

## **Reduction of nitrate in groundwater by hematite supported bimetallic catalyst**

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### **Abstract**

In this study, nitrate reduction of real groundwater sample by 2.2%Cu-1.6%Pd-hematite catalyst was evaluated at different nitrate concentrations, catalyst concentrations, and recycling. Results show that the nitrate reduction is improved by increasing the catalyst concentration. Specific nitrate removal by 2.2%Cu-1.6%Pd-hematite increased linearly with the increase of nitrate concentration showing that the catalyst possesses significantly higher reduction capacity. More than 95% nitrate reduction was observed over five recycles by 2.2%Cu-1.6%Pd-hematite with ~56% nitrogen selectivity in all recycling batches. The results from this study indicate that stable reduction of nitrate in groundwater can be achieved by 2.2%Cu-1.6%Pd-hematite over the wide range of initial nitrate inputs.

**Keywords:** Bimetallic catalyst, Cu-Pd-hematite, Nitrate reduction in groundwater, Specific nitrate removal, Catalyst recycling

### **1. Introduction:**

Groundwater is an important source of potable, agricultural, and industrial water. Its resources have been facing severe anthropogenic deterioration during recent decades. Nitrate contamination in groundwater is one of the most critical problems arising from increased agricultural inputs (fertilizers, livestock, etc.) and insufficient treatment of industrial wastes (Jung *et al.* 2014; Choi *et al.* 2012; Pirkanniemi and Sillanpaab 2002). Consumption of water polluted with nitrate is hazardous to human health because 1) it causes blue baby syndrome in infants and 2) it is a potential precursor of carcinogenic amines (Jung *et al.* 2014). From ecological point of view, nitrate pollution enhances eutrophication in water bodies. Due to these potential threats of nitrate pollution, enormous

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efforts have been made to invent and devise denitrification techniques and processes. Recently, catalytic nitrate reduction using bimetallic catalysts have attracted an attention due to its high efficiency, selectivity, stability, and reliability (Pintar 2004, Shin *et al.* 2014). However, more research is continuously required to develop environmentally benign catalysts and to optimize the catalytic processes to achieve successful recovery of the polluted water. Most of the catalyst research works have been conducted in laboratory environments using artificial nitrate solution (Jung *et al.* 2014; Hamid *et al.* 2015; Shin *et al.* 2014). However, the composition of groundwater is usually very complex due to dissolution of anions, cations, and organic matter from soil. Thereby, such evaluations are needed to investigate the catalytic performance of bimetallic catalysts in the groundwater conditions. Our recent work demonstrated the development of a highly reactive and selective bimetallic catalyst supported by eco-friendly and inexpensive hematite for nitrate reduction. In this study, we report the investigation of nitrate reduction in real groundwater sample by Cu-Pd-hematite catalyst in batch mode. The objectives of this study are 1) to investigate the reactivity of Cu-Pd-hematite catalyst in groundwater, 2) to evaluate the removal capacity of Cu-Pd-hematite for the nitrate reduction, and 3) reusability of Cu-Pd-hematite for the removal of nitrate in groundwater.

## **2. Materials and Methods**

### *2.1. Chemicals*

Copper (II) chloride dihydrate (97.5%, Samchun Pure Chemical Co., Korea) and palladium (II) chloride (99.9%, Sigma-Aldrich Inc., USA) were used as Cu and Pd precursors. Pd precursor solution was prepared with 0.5 M HCl (37%, Samchun Pure Chemical Co., Korea). Sodium borohydride (98.0%, Samchun Pure Chemical Co., Korea) was used to reduce fresh Cu-Pd-hematite catalyst. Potassium nitrate (99.0%, Duksan Pure Chemical Co., Korea), potassium nitrite (97.0%, Samchun Pure Chemical Co., Korea), and ammonium chloride (98.5%, Duksan Pure Chemical Co., Korea) were used to prepared nitrate, nitrite, and ammonium stock and standard solutions, respectively. Sodium bicarbonate (99.7%, Sigma-Aldrich Inc., USA) and sodium carbonate (99.5%, Sigma-Aldrich Inc., USA), and nitric acid (60%, Samchun Pure Chemical Co., Korea) were used to prepare an eluent for nitrite, nitrate, and ammonium determination via ion chromatography (IC). Deionized water (DIW, ELGA PURELAB Classic system) was purged with argon gas overnight to prepare deaerated deionized water (DDIW). The DDIW was used to prepare all solution and standards.

~20 L groundwater sample was collected in the middle of farming land near Wonju, South Korea using air tight PVC container. The containers were wrapped in aluminum foil and stored in refrigerator to avoid nutrient losses due to photosynthesis and photocatalysis.

### *2.2 Catalyst synthesis*

The 2.2%Cu-1.6%Pd-hematite catalyst was prepared as reported in our previous work (Jung *et al.*, 2014). Briefly, 1.5 g hematite was mixed in 200 mL of DIW via ultra-sonication

for 6 min. Then 2.2%Cu precursor solution was added drop-wise and stirred for two hours. Subsequently, Pd precursor solution (1.6% Pd in 0.5 M HCl) was sequentially added drop-wise and mixed for two hours under continuous stirring. The Cu-Pd hematite suspension was then dried in oven at 105 °C for 24 h, followed by calcination at 350 °C for 2 h to stabilize the precursors on hematite surface. The freshly calcined 2.2%Cu-1.6%Pd-hematite catalyst was mixed in DDIW and reduced through the drop-wise addition of 0.01M NaBH<sub>4</sub>. The reduced catalyst was then filtered by membrane filter (0.2 μm, Advantech, Japan), washed three times with DDIW to remove unwanted impurities, and then transferred to reactor system for the removal of nitrate in groundwater.

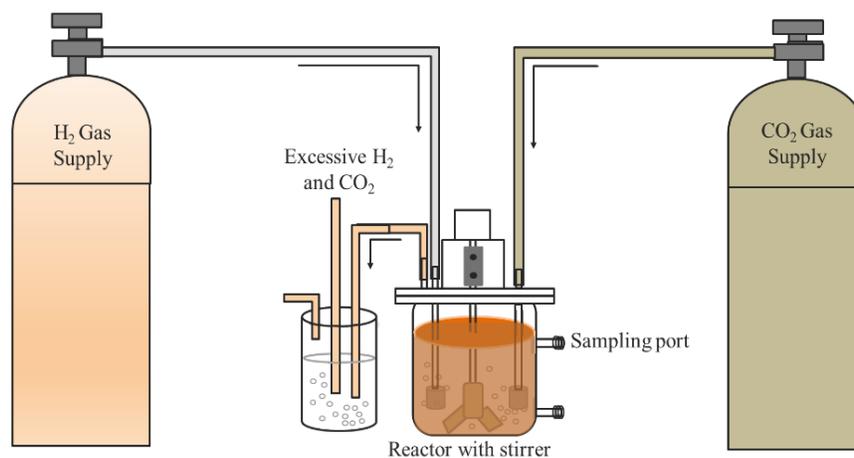


Fig. 1 Schematic of reactor system

Table 1. Reaction condition

Catalyst Loading (g)	0.25, 0.5, 0.75, 1
H <sub>2</sub> Flow rate (mL/min)	40
CO <sub>2</sub> flow rate (mL/min)	30
Initial NO <sub>3</sub> -N conc. (mg/L)	40, 60, 80, 120, 160, 300, 600
Cu loading (%)	2.2
Pd loading (%)	1.6

### 2.3 Experimental procedure of catalytic nitrate reduction

The nitrate reduction experiments were performed in a 500 mL glass batch reactor as shown in Fig. 1 (Jung et al., 2014, Hamid and Lee, 2015). Groundwater (230mL) was

taken into the reactor and purged with H<sub>2</sub> gas to ensure anaerobic conditions (Hamid et al., 2015). Then a measure amount of previously reduced 2.2%Cu-1.6%Pd-hematite was introduced to the reactor and dispersed by ultra-sonication for 3 min. Then respective amount of nitrate stock solution (20,000 mg/L as NO<sub>3</sub>-N) was introduced into the reactor to start the catalytic reaction. CO<sub>2</sub> and H<sub>2</sub> gases were continuously supplied for buffering and reduction, respectively. The detailed experimental conditions are given in table 1.

#### 2.4 Analysis

Concentrations of nitrate, nitrite, and ammonium were determined by an ion chromatograph (IC; 883 basic IC plus, Metrohm, U.K.) equipped with a compact auto sampler (863 Compact IC, Metrohm USA), anion column (Metrosep A Supp 4-250/4.0), and cation column (Metrosep C4-150/4.0) (Hamid *et al.* 2015; Hamid and Lee, 2015). The nitrate removal ( $R_{NO_3^-}$ ) and byproducts selectivity ( $S_{by-product}$ ) were calculated on mass balance basis as given in following equations (Hamid *et al.* 2015, Jung *et al.* 2014, Jung *et al.* 2012).

$$R_{NO_3^-} (\%) = \frac{[NO_3^- - N]_i - [NO_3^- - N]_f}{[NO_3^- - N]_i} \quad (1)$$

$$S_{NO_2^-} (\%) = \frac{[NO_2^- - N]_f}{[NO_3^- - N]_i - [NO_3^- - N]_f} \quad (2)$$

$$S_{NH_3^+} (\%) = \frac{[NH_3^+ - N]_f}{[NO_3^- - N]_i - [NO_3^- - N]_f} \quad (3)$$

$$S_{N_2^-} (\%) = \frac{[NO_3^- - N]_i - [NO_3^- - N]_f - [NO_2^- - N]_f - [NH_4^+ - N]_f}{[NO_3^- - N]_i - [NO_3^- - N]_f} \quad (4)$$

Where, initial and final concentrations are denoted by subscripts *i* and *f*, respectively.

### 3. Results and discussions

#### 3.1 Composition of groundwater

We checked 47 physico-chemical factors to characterize the groundwater. The characterization results revealed that higher contents of Ca (31.02mg/L), K (3.309 mg/L), Mg (11.06 mg/L), Na (33.10 mg/L), KMnO<sub>4</sub> (1 mg/L), Cl<sup>-</sup> (103 mg/L), and SO<sub>4</sub><sup>-</sup> (4 mg/L) were present in the groundwater as shown in the table 2. Nitrate concentration was found to be 12.6 mg/L NO<sub>3</sub>-N, while its allowable content in groundwater is 10mg/L. For evaluation of reactivity of 2.2%Cu-1.6%Pd-hematite catalyst, nitrate concentration in the groundwater sample was increased to 40 mg/L NO<sub>3</sub>-N by adding a stock solution prior to the start of reduction by the Cu-Pd-hematite catalyst. Unless otherwise stated, the initial concentration of nitrate was fixed by such an addition. Ammonium was not detected in the groundwater sample. The pH (6.1) and turbidity (0.31 NTU) was found in the permissible range and no taste and color was detected. Among organic chemical compounds analyzed for Diazinon, Parathion, Fenitrothion, Carbaryl, 1.1.1-Trichloroethane, Tetrachloroethylene, Trichloroethylene, Dichloromethane, Benzene, Toluene, Ethylbenzene, Xylene, 1.1-dichloroethylene, Carbon tetrachloride, Phenol, Formaldehyde,

1.2-dibromo-3-chloropropane, and 1.4-dioxane, however, only Dichloromethane was detected in 0.004 mg/L.

### 3.2 Evaluation of catalytic reactivity

It is well known that impurities (i.e. anions, cations etc.) present in groundwater inhibit the catalytic activity of bimetallic catalysts (Chaplin et al. 2006; Prusse et al. 2000; Pintar et al. 1998).

Table 2. Characterization of groundwater sample for physical and chemical parameters

Name	*Con. (mg/L)	Name	*Con. (mg/L)	Name	Con. (mg/L)
Ca	31.02	Diazinon	ND	Phenol	ND
Fe	0.048	Parathion	ND	Formaldehyde	ND
K	3.309	Fenitrothion	ND	1.2-dibromo-3-chloropropane	ND
Mg	11.06	Carbaryl	ND	KMnO <sub>4</sub>	1
Na	33.1	1.1.1-Trichloroethane	ND	B	ND
P	0.041	Tetrachloroethylene	ND	Cu	0.016
As	ND	Trichloroethylene	ND	Anionic surfactant	ND
Se	ND	Dichloromethane	0.004	Zn	0.031
Hg	ND	Benzene	ND	Cl <sup>-</sup>	103
Cyan	ND	Toluene	ND	Mn	ND
Cr	ND	Ethylbenzene	ND	SO <sub>4</sub> <sup>2-</sup>	4
NH <sub>3</sub> -N	ND	Xylene	ND	Al	ND
NO <sub>3</sub> -N	12.6	1.1-dichloroethylene	ND	1.4-dioxane	ND
Cd	**ND	CCl <sub>4</sub>	ND	Hardness	228mg/L
<b>Other physical parameters</b>					
Odor	ND	Color	1	pH	6.1
Taste	ND	Turbidity	0.31 NTU		

\* Concentrations (mg/L)

\*\*Not detected

A slow removal rate of nitrate was expected in this study due to presence of anions, cations, and hardness. Initially, we investigated  $\text{NO}_3\text{-N}$  reduction (40 mg/L) in groundwater by 1.1 g/L catalyst (Fig. 2) which showed a very slow and incomplete reduction (about 55% removal), while the nitrate reduction in DDIW was complete (100%). This confirms an inhibitory effect of anions and cations along with other impurities in the groundwater sample. To enhance the nitrate removal, the 2.2%Cu-1.6%Pd-hematite catalyst loading was systematically increased (i.e. 1.1, 2.2, 3.3, and 4.4 mg/L). Results show that nitrate removal and kinetics were significantly improved with the increase of catalyst loading (Fig. 2). It has been reported that  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and other groundwater constituents can inhibit the nitrate reduction rates by competing for active sites of catalyst (Chaplin et al. 2012; Pintar et al. 2004; Lemaigen et al. 2002; Pintar et al. 2001; Deganello et al. 2000). As the catalyst loading increased, the relative reactive sites of Cu-Pd increased. Therefore, complete nitrate removal can be achieved by the abundant reactive sites as the catalyst loading reach  $\geq 2.2\text{g/L}$  (Fig. 2). It is interesting to note that nitrite selectivity decreased from 5% to  $\leq 1\%$  as the catalyst loading increased from 1.1 to 4.4g/L (table 3). It shows that at low catalyst loading, groundwater constituents may inhibit the nitrate reduction to nitrite and further reduction of nitrite to nitrogen and/or ammonium.

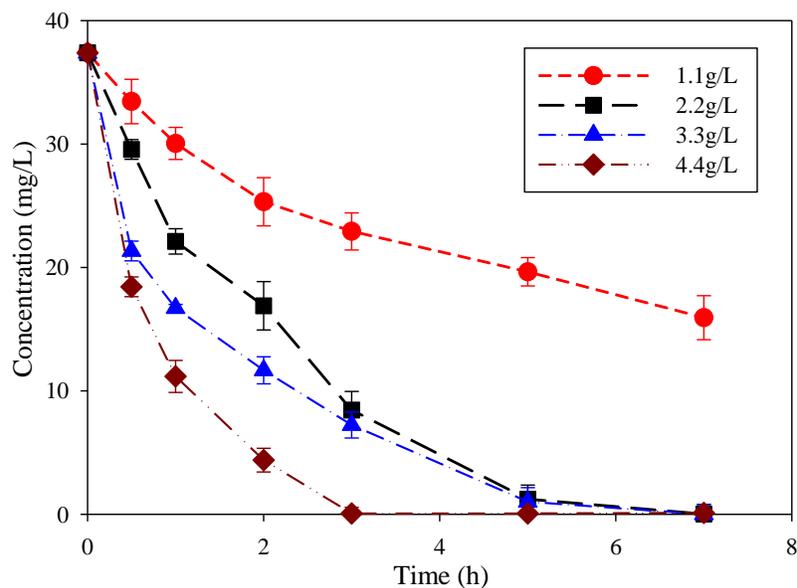


Fig. 2 Nitrate removal by different catalyst concentrations

Ammonium selectivity decreased (from 47.5% to 43.87%), while nitrogen selectivity increased (from 52% to 56.13%) with the increase of catalyst loading (from 2.2g/L to 4.4g/L, table 3). On the other hand, nitrogen selectivity was about 52% in the same range. The current nitrogen selectivity is lower than our previously reported one for DDIW

experiments (i.e. 72%). This increase in ammonium selectivity and decrease in nitrogen selectivity could be due to the presence of hardness (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in groundwater samples, which support  $\text{NH}_4^+$  formation over nitrogen. This result shows that groundwater constituents may not only inhibit the reduction step but also influence the formation of nitrogen and/or ammonium in overall process. Although higher catalyst loadings reduced nitrate at higher rates, we selected 2.2 g/L catalyst loading due to economic values and high nitrogen selectivity for further evaluation and experiments.

Table 3. Comparison of nitrate removal and byproduct selectivities at different catalyst concentrations

Amount of catalyst (g/L)	Nitrate removal (%)	Nitrite selectivity (%)	Ammonium selectivity (%)	Nitrogen selectivity (%)
1.1	57.41	4.97	18	77.03
2.2	100	0.5	47.5	52
3.3	100	0.23	45.31	54.46
4.4	100	0	43.87	56.13

### 3.3 Evaluation of removal capacity

In order to evaluate the removal capacity of 2.2%Cu-1.6%Pd-hematite catalyst, seven concentrations of initial nitrate (40, 60, 80, 120, 160, 300, and 600 mg/L  $\text{NO}_3\text{-N}$ ) were tested at same catalyst loading (i.e., 2.2 g/L, Fig. 3). The initial nitrate input and resulting total nitrate removal was converted to “specific nitrate input (mg  $\text{NO}_3\text{-N/g}$  catalyst)” and “specific nitrate removal (mg  $\text{NO}_3\text{-N/g}$  catalyst)”, respectively to comprehend the reaction on unitary basis (Hamid et al., 2015; Hamid and Lee, 2015). The specific nitrate input is shown in black color and specific nitrate removal is shown in blue color, while overall removal efficiency is depicted in red color in Fig. 3.

Remarkable removal efficiency (>95%) was observed for all nitrate concentrations (Fig. 3, red line). It is interesting to note that specific nitrate removal increases with the increase of specific nitrate input, showing that 2.2%Cu-1.6%Pd-hematite is a stable catalyst with high nitrate removal capacity. It has been reported that the removal capacity of catalyst declines due to oxidation of  $\text{Cu}(0)$  to  $\text{Cu}_2\text{O}$  ( $\text{NO}_3^- + 2\text{Cu}(0) \rightarrow \text{Cu}_2\text{O} + \text{NO}_2^-$ ) and  $\text{CuO}$  ( $\text{NO}_3^- + \text{Cu}_2\text{O} \rightarrow 2\text{CuO} + \text{NO}_2^-$ ) during nitrate reduction (Shin et al. 2014; Jung et al. 2014; Bae et al. 2013; Jung et al. 2012). The stable and complete nitrate reduction by 2.2%Cu-1.6%Pd-hematite during nitrate reduction. On the other hand, the valence of Pd does not change and is kept constant at  $\text{Pd}(0)$  state due to hydrogen chemisorption and activation. The stable and complete nitrate reduction by 2.2%Cu-1.6%Pd-hematite also indicates that the catalyst is continuously activated by via rejuvenation of Cu and Pd by the hydrogen.

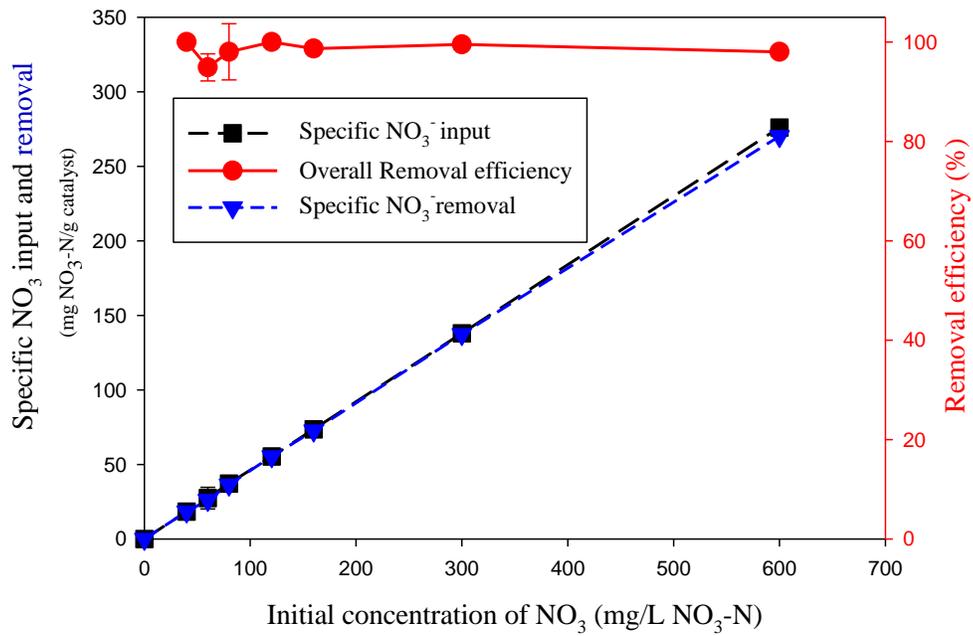


Fig. 3 Evaluation of nitrate removal capacity of 2.2%Cu-1.6%Pd-hematite at different nitrate concentrations.

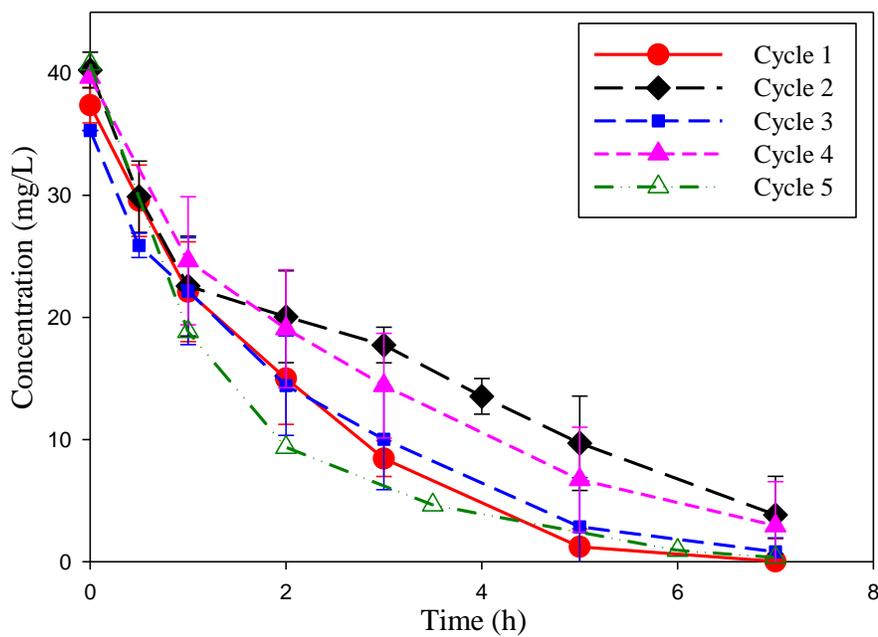


Fig. 4 Nitrate removal by 1.6% Pd-2.2% Cu/hematite catalyst over five recycles

### 3.4 Recycling of catalyst for nitrate reduction

Reactivity of catalyst in groundwater is strongly affected by several factors, i.e. 1) temporary or permanent fouling by groundwater impurities, 2) dilution of promoter metal, noble metal, and/or support material due to leaching in treated discharges, and 3) sintering of bimetallic nano-particles during recycling (Hamid et al., 2016; Chaplin et al, 2012; Jung et al, 2012). In order to further evaluate the stability of hematite supported bimetallic catalyst, 2.2% Cu-1.6%Pd-hematite catalyst was recycled for five times (Fig. 4). At every recycling experiment, the same catalyst was subjected to reduce NO<sub>3</sub>-N at same initial concentration (40 mg/L NO<sub>3</sub>-N). At the end of every recycling experiment, the catalyst in the reactor was collected, washed, dried, and calcined under same procedures and conditions. Due to loss of catalyst during sampling and processing, the catalyst to nitrate ratio was adjusted (when needed) to keep the same conditions. Results from recycling experiments show that catalyst achieved stable nitrate removal (i.e. >95%) during all five recycles (Fig. 4). Furthermore, nitrite selectivity was found at ≤ 6%, ammonium selectivity was at ≤ 42% and the nitrogen selectivity was at ≥56% in all cycles (Table 4).

Table 4. Nitrate removal and byproducts selectivity of 2.2%Cu-1.6%Pd-hematite for five cycles

No. of cycles	Nitrate removal (%)	Nitrite selectivity (%)	Ammonium selectivity (%)	Nitrogen selectivity (%)
1	99.94	0.78	42.63	56.59
2	98.51	6.02	37.22	56.76
3	99.71	0	42.16	57.84
4	94.80	3.19	40.56	56.25
5	97.43	0	42.84	57.16

The stability of 2.2%Cu-1.6%Pd-hematite catalyst during the recycling experiments shows that this catalyst is not only chemically stable against leaching but also resistant to permanent fouling due to the impurities of groundwater. The catalyst may have suffered from temporary fouling which could have been simply addressed by washing or reducing again using NaBH<sub>4</sub>. It has been reported that some catalysts suffer from strong fouling due to reduced sulfur species (i.e. HS<sup>-</sup> and SO<sub>3</sub><sup>2-</sup>), while weak fouling due to HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and OH<sup>-</sup>. The strong fouling could be reversed by oxidative regeneration, while weak fouling could be addressed by washing the catalyst by deionized water (Chaplin et al. 2012; Chaplin et al. 2006; Shindler et al. 2001; Lemaigen et al., 2002). The stable nitrate removal with high nitrogen selectivity and consistent composition after every recycling experiment indicate that the 2.2%Cu-1.6%Pd-hematite is resistant to permanent fouling. The results also imply that 2.2%Cu-1.6%Pd-hematite is suitable for the application to

nitrate contaminated groundwater treatment due to its stability, higher reactivity, economical and environmentally benign nature.

#### 4. Conclusions

The experimental results presented in this study show that 2.2%Cu-1.6%Pd-hematite is stable and has high capacity for groundwater denitrification. The nitrate removal in the groundwater was found directly proportional to catalyst loadings. The catalyst recycling experiments show that its chemical composition and structure did not change, indicating the proper catalyst for the treatment of nitrate in groundwater. This study can help improve and develop efficient nitrate removal treatment technologies by providing the basic understanding and examples of catalytic reactions of nitrate in groundwater.

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