



Evaluation of a hybrid ion exchange-catalyst treatment technology for nitrate removal from drinking water



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ABSTRACT

Ion exchange (IX) is the most common approach to treating nitrate-contaminated drinking water sources, but the cost of salt to make regeneration brine, as well as the cost and environmental burden of waste brine disposal, are major disadvantages. A hybrid ion exchange-catalyst treatment system, in which waste brine is catalytically treated for reuse, shows promise for reducing costs and environmental burdens of the conventional IX system. An IX model with separate treatment and regeneration cycles was developed, and ion selectivity coefficients for each cycle were separately calibrated by fitting experimental data. Of note, selectivity coefficients for the regeneration cycle required fitting the second treatment cycle after incomplete resin regeneration. The calibrated and validated model was used to simulate many cycles of treatment and regeneration using the hybrid system. Simulated waste brines and a real brine obtained from a California utility were also evaluated for catalytic nitrate treatment in a packed-bed, flow-through column with 0.5 wt%Pd–0.05 wt%In/activated carbon support (Pd–In/AC). Consistent nitrate removal and no apparent catalyst deactivation were observed over 23 d (synthetic brine) and 45 d (real waste brine) of continuous-flow treatment. Ion exchange and catalyst results were used to evaluate treatment of 1 billion gallons of nitrate-contaminated source water at a 0.5 MGD water treatment plant. Switching from a conventional IX system with a two bed volume regeneration to a hybrid system with the same regeneration length and sequencing batch catalytic reactor treatment would save 76% in salt cost. The results suggest the hybrid system has the potential to address the disadvantages of a conventional IX treatment systems.

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1. Introduction

Sustainably addressing nitrate-contaminated groundwater sources is a serious and growing issue due to its well-documented health effects (Cantor, 1997; European Union, 2000; Fewtrell, 2004; Lee, 1970; Sadeq et al., 2008; US EPA, 2016; Walter, 1951; Ward and Brender, 2011) and ever increasing use in agriculture (Crews and Peoples, 2004; Galloway et al., 2008; Snyder et al., 2009). Ion exchange (IX) is the predominant technology used in the U.S. for removing nitrate from drinking water sources, and has proven very effective in small to medium sized treatment plants (Kapoor and Viraraghavan, 1997). However, when the IX resin is exhausted,

regeneration is accomplished by flushing a concentrated salt brine (5–12 wt% NaCl) through the resin bed. The purchase of salt used for this regeneration step and disposal of the resulting nitrate-contaminated waste brines is expensive and leads to negative environmental impacts (Kapoor and Viraraghavan, 1997; Wang et al., 2011). Current treatment practices involve using fresh brine for each regeneration cycle, leading to inefficiency in the use of NaCl. The results of a 2011 study found that salt costs accounted for 78% of the overall operations and maintenance (O&M) at an IX treatment demonstration plant in Vale, OR (Wang et al., 2011). Thus, treating waste brine to enable reuse could decrease both the economic costs and environmental burdens of IX treatment processes.

Biological denitrification of ion exchange waste brine has been extensively studied and is a viable option for waste brine treatment (Clifford and Liu, 1993; Lehman et al., 2008; van der Hoek et al.,

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1988; van der Hoek and Klapwijk, 1989). However, biological treatment is sensitive to influent nitrate loading, and raises concerns over pathogens in drinking water. Results from a recent life cycle assessment suggest that a hybrid IX-catalyst system, in which waste brine reuse is enabled by catalytic denitrification, is another promising option for addressing IX inefficiencies (Choe et al., 2015). In the proposed catalytic reactor, hydrogen is supplied as an electron donor to reduce nitrate over a bimetallic catalyst, converting the toxic oxyanion primarily to inert dinitrogen gas ($\text{NO}_3^- + 2.5\text{H}_2 \rightarrow 0.5\text{N}_2 + \text{OH}^- + 2\text{H}_2\text{O}$). Among the materials tested, the combination of the hydrogenation metal palladium and the promoter metal indium immobilized on an activated carbon support (Pd–In/AC) has shown both high activity and selectivity for dinitrogen gas (Al Bahri et al., 2013; Barrabés and Sá, 2011; Marchesini et al., 2008; Soares et al., 2010). In addition, unlike Pd–Cu catalysts, the Pd–In catalysts are stable during oxidative regeneration processes that could be periodically required to reverse sulfide poisoning (Chaplin et al., 2007).

Pintar et al. (Pintar et al., 2001) proposed and later modified (Pintar and Batista, 2006) a closed loop hybrid IX-catalyst system for brine reuse, in which a 1 wt% NaCl brine was continually recirculated through both the catalyst column and IX resin until all nitrate was removed. In contrast, Choe et al., (Choe et al., 2015) proposed a 2-stage hybrid treatment system using IX for treatment of the contaminated source water followed by resin regeneration using waste brine that is catalytically treated in a separate reactor (either packed bed or sequencing batch catalyst reactor) between regeneration cycles. One concern, though, is that IX model simulations predicted buildup of unreactive bicarbonate and sulfate ions in waste brines over repeated catalyst treatment and reuse cycles, and previous experiments in batch reactor systems suggest that elevated levels of these non-target ions may inhibit catalyst reactions with nitrate (Chaplin et al., 2006; Choe et al., 2015; Pintar et al., 2001; Yang et al., 2013). It is not clear how these findings translate to continuous flow reactors, whether the reduction in catalyst activity is simply competitive inhibition or leads to more progressive loss in activity (i.e., deactivation), and how residual nitrate levels remaining after catalytic treatment affects IX performance. Prior work indicates that the elevated levels of bicarbonate and sulfate in waste brine will have minimal effect on IX performance during treatment with nitrate-selective resins (Clifford and Liu, 1993; van der Hoek et al., 1988) because a selectivity reversal at high ionic strength favors chloride sorption over bicarbonate or sulfate during resin regeneration (Chiavola et al., 2014; Flodman and Dvorak, 2012). However, the effects of very high sulfate and bicarbonate levels expected for repeated reuse cycles (e.g., 8000–30,000 mg/L) have not been experimentally evaluated, and our prior IX model simulations (Choe et al., 2015) that considered this scenario used literature values for selectivity coefficients that did not consider selectivity reversal during regeneration.

The overall goal of this contribution is to employ a combination of process modeling and experimentation to evaluate the technical feasibility of the hybrid IX-catalyst technology for treatment of nitrate-contaminated drinking water (see Fig. 1 for diagram). The specific objectives are to: 1) Calibrate and validate an ion exchange model for treating nitrate-contaminated water that includes repeated treatment and regeneration cycles using treated waste brine; 2) Use the calibrated model to simulate multiple treatment/regeneration cycles to predict the buildup of bicarbonate and sulfate ions in waste brine that occurs with brine reuse and the impact of these ions on IX performance for nitrate removal; 3) Evaluate the effects of elevated levels of bicarbonate and sulfate in synthetic and real waste brines on long-term catalyst performance in a continuous-flow packed-bed reactor; and 4) Estimate input salt and catalyst metal requirements for the conventional versus hybrid

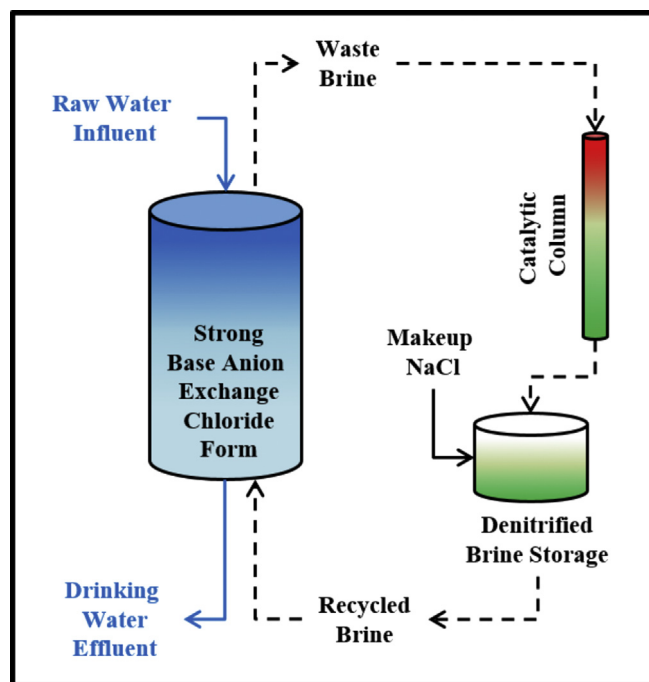


Fig. 1. Flow diagram of the hybrid ion exchange-catalyst treatment system.

IX systems as a function of regeneration bed volumes. Results from the work are used to recommend an optimum hybrid treatment strategy, and the use of separate selectivity coefficients for IX treatment and IX regeneration steps yields new insights into how the IX system must be operated to maintain performance. In addition, long-term catalyst tests with synthetic and real brines provide important performance data needed to advance the development of a practical hybrid system.

2. Methods

2.1. Materials

Reagent-grade sodium salts ($\geq 99\%$ purity) of nitrate, chloride, bicarbonate, and sulfate were obtained from Fisher or Sigma-Aldrich. All synthetic brines were prepared with either deionized (DI) water or Nanopure water (18.2 M Ω -cm resistivity, Millipore system). A nitrate selective ion exchange resin (CalRes 2105) was supplied by the Calgon Carbon Corporation with a reported resin capacity of 1000 meq/L. A 0.5 wt%Pd–0.05 wt%In/C was provided by Johnson Matthey.

2.2. IX and catalyst experimental setups

IX columns were constructed from 101.6 cm (40") long sections of 1.9 cm (0.75") OD, 1.27 cm (0.5") ID UV-stabilized acrylic tubing and filled with 116 mL resin. A Masterflex peristaltic pump with three pump-heads was used to deliver all solutions, and up to three IX columns were run in parallel. More details and a simple diagram are shown in Figure S1.

The packed bed catalyst reactor column was constructed from 50.8 cm (20") of 2.54 cm (1") OD, 1.9 cm (0.75") ID UV-stabilized acrylic tubing and packed with 80.7 g of Pd–In/AC catalyst. It was equipped with stainless steel Swagelok fittings and PTFE tubing. More details and a simple diagram are shown in Figure S2.

All fresh brines and simulated waste brines were prepared with Nanopure water. Solutions for IX treatment cycle experiments

(150–210 L feeds) were prepared with deionized (DI) water using a high pressure DI faucet to ensure proper mixing of the large volumes required (150–210 L). All experiments were conducted at ambient laboratory temperatures. IX experiments were conducted at $27 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$, and catalyst experiments were conducted at $20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$. Previous reports indicate that IX performance varies little with temperature. In one study, anion selectivity coefficients were not significantly impacted between 5 and $25 \text{ }^\circ\text{C}$ (Gregor et al., 1955). In another study, there was no change in the nitrate-bromide selectivity coefficient between 0 and $50 \text{ }^\circ\text{C}$ (Morgan et al., 1995). Hence, the $\pm 5 \text{ }^\circ\text{C}$ temperature variation in our runs had little effect on the results.

2.2.1. IX experiment protocol

IX experiments were conducted with alternating treatment and regeneration cycles. During treatment cycles, feed was pumped down-flow at 80 mL/min (EBCT = 1.45 min); during regeneration cycles, brine was pumped up-flow at 3.3 mL/min (EBCT = 35.15 min). Experiments used for model calibration also included an intermediate DI water flush cycle before each treatment cycle and each regeneration cycle; this was pumped at 19 mL/min (EBCT = 6.1 min) for 5 BV (empty bed volumes) in the same direction as the subsequent cycle (i.e., down-flow if preceding the treatment cycle). These BV and hydraulic retention times (based on flow rates) were selected in consultation with personnel from Calgon Carbon Corporation and are representative of those used in practice (Calgon Corporation, 2014).

Table 1 summarizes the three sets of IX experiments performed: one set of four experiments for treatment cycle model calibration (labeled Model Treatment Exp. 1–4), one set of four experiments for brine cycle model parameterization (labeled Model Brine Exp. 1–4), and one set of six experiments for testing 2-cycle IX performance for model refinement and validation (labeled 2-Cycle Exp. 1–6). Further protocol details and diagrams are provided in Supplemental Information (SI). Three different bed volumes of brine regeneration were considered in experiments (2, 5 and 10 BV); partial resin regeneration is expected with 2 BV and nearly complete regeneration (i.e., return resin to fully chloride-loaded state) with 10 BV.

2.2.2. Catalyst experimental protocol

Continuous catalytic nitrate treatment experiments were performed for 23–45 d to evaluate catalyst activity and longevity. A

two-phase flow packed-bed reactor was used because sufficient hydrogen for stoichiometric nitrate reduction could not be delivered in the liquid phase alone. The brine flow rate was 0.2 mL/min, the hydrogen gas flow rate was 6.8 mL/min, and the carbon dioxide gas (pH buffer) flow rate was 1.6 mL/min. At the column inlet, the H₂/N molar ratio was ca. 7.5. The minimum required stoichiometric molar ratio for nitrate reduction to dinitrogen gas is 2.5, and for nitrate reduction to ammonium is 4.0. Two experiments were performed: one with a series of synthetic brines and one with a real waste brine obtained from a California utility (see Table S1). Further details concerning the protocols and brines are available in SI.

Batch experiments were also performed to evaluate catalyst activity in a rapidly mixed (800 rpm) and vigorously H₂ sparged (250 mL/min) solution using a system described previously (Choe et al., 2015). A synthetic waste brine containing 11,500 mg/L nitrate and 4.5 wt% NaCl was introduced to a 250 mL, round bottom, five-neck reaction flask containing 40 g/L catalyst. Solution pH was maintained at 5.0 with HCl addition by an automatic pH stat during reactions. Suspension samples were periodically collected for analysis and immediately filtered (0.45 μm) to quench further reaction.

2.2.3. Analytical methods

Aqueous chloride, nitrate and sulfate concentrations were quantified using ion chromatography with conductivity detection (Dionex ICS-2000/2100, 4 \times 250 mm IonPac AS-19). A flow rate of 1.0 mL/min, 32 mM KOH eluent concentration and 96 mA suppressor current were used. Internal and external standards were used to calibrate the results. All brine samples and reference standards were diluted 50-fold prior to IC analysis. Bicarbonate concentrations were estimated by alkalinity pH titration using reference 0.1 N, 0.01 N and 0.001 N HCl solutions. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was used to quantify total calcium, magnesium, phosphorous, iron and manganese in the real waste brine obtained from the California utility.

2.3. IX modeling

2.3.1. IX model development

An IX model was developed using the three mass action and five mass balance relationships listed in Table 2, which have eight

Table 1
Summary of IX experiments used for model calibration and validation.

Experiment number	Water composition				BV of brine	# Feed cycles	Brine composition			
	[Cl ⁻] mg/L	[NO ₃ ⁻] mg/L	[HCO ₃ ⁻] mg/L	[SO ₄ ²⁻] mg/L			[NaCl] mg/L	[NO ₃ ⁻] mg/L	[HCO ₃ ⁻] mg/L	[SO ₄ ²⁻] mg/L
Experiments used to parameterize the model during the feed cycle										
Model Treatment Exp. 1	0	0	0	200	NA	1	NA	NA	NA	NA
Model Treatment Exp. 2	0	0	200	0	NA	1	NA	NA	NA	NA
Model Treatment Exp. 3	0	200	0	0	NA	1	NA	NA	NA	NA
Model Treatment Exp. 4	0	200	200	200	NA	1	NA	NA	NA	NA
Experiments used to parameterize the model during the regeneration cycle										
Model Brine Exp. 1	0	200	0	0	9BV	1	100,000	0	0	0
Model Brine Exp. 2	0	200	0	0	9BV	1	100,000	1500	30,000	0
Model Brine Exp. 3	0	200	0	0	9BV	1	100,000	1500	0	30,000
Model Brine Exp. 4	0	200	0	0	9BV	1	100,000	1500	30,000	30,000
Experiments used to refine regeneration parameters and validate model										
2-Cycle Exp. 1	70	200	131	48	2BV	2	100,000	0	0	0
2-Cycle Exp. 2	70	200	131	48	5BV	2	100,000	0	0	0
2-Cycle Exp. 3	70	200	131	48	10BV	2	100,000	0	0	0
2-Cycle Exp. 4	70	200	131	48	2BV	2	100,000	1500	30,000	30,000
2-Cycle Exp. 5	70	200	131	48	5BV	2	100,000	1500	30,000	30,000
2-Cycle Exp. 6	70	200	131	48	10BV	2	100,000	1500	30,000	30,000

NA = Not applicable.

Table 2
Ion exchange model.

Equations	Unknowns	Definitions
(1) $Cl_{tot} = [Cl^-] + RCl$	$[Cl^-]$, RCl	$[Cl^-]$ = chloride aqueous conc. RCl = chloride resin conc. Cl_{tot} = total chloride
(2) $NO_{3,tot} = [NO_3^-] + RNO_3$	$[NO_3^-]$, RNO_3	$[NO_3^-]$ = nitrate aqueous conc RNO_3 = nitrate resin conc. $NO_{3,tot}$ = total nitrate
(3) $HCO_{3,tot} = [HCO_3^-] + RHCO_3$	$[HCO_3^-]$, $RHCO_3$	$[HCO_3^-]$ = bicarbonate aqueous conc $RHCO_3$ = bicarbonate resin conc. $HCO_{3,tot}$ = total bicarbonate
(4) $SO_{4,tot} = [SO_4^{2-}] + R_2SO_4$	$[SO_4^{2-}]$, R_2SO_4	$[SO_4^{2-}]$ = sulfate aqueous conc R_2SO_4 = sulfate resin conc. $SO_{4,tot}$ = total sulfate
(5) $K_C^N = \frac{[Cl^-]RNO_3}{[NO_3^-]RCl}$	$[Cl^-]$, RCl $[NO_3^-]$, RNO_3	K_C^N = resin nitrate-chloride selectivity, different for feed and regeneration
(6) $K_C^S = \frac{[Cl^-]^2 R_2SO_4}{[SO_4^{2-}]RCl^2}$	$[Cl^-]$, RCl $[SO_4^{2-}]$, R_2SO_4	K_C^S = resin sulfate-chloride selectivity, different for feed and regeneration
(7) $K_C^H = \frac{[Cl^-]RHCO_3}{[HCO_3^-]RCl}$	$[Cl^-]$, RCl $[HCO_3^-]$, $RHCO_3$	K_C^H = resin bicarb-chloride selectivity, different for feed and regeneration
(8) Resin capacity = $RCl + RNO_3 + RHCO_3 + R_2SO_4$	RCl , RNO_3 , $RHCO_3$, R_2SO_4	Resin capacity = total equivalence that can be absorbed onto the resin

unknown variables (RCl , RNO_3 , $RHCO_3$, R_2SO_4 , $[Cl^-]$, $[NO_3^-]$, $[HCO_3^-]$, $[SO_4^{2-}]$) evaluated in meq/L, and seven model parameters (i.e., K_C^N , K_C^S , K_C^H , rK_C^N , rK_C^S , rK_C^H , Resin Capacity). The IX column was discretized spatially into a series of theoretical “plates”. The eight equations and eight unknown variables were solved at each plate as a system of non-linear equations in MATLAB assuming instantaneous equilibrium. The mathematical solution of the eight unknown variables from one plate became the initial conditions for the next plate. The number of plates required for model simulations was increased until model output was constant and a mass balance was obtained; 25 plates were determined to be sufficient to meet these criteria. The supplier-provided resin capacity of 1000 meq/L was used as an initial guess during parameter fitting. The model code was validated by matching simulated nitrate breakthrough results provided in (Guter, 1995) using the same initial conditions, treatment selectivity coefficients and resin capacity.

Ion selectivity coefficients vary depending on solution ionic strength (Boari et al., 1974; Fernandez et al., 1994). Hence, breakthrough of ions during the IX treatment (i.e., low ionic strength feed) and resin regeneration (i.e., high ionic strength brine feed) stages were modeled separately, resulting in the two different sets of selectivity coefficients (a single resin capacity value was optimized). Optimization was conducted in three distinct stages by minimizing the relative least square error between model and experimental results using a genetic algorithm (details provided in SI). First, treatment cycle parameters were determined by fitting Model Treatment Exp. 1–4 data (see SI for details). This resulted in an optimized set of treatment cycle selectivity coefficients. Second, regeneration cycle parameters were initially determined by fitting Model Brine Exp. 1–4 data (see SI for details), and the challenges encountered are discussed in Section 3.1. Finally, regeneration cycle parameters were optimized by fitting 2-Cycle Exp. 1 data. The best-fit regeneration parameters were then validated by predicting nitrate breakthrough curves for 2-Cycle Exp. 2–6 experiments (see Fig. 3b–f). The 95% confidence intervals were calculated for the best-fit parameters (see SI for parameter optimization details).

Catalytic denitrification was incorporated into the IX model by (numerically) reducing the level of nitrate to 1500 mg/L in the composite waste brine collected during a regeneration cycle. A nitrate level of 1500 mg/L was chosen to balance subsequent treatment length with catalyst reactor requirements. Treating to a lower nitrate level would allow longer treatment time in the subsequent IX cycle (as model results will indicate), but would also

require more catalyst and increase the price of the reactor. With the loss of nitrate ions from the treated brine, electroneutrality was maintained by assuming an equivalent addition of bicarbonate anions resulting from the carbon dioxide buffering agent used. Since chloride is lost from brine to the resin during IX regeneration, makeup NaCl was (numerically) added to the composite waste brine to maintain a constant chloride level during each regeneration cycle. The modified composite waste brine (with reduced nitrate level and constant chloride level) was used in the next simulated regeneration cycle.

We note that our modeling approach assumes ideal plug flow through the IX column, i.e., dispersion is ignored. There are examples of IX models in the literature that have considered (Flodman and Dvorak, 2012; Hekmatzadeh et al., 2012) and neglected dispersion (Choe et al., 2015; Hekmatzadeh et al., 2012; Kim and Benjamin, 2004). We note that Hekmatzadeh et al. (2012) compared IX model results for nitrate breakthrough with and without dispersion for a nitrate-selective resin, and determined that models neglecting dispersion were sufficient for modeling dynamic systems for diverse operating conditions.

2.3.2. IX model application

After calibration and validation, the IX model was applied to simulate a range of scenarios with multiple cycles of regeneration and treatment as a function of two important design considerations, the BV used for resin regeneration and addition (or no addition) of NaCl makeup (see Table S3). Water containing 10 wt% NaCl only was used for the first regeneration cycle of all scenarios. Regeneration waste brines from this and later cycles were used for all subsequent regeneration cycles, after adjustment to reduce nitrate to 1500 mg/L, and increase chloride to the original level via numerical NaCl addition. Each treatment cycle was modeled until nitrate breakthrough reached 44 mg/L as nitrate. A full list of the scenarios considered is provided in Table S3.

3. Results and discussion

3.1. IX model calibration and validation

Data from selected treatment (Model Treatment Exp. 4) and resin regeneration (Model Brine Exp. 4) experiments, along with model fits, are shown in Fig. 2. The simulated treatment profiles (Fig. 2a) and regeneration profiles (Fig. 2b) appear to adequately

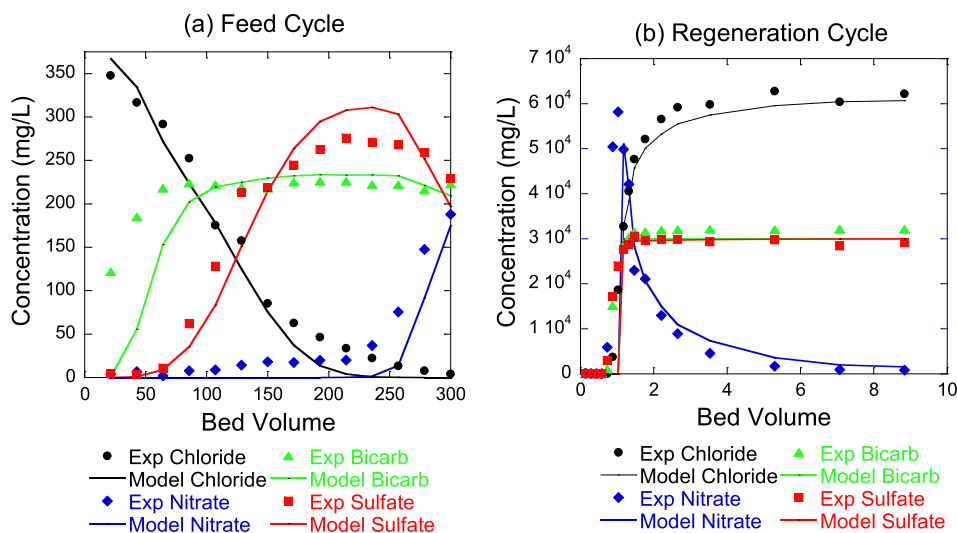


Fig. 2. IX measurements and model fits of (a) nitrate treatment cycle and (b) resin regeneration cycle. Experiments used for model calibration are listed in Table 2.

match the measured profiles, with the exception of a discrepancy at early time during regeneration when experimental breakthrough is observed before 1 BV (model breakthrough starts at exactly 1 BV). This offset likely results from the assumption of ideal plug flow without dispersion (dispersion is required for breakthrough before 1 BV). Preferential flow through channels or near sidewalls could also have caused early breakthrough. Another discrepancy occurs at the beginning of treatment when model predictions of bicarbonate breakthrough (using treatment selectivity coefficients) lag behind the measured breakthrough by roughly 25 BV. This likely results from a combination of the high treatment flow rate preventing full equilibration time and the very low bicarbonate selectivity.

The initial best-fit resin capacity parameters and selectivity coefficients for the one cycle treatment and regeneration experiments (see Table S2) were used to model the 2-Cycle Exp. 1, which was characterized by two treatment cycles separated by a regeneration cycle. This resulted in inaccurate prediction of nitrate breakthrough during the second treatment cycle (see Figure S6a), indicating model calibration using only one treatment cycle is not adequate to predict multi-cycle treatment breakthrough. A model sensitivity analysis (see Figure S5 in SI) indicated that the spatial distribution of sorbed anions in the IX column at the end of the regeneration cycle has a large effect on nitrate breakthrough during the subsequent treatment cycle. Therefore, the selectivity coefficients during brine regeneration and the resin capacity initially estimated from fits of one cycle regeneration experiments were further adjusted to optimize model fits of nitrate breakthrough during the second cycle of the 2-Cycle Exp. 1; the treatment cycle selectivity coefficients were held constant at values determined above. Results are shown in Fig. 3a, and the best-fit resin capacity and selectivity coefficients are listed in Table 3. While the fit is not exact, the simulated time to breakthrough (i.e., time when nitrate reaches the MCL of 44 mg/L) is within 17% of that measured experimentally, and major features of the breakthrough profiles (i.e., shape, plateau) are matched. The 95% confidence intervals for treatment parameters are less than 10% of fit-derived values. However, the 95% confidence interval values for regeneration parameters are up to 60% of fit-derived values. A model sensitivity analysis suggests this level of uncertainty can lead to a deviation in the cycle 2 breakthrough time of up to 22%, so the best fit parameters were further tested by using them to predict nitrate breakthrough profiles of the remaining 2-Cycle (i.e., 2–6) experiments.

Treatment results for 2-Cycle Exp. 2–3 are shown in Fig. 3b–c. Here, regeneration was performed with a 10 wt% NaCl brine. The predicted breakthrough times in Fig. 3b–c are within 2% and 0.8%, respectively, of experimental breakthrough times, and the profiles are well matched. In addition, the match improves with increasing BV used for regeneration, which is not surprising given that the IX bed becomes more uniformly chloride-saturated (i.e., closer to the initial state of the virgin resin). The results suggest the separate selectivity coefficients listed in Table 3 for the treatment and regeneration cycles allow adequate determination of sulfate, bicarbonate, and nitrate breakthrough in treatment and waste brines for multiple cycles of reuse under a variety of conditions, and that model accuracy improves when using greater BV for regeneration. The relatively large differences in treatment and regeneration selectivity coefficients for the same anion also call into question results from prior work (Choe et al., 2015) that used the same selectivity coefficients for both stages of the IX process.

Treatment results for 2-Cycle Exp. 4–6 are shown in Fig. 3d–f. Here, regeneration was performed with a synthetic “treated waste brine” containing 10 wt% NaCl, 1500 mg/L nitrate, 30,000 mg/L bicarbonate, and 30,000 mg/L sulfate. Predicted breakthrough profiles accurately simulate the earlier breakthrough of the second IX treatment cycle, resulting primarily from lower regeneration efficiency (i.e., mass of nitrate removed per mass of sodium chloride used in the brine) due to nitrate left in the brine. A comparison of Fig. 3c and f provide the most noticeable example, as even a 10 BV regeneration with the synthetic treated brine (Fig. 3f) does not provide full resin regeneration. A similar comparison between Fig. 3b and e reveals a similar result.

3.2. Multi-cycle IX model scenarios

The calibrated and validated IX model was then used to simulate multiple cycles of alternating IX treatment and regeneration for different brine reuse scenarios, with an assumed treatment of the waste brine nitrate down to a residual concentration of 1500 mg/L after each regeneration cycle (to simulate catalytic treatment where ~90% of 15,000 mg/L is removed before reusing). The model runs are listed in Table S3, and allowed us to determine realistic operating conditions that would result in the most efficient design of the hybrid IX-catalyst treatment system. The buildup of unreactive bicarbonate and sulfate ions in the reused waste brine

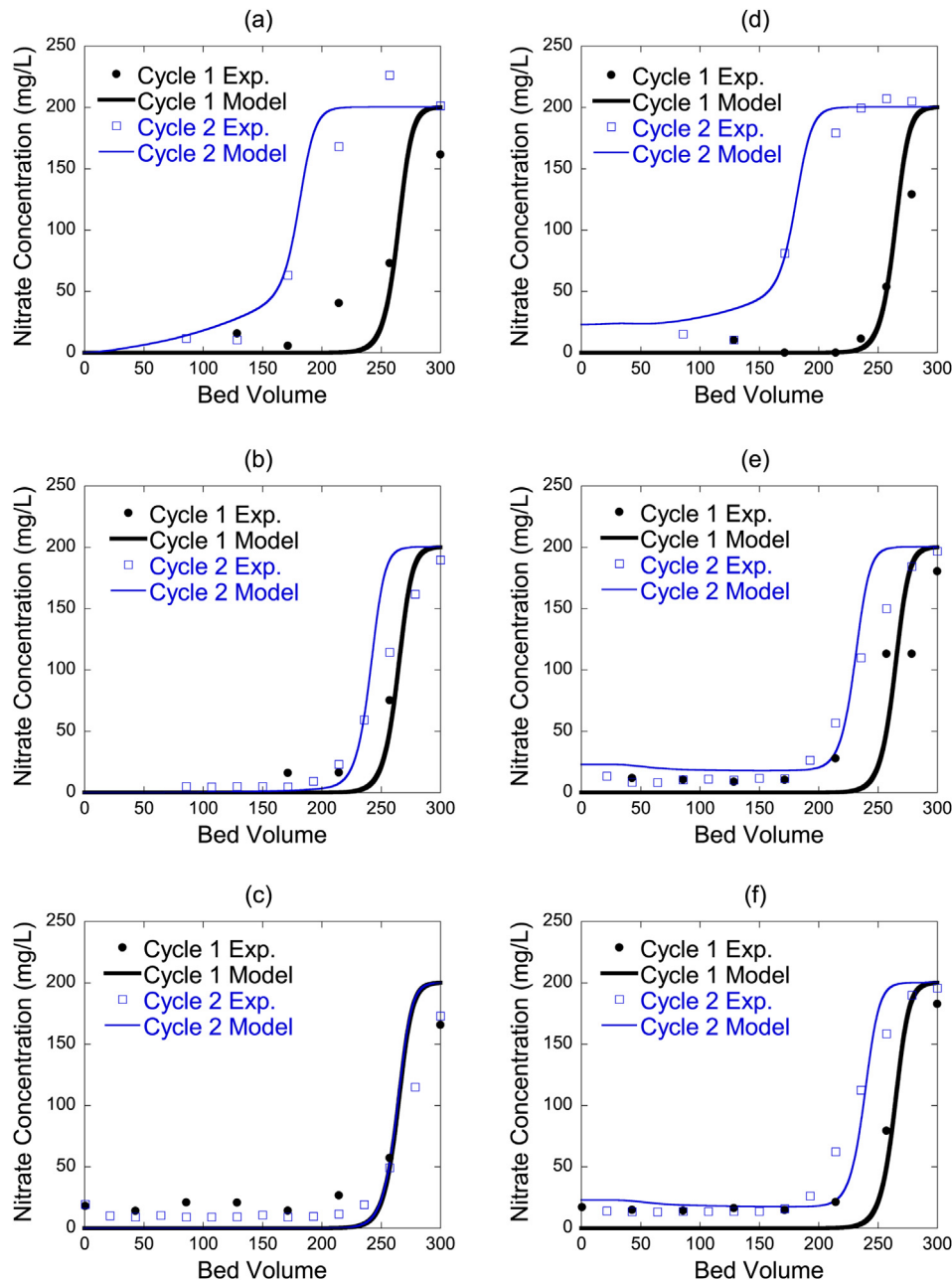


Fig. 3. Measured versus predicted nitrate breakthrough curves during two sequential treatment cycles separated by a resin regeneration cycle using two different brines for regeneration: (a) Experimental data used to refine the regeneration selectivity parameters with 2 BV of regeneration (2-Cycle Exp. 1), and model validation (b)–(c) for 2-cycle experiments with 5 BV and 10 BV of regeneration with 10 wt% NaCl brine, (d)–(f) for 2-cycle experiments with 2 BV, 5 BV, and 10 BV regeneration with synthetic “treated waste brine” contained 10 wt% NaCl, 1500 mg/L nitrate, 30,000 mg/L bicarbonate, and 30,000 mg/L sulfate.

Table 3
Best fit IX model parameters.

Ion exchange resin characteristics	
Resin Name: CalRes 2105	
Resin Type: SBA Cl ⁻ form	
Resin Selectivity: nitrate selective	
Resin Capacity: 1096 meq/L	
Treatment parameters	Regeneration parameters
$K_C^N = 3.52 \pm 0.11$	$rK_C^N = 12.0 \pm 5.8$
$K_C^S = 0.0056 \pm 0.0002$	$rK_C^S = 0.15 \pm 0.09$
$K_C^H = 0.41 \pm 0.04$	$rK_C^H = 0.002 \pm 0.001$

over ten cycles of treatment/regeneration is shown in Fig. 4a for scenarios where 2 BV and 10 BV of denitrified waste brine are used for regeneration each cycle. The simulated source water was modeled after that used by a participating utility in California, 10 wt % NaCl brine was used for the first regeneration cycle, and used brine was amended with NaCl to maintain 10 wt% NaCl. As expected, the sulfate and bicarbonate concentrations buildup occurs more rapidly when using 2 BV of regeneration compared to 10 BV because more waste brine volume is required for the latter, resulting in dilution of the non-target ions removed from the resin. Bicarbonate and sulfate both reach or exceed 30,000 mg/L by the tenth cycle when using 2 BV for regeneration, which led us to use 30,000 mg/L of bicarbonate and sulfate in synthetic brines for IX

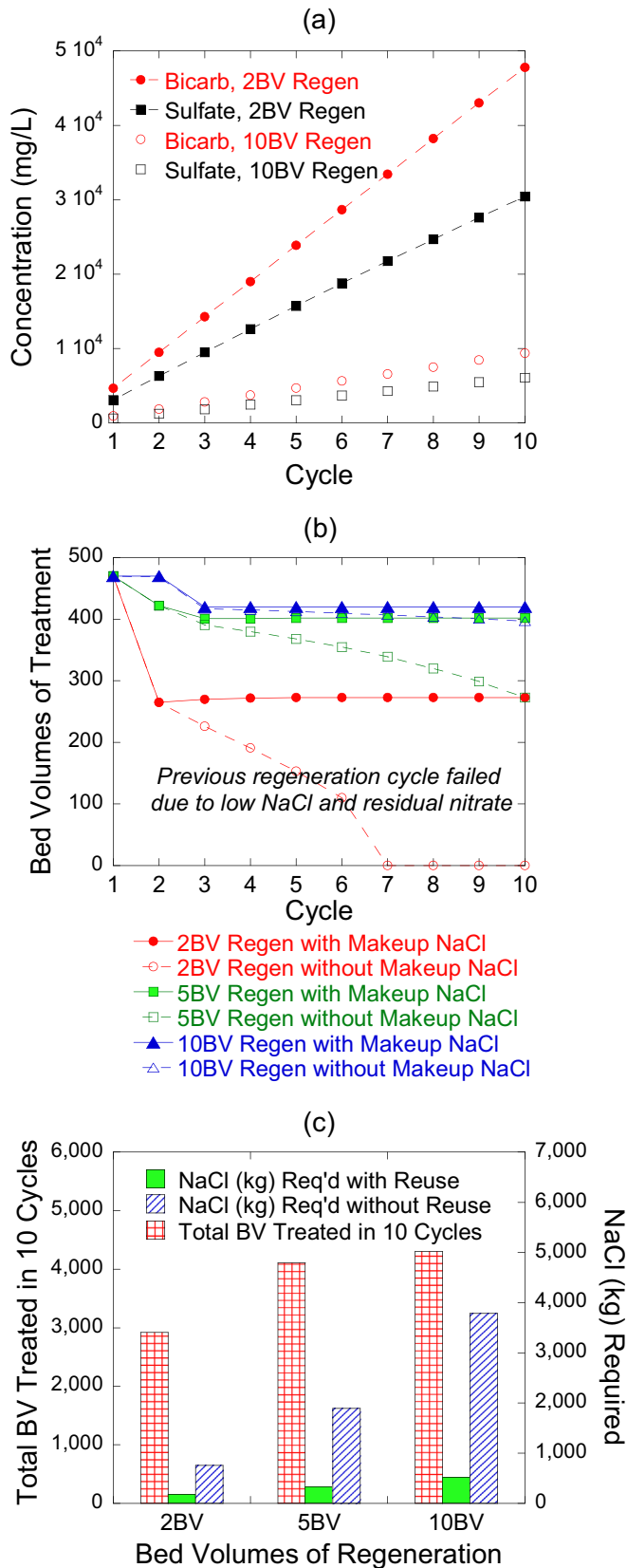


Fig. 4. Model simulation results showing (a) buildup of bicarbonate and sulfate in waste brine when using 2 BV and 10 BV regeneration scenarios, (b) impact of the number of regeneration BVs and NaCl makeup addition on the number of BV before nitrate breakthrough during the next treatment cycle, (c) total bed volumes of groundwater treated over ten treatment/regeneration cycles as a function of the

experiments.

The corresponding BV of feedwater treated before nitrate breakthrough is shown in Fig. 4b (solid lines) for cycles 1 through 10, with 5 BV of regeneration also included. Also shown is the case with no makeup NaCl addition to the denitrified brines (dashed lines). As expected, the BV treated are less for the tenth cycle than the first cycle with makeup NaCl addition, and they increase with BV of resin regeneration. Only 274 BV are treated in the tenth cycle with 2 BV of regeneration compared to 470 BV for the first cycle; breakthrough during the tenth cycle increases to 402 BV and 420 BV, respectively when 5 BV and 10 BV of treated waste brine are used for regeneration, respectively. Despite 10 BV providing complete regeneration, the expected presence of residual nitrate in the treated waste brine (1500 mg/L) degrades the regeneration cycle slightly and results in less nitrate treatment before breakthrough (420 BV versus 470 BV for virgin resin). Results from earlier cycles indicate that the decrease in BV of treatment before nitrate breakthrough occurs mainly between cycles 1 and 2 for all scenarios, and then levels off. This indicates that the 1500 mg/L residual nitrate in the treated waste brine is principally responsible for the lower regeneration efficiency and reduced number of BV for breakthrough in the subsequent cycle rather than the buildup of sulfate or bicarbonate in the waste brine.

Model simulations show that without addition of makeup NaCl to the brine following each regeneration cycle, the salt's concentration will eventually be depleted and no resin regeneration can occur. Not adding makeup NaCl to the brine limited the number of times it could be reused before failing to regenerate the resin, due to the loss in NaCl during each cycle. As shown in Fig. 4b, longer regeneration time extends the number of brine reuse opportunities, with 2 BV being reused five times, while 5 BV and 10 BV can be reused for all ten cycles, but to different levels of success. The increased reuse capability without makeup NaCl between 2 BV and 10 BV is simply a byproduct of the larger initial volume of brine used and the relatively small fraction of total chloride lost from brine during each resin regeneration cycle (3.2% for 10 BV versus 11.5% for 2 BV). Hence, makeup salt addition is very important for all regeneration BV below 10 for up to 10 cycles of treatment/regeneration before brine replacement. It is important to note that makeup NaCl has only a marginal effect when using a 10 BV regeneration, given the small fraction chloride lost each cycle.

The total number of treatment BV after 10 cycles is shown in Fig. 4c (red line boxes), along with NaCl requirements with reuse (solid green). Also shown are the NaCl requirements for IX treatment when brine reuse is not considered (blue diagonal lines). As expected, more regeneration BV allow for more BV of nitrate treatment over 10 cycles, and more regeneration BV incur higher NaCl requirements. However, the increase in NaCl with more regeneration BV is only a small fraction of the NaCl required when reuse is not considered, regardless of the number of regeneration BV used. These results suggest that there is a tradeoff between more treatment and higher NaCl demands with or without brine reuse.

3.3. Packed bed catalytic reactor experiments

Continuous nitrate reduction in both synthetic and real waste brines was evaluated in a packed bed, flow-through catalytic column reactor (see Table S1). A schematic of the experimental set-up is shown in Figure S2. The NaCl and nitrate levels in the synthetic brine mimicked those obtained from a real waste brine sent to our

number of BV used for regeneration, and total mass of NaCl required for resin regeneration with and without brine reuse.

laboratory in 2011. The synthetic brine was amended with elevated concentrations of bicarbonate and sulfate to mimic concentrations produced in model simulations where waste brine was subjected to many cycles of reuse (see previous sections).

For all synthetic brine formulations, the reactor effluent nitrate concentrations were relatively constant, with fluctuations ranging between 40 and 60% of the influent concentration that did not trend with time (see Fig. 5). At least some of the fluctuations are related to the flow rate, i.e., when the flow rate decreases slightly, so does the effluent nitrate concentration (due to a longer retention time). Apparent zero order rate constants were calculated for each day based on the retention time plus influent and effluent measurements; an average value of $13.35 \pm 3.27 \text{ mg NO}_3^- \text{ min}^{-1} \text{ L}^{-1}$ was obtained. The corresponding Pd-mass normalized rate constant was $2.07 \pm 0.26 \text{ mg NO}_3^- \text{ g}_{\text{Pd}}^{-1} \text{ min}^{-1}$. The selectivity for dinitrogen gas ranged between 73 and 87% for the samples tested (see Table S1). We note that the column reactor could have been designed with a longer retention time to achieve a higher level of nitrate reduction, but the intermediate level achieved was targeted to evaluate potential inhibitory effects of sulfate and bicarbonate. Zero order kinetics were assumed based on batch results that showed this behavior when treating elevated nitrate concentrations. The lack of any notable effect of either high concentrations of sulfate or bicarbonate contrasts with results reported previously in completely mixed batch experiments (Choe et al., 2015).

The results of nitrate reduction in the real brine are shown in Fig. 6. The real brine was not recycled and contained the same anions as the synthetic brine plus lesser concentrations of other constituents (ICP analysis showed 11.1 mg/L calcium, 3.14 mg/L magnesium, 2.94 mg/L phosphorous, 0.09 mg/L iron, and 0.014 mg/L manganese). Over the 23-day study period, no change in activity for nitrate reduction was observed, with an average mass-normalized rate constant of $2.24 \pm 0.22 \text{ mg NO}_3^- \text{ g}_{\text{Pd}}^{-1} \text{ min}^{-1}$, and $81 \pm 11\%$ selectivity for the dinitrogen product (see Table S1). Thus,

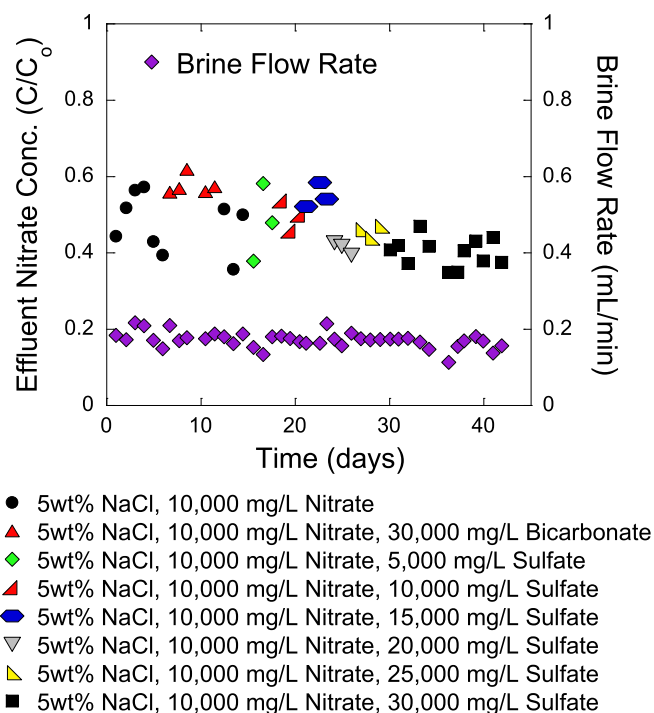


Fig. 5. Nitrate reduction in synthetic brines by treatment in a continuous flow fix-bed catalytic reactor for 45 d with 0.5 wt% Pd–0.05 wt% In/C catalyst. NaCl concentration was fixed at 5 wt% and nitrate at 10,000 mg/L.

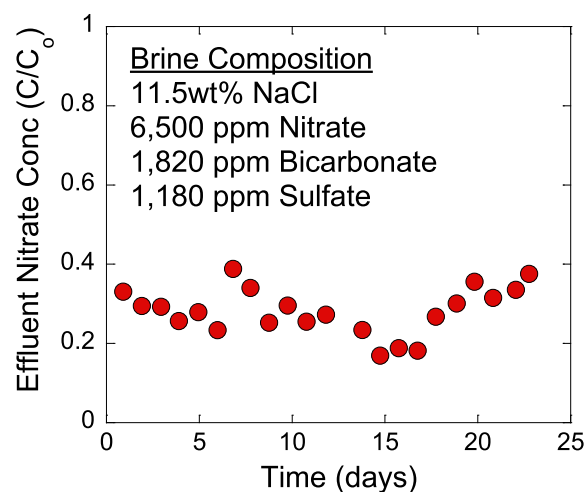


Fig. 6. Nitrate reduction in a real waste IX brine from a California utility in a continuous flow fix-bed catalytic reactor for 23 d with 0.5 wt% Pd–0.05 wt% In/C catalyst.

results with the real waste brine are consistent with experiments conducted in the synthetic brines.

The same catalyst packed into the column reactor (0.5% Pd–0.05%In/AC) was also tested in a batch reactor, where rapid mixing and excess hydrogen addition minimize mass transfer limitations. Under these conditions, an apparent zero order rate constant of $57.32 \pm 6.31 \text{ mg NO}_3^- \text{ g}_{\text{Pd}}^{-1} \text{ min}^{-1}$ was obtained, approximately 25 times greater than the corresponding rate constant obtained from data collected in the continuous-flow column reactor experiments. Based on the flow rates of hydrogen gas (6.8 mL/min) and brine (10,000 mg/L nitrate at 0.2 mL/min) in the column reactor, the stoichiometric ratio of hydrogen to nitrate-N entering the column was 8.6H:1N, a value more than three times the minimum stoichiometric ratio required for nitrate reduction to dinitrogen gas. Since H_2 was present in excess, the low column reaction rates indicate hydrogen mass transfer is likely limiting nitrate reduction. This is not surprising given the low aqueous solubility of hydrogen (0.8 mM at ambient temperature in equilibrium with 1 atm P_{H_2}), which at saturation provides only 0.4–1% of the stoichiometric hydrogen needs for reduction of aqueous nitrate in the waste brine (80 mM–160 mM). The H_2 mass transfer limitations may also explain why no apparent loss in nitrate reduction activity was observed in the presence of elevated bicarbonate and sulfate in the packed bed reactor experiments. Although these ions might lower the intrinsic rate of nitrate reduction on the catalyst surface (Choe et al., 2015), this effect would be masked by the fact that the overall rate is limited by the much lower rate of H_2 mass transfer in the column reactor, rather than the surface reactions in the well-mixed batch system.

Although H_2 mass transfer limitations appear to affect apparent nitrate reduction rates, the results suggest that elevated sulfate and bicarbonate in the synthetic brine, and the many constituents present in real brine, do not progressively degrade catalyst performance over time. However, further experiments are required to confirm these results, as longer times need to be evaluated to ensure that any progressive losses are not being masked by H_2 mass transfer limitations.

Pintar et al. (2001) tested Pd–Cu/ γ - Al_2O_3 in a column system and experienced a loss in catalytic activity after many cycles. They ruled out copper leaching as an explanation, and instead postulated that the loss in activity occurred as a result of the build-up of chloride in their brine, or hydroxide ions as nitrate reduction proceeds. Prior work (Choe et al., 2015) indicates high chloride levels

may lower Pd–In/C activity, but chloride levels are maintained constant in the hybrid system proposed here and pH is buffered by CO₂ addition to the feed gas.

3.4. Hybrid IX-catalyst system considerations

The IX and catalyst results described above suggest that the choice of brine regeneration BV affects the economics and environmental impact of the hybrid system. It affects not only total salt use and BV treated, but also the amount of catalyst required in the reactor design. The effects of the number of BV used for regeneration on the treatment of one billion gallons of water with the hybrid system was simulated (Fig. 7) and compared to simulations for conventional IX treatment without brine reuse. Calculations were based on multi-cycle model simulations and IX system information from the Vale, OR demonstration plant study (0.5 MGD), which had a single-pass IX configuration that treated water at 540 gpm (Wang et al., 2011). The IX bed volume size at the Vale, OR site is 5266 L (1391 gal), and the cost of NaCl was \$0.076/lb (Wang et al., 2011), and waste brines were disposed and replaced with fresh brine after every 10 treatment/regeneration cycles. Catalyst requirements for denitrifying the simulated waste brine to a level of 1500 mg/L NO₃⁻ were estimated using the zero-order rate constants from the fixed-bed reactor (2.24 mgNO₃⁻gPd⁻¹min⁻¹) and sequencing batch reactor (57 mgNO₃⁻gPd⁻¹min⁻¹), which both used the same 0.5 wt% Pd–0.05 wt%In/C catalyst. The catalyst reactors were sized according to the need to treat the generated waste brine volume before nitrate breakthrough from the IX reactor occurs. For example, 2 BV of waste brine required a flow rate through the catalyst reactor of 15 L/min in order to complete waste brine treatment in 11.7 h, the time corresponding to breakthrough at 274

BV of IX run time. The price of palladium was assumed to be \$800/oz, taken from a one year average between May 6, 2014 and May 6, 2015 (Kitco Metals, 2015). The price of In is small compared to Pd (ca. \$21/oz (USGS, 2014)) and was neglected.

The cost of NaCl with and without brine reuse with respect to different regeneration volume is shown in Fig. 7a. When brine is not reused, a 10 BV regeneration strategy requires more than three times as much NaCl as a 2 BV regeneration strategy (2591 ton vs 8793 ton). Alternately, when brine is reused, the quantities are much lower and the difference is much smaller (612 ton vs 1204 ton). Thus, by switching from 2 BV regen without brine reuse to 10 BV regen with brine reuse, the plant operator would see a 53% reduction in total NaCl required and 150% increase in treatment length each cycle (274 BV to 420 BV). The efficiency of NaCl use as a ratio of BV of water treated per kilogram of NaCl used is shown in Fig. 7b. The results show a clear benefit to brine reuse (solid red), which leads to an increase in the volume of water treated per unit mass of NaCl used by a factor ranging between 4.2 and 7.3. The results also show a clear benefit in reduced salt costs when regenerating resins with only 2 BV compared to 5 or 10 BV.

The average nitrate concentration in the waste brine prior to catalytic treatment (diagonal red lines), as well as the total mass of nitrate removed from the waste brine to treat 1B gallons from the waste brine to treat 1B gallons (solid blue), are shown in Fig. 7c. Nitrate concentration in the waste brine, as well as volume of waste brine to be treated and time available for treatment, are all impacted by the volume of brine used for regeneration. Together, these variables impact one of the most expensive parts of the hybrid system capital costs, which is palladium metal for the catalyst reactor. These estimated costs are shown in Fig. 7d for 2, 5, and 10 BV of regeneration. A 2 BV regeneration produces a smaller volume of waste brine with a

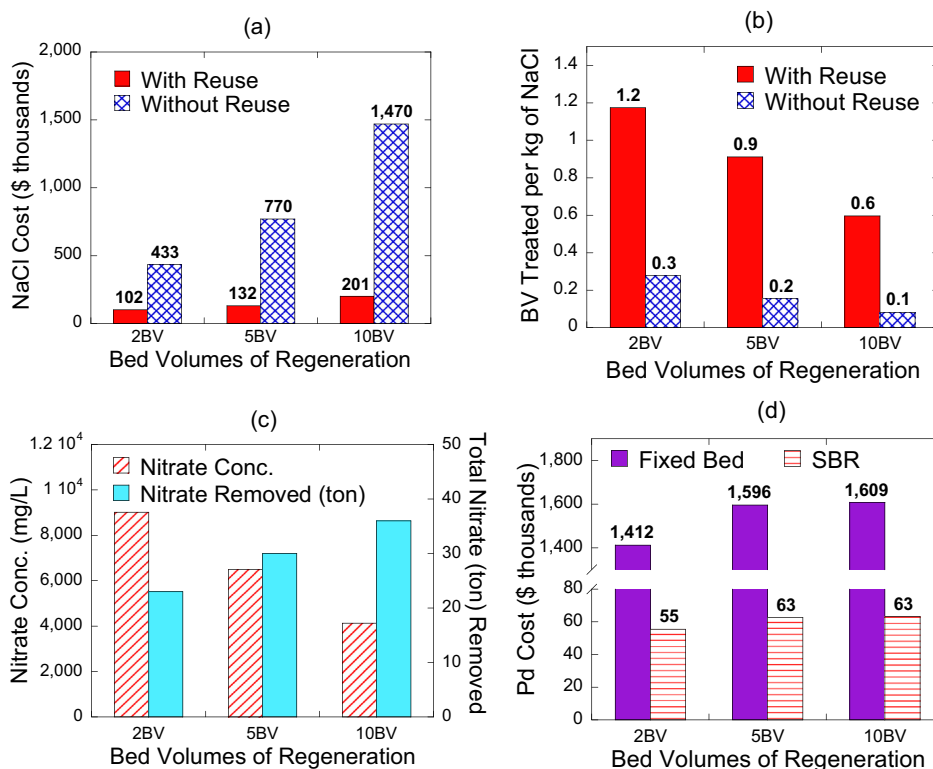


Fig. 7. Analysis of hybrid system requirements to treat one billion gallons of water using different BV for regeneration between each nitrate treatment cycle with and without brine reuse. (a) Cost of NaCl required. (b) Efficiency of NaCl use – defined as BV water treated per kilogram of NaCl required. (c) Nitrate concentration in the waste brine before catalytic reduction and total mass of nitrate removed from waste brine when treating 1 billion gallons of water. Higher concentrations require more reduction to reach the desired 1500 mg/L level, which impacts the catalyst required. (d) Catalyst cost as a function of regeneration BV for fixed bed and sequencing batch reactor configurations.

higher nitrate concentration compared to a 5 or 10 BV regeneration. Treating a smaller volume of waste brine requires a smaller catalyst reactor (and hence less Pd mass), while a higher nitrate concentration requires more catalyst. The simulation indicates the former factor dominates overall Pd metal costs, so Pd metal costs tend to decrease with decreasing BV used for resin regeneration.

Catalyst costs are also influenced directly by catalyst activity level. The anticipated costs of Pd required to reduce nitrate in the waste brine to 1500 mg/L nitrate using the mass normalized zero order rate constant for both the fixed bed system and sequencing batch reactor are also shown in Fig. 7d. As discussed above, catalyst activity in the fixed bed is relatively low compared to the batch system due to hydrogen mass transfer limitations, resulting in prohibitively high palladium costs (solid purple), i.e., costs that far exceed the savings associated with reduced salt usage. However, costs for Pd are much lower when the catalyst activity from the SBR is used to estimate Pd mass requirements (horizontal red lines). Considering the SBR activity, a 2 BV regeneration leads to nitrate concentrations around 9000 mg/L and an anticipated reactor palladium cost of \$55.5k; whereas 10 BV regeneration leads to nitrate concentrations around 4100 mg/L and a palladium cost of about \$63.2k. These capital costs are 50% or lower than the savings resulting from reduced salt requirements when treating 1 billion gallons of sourcewater, and highlight the promise of the hybrid system. Also important to note is that the savings from brine reuse would increase, while catalyst costs would remain unchanged, if a larger volume of sourcewater was considered (i.e., more than 1 billion gallons) or waste brine were reused for more than ten treatment/regeneration cycles before replacing with fresh brine. The actual volume treated with the same catalyst depends on catalyst longevity, and results from this study suggest the catalyst is stable over at least 45 days of continuous treatment.

Activity differences between the batch and fixed bed reactors, and their resulting impact on catalyst costs, highlight limitations of the latter. Improved fixed-bed reactor design is crucial in order to minimize hydrogen mass transfer limitations. This would decrease both the amount of excess hydrogen and the amount of Pd metal required. Minimizing both hydrogen and Pd usage are critical for reducing costs and the environmental impact of the hybrid system (Choe et al., 2015).

Several factors associated with the hybrid system may necessitate re-thinking IX operations to maximize benefits. Longer regeneration times increase the number of BV treated during each cycle and decrease the nitrate concentration reduction required via catalytic treatment. However, longer regeneration times also increase the salt required for regeneration and the amount of Pd metal needed for nitrate reduction. Hence, a 2 BV regeneration length results in the lowest IX and catalytic treatment costs in the hybrid system compared to 5 and 10 BV. These results may change if brines can be reused more than the assumed 10 treatment/regeneration cycles before disposing and replacing with a fresh regenerant brine. Other salt-related factors such as unit price, delivery frequency, delivery size, plant storage capacity and use rate are important in determining plant operations and may constrain the hybrid system. Larger regeneration brine BV would also require larger volume storage tanks with associated higher capital costs.

Near-complete nitrate removal from the waste brine would be ideal, particularly given the results discussed above. Regardless of IX configuration and regeneration strategy, the nitrate level remaining in the waste brine has an impact on future treatment length. Research focused on biological denitrification of waste brine achieved near-complete removal of nitrate in the waste brine (Clifford and Liu, 1993; Lehman et al., 2008), which undoubtedly aided in the hybrid process's successful results. Near-complete nitrate removal via catalysis is achievable; however, balancing the

requirements to do so and the associated life cycle impacts are critical to developing a hybrid system that is a more sustainable option compared to a conventional IX system. For example, Choe et al. (2015) showed 87–95% nitrate reduction in a packed bed reactor, but the LCA results determined the packed-bed hybrid-IX design had higher environmental impacts than the conventional IX design. Catalytic reactor optimization and iterative Life Cycle Assessment will both be important in future work on the hybrid system.

4. Conclusions

A hybrid ion exchange-catalytic process for nitrate treatment leveraging brine reuse shows promise for reducing economic costs and environmental burdens associated with large salt inputs and waste brine disposal. Key conclusions include:

- Integrated models for hybrid IX/catalyst treatment systems can be used to examine critical factors influencing the cost, performance, and environmental impact.
- Model simulations indicate that non-target ions like sulfate and bicarbonate will buildup in waste brines over repeated cycles of reuse, but this buildup will not negatively impact IX performance or lead to permanent deactivation of the Pd metal catalyst.
- Adding makeup salt to treated waste brines is necessary to maintain long treatment cycle run times between regeneration.
- Salt costs and waste brine volumes can be decreased by up to 80% with the hybrid system.
- Achieving high catalyst activity and stability is critical for reducing the cost of the hybrid system.
- Reactor design plays an important role in the effectiveness of hydrogen mass transfer.
- Tradeoffs between regeneration length, treatment time, and salt warrant reevaluation in a hybrid system compared to a conventional system.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.03.054>.

References

- Al Bahri, M., Calvo, L., Gilarranz, M.A., Rodriguez, J.J., Epron, F., 2013. Activated carbon supported metal catalysts for reduction of nitrate in water with high selectivity towards N₂. *Appl. Catal. B Environ.* 138–139, 141–148. <http://dx.doi.org/10.1016/j.apcatb.2013.02.048>.
- Barrabés, N., Sá, J., 2011. Catalytic nitrate removal from water, past, present and future perspectives. *Appl. Catal. B Environ.* 104, 1–5. <http://dx.doi.org/10.1016/j.apcatb.2011.03.011>.

- Boari, G., Liberti, L., Merli, C., Passino, R., 1974. Study of the SO₄²⁻/Cl⁻ exchange on a weak anion resin. *Desalination* 145–166.
- Calgon Corporation, 2014. Strong Base Anion Resin Regeneration Efficiency with Catalytically Treated Recycled Spent Brine: Laboratory Test Procedure, Revision B.
- Cantor, K.P., 1997. Drinking water and cancer. *Cancer Causes Control* 8, 292–308. <http://dx.doi.org/10.1023/A:1018444902486>.
- Chaplin, B.P., Roundy, E., Guy, K.A., Shapley, J.R., Werth, C.J., 2006. Effects of natural water ions and humic acid on catalytic nitrate reduction kinetics using an alumina supported Pd–Cu catalyst. *Environ. Sci. Technol.* 40, 3075–3081. <http://dx.doi.org/10.1021/es0525298>.
- Chaplin, B.P., Shapley, J.R., Werth, C.J., 2007. Regeneration of sulfur-fouled bimetallic Pd-based catalysts. *Environ. Sci. Technol.* 41, 5491–5497. <http://dx.doi.org/10.1021/es0704333>.
- Chiavola, A., Baciocchi, R., D'Amato, E., 2014. Application of a two-site ideal model for the prediction of As–SO₄–Cl ion exchange equilibria. *Water. Air. Soil Pollut.* 225. <http://dx.doi.org/10.1007/s11270-013-1810-z>.
- Choe, J.K., Bergquist, A.M., Jeong, S., Guest, J.S., Werth, C.J., Strathmann, T.J., 2015. Performance and life cycle environmental benefits of recycling spent ion exchange brines by catalytic treatment of nitrate. *Water Res.* 80, 267–280. <http://dx.doi.org/10.1016/j.watres.2015.05.007>.
- Clifford, D., Liu, X., 1993. Biological denitrification of spent regenerant brine using a sequencing batch reactor. *Water Res.* 27, 1477–1484. [http://dx.doi.org/10.1016/0043-1354\(93\)90028-G](http://dx.doi.org/10.1016/0043-1354(93)90028-G).
- Crews, T., Peoples, M., 2004. Legume versus fertilizer sources of nitrogen: ecological tradeoffs and human needs. *Agric. Ecosyst. Environ.* 102, 279–297. <http://dx.doi.org/10.1016/j.agee.2003.09.018>.
- European Union, 2000. Report from the Commission Implementation of Council Directive 91/676/EEC Concerning the Protection of Waters against Pollution Caused by Nitrates from Agricultural Sources.
- Fernandez, A., Rendueles, M., Rodrigues, A., Diaz, M., 1994. Co-ion behavior at high concentration cationic ion exchange. *Ind. Eng. Chem. Res.* 33, 2789–2794.
- Fewtrell, L., 2004. Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion. *Environ. Health Perspect.* 112, 1371–1374. <http://dx.doi.org/10.1289/ehp.7216>.
- Flodman, H.R., Dvorak, B.I., 2012. Brine Reuse in ion-exchange softening: salt discharge, hardness leakage, and capacity tradeoffs. *Water Environ. Res.* 84, 535–543. <http://dx.doi.org/10.2175/106143012X13373550427354>.
- Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. *Science* 320, 889–892. <http://dx.doi.org/10.1126/science.1136674>.
- Gregor, H.P., Belle, J., Marcus, R.A., 1955. Studies on ion-exchange resins. XIII. Selectivity coefficients of quaternary base anion-exchange resins toward univalent anions. *J. Am. Chem. Soc.* 77, 2713–2719.
- Guter, G., 1995. Nitrate removal from contaminated groundwater by anion exchange. In: Sengupta, A. (Ed.), *Ion Exchange Technology: Advances in Pollution Control*, pp. 61–113.
- Hekmatzadeh, A.A., Karimi-Jashani, A., Talebbeydokhti, N., Kløve, B., 2012. Modeling of nitrate removal for ion exchange resin in batch and fixed bed experiments. *Desalination* 284, 22–31. <http://dx.doi.org/10.1016/j.desal.2011.08.033>.
- Kapoor, A., Viraraghavan, T., 1997. Nitrate removal from drinking water—review. *J. Environ. Eng.* 123, 371–380. [http://dx.doi.org/10.1061/\(ASCE\)0733-9372\(1997\)123:4\(371\)](http://dx.doi.org/10.1061/(ASCE)0733-9372(1997)123:4(371)).
- Kim, J., Benjamin, M.M., 2004. Modeling a novel ion exchange process for arsenic and nitrate removal. *Water Res.* 38, 2053–2062. <http://dx.doi.org/10.1016/j.watres.2004.01.012>.
- Kitco Metals, 2015. 24 Hours spot chart of palladium prices, 1 year price chart.
- Lee, D.H.K., 1970. Nitrates, nitrites, and methemoglobinemia. *Environ. Res.* 3, 484–511. [http://dx.doi.org/10.1016/0013-9351\(70\)90042-3](http://dx.doi.org/10.1016/0013-9351(70)90042-3).
- Lehman, S.G., Badruzzaman, M., Adham, S., Roberts, D.J., Clifford, D.A., 2008. Perchlorate and nitrate treatment by ion exchange integrated with biological brine treatment. *Water Res.* 42, 969–976. <http://dx.doi.org/10.1016/j.watres.2007.09.011>.
- Marchesini, F.A., Irusta, S., Querini, C., Miró, E., 2008. Spectroscopic and catalytic characterization of Pd–In and Pt–In supported on Al₂O₃ and SiO₂, active catalysts for nitrate hydrogeneration. *Appl. Catal. Gen.* 348, 60–70. <http://dx.doi.org/10.1016/j.apcata.2008.06.026>.
- Morgan, J.D., Napper, D.H., Warr, G.G., 1995. Thermodynamics of ion exchange selectivity at interfaces. *J. Phys. Chem.* 99, 9458–9465. <http://dx.doi.org/10.1021/j100023a024>.
- Pintar, A., Batista, J., 2006. Improvement of an integrated ion-exchange/catalytic process for nitrate removal by introducing a two-stage denitrification step. *Appl. Catal. B Environ.* 63, 150–159. <http://dx.doi.org/10.1016/j.apcatb.2005.10.006>.
- Pintar, A., Batista, J., Levec, J., 2001. Catalytic denitrification: direct and indirect removal of nitrates from potable water. *Catal. Today* 66, 503–510.
- Sadeq, M., Moe, C.L., Attarassi, B., Cherkaoui, I., ElAouad, R., Idrissi, L., 2008. Drinking water nitrate and prevalence of methemoglobinemia among infants and children aged 1–7 years in Moroccan areas. *Int. J. Hyg. Environ. Health* 211, 546–554. <http://dx.doi.org/10.1016/j.ijheh.2007.09.009>.
- Snyder, C.S., Bruulsema, T.W., Jensen, T.L., Fixen, P.E., 2009. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. *Agric. Ecosyst. Environ.* 133, 247–266. <http://dx.doi.org/10.1016/j.agee.2009.04.021>.
- Soares, O.S.G.P., Órfão, J.J.M., Ruiz-Martínez, J., Silvestre-Albero, J., Sepúlveda-Escribano, A., Pereira, M.F.R., 2010. Pd–Cu/AC and Pt–Cu/AC catalysts for nitrate reduction with hydrogen: influence of calcination and reduction temperatures. *Chem. Eng. J.* 165, 78–88. <http://dx.doi.org/10.1016/j.cej.2010.08.065>.
- US EPA, O., 2016. Drinking Water Contaminants – Standards and Regulations [WWW Document]. <http://www.epa.gov/dwstandardsregulations> (accessed 01.09.16).
- USGS, 2014. *USGS Mineral Commodity Summary. January 2015.*
- van der Hoek, J.P., Klapwijk, A., 1989. Reduction of regeneration salt requirement and waste disposal in an ion exchange process for nitrate removal from ground water. *Waste Manag.* 9, 203–210. [http://dx.doi.org/10.1016/0956-053X\(89\)90404-2](http://dx.doi.org/10.1016/0956-053X(89)90404-2).
- van der Hoek, J.P., van der Ven, P.J.M., Klapwijk, A., 1988. Combined ion exchange/biological denitrification for nitrate removal from ground water under different process conditions. *Water Res.* 22, 679–684. [http://dx.doi.org/10.1016/0043-1354\(88\)90178-9](http://dx.doi.org/10.1016/0043-1354(88)90178-9).
- Walter, G., 1951. Survey of literature relating to infant methemoglobinemia due to nitrate-contaminated water. *Am. J. Public Health* 41, 986–996.
- Wang, L., Chen, A.S., Wang, A., Condit, W.E., Battelle, C., Sorg, T.J., Supply, W., 2011. Arsenic and Nitrate Removal from Drinking Water by Ion Exchange US EPA Demonstration Project at Vale (OR Final Performance Evaluation Report).
- Ward, M.H., Brender, J.D., 2011. Drinking water nitrate and health. *Environ. Health* 167–178.
- Yang, T., Doudrick, K., Westerhoff, P., 2013. Photocatalytic reduction of nitrate using titanium dioxide for regeneration of ion exchange brine. *Water Res.* 47, 1299–1307. <http://dx.doi.org/10.1016/j.watres.2012.11.047>.