

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 ₄	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 ⁻	103
Cyan	ND	Toluene	ND	Mn	ND
Cr	ND	Ethylbenzene	ND	SO ₄ ²⁻	4
NH ₃ -N	ND	Xylene	ND	Al	ND
NO ₃ -N	12.6	1,1-dichloroethylene	ND	1,4-dioxane	ND
Cd	**ND	CCl ₄	ND	Hardness	228mg/L
Other physical parameters					
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 HCO_3^- , Cl^- , 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.

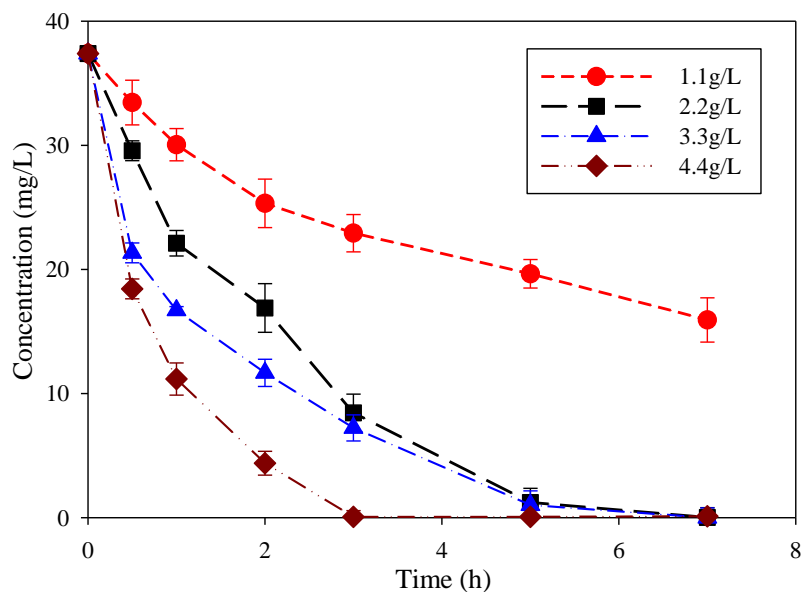


Fig. 2 Nitrate removal by different catalyst concentrations

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. Ca^{2+} , Mg^{2+}) in groundwater samples, which support 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 Cu_2O ($\text{NO}_3^- + 2\text{Cu}(0) \rightarrow \text{Cu}_2\text{O} + \text{NO}_2^-$) and 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 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.

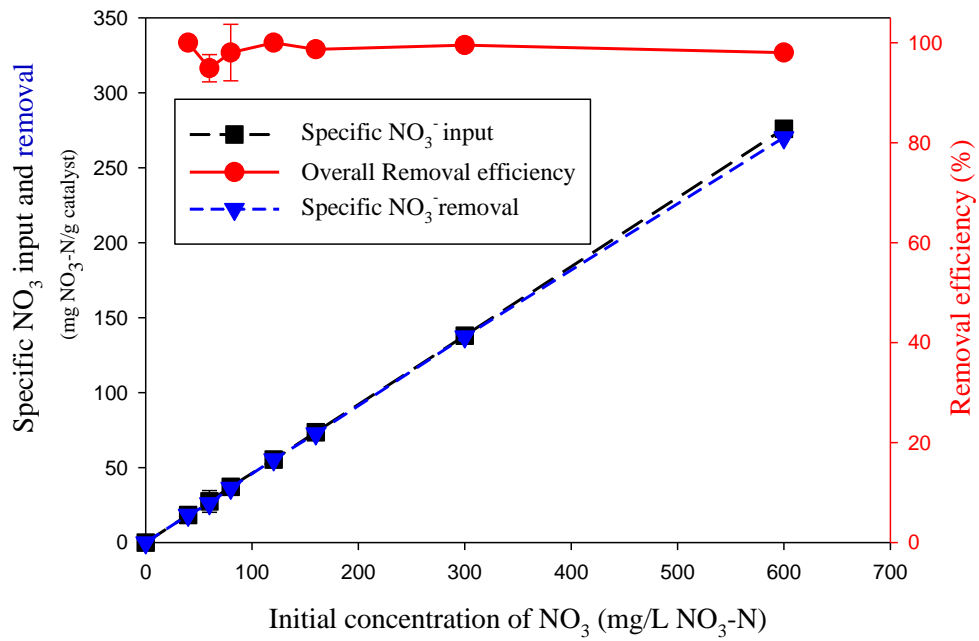


Fig. 3 Evaluation of nitrate removal capacity of 2.2%Cu-1.6%Pd-hematite at different nitrate concentrations.

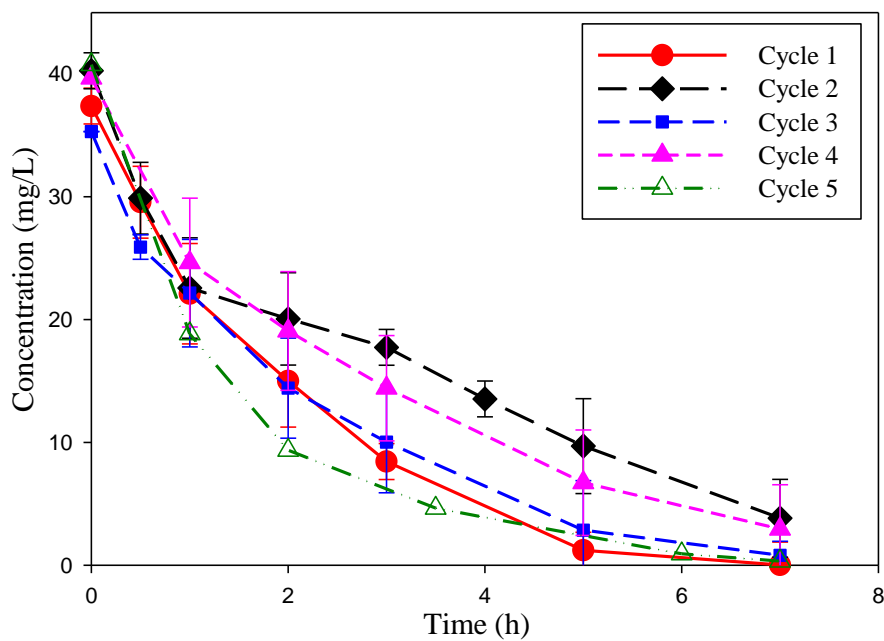


Fig. 4 Nitrate removal by 1.6% Pd-2.2% Cu/hematite catalyst over five recycles

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 NO₃-N at same initial concentration (40 mg/L NO₃-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 NaBH₄. It has been reported that some catalysts suffer from strong fouling due to reduced sulfur species (i.e. HS⁻ and SO₃²⁻), while weak fouling due to HCO₃⁻, SO₄²⁻, and OH⁻. 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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