient condition (Fig. 4), due to its faster formation than its reduction. Nitrite accumulation during carbon-sufficient denitrification was also observed by many other researchers (Chung et al., 2009; Peyton et al., 2001; Show et al., 2013; Tavares et al., 2006; Xiao et al., 2010). Hence, without proper acclimation of DAS, it would be difficult to operate carbon-limited denitrification without nitrite accumulation at the end. In this study, sulfide was used to promote the synchronization of bacterial nitrite formation and reduction under carbon limitation. After 14-day acclimation of hematite-enriched DAS with sulfide under carbon limitation, synchronization of bacterial nitrite formation and reduction was obtained, as evidenced by the greatly minimized variation of nitrite level during the operation of carbon-limited denitrification after sulfide acclimation (Fig. 5). In each cycle of operation, the nitrate level decreased quickly each time after the addition of carbon source while the nitrite level only increased slightly and was constantly below detection at the end of operation, indicating that synchronized nitrite formation and reduction were basically maintained under carbon limitation. Synchronized nitrite formation and reduction still remained even after an intentional 7-day idling interruption (Fig. 5). Sulfide might have double roles in DAS acclimation, on one hand to lower nitrite formation, and on the other hand to increase nitrite reduction (Cang et al., 2004; Mahmood et al., 2007; Show et al., 2013; Tavares et al., 2006), overall promoting synchronized nitrate and nitrite reduction. The intermittently dosing of sulfide might also improve the availability of trace metals to better favor nitrite reducers against nitrate reducers. For long-term operation, it might be better to intermittently dose sulfide of small amount after several cycles of operation to maintain synchronized nitrate and nitrite reduction for carbon-limited denitrification.

The benefits of carbon-limited brine biotreatment were apparent. The levels of residual nitrate below 10 mM and residual nitrite below detection after carbon-limited brine biotreatment did not much affect brine reuse for resin regeneration, but reduced the formation of bacterial derivatives. The soluble organic carbon (SOC) level in the biotreated effluent decreased from 189 mg/L to 136 mg/L when the addition of carbon source changed from being sufficient to being 20% of shortage, not only lowering the cost of carbon source, but also lowering the cost of post treatment. Nevertheless, due to the delay of perchlorate bioreduction relative to nitrate bioreduction (Lehman et al., 2008; Xiao et al., 2010), carbon-limited denitrification is not suitable for bioregeneration of nitrate- and perchlorate-laden ion exchange brine.

3.5. Post treatment of biotreated brine

The biotreated brine needs further processing to remove suspended and soluble undesired organics before reuse for resin regeneration (Bae et al., 2002; Clifford and Liu, 1993). CaCl₂-induced CaCO₃ flocculation was much more effective in removal of SOC from the biotreated brine than filtration with CaCO₃ powder or fine sands, and comparable to filtration with activated carbon (Fig. 6). When the biotreated brine was sequentially treated with CaCl₂-induced CaCO₃ flocculation and activated carbon filtration, overall 89% of SOC present in
the biotreated brine was removed, much higher than the percentage of SOC removal by filtration with activated carbon alone (Fig. 6). In the process of CaCl$_2$-induced CaCO$_3$ flocculation, Ca$^{2+}$ as cation might react with a large portion of anion-rich SOC to co-precipitate with CaCO$_3$. In addition, the flocculation of the newly formed CaCO$_3$ simultaneously consumed 73% of biogenic bicarbonate, and would also co-precipitate heavy metals and inorganic anions including arsenate if present in the treated brine (Tang et al., 2012). Hence, CaCO$_3$ flocculation not only reduced the cost of activated carbon but also enhanced the post treatment quality.

3.6. Reuse of bioregenerated brine

The performances of the resins regenerated with freshly prepared and bioregenerated brines were compared regarding the time for resin regeneration and the capacity for processing nitrate-polluted water. The durations for resin regeneration with the recycled and freshly prepared brines for 10 cycles were quite close, with a relative difference averagely below 7%. The exhaustion capacities of the resins regenerated with the recycled and freshly prepared brines were also very similar, with a relative difference averagely below 5%. Use of the recycled brine for even more cycles is possible (Bae et al., 2002; Clifford and Liu, 1993; Lehman et al., 2008) but attention should be paid to possible accumulation of other undesirable substances in it (Lehman et al., 2008).

3.7. Comparison of brine bioregeneration with and without bicarbonate incorporation

Based on experimental results obtained from this study, the differences in brine bioregeneration with and without bicarbonate incorporation are compared (Table 1). Ten-cycle brine reuse with and without bicarbonate incorporation similarly decreased the SB volume by >80% compared to the direct brine disposal route, but differed much in consumption of chemicals in resin regeneration and brine bioregeneration (Table 1). When one BV of brine was considered to be lost in resin cleaning after each cycle of regeneration, 44%–46% of salt consumed in resin regeneration with recycled brine was actually lost due to resin cleaning. In practical operation, to reduce such salt loss, the first BV of spent resin washwater, containing a relative level of salinity, may be collected for preparing supplemental brine, and the remaining spent...
washwater, with a relatively low salinity, may be used for other purposes with reduced impact on the environment when discharged.

The deliberate incorporation of bicarbonate in chloride-based brine was primarily to favor its bio-based regeneration with changes in use of chemicals. The CaCl₂-induced sulfate removal in bicarbonate-incorporated brine, with the efficiency of CaCl₂ for sulfate removal being >80% and the residual Ca²⁺ level being <2 mM, would be cheaper and safer than BaCl₂-induced sulfate removal. Compared to the treatment of BaSO₄ precipitated in sulfate removal, CaSO₄ precipitated in CaCl₂-induced sulfate removal could be easily separately harvested and collectively treated as solid waste with little environmental risks. Instead of using HCl to control pH and neutralize alkalinity generated in nitrate bioreduction, maintaining 0.5–2.5 mM dissolved CO₂ in the bicarbonate-incorporated brine not only buffered the pH between 8.3 and 8.8 to support high-rate nitrate bioreduction by hematite-enriched activated sludge, but also retained the biogenic alkalinity in the benign form of bicarbonate. A minor part of the retained biogenic alkalinity was to compensate the consumption of alkalinity in CaCO₃ precipitation for limiting residual Ca²⁺ after sulfate removal. The remaining biogenic alkalinity was to balance the need of alkalinity in CaCl₂-induced CaCO₃ flocculation for SOC removal during post treatment (Table 1), so that the bicarbonate level in brine was well stabilized before and after brine bioregeneration. External input of CO₂ was mainly needed for adjusting the pH of brine prior to denitrification while CO₂ internally derived from acetic acid-supported denitrification was sufficient to maintain the pH during denitrification (Huang et al., 2011). It should be noted that either BaCl₂ used for sulfate removal and HCl used for pH control in nitrate reduction, or CaCl₂ used in sulfate removal and in CaCO₃ precipitation/flocculation, also compensates chloride consumed in resin regeneration.

The competitiveness of brine bioregeneration largely depends on the expense and difficulty of direct brine disposal in a specific area. However, when brine bioregeneration is considered, stable brine biotreatment and cost-effective removal of biogenic SOC are the essential parts of the operational challenge. Compared to the brine bioregeneration without bicarbonate incorporation, even sulfate removal is not critically needed when nitrate-selective resins are used, the cost on sodium bicarbonate, calcium chloride and maintenance of CO₂/HCO₃⁻/CO system buffered pH condition as required by the bicarbonate incorporation approach, could be greatly offset by high-rate nitrate bioreduction by hematite-enriched well-settled DAS and much reduced post treatment cost in SOC removal through biogenic alkalinity and CaCl₂-induced CaCO₃ flocculation.

### 4. Conclusions

Deliberate incorporation of a high level of bicarbonate created a benign alkaline condition for long-term cost-effective bioregeneration of nitrate-laden ion exchange brine. Acidifying the first-quarter sulfate-enriched SB with carbon source acetic acid permitted CaCl₂-induced sulfate removal and mixing it with remained SB limited the residual Ca²⁺ level to favor brine

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<td>CO₂, consumed</td>
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<td>0</td>
<td>0.5–1.2²¹</td>
</tr>
<tr>
<td>HCO₃⁻, produced</td>
<td></td>
<td>0</td>
<td>7.3</td>
</tr>
<tr>
<td>SOC removal</td>
<td>CaCl₂, consumed</td>
<td>0</td>
<td>2.9</td>
</tr>
<tr>
<td>HCO₃⁻, consumed</td>
<td></td>
<td>0</td>
<td>5.8</td>
</tr>
<tr>
<td>CaCO₃, precipitated</td>
<td></td>
<td>0</td>
<td>2.9</td>
</tr>
<tr>
<td>Activated carbon, consumed</td>
<td></td>
<td>100</td>
<td>33</td>
</tr>
</tbody>
</table>

³ In each cycle, nitrate and sulfate were enriched at 42 and 27 mM in spent brine, respectively.

⁴ Compared to NaCl consumption in the direct brine disposal route.

⁵ Ten-cycle brine reuse with one bed volume of brine loss in resin cleaning after regeneration.

⁶ Volumetric basis, compared to spent brine produced in the direct brine disposal route.

⁷ HCO₃⁻ incorporation from 100 to 250 mM.

⁸ BaCl₂ efficiency for sulfate removal: 100%; averaged percentage of sulfate removal: 80%.

⁹ CaCl₂ efficiency for sulfate removal: 80%; averaged percentage of sulfate removal: 80%.

¹⁰ Averaged percentage of residual Ca²⁺ removal: 75%.

¹¹ Based on the molar ratio of dissolved CO₂ to HCO₃⁻ level of 2.5%.

¹² Mass basis, compared to activated carbon consumption without HCO₃⁻ incorporation.
briotreatment. The use of hematite enriched well-settled high-density activated sludge for efficient nitrate bioreduction and the sludge accretion with sulfate synchronized nitrate and nitrite reduction to allow carbon-limited denitrification with reduced formation of undesired organics. Biogenic alkalinity produced in nitrate bioreduction was retained in the benign form of bicarbonate under CO\textsubscript{3}−−HCO\textsubscript{3}− system buffered pH condition. Removal of bacterial derivatives produced from nitrate bioreduction through biogenic alkalinity and CaCl\textsubscript{2}− induced CaCO\textsubscript{3} flocculation lowered the cost and enhanced the quality of post treatment. This bicarbonate incorporation approach, stabilizing brine salinity and alkalinity to well maintain well-settled high-density activated sludge and economically remove undesired organics, is good for long-term bioregeneration of nitrate-laden ion exchange brine.

**REFERENCES**


