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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.

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 ($NO_3^- + 2.5H_2 \rightarrow 0.5N_2 + OH^- + 2H_2O$). 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 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.

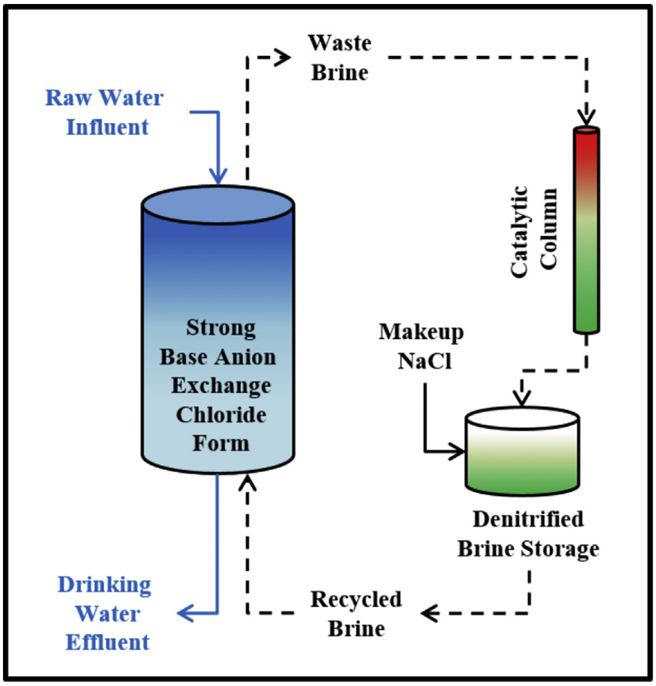

Fig. 1. Flow diagram of the hybrid ion exchange-catalyst treatment system.

2. Methods

2.1. Materials

Reagent-grade sodium salts (≥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 MΩ-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