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The Selectivity and Sustainability of a Pd–In/γ-Al_2O_3 Catalyst in a Packed-Bed Reactor: The Effect of Solution Composition

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Abstract This study tested the selectivity and sustainability of an alumina-supported Pd–In bimetallic catalyst for nitrate reduction with H_2 in a continuous-flow packed-bed reactor in the presence of: (i) dissolved oxygen (DO), an alternative electron acceptor to nitrate, (ii) variable NO_3^-:H_2 influent loadings, and (iii) the presence of a known foulant, sulfide. The sustainability of the catalyst was promising, as the catalyst was found to be stable under all conditions tested with respect to metal leaching. The presence of DO at concentrations typical of treatment conditions will increase H_2 demand for NO_3^- reduction, but has no negative impact on the selectivity of the catalyst. Under optimal conditions, i.e., a pH of 5.0 and a high NO_3^-:H_2 influent loading, low NH_3 selectivity (5%) was achieved for extended periods (36 days), resulting in sustained levels of NH_3 that approached the European legal limit. The biggest challenge to the sustainability of the catalyst was the addition of sulfide, that initially increased NH_3 selectivity and ultimately resulted in complete deactivation of the catalyst. Further work is required to identify regeneration methods to restore sulfide-fouled catalyst activity and selectivity; however, the most effective use would be to remove sulfide prior to catalytic treatment.

Keywords Nitrate reduction · Catalysis · Drinking water treatment · Sulfur fouling · Palladium · Indium

1 Introduction

Nitrate conversion to nitrogen proceeds with exquisite selectivity in the natural environment through a series of metalloenzyme-controlled steps (denitrification). However, nitrate overload from anthropogenic sources can lead to contaminated drinking water in which the nitrate level exceeds the legal limit (USEPA MCL, 714 μM) [1]. The use of Pd-based heterogeneous catalysts with hydrogen as the electron donor has emerged as an attractive treatment strategy for nitrate-contaminated water [2], but the issues of *selectivity* (formation of significant amounts of ammonia as well as nitrogen) [2–11] and *sustainability* (activity maintenance when confronted with potential foulants in the source water) [10, 11] remain formidable barriers to widespread adoption. We have examined how three critically important solution conditions affect the operation of a Pd–In/γ-Al_2O_3 catalyst for nitrate reduction: (i) the concentration of dissolved oxygen (DO), an alternative electron acceptor to nitrate, (ii) the specific NO_3^-:H_2 influent loading; and (iii) the presence of a known foulant, sulfide. This is the first reported study of these parameters in an open system characteristic of a water treatment

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process (a packed-bed flow reactor), and it provides a unique, quantitative demonstration of the link between input and output water properties in the presence of the catalyst.

2 Materials and Methods

2.1 Catalyst Preparation

The catalyst was prepared using the incipient wetness method. A bulk 5 wt%Pd/γ-Al_2O_3 catalyst (Aldrich) was wet sieved to obtain a particle size between 63 and 125 μm. Analysis of this particle size fraction with ICP-MS revealed a Pd loading of approximately 3 wt%. The In promoter was added by pore volume impregnation with an $In(NO_3)_3$ salt solution [11]. The Pd–In catalyst was dried in air at 120 °C for 3 h and reduced with H_2 at 120 °C for 1 h. Previous XPS analysis has shown that this preparation method yields metallic Pd and In_2O_3 [11]. The catalyst had a final metal loading of 3wt%Pd and 0.6 wt%In (3.0Pd–0.6In), as determined by ICP-MS and a surface area of 112 m^2/g (ASAP 2020, Micromeritics).

2.2 Reagents

All chemicals used were reagent grade sodium salts (Fisher). Deionized, nanopure water (DNW) was obtained by purification of tap water by ion exchange (resistivity 16 MΩ cm at 25 °C) and then subsequent filtration through a nanopure membrane (Barnstead) until the product water achieved a resistivity of 18 MΩ cm (25 °C). Gas tanks of H_2 (99.999%), He (99.999%), CO_2 (99.9%) and 50%CO_2/50%O_2 were purchased from Matheson Tri-Gas (Joliet, IL).

2.3 Analytical Methods

Nitrate, nitrite, and sulfate concentrations were determined by ion chromatography (Dionex ICS-2000; Dionex IonPac AS18 column; 32 mM KOH eluent; 1 mL/min eluent flow rate). Hydrogen sulfide was measured by ion chromatography by converting it to sulfate with the addition of NaOCl (0.35 mM). A gas sensitive ammonia probe (Orion 9512) was used for ammonia determination, after raising the sample pH to 13 by NaOH addition (detection limit of 0.03 mg/L as N). Metals were determined by ICP-MS (OES Optima 2000 DV, Perkin Elmer) at the School of Chemical Sciences Microanalysis Laboratory (University of Illinois at Urbana-Champaign). The pH was measured with a pH electrode (Cole Parmer). Hydrogen, nitrogen, and nitrous oxide were analyzed on an HP-6890a GC with a Carboxen 1004 stainless steel micropacked column (Supelco) and a TCD detector. Dissolved oxygen was monitored by a probe and meter (WTW).

2.4 Packed-bed Reactor Setup

The reactor (Fig. 1) was a 1 cm ID glass HPLC column equipped with an adjustable plunger (Altech) and packed with 2.0 g of the 3Pd–0.6In catalyst. All experiments were maintained at 21.0 ± 0.8 °C, and aqueous solution was purged through the column at 1.0 mL/min. The aqueous nitrate solution was stored in a 19 L stainless steel reservoir (Alloy Products Corp; Waukesha, Wisconsin) pressurized by UHP He at 40 psi, previously degassed by sparging with UHP He for 60 min. Gases were delivered to the liquid using a membrane module gas exchanger (Liqui-cell). Hydrogen was used as the electron donor and CO_2 was used to buffer the pH. When oxygen was added to solution, a 50%CO_2/50%O_2 gas blend was used. The porosity of the reactor was determined gravimetrically to be 0.40, resulting in a single pore volume residence time of 1.6 min. The liquid outlet was pressurized to approximately 55 psi by an adjustable check valve (Swagelok). An inline pH probe (Cole Parmer) was used to record the pH of the solution. Liquid and gas sampling ports were located both upstream and downstream of the reactor.

A tracer test was conducted to determine the absorption of NO_3^- and NH_3 in the packed-bed reactor. An NH_4NO_3 concentration of 10 mM and a tritium concentration of 5,000 dpm/mL was pumped through the column at a flow rate of 1 mL/min. Tritium was assumed to be the conservative tracer.

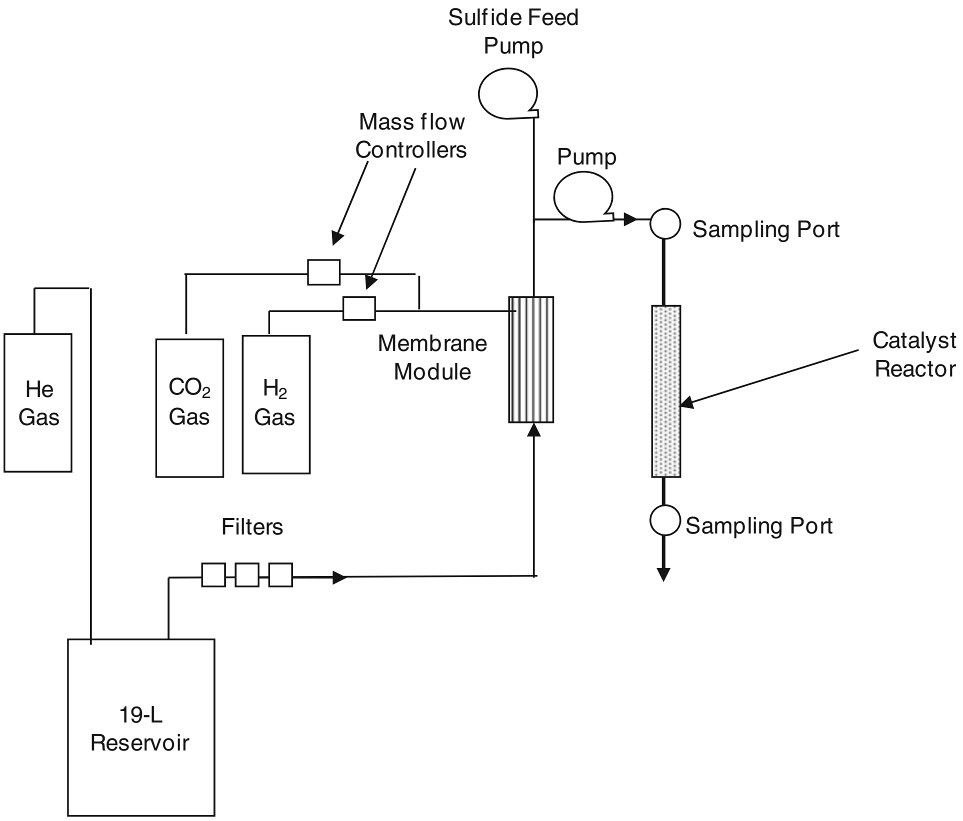
2.5 Sulfide Isotherm

A batch adsorption isotherm was conducted to determine the distribution coefficient (K_d) for sulfide to the catalyst. Liquid concentrations were monitored during step-wise injections of a sulfide solution to a sealed flask containing 1 g/L of catalyst under anaerobic conditions and vigourous stirring.

2.6 Packed-bed Nitrate Reduction Experiments

Influent NO_3^- was either 1.0 or 1.4 mM. Solution pH values of 5.0 and 9.0 were achieved by buffering with 2.09 mM CO_2 and 3.28 mM $NaHCO_3$, respectively. The $NaHCO_3$ was added directly to the nitrate-reservoir. The DO was added at a concentration of 82 and 124 μM (2.6 and 4.0 mg/L). The H_2 concentration was varied between 1.95 and 2.54 mM. Dissolved HS^- was added via a syringe pump at a flow rate of 0.1 mL/h to obtain a concentration of 164 μM S (5.6 mg/L) in the influent solution.

Fig. 1 Fixed-bed reactor schematic



3 Results and Discussion

3.1 Experimental Reproducibility

Packed-bed reactor results are shown in Fig. 2, and product distribution results (in percentages) are documented in Table 1. The reactor was operated initially at pH 5.0, increased to pH 9.0, and returned back to pH 5.0. At both pH values, the product distribution consisted only of nitrogen gas and ammonia and the total N balance was between 99.8 and 103.9%. Nitrite and nitrous oxide were not detected in the reactor effluent (detection limit of 5 and 1.4 µM, respectively), and H_2 was completely consumed (detection limit of 60 µM). Ammonia levels were elevated at the higher pH, which is to be expected based on prior research [5, 11]. When the pH in the influent was lowered again to 5.0 (Fig. 2a), both the effluent nitrate concentration and product distribution returned to their previous levels. This result indicates that the effect of pH is temporary, it does not permanently change the catalyst

Fig. 2 Nitrogen product distribution from fixed bed reactor. **a** pH = 5.0, H_2 = 2.54 mM, NO_3^- = 1.0 mM; **b** pH = 5.0, H_2 = 2.54 mM, DO = 82 µM, NO_3^- = 1.0 mM; **c** pH = 5.0, H_2 = 2.54 mM, DO = 124 µM, NO_3^- = 1.0 mM; **d** pH = 5.0, H_2 = 2.30 mM, NO_3^- = 1.0 mM; **e** pH = 5.0, H_2 = 1.95 mM, NO_3^- = 1.4 mM

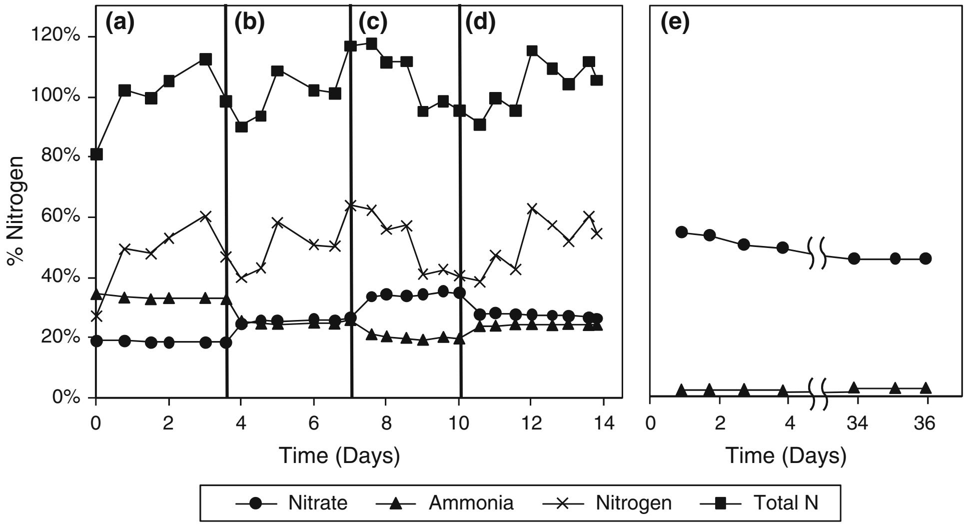


Table 1 Summary of the influent and effluent solution conditions for steady state packed-bed reactor experiments

Influent				[a]Effluent									
Data on figure	pH	H_2 mM	Do 6 M	pH	%NO_3^-	%NO_2^-	%N_2O	%N_2	%NH_3	%Total N	%H_2	[b]Stoich H_2 used (mM)	[c]Normalized %NH_3
NA	5	2.54	0	5.9	18.8(1.0)	0.0	0.0	52.9(9.0)	32.2(1.1)	103.9(9.2)	0.0	2.57(0.13)	39.7(1.0)
NA	9	2.54	0	9.1	26.9(0.7)	0.0	0.0	23.1(4.1)	52.3(0.9)	102.2(3.8)	0.0	2.65(0.06)	71.5(1.5)
2a	5	2.54	0	5.8	18.9(0.3)	0.0	0.0	47.5(8.9)	33.4(0.5)	99.8(8.4)	0.0	2.53(0.13)	41.1(0.7)
2b	5	2.54	82	5.7	25.8(0.4)	0.0	0.0	51.1(5.2)	25.1(0.5)	102.0(5.8)	0.0	2.43(0.09)	33.9(0.8)
2c	5	2.54	124	5.7	34.4(0.5)	0.0	0.3(0.04)	50.0(6.4)	20.2(0.3)	105.0(6.2)	0.0	2.27(0.10)	30.9(0.6)
2d	5	2.30	0	5.8	27.5(0.4)	0.0	0.0	52.1(5.0)	24.3(0.1)	104.0(4.8)	0.0	2.24(0.08)	33.6(0.3)
2e[d]	5	1.95	0	5.6	48.1(1.7)	0.0	ND	ND	2.4(0.5)	ND	0.0	1.90(0.03)	5.1(0.7)
3a	5	2.54	0	5.9	18.5(0.4)	0.0	0.0	64.9(5.5)	26.2(0.4)	109.6(5.4)	0.0	2.57(0.07)	32.1(0.5)

Results from sulfide fouling experiments are not shown because the reactor was not at steady state

[a] Effluent concentrations represent percent of influent nitrate on a N atom basis and percent hydrogen remaining

[b] Hydrogen used was calculated based on the observed product distribution and the stoichiometry shown in Eqs. 1–5

[c] Ammonia was normalized by dividing the moles of ammonia produced by the moles of nitrate degraded

[d] Influent nitrate was 1.4 mM

surface, and reactor operation is stable and reproducible. This result also indicates that pH changes over the range and duration studied do not affect the sustainability of the catalyst.

3.2 Dissolved Oxygen

The effects of DO on catalytic NO_3^- reduction has not been previously investigated in a packed-bed flow-through reactor. Dissolved oxygen was added to the reactor influent at either 82 or 124 µM (Fig. 2b, c) concentrations in the range of those found in natural waters. Increases in DO resulted in increases in effluent NO_3^- and decreases in effluent NH_3. Nitrite was not detected in the reactor effluent, and only trace N_2O was observed in the case of the higher DO concentration. Normalization of NH_3 produced by the amount of NO_3^- transformed (Table 1) showed that DO limited NH_3 production. To test whether the presence of DO or lower H_2 levels created by the reaction of DO and H_2 were responsible for the lower NH_3 production, an experiment was conducted at a H_2 concentration (2.30 mM) corresponding to the H_2 that would remain after 124 µM of DO was consumed, according to the stoichiometry shown in Eq. 1 below.

$$O_2 + 2.0H_2 \xrightarrow{Pd\text{–}In/\gamma\text{–}Al_2O_3} 2.0H_2O \tag{1}$$

Under these conditions, effluent NO_3^- decreased and NH_3 increased (Fig. 2d; Table 1) relative to the 124 µM DO experiment. However, the increase in NH_3 levels was small (~4%) relative to the reduction in effluent NO_3^- (~9%) caused by eliminating effluent DO and decreasing H_2 from 2.54 to 2.30 mM. The higher overall NO_3^- conversion in the absence of DO suggests that DO has a fouling effect with regard to NO_3^- reduction, causing the chemisorbed H_2 to not be readily available for reaction. The lower NH_3 production in the presence of 124 µM DO, illustrates that DO contributes to reducing NH_3 production primarily (but not exclusively) by reaction with H_2. These results are consistent with the proposed mechanism that a higher ratio of N:H species on the catalyst surface lowers the overall NH_3 production [5].

The H_2 consumption was calculated for all solution conditions shown in Fig. 2 based on the observed product distribution and the stoichiometry presented in Eqs. 1–5 (Table 1).

$$NO_3^- + H_2 \xrightarrow{Pd\text{–}M/\gamma\text{–}Al_2O_3} NO_2^- + H_2O \tag{2}$$

$$NO_2^- + 3.0H_2 \xrightarrow{Pd\text{–}M/\gamma\text{–}Al_2O_3} NH_3 + H_2O + OH^- \tag{3}$$

$$NO_2^- + H_2 \xrightarrow{Pd\text{–}M/\gamma\text{–}Al_2O_3} 0.5N_2O + 0.5H_2O + OH^- \tag{4}$$

$$N_2O + H_2 \xrightarrow{Pd\text{–}M/\gamma\text{–}Al_2O_3} N_2 + H_2O \tag{5}$$

In the absence of DO, the calculated H_2 consumption was close to influent concentrations and H_2 was not observed in the effluent. However, when DO was added, calculated H_2 consumption (by Eqs. 1–5) was lower than the influent H_2 concentration (2.54 mM) (Table 1). Neither DO (detection limit 17 µM) nor H_2 was detected in the effluent, suggesting that DO limits the availability of H_2 for reaction with nitrogen species. Studies looking at the H_2-O_2 reaction on Pd(100) have shown that the rate limiting step involves the reaction of two adsorbed OH molecules to form H_2O [12], and the H_2-O_2 reaction rate is also limited by the formation of adsorbed OH at Pd(111) step edge sites [13]. Thus, it is possible that the reaction between H_2 and O_2 on the 3.0Pd–0.6In catalyst resulted in adsorbed oxygenated species on Pd sites that blocked the spillover of chemisorbed hydrogen to oxygenated-In sites, which are the active sites for NO_3^- reduction [5]. The slow regeneration of In sites could explain the lower NO_3^- conversion observed in the presence of DO. The effect was not permanent, as removal of DO from the influent resulted in a similar nitrogen distribution as shown in Fig. 2a. Therefore, the catalyst proved to be sustainable to periodic exposure to DO.

The effects that DO has on NO_3^- reduction was recently evaluated in a semi-batch reactor using a Pd–Cu/TiO_2–Al_2O_3 catalyst [14]. The authors found that the addition of between 2 and 6%O_2 (added as air) to the gas inlet stream did not significantly affect the NO_3^- reduction rate, but lowered NH_3 production by as much as 80% [14]. The study inferred high selectivity towards N_2, but did not measure N_2O in the solution or off-gas [14], which has previously been shown to be present in the off-gas in high concentrations [11, 15, 16]. The intentional injection of oxygen as a strategy to limit NH_3 production has limited value in either a packed-bed or semi-batch system. Under semi-batch conditions, low NH_3 can be achieved, but at the expense of wasting large amounts of H_2 and off-gasing large amounts of N_2O, which is a potent greenhouse gas [17]. Most importantly, our results indicate that DO present in natural waters must be accounted for during system design, as it will increase H_2 demand beyond stoichiometric requirements but has no negative impact on effluent water quality. A packed-bed reactor however, has the advantage of preventing H_2 loss from solution and N_2O out-gasing is prevented because it stays in solution and subsequently reacts to form N_2.

3.3 Hydrogen Concentration

The local concentrations of both NO_3^- and H_2 have been shown to be a key operating condition to maintain low levels of NH_3 during catalytic NO_3^- reduction [5, 9, 18]. In an attempt to minimize NH_3 production, influent concentrations of 1.4 mM NO_3^- and 1.95 mM H_2 were used (Fig. 2e; Table 1). During 36 days of operation, effluent NO_3^- and NH_3 concentrations were 667 ± 39 and 33 ± 11 μM, respectively; the NH_3 concentration represents only 5.1 ± 0.7% of nitrate converted. These concentrations are below the U.S. EPA MCL for NO_3^- (714 μM) and are only 18% greater than the European Union limit for NH_3 (28 μM). The very low levels of NH_3 obtained under these conditions were achieved because the effluent NO_3^- concentrations were maintained higher than previous operating conditions and influent H_2 concentrations were lower. Thus the N:H ratio on the catalyst surface was always low and the production of N_2 was favored over NH_3 [5]. The measurement of N_2 and N_2O was not performed. However, results from the first 14-day column experiment (i.e., Fig. 2) show that the balance of NO_3^- likely went to N_2. This is supported by calculations of H_2 consumption based on the nitrogen distribution (shown in Fig. 2e); the stoichiometric H_2 consumption is 1.90 ± 0.03 mM, which is almost identical to the influent H_2 concentration (1.95 mM) (Table 1). These results indicate that in a continuously operating flow-through system, representative of those in a water treatment plant, optimization of system parameters can result in high selectivity for N_2 and in NH_3 levels approaching regulatory limits. Further system optimization is possible and is expected to reduce NH_3 levels even further. For example, delivering a low concentration of H_2 along the catalyst bed via a membrane would insure that the N:H ratio on the catalyst surface was always high and would thus favor N_2 over NH_3.

3.4 Sulfide Fouling

The effect of sulfide fouling on the product distribution during catalytic NO_3^- reduction has been demonstrated in batch studies, but not in a packed-bed reactor. The primary difference is that in packed-bed studies, the effects of sulfide on the complete product distribution can be quantified. The results of sulfide fouling are shown in Fig. 3 and summarized in Table 1. Before sulfide was added to the influent, the solution consisted of NO_3^- at a pH of 5.0. Upon the addition of 164 μM H_2S (5.6 mg/L) to the influent solution, NO_3^- conversion decreased and was close to zero after 2 days of sulfide fouling (Fig. 3b). A sharp increase in the effluent NH_3 concentration was observed, and neither NO_2^- nor N_2O were detected. The increase in NH_3 concentrations was attributed to a shift in the selectivity of the catalyst caused by sulfide fouling, as was reported previously [11]. The release of adsorbed NH_3 could not be a significant source for increased effluent NH_3 concentrations, as the K_d value found for NH_3 from the tracer test would result in neglible NH_3 adsorption. Values for K_d were 0.15 and 0.26 L/kg for NO_3^- and NH_3, respectively. A high nitrogen mass balance was also observed during this period (138.5 ± 14.8%; Fig. 3b), and was attributed to the fact that the gas sampling port was not at equilibrium with respect to N_2 partitioning between the liquid and gas phases.

Sulfide concentrations in the reactor effluent were at 37% of their influent value after approximately 4 days of sulfide fouling (Fig. 3b). The total sulfur loading during this period was 475 μmol S/g catalyst, which was about half the value (836 μmol S/g catalyst) that was predicted

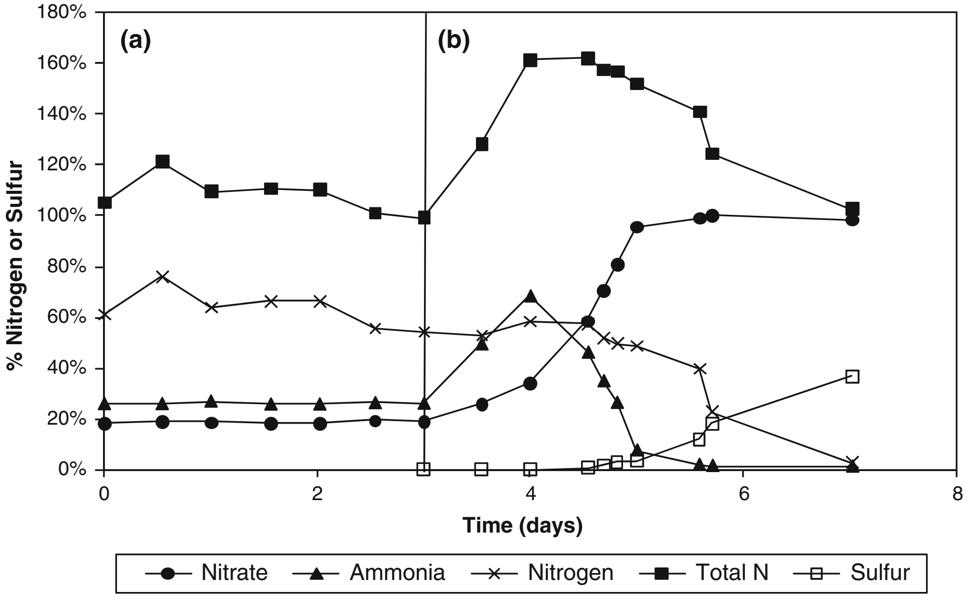


Fig. 3 Product distributions from nitrate reduction under sulfide fouling conditions: **a** pH = 5.0, $H_2 = 2.54$ mM; **b** pH = 5.0, $H_2 = 2.54$ mM, $H_2S = 164$ μM. Sulfur data represents percent of influent (164 μM)

by the K_d (5,110 L/kg) from the sulfide isotherm and the influent sulfide concentration (164 mM). Nitrate reduction was completely inhibited before the total sulfur capacity was reached because sulfide adsorption to non-active sites on the catalyst also occurred (e.g., alumina support).

Sulfide was eliminated from the influent, but no recovery of NO_3^- reduction was observed (Results not shown). These results are consistent with our previous findings in a batch system that showed a sulfide fouled Pd–In/γ-Al_2O_3 catalyst resulted in the formation of PdS and In_2S_3 species on the catalyst surface that required oxidative regeneration to remove the bound S [11]. A variety of regeneration strategies were evaluated; the results can be found in Chaplin [19] and are the subject of another paper.

3.5 Catalyst Stability

Periodic measurements of effluent samples during the course of nearly 2 months of operation did not result in detectable amounts of Pd, In, or Al during NO_3^- reduction, indicating that the catalyst was stable during operation. This is a key result for the sustainability of the catalyst, as it will assure longevity of operation and alleviate health concerns from the ingestion of metal nanoparticles.

4 Conclusions

The work presented here examined the *selectivity* and *sustainability* of a 3 wt%Pd–0.6 wt%In/γ-Al_2O_3 catalyst during NO_3^- reduction with dissolved H_2. The production of NH_3 was observed to be highly dependent on the influent solution conditions. Increases in NH_3 were observed in accordance with increases in H_2 concentration and sulfide concentration, and NH_3 production decreased slightly with the addition of DO. The production of NH_3 was low under optimal solution conditions (5% of NO_3^- reduced at pH 5 and $H_2 = 1.95$ mM) for over a month of operation, for an influent NO_3^- concentration of 1.4 mM. Sulfide quickly fouled the catalyst resulting in increased NH_3 production and ultimately no activity for NO_3^- reduction. The catalyst was shown to be stable with respect to metal leaching for the duration of these experiments. Therefore, this catalyst has several critical characteristics needed for potential use in drinking water purification. However, it would likely be more sustainable with pretreatment of the water to remove any contaminant sulfide. The possible effects of ubiquitous dissolved organic matter (DOM) have not been examined in this study, but previous work with a Pd–Cu/γ-Al_2O_3 catalyst exposed to humic acid in a batch mode showed only moderate inhibition that was largely reversible [10].

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