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Performance and life cycle environmental benefits of recycling spent ion exchange brines by catalytic treatment of nitrate

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ABSTRACT

Salt used to make brines for regeneration of ion exchange (IX) resins is the dominant economic and environmental liability of IX treatment systems for nitrate-contaminated drinking water sources. To reduce salt usage, the applicability and environmental benefits of using a catalytic reduction technology to treat nitrate in spent IX brines and enable their reuse for IX resin regeneration were evaluated. Hybrid IX/catalyst systems were designed and life cycle assessment of process consumables are used to set performance targets for the catalyst reactor. Nitrate reduction was measured in a typical spent brine (i.e., 5000 mg/L NO_3^- and 70,000 mg/L NaCl) using bimetallic Pd–In hydrogenation catalysts with variable Pd (0.2–2.5 wt%) and In (0.0125–0.25 wt%) loadings on pelletized activated carbon support (Pd–In/C). The highest activity of 50 $mgNO_3^-/(min - g_{Pd})$ was obtained with a 0.5 wt%Pd–0.1 wt%In/C catalyst. Catalyst longevity was demonstrated by observing no decrease in catalyst activity over more than 60 days in a packed-bed reactor. Based on catalyst activity measured in batch and packed-bed reactors, environmental impacts of hybrid IX/catalyst systems were evaluated for both sequencing-batch and continuous-flow packed-bed reactor designs and environmental impacts of the sequencing-batch hybrid system were found to be 38–81% of those of conventional IX. Major environmental impact contributors other than salt consumption include Pd metal, hydrogen (electron donor), and carbon dioxide (pH buffer). Sensitivity of environmental impacts of the sequencing-batch hybrid reactor system to sulfate and bicarbonate anions indicate the hybrid system is more sustainable than conventional IX when influent water contains <80 mg/L sulfate (at any bicarbonate level up to 100 mg/L) or <20 mg/L bicarbonate (at any sulfate level up to 100 mg/L) assuming 15 brine reuse cycles. The study showed that hybrid IX/catalyst reactor

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systems have potential to reduce resource consumption and improve environmental impacts associated with treating nitrate-contaminated water sources.

1. Introduction

Nitrate (NO_3^-) is the most common groundwater contaminant in the world (Spalding and Exner, 1993). Consumption of high levels of nitrate can adversely affect human health, e.g., methemoglobinemia in infants (a.k.a. blue baby syndrome) (Sadeq et al., 2008). Nitrate ingestion can also promote physiological production of potentially carcinogenic nitrosamines (Magee, 1982). Nitrate occurrence in drinking water sources results primarily from agricultural activities (fertilizer and livestock manure) (Carle et al., 2004). In the U.S., up to 50% of surveyed well water had nitrate levels exceeding the USEPA maximum contamination level (MCL) of 44 mg/L as NO_3^- (10 mg/L as N) (Carle et al., 2004; U.S. EPA, 2002). European surveys also showed that 14.4% of groundwater monitoring stations exceed the recommended nitrate level (European Commission, 2013; World Health Organization, 2008). The problem is expected to grow worldwide due to continuously increasing fertilizer use to meet the food production demands of a growing population (Dobermann and Cassman, 2005).

Treating nitrate-contaminated water in an economically and environmentally sustainable manner is a challenge. In the U.S., the most common nitrate treatment technology is ion exchange (IX) (Clifford and Liu, 1993a; Kapoor and Viraraghavan, 1997). While effective, IX only separates the contaminant from water without destroying it. When the IX resin's capacity is exhausted, resin is regenerated by flushing with a high salt-content brine (Kapoor and Viraraghavan, 1997). This produces a nitrate-contaminated waste brine stream. The disposal (and potential treatment) of waste brine and cost of salt for preparing fresh brine are the two primary drawbacks of conventional IX systems (Kapoor and Viraraghavan, 1997). For example, approximately 1.4 tons of salt per day is used for IX resin regeneration at a small treatment plant (0.77 MGD) in Vale, Oregon, and the cost of salt represents 77% of the total operation and maintenance cost of the system (Wang et al., 2011). Beyond costs, waste brine disposal methods (e.g., discharge to sewer or surface water) raise environmental concerns and local restrictions are limiting the practice, especially for inland treatment facilities.

Developing effective methods for treating waste brines to enable reuse is economically and environmentally beneficial. Studies demonstrated biological denitrification in high salt solutions, enabling reuse of waste brines for resin regeneration (Lehman et al., 2008). Clifford and colleagues demonstrated heterotrophic biological denitrification in a bench-scale sequencing batch reactor, allowing reuse of waste brine for at least 15 cycles of IX resin regeneration and reducing brine waste volumes and salt requirements by 90% and 50%, respectively (Clifford and Liu, 1993a, 1993b). However, biological treatment of waste brines presents its own challenges, including slow start up times that make intermittent treatment applications problematic, and the unpredictability of the bacterial culture in the presence of non-target water constituents (Lehman et al., 2008).

Recently, the application of catalytic technologies for nitrate treatment has been investigated, using hydrogen as an electron donor in combination with supported palladium-based catalysts (Chaplin et al., 2006; Pintar et al., 2001; Prüsse and Vorlop, 2001; Salazar et al., 2012; Zhang et al., 2013). Our recent study demonstrated that hydrogen has lower life cycle environmental impacts than acetate and other organic donors used for biological reduction of contaminants (Choe et al., 2013). Additional potential advantages of catalytic reduction over biological denitrification include lower maintenance requirements, automated operation at drinking water treatment facilities (especially an advantage for a small water treatment plants), and faster start up times allowing intermittent brine treatment. Although previous studies have shown that Pd-based catalysts efficiently reduce nitrate in freshwater and in low saline water (~1.8 g/L NaCl) (Chaplin et al., 2007, 2006; Pintar et al., 2001), their application for brine treatment requires efficient activity in the presence of >40 g/L NaCl. Our recent work focusing on treating perchlorate in waste IX brines revealed that nitrate co-contaminants can also be reduced by Pd-based bimetallic catalysts (Liu et al., 2013). While direct treatment of nitrate contaminated water using catalytic reduction technology is also promising, acceptance of new technologies for direct treatment purposes is limited, in part, by concerns about robustness of the unproved technology. Ion exchange, on the other hand, is an established technology, so application of catalytic treatment for off-stream brine management will be more acceptable to public utility clients in the near term. In this study, we apply for the first time palladium–indium catalysts on activated carbon supports (Pd–In/C; granular and powdered support materials) to reduce nitrate in high salt content brine solutions, thereby enabling reuse of the waste brines. Complementary batch and continuous-flow packed-bed reactor experiments are used to identify optimal bimetal formulations and demonstrate catalyst longevity in brine matrices.

The goal of this contribution is to elucidate the environmental sustainability of catalytic reduction technologies for treating nitrate in spent IX brines to enable their reuse for IX resin regeneration (as compared to IX without brine regeneration), and set performance targets (including catalyst activity and longevity) for this developing technology. While the benefits of reducing salt consumption in IX systems have been discussed in the literature, no study has systematically evaluated and compared the environmental impacts of brine treatment technologies (e.g., catalyst metals and electron donors for catalytic reduction) with conventional IX. Specific