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Photocatalytic reduction of nitrate using titanium dioxide for regeneration of ion exchange brine

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Abstract

Nitrate is often removed from groundwater by ion exchange (IX) before its use as drinking water. Accumulation of nitrate in IX brine reduces the efficiency of IX regeneration and the useful life of the regeneration brine. For the first time, we present a strategy to photocatalytically reduce nitrate in IX brine, thereby extending the use of the brine. Titanium dioxide (Evonik P90), acting as photocatalyst, reduced nitrate effectively in both synthetic brines and sulfate-removed IX brine when formic acid (FA) was used as the hole scavenger (i.e., electron donor) and the initial FA to nitrate molar ratio (IFNR) was 5.6. Increasing the NaCl level in the synthetic brine slowed the nitrate reduction rate without affecting byproduct selectivity of ammonium and gaseous N species (e.g., N₂, N₂O). In a non-modified IX brine, nitrate removal was greatly inhibited owing to the presence of sulfate, which competed with nitrate for active surface sites on P90 and induced aggregation of P90 nanoparticles. After removing sulfate through barium sulfate precipitation, nitrate was effectively reduced; approximately 3.6×10^{24} photons were required to reduce each mole of nitrate to 83% N Gases and 17% NH₄⁺. To make optimum use of FA and control the residual FA level in treated brine, the IFNR was varied. High IFNRs (e.g., 4, 5.6) were found to be more efficient for nitrate reduction but left higher residual FA in brine. IX column tests were performed to investigate the impact of residual FA for brine reuse. The residual FA in the brine did not significantly affect the nitrate removal capacity of IX resins, and formate contamination of treated water could be eliminated by rinsing with one bed volume of fresh brine.

Keywords

Photocatalytic denitrification; Ion exchange brine; Nitrate; Titanium dioxide; Formic acid

1. Introduction

Nitrate contamination of groundwater, mainly resulting from intensive agricultural activities using nitrogen fertilizers, has become a widespread problem throughout the world (Singh

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and Sekhon, 1979; Strebel et al., 1989; Zhang et al., 1996; Burow et al., 2010). High levels of nitrate NO_3^- in groundwater pose a great risk to human health when groundwater is used as a supply of drinking water. Intake of excess nitrate may cause infant methemoglobinemia (i.e., blue baby syndrome) and increase the risk for gastric cancer and other diseases (Mirvish, 1985). To limit the health impact of nitrate, 10 mg-N/L as NO_3^- was recommended by the United States Environmental Protection Agency (U.S. EPA) as the maximum contaminant level (MCL) in drinking water.

Among available nitrate removal technologies, ion exchange (IX) is used frequently in drinking water applications because of its effectiveness, low cost, and operational simplicity in producing reliable drinking water. The ion exchange media used for nitrate removal include non-selective resins and nitrate-to-sulfate selective resins (e.g., Purolite A-520E). But the IX process generates large volumes of waste brine containing nitrate, chloride, sulfate, and other oxyanions (McAdam and Judd, 2008). Disposal of IX brine has become a costly challenge from economic and environmental standpoints. Various other technologies aim to convert nitrate into harmless nitrogen gas (N_2); these include biological denitrification (McAdam and Judd, 2006; Karanasios et al., 2010; Soares, 2000), catalytic reduction (Pintar et al., 2004; Gasparovicova and Kralik, 2000), and electrochemical reduction (Li et al., 2009; Inam Ul and Tariq, 2010). Biological denitrification has not been widely adopted for drinking water applications because of its high capital costs, lengthy lead times for biofilm establishment, and post-treatment requirements for the removal of biomass and dissolved organics. Other reduction technologies also have serious disadvantages (e.g., poor selectivity to nitrogen, hydrogen availability, energy intensiveness) that limit their practical applications and will not soon replace IX in drinking water treatment.

Integration of IX with brine denitrification processes is promising because the combination could reduce IX costs for brine disposal and minimize problems associated with each denitrification approach for drinking water treatment. Biological denitrification to remove nitrate from IX brine has been studied extensively (McAdam and Judd, 2008; Vanderhoek et al., 1988; Bae et al., 2002; Cang et al., 2004; Lehman et al., 2008; Van Ginkel et al., 2008; McAdam et al., 2010; Clifford and Liu, 1993). By treating IX brine instead of the drinking water itself, quality concerns, such as bacterial, organic matter, and hazardous by-product contamination caused by bio-processes, are minimized. However, IX systems are often operated intermittently (i.e., a few times per month to meet peak water demands), which makes inclusion of biological processes challenging. Electrochemical reduction can selectively treat nitrate in high salt solutions, but it may produce Cl_2 , which can damage the structure of IX resins (Paidar et al., 2004; Dortsiou et al., 2009). An attempt to reduce nitrate using zerovalent iron nanoparticles showed that the nitrate removal rate was greatly slowed in 6% NaCl solution, and ammonium was the predominant by-product accounting for 62% of the reduced nitrate (Xiong et al., 2009). Therefore, a need exists to develop an effective nitrate reduction technology for IX brine treatment that overcomes these disadvantages.

Photocatalytic reduction of nitrate over semiconductor materials is a relatively new technique, but it has shown high efficacy and great potential for nitrate removal. Titanium dioxide (TiO_2) is the most frequently studied photocatalyst; such studies include applications using metal-modified TiO_2 to improve the kinetics and selectivity away from

undesirable aqueous by-products (NO_2^- , NH_4^+) (Kudo et al., 1987; Ranjit and Viswanathan, 1997; Kominami et al., 2001; Gao et al., 2004; Zhang et al., 2005; Sa et al., 2009; Hirayama et al., 2012; Anderson, 2012; Rengaraj and Li, 2007; Gao et al., 2006; Kominami et al., 2005; Li et al., 2010). When irradiated with incident light whose energy is larger than that of the band gap of the semiconductor, electrons are excited to the conduction band e_{cb}^- and positive holes form in the valence band h_{vb}^+ . The electrons and holes generated can be utilized for reduction and oxidation, respectively. However, the photogenerated electron-hole pairs can recombine within a few nanoseconds (Rothenberger et al., 1985; Serpone et al., 1995); this can be overcome by adding a hole scavenger (i.e., electron donor) to trap the holes, leaving the photogenerated electrons available for nitrate reduction. Common hole scavengers such as methanol (Mori et al., 1999), ethanol (Hirayama et al., 2012), oxalic acid (Kominami et al., 2001; Gao et al., 2004), acetic acid (Sa et al., 2009), formic acid (FA), and sodium formate (Zhang et al., 2005; Sa et al., 2009) have been investigated for nitrate reduction. Among them, FA exhibits the highest activity (Zhang et al., 2005; Sa et al., 2009). The overall redox reactions between nitrate and FA with photocatalysts under UV irradiation can be expressed as follows:

Both FA and protons are consumed during nitrate reduction. The theoretical FA to nitrate stoichiometric ratios (FNRs) to reduce nitrate to nitrite, to dinitrogen, and to ammonium are 1, 2.5, and 4, respectively. Though a FNR of 2.5 is an ideal stoichiometric ratio for 100% N_2 selectivity, a higher FNR value than 2.5 is usually necessary for effective nitrate reduction. For example, an initial FA to nitrate molar ratio (IFNR) of 5.6 was reported to be optimal in terms of both nitrate reduction kinetics and by-product selectivity (Zhang et al., 2005; Sa et al., 2009). Thus, complete removal of nitrate and FA simultaneously is currently difficult to achieve, though recent research shows it may be possible to control the residual FA levels (Anderson, 2012). In addition, 100% dinitrogen selectivity is hard to achieve on bare or modified photocatalysts (e.g., TiO_2), and ammonium is commonly formed as the aqueous by-product of photocatalytic nitrate reduction (Ranjit and Viswanathan, 1997; Gao et al., 2004; Sa et al., 2009; Anderson, 2012; Rengaraj and Li, 2007). Although these biologically unstable hole scavengers (e.g., FA) and aqueous nitrogen by-products (e.g., ammonium) are not desirable in drinking water, indirect contact with drinking water through photocatalytic nitrate reduction of spent IX brine may make them acceptable.

This study is the first to evaluate the ability of photocatalytic reduction using TiO_2 to remove nitrate from IX brine wastes. The specific objectives of this study were to (1) investigate the ability of TiO_2 and silver-modified TiO_2 to remove nitrate from IX brines

and (2) evaluate the possibility of reusing the photocatalytically treated brine for IX resin regeneration.

2. Materials and methods

2.1. Materials

Titanium dioxide (Evonik P90) was obtained in powder form and used as received. P90 is a commercially available product containing both anatase (88%, 12 nm) and rutile (12%, 18 nm) crystal phases; compared with P25 (the most frequently used TiO_2), it has a higher surface area and was previously found to have a higher rate of nitrate reduction (Doudrick et al., 2012). P90 loaded with silver (P90/Ag) was synthesized according to a method reported elsewhere (Doudrick et al., submitted for publication). Sodium nitrate (NaNO_3 , 99% EMD) and FA (HCOOH , 98% Fluka) were used as the nitrate source and hole scavenger, respectively. Sodium hydroxide (NaOH , EMD) was used for pH adjustment. A model water was prepared using a Nanopure[®] (18.3 M Ω -cm) treatment system. Sodium chloride (NaCl , 99.5% Sigma-Aldrich) was added to model water to create synthetic NaCl brines. A real IX brine was obtained from a nitrate IX system for groundwater treatment used by a confidential water company in California. A nitrate selective resin (Purolite A-520E) was used on site to generate the IX brine. The major characteristics of this brine are summarized in Table 1.

2.2. Photocatalytic experiments

Different concentrations of synthetic NaCl brines (0%, 3%, 6%, and 10% by weight) were prepared by adding NaCl to model water spiked with 500 mg-N/L nitrate (35.7 mM). The real IX brine contained a much higher nitrate level of 1740 mg NO_3^- -N/L (124.3 mM). Then, 1 g/L P90 was mixed into the brines as the photocatalyst. An IFNR of 5.6 was used in all experiments except those in which IFNR values were varied. 200- and 700-mM FA were added to the synthetic brines and the real brine, respectively. In select experiments using the real IX brine, barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, 99% Aldrich) was added to the brine for sulfate precipitation. The mixture was sonicated for 20 min, vigorously stirred for 2 h, and allowed to sit for 30 min to settle out the precipitate. Then, the supernatant was filtered using a GF/F glass fiber filter. Barium sulfate precipitation brought the dissolved sulfate concentration in IX brine down to less than 50 mg/L.

Photocatalytic reactions were carried out in a double-wall quartz reactor. A 450-W medium-pressure mercury lamp (Ace Glass, 7825-34) was put in a double-walled quartz immersion well (Ace Glass, 7854-25), which was placed in the middle of the reactor for irradiation. In different experiments, 200-mL samples of real or synthetic brine with different P90 and FA concentrations were prepared and poured into the reactor after sonication. No effort was made to remove dissolved oxygen. A chiller was used to maintain a constant solution temperature of 25 °C. A magnetic stir bar was used to keep the suspension well dispersed. A small part of the solution was withdrawn periodically, filtered with a 0.45- μm nylon membrane, and then diluted and analyzed.

Using an Avantes UV-VIS Fiber Optic Spectrometer (AvaS-pec-2048) with a cosine corrector, the lamp intensity was measured in water at multiple points between the bottom

and the top of the reactor to obtain the average irradiance. The lamp irradiance starts at approximately 230 nm, and the irradiance absorbable by TiO_2 (230–388 nm) is 7.1 mW/cm², which is used here as the actual energy consumed by P90. Variation of fluence was used instead of accumulation of operating time to make our results comparable to other studies. Because a polychromatic lamp was used, the irradiation is shown as photon fluence (i.e., photons/cm²) instead of energy fluence (e.g., J/cm²) to account for the energy difference at different wavelengths.

2.3. IX system

Purolite A-520E, a commercially available macroporous strong base anion exchange resin, was used. This resin has quaternary ammonium functional groups and is specifically designed for the removal of nitrate. The resin particles have sizes between 0.3 and 1.2 mm. 50-mL of resin were packed into an IX column (OD = 2.5 cm), regenerated using 6% NaCl, and rinsed prior to use. Model water spiked with 200 mg-N/L nitrate was pumped downward at a flow rate of 48 BV/h (40 mL/min), which corresponds to an empty bed contact time of 1.25 min. After nitrate breakthrough, the resins were rinsed and regenerated using 10 BVs of 6% NaCl containing 400-mM FA (the pH was adjusted to 3.0 using sodium hydroxide) at a flow rate of 12 BV/h. In select experiments, an additional regeneration process was followed using 1 BV of 6% NaCl at a flow rate of 6 BV/h.

2.4. Analytical methods

Concentrations of nitrate, chloride, and sulfate were analyzed using ion chromatography (Dionex DX-120; AS12A column). Nitrite and ammonium in brines could not be analyzed using our ion chromatography setup due to overlapping of chloride and sodium peaks with nitrite and ammonium peaks, respectively. Thus, nitrite and ammonium concentrations were measured using colorimetry (Hach nitrite reagent, TNT plus 839; Hach ammonium reagent TNT plus 830) on an ultraviolet–visible light absorption spectrometer (Hach DR5000, Loveland, CO). Total dissolved nitrogen (TDN) was measured, along with dissolved organic carbon (DOC), using a Shimadzu TOC-V instrument. Samples were acidified and purged with air prior to TDN analysis. TDN measures the sum of non-volatile N species (e.g., NO_3^- , NO_2^- , NH_4^+ , or other aqueous N-species). DOC indicates the concentration of FA added initially as the hole scavenger. X-ray photoelectron spectroscopy (XPS) was performed on an ESCA-LAB 220i-XL (Vacuum Generators) with a monochromatic Al K_{α} source at $h\nu = 1486$ eV and a base pressure = 7×10^{-10} mbar. Conductivity and pH were measured using VWR model 2052 and Beckman model PHI 410 m, respectively.

3. Results and discussion

3.1. Nitrate reduction in synthetic NaCl brines

Fig. 1 compares the rate of nitrate reduction with UV irradiation only (UV alone) and of photocatalytic reduction using P90 (1 g/L) and FA (200 mM) under irradiation (P90 + FA + UV). Nitrate was slowly reduced with UV alone (Fig. 1(a)), which suggests photolysis of nitrate occurred; nitrite was the major by-product, accounting for more than 90% of the reduced nitrate. Inclusion of P90 and FA substantially increased the rate of nitrate reduction (Fig. 1(b)). Approximately 25% of the reduced nitrate converted to ammonium and 75% to

unknown non-aqueous N species (e.g., N_2 , N_2O). No nitrite concentration was detected throughout the experiment. In separate experiment in which nitrite (500 mg-N/L) was added initially to model water instead of nitrate, the rate of nitrogen loss in the presence of P90 and FA was significantly enhanced. For example, the first-order rate k_{nitrite} ($3.5 \text{ cm}^2/10^{19}$ photons) was an order of magnitude higher than k_{nitrate} ($0.4 \text{ cm}^2/10^{19}$ photons). This could suggest that nitrite may be produced as an intermediate during nitrate reduction but was rapidly reduced and unlikely to be detected in solution. The sum of nitrate, nitrite and ammonium concentrations agreed well with measured TDN levels in all conditions, indicating that levels of other aqueous N species were negligible. In the absence of FA, P90 had a slower nitrate reduction rate than did UV alone, probably because the presence of P90 particles created a light scattering effect that reduced the photon absorption of nitrate. The nitrate removal efficiency of P90 + UV was greatly slowed in comparison with that of P90 + FA + UV, thus verifying the indispensable role of FA as a hole scavenger in the photocatalytic system.

Fig. 1 also reveals the influence of NaCl concentration (0%, 3%, 6%, and 10% by weight) on nitrate removal efficiency. With UV alone, increasing the ionic strength through NaCl addition slightly increased the rate of nitrate removal (Fig. 1(a)), which is probably due to the stabilizing effect of chloride on the photolytic formation of nitrite from nitrate (Petriconi et al., 1969). In contrast, the nitrate removal efficiency decreased as the NaCl concentration increased from 0% to 3% with P90 + FA + UV, but additional NaCl addition up to 10% further decreased nitrate removal little (Fig. 1(b)). The first-order rate constant k_{nitrate} at different NaCl concentrations (0%, 3%, 6%, and 10%) was calculated to be 3.6, 2.4, 2.1, 1.9 $\text{cm}^2/10^{20}$ photons, respectively. An increase in ionic strength in solution could induce interparticle aggregation by compressing electrostatic double layer (EDL) thickness around nanoparticles (French et al., 2009; Shih et al., 2012; Mukherjee and Weaver, 2010). The interference effect brought from the elevating NaCl levels is likely attributed to the aggregation on TiO_2 nanoparticles, which decreased the total surface area of P90. Greater than 98% nitrate reduction was achieved at all NaCl levels studied after 1.3×10^{20} photons/ cm^2 irradiation. This suggests that the existence of high levels of chloride slowed the rate of nitrate reduction, but P90 is still capable of effectively reducing nitrate in NaCl brines and is especially competitive in extremely high NaCl concentrations, e.g., 10%. Addition of NaCl did not significantly change the selectivity toward N-species by-products for either UV alone or P90 + FA + UV.

In an effort to increase the nitrate reduction rate and improve selectivity toward gaseous N species, experiments were conducted using P90/Ag. Titanium dioxide loaded with silver nanoparticles has been shown to have much faster kinetics and higher innocuous by-product selectivity in model water (Zhang et al., 2005; Sa et al., 2009; Doudrick et al., submitted for publication). When P90/Ag was tested in a synthetic NaCl brine, however, no better performance was observed in contrast to non-modified P90. This may be due to chloride interacting with the silver and causing it to dissolve; a similar phenomenon is seen with chloride and copper (Chaplin et al., 2006). Dissolution of the silver into AgCl would eliminate its ability to enhance the rate of nitrate reduction, thus explaining the similar reduction rates of P90 and P90/Ag.

3.2. Nitrate reduction in a real IX brine

Fig. 2 shows the conversion of nitrate in a non-modified real IX brine in the presence of P90 + FA + UV. Nitrate removal was also tested in a synthetic brine (4.2% NaCl solution, 1740 mg-N/L nitrate) for comparison. The difference between the IX brine and synthetic brine suggested a potential role of anions other than chloride in nitrate reduction. Previous studies have shown that the presence of sulfate or carbonate anions decreases the kinetics of photocatalytic nitrate reduction employing TiO_2 (Zhang et al., 2005). In this IX brine, carbonate and bicarbonate anions were unlikely to cause interference because they were converted to carbonic acid by the addition of 700-mM FA before irradiation. The sulfate concentration in the IX brine was 6000 mg/L, and its concentration did not decrease during the photocatalytic treatment process. After removing sulfate from the IX brine through barium sulfate precipitation, the nitrate reduction efficiency was significantly improved (the first order rate constant k_{nitrate} tripled from 2.2 to 6.9 $\text{cm}^2/10^{21}$ photons), and the nitrate removals of the sulfate-removed brine and synthetic 4.2% NaCl brine were in good agreement (Fig. 2), which indicates that sulfate is the dominating disturbance factor for nitrate removal in brine. XPS results for P90 after photocatalytic treatment of nonmodified real brine (with sulfate) showed no fouling of the photocatalyst (Fig. SI-1). This indicates that the presence of chloride, sulfate, and other components of the brine did not deactivate the photocatalyst surface and that P90 could be used as a stable photocatalyst for brine treatment. Fig. SI-2 shows the impact of different sulfate concentrations (<50, 550, 1000, 6000 mg/L) on nitrate removal by lowering sulfate in brine through precipitation. Nitrate reduction was sensitive to sulfate concentrations. For example, 550 mg/L sulfate (a sulfate-to-nitrate molar ratio of 0.05) was sufficient to decrease the k_{nitrate} by 27.7% in the real brine. The isoelectric point for P90 is approximately 6.4 (Doudrick et al., 2012), which suggests that the surface of P90 is positively charged in acidic media ($\text{pH} < 6.4$) owing to presence of titanol (Ti-OH) on the surface (Hoffmann et al., 1995; Kormann et al., 1991) and that anions (i.e., NO_3^- , NO_2^- , and formate) are adsorbed to surface sites of P90 particles before photocatalytic reaction occurs. SO_4^{2-} is divalent and may be preferentially adsorbed by P90 under acidic conditions. Sulfate and chloride compete with nitrate for available surface sites on P90, which slows the rate of nitrate reduction in the brine. In addition, it is reported that the presence of a small concentration of sulfate (e.g., 115 mg/L) resulted in huge aggregation of TiO_2 nanoparticles (Shih et al., 2012), which could further explain the interference effect brought from sulfate in brine. Removal of sulfate from the real brine prior to photocatalysis allowed nitrate to be effectively removed. On average, approximately 3.6×10^{24} photons were required to reduce 1 mol of nitrate. No nitrite was detected, and the selectivity of ammonium and gaseous nitrogen compounds was 17% and 83%, respectively (Fig. SI-3). According to DOC measurement, nearly 400-mM FA was left at 2.6×10^{20} photons/ cm^2 of irradiation.

To make optimum use of FA as the hole scavenger and control the residual FA in the treated brine, the initial FA concentration added to the sulfate-removed brine was varied at IFNR = 1, 2.5 and 4 other than IFNR of 5.6 (shown above); the results are shown in Fig. 3. Fig. 3(a) compares the nitrate removal efficiency in brine at different IFNR values. The nitrate reduction rate was fastest for IFNR 5.6. For all IFNR values, similar initial nitrate removal rates were observed at less than 7.9×10^{19} photons/ cm^2 of irradiation. However, whereas

IFNR 5.6 and IFNR 4 maintained the same nitrate removal rate throughout the experiment, nitrate reduction at IFNR 1 and IFNR 2.5 became much slower after 0.8×10^{20} photons/cm² and 1.6×10^{20} photons/cm² of irradiation, respectively. Table SI-1 shows the changes in FNR and pH as the nitrate reduction proceeds. For IFNR 4 and IFNR 5.6, FNR values increased as nitrate concentration decreased, which suggests sufficient FA was available during the nitrate reduction process. The pH values for IFNR 4 and IFNR 5.6 increased from 2.0 to 3.3 and 1.9 to 3.0, respectively, indicating that adequate protons were available to be consumed. Thus, complete nitrate removal may be achieved with prolonged irradiation. For IFNR 1 and IFNR 2.5, FNR values gradually decreased as the nitrate in the brine decreased. A sharp increase in pH occurred with IFNR 1 (2.6–8.1) and IFNR 2.5 (2.2–7.8), which suggests a deficiency of protons in the solution. As shown in Equations (1)–(3), FA and protons are indispensable factors on photocatalytic nitrate reduction. Lack of FA as a hole scavenger and insufficient protons at neutral pH could explain the slower nitrate reduction rates for IFNR 1 and IFNR 2.5 in the later period (e.g., more than 1.6×10^{20} photons/cm² of irradiation). Moreover, in experiments with sufficient FA and protons (IFNR 4, IFNR 5.6), nitrate was converted into N gases and a small portion of ammonium (~17%) without detection of nitrite. However, in experiments with IFNR 1 and IFNR 2.5, nitrite was formed (>40 mg-N/L); a similar portion of ammonium was produced. The presence of nitrite in treated brine may cause drinking water contamination if the treated brine was reused for IX resin regeneration. Therefore, a higher IFNR value (e.g., 4, 5.6) seems more appropriate for nitrate reduction in IX brine. Fig. 3(c) reveals the linear relationship between nitrate removal and FA consumed. A FNR of 2.7 (larger than 2.5 as shown in Equation (2)) was found to be constantly consumed because of yielding NH₄⁺ (following Equation (3)). After 2.4×10^{20} photons/cm² irradiation, 11, 83, 240, 400 mM of FA remained in the treated brine for IFNR = 1, 2.5, 4, and 5.6 (Fig. 3(b)), respectively.

3.3. Managing FA during IX resin regeneration

Photocatalytic reduction using P90 can remove nitrate from IX brines with higher IFNRs (e.g., 4, 5.6), with formation of approximately 17% ammonium as the aqueous by-product. As anion exchange resins are used for nitrate removal, accumulation of ammonium has an insignificant effect on IX resin performance and the treated drinking water quality, as proved by Paidar and co-workers (Paidar et al., 2004). Thus, a scheme combining IX with photocatalytic nitrate treatment of IX brine may be able to remove nitrate from drinking water sources (Fig. 4). The subsequent question is what influence the residual FA from photocatalytic denitrification has on IX resin regeneration. Oxidation of all of the FA to CO₂ during photolysis may be feasible, but we wanted to investigate the fate of any residual FA by measuring DOC. An IX column was operated to study the impact of residual FA in the brine on IX resin regeneration. The higher residual FA of 400 mM from the IFNR 5.6 experiment was added to synthetic brine (6% NaCl) for IX resin regeneration. To maintain the same formate concentration, the pH of the synthetic brine was adjusted using sodium hydroxide to 3.0, the pH of the treated brine from the IFNR 5.6 experiment.

Fig. 5 shows the nitrate and formate breakthrough curves as a function of bed volumes (BVs) of treated water. We used a high influent nitrate concentration (200 mg-N/L) to accelerate IX column tests. Similar nitrate breakthrough curves were observed for fresh resin

(a) and regenerated resin (b, c). Using 10 mg-N/L (EPA MCL) as the breakthrough threshold, the amount of nitrate-containing model water can be treated during (a), (b), and (c) is 62, 61, and 59 BVs, respectively. The small differences indicate that the residual formate in treated IX brine resulted in minimal loss of the nitrate removal capacity of IX resins. However, after regeneration using FA-containing brine, formate was detected in treated water (Fig. 5(b)) in the first 40 BVs, with a maximum of 2.8 mM (127.5 mg/L) at approximately 6 BVs. We speculate that formate anions in the brine occupied resin exchange sites during the regeneration process and were displaced by nitrate in the model water in the following exhaustion runs, causing treated water contamination. Assuming the impact of FA in treated brine is exchange based, 50 mL (1 BV) of fresh 6% NaCl was applied as a follow-up regeneration process to replace formate brought from regeneration using FA-containing brine. This approach eliminated formate leakage into treated water (Fig. 5(c)), which further supported the exchange based assumption. As a result, the negative effect of a high concentration of residual FA in IX brine was completely overcome, and the reliable performance of the IX process could be ensured. By reusing the photocatalytically treated brine for regeneration, costs for NaCl consumption and brine disposal can be greatly reduced.

4. Conclusions

This study investigated the feasibility of photocatalytic reduction using TiO₂ (Evonik P90) to remove nitrate from IX brine and analyzed the possibility of reusing the treated brine containing residual FA for resin regeneration. Photocatalytic reduction using P90 could effectively remove nitrate from synthetic NaCl brines and real IX brine. No nitrite was detected as a by-product. Most of the reduced NO₃⁻ converted to volatile N species and a small portion to ammonium. High levels of chloride slowed the rate of nitrate reduction, but the presence of sulfate in IX brine is the dominating interference factor that inhibited nitrate removal, likely because sulfate competes with nitrate for available surface sites on TiO₂ and induces aggregation of TiO₂ nanoparticles. A higher IFNR (e.g., 4, 5.6) was found to be more appropriate for nitrate reduction but left higher residual FA in the treated brine. IX column tests showed that 400-mM residual FA in treated brine had an insignificant effect on IX resin capacity loss, and its contamination of treated water could be eliminated by rinsing with 1 BV of fresh NaCl. For this proof of concept treatment option, we have shown that sulfate precipitation using barium chloride is one option for mitigating high sulfate concentrations. Because the IX sites are anion specific, residual cations (e.g., Ba²⁺; NH₄⁺) in the regenerant solution will not have a negative impact on the removal efficiency. Based upon a K_{sp} of 1.1 × 10⁻¹⁰ for BaSO_{4(s)} and a measured sulfate ion residual of below 50 mg/L, the calculated residual dissolved barium concentration would be on the order of 0.03 mg/L. Although the EPA has set a limit for barium in drinking water at 2 mg/L, the residual concentration remaining in the treated IX brine will have minimal impact on drinking water quality. While we utilized barium sulfate precipitation, other methods to separate sulfate from ion exchange brines exist (e.g., nanofiltration of the brine). Thus, the photocatalytically treated brine is potentially suitable for continuous reuse after separating the TiO₂ nanoparticles.

Physical treatment options for nitrate, such as reverse-osmosis and ion-exchange, are simple and effective, yet their brine wastes must still be treated. Typically, these nitrate wastes are discharged to the municipal wastewater treatment plant at a specified charge. This proof of concept study has shown that photocatalysis is a very viable alternative for treating these wastes, especially if improvements are made to the visible-light absorption performance of photocatalysts such that the brine treatment can be done using natural sunlight. Adequately sized photocatalytic systems (e.g., the Photo-Cat system from Purifics) that include photoreactors and ceramic membranes for catalyst recovery are commercially available and could be used to treat sulfate removed brines. The next step would be to conduct pilot tests to obtain performance data and information for an economic analysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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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.2012.11.047>.

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Fig. 1.

Nitrate removal in synthetic NaCl brines (0%, 3%, 6%, and 10% by weight) as a function of photon fluence absorbable by TiO₂ using (a) UV alone and (b) P90 + FA + UV. The initial concentration of nitrate was ~500 mg-N/L for all samples. For P90 + FA + UV samples, 1-g/L P90 and 200-mM formic acid were initially added to the solution.

Fig. 2. Nitrate removal in a non-modified IX brine, synthetic brine (4.2% NaCl solution, 1740 mgN/L nitrate), and sulfate-removed IX brine as a function of photon fluence absorbable by TiO₂. The nitrate concentration in the IX brine was 1740 mgN/L. The concentration of P90 in solution was constant at 1 g/L. In all samples, 700 mM formic acid was added initially.

Fig. 3.

Nitrate removal (a) and FA removal (b) as a function of photon fluence absorbable by TiO₂ in sulfate-removed brine for varying initial FA to nitrate molar ratios (IFNRs), as well as nitrate removal versus FA removal (c). The concentration of P90 in solution was constant at 1 g/L.

Fig. 4. Schematic of an ion exchange system integrated with photocatalytic nitrate reduction of IX brine for reuse. FA represents formic acid.

Fig. 5. Breakthrough curves of nitrate and formate for fresh IX resin (a) and regenerated resin (b, c). The regenerant used before (b) was 6% NaCl containing 400-mM FA (500 mL), pH = 3.0; the regenerant used before (c) was 6% NaCl containing 400-mM FA (500 mL), pH = 3.0, followed by 50 mL fresh 6% NaCl.

Table 1

Characteristics of real IX brine.

Parameter	Value	Unit	Parameter	Value	Unit
pH	7.81	–	Conductivity	127.4	mS
Dissolved organic carbon	23.9	mg-C/L	Sulfate	6000	mg/L
Total dissolved nitrogen	1793	mg-N/L	Sodium chloride	4.2%	–
Nitrate	1740	mg-N/L	Magnesium	20.6	mg/L
Nitrite	1.1	mg-N/L	Calcium	27.2	mg/L
Ammonium	3.6	mg-N/L	Total hardness	350	mg/L as CaCO ₃