Selective reduction of nitrate into nitrogen using Fe–Pd bimetallic nanoparticle supported on chelating resin at near-neutral pH

Jialu Shi [a], Chao Long [a,b,*], Aimin Li [a,b]

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, 163 Xianlin Avenue, Nanjing 210023, China
[b] Nanjing University Yancheng Environmental Protection Technology and Engineering Research Institute, 888 Yingbin Road, Yancheng 22400, China

HIGHLIGHTS

- Bimetallic Fe–Pd nanoparticles were immobilized effectively onto resin DOW 3N.
- Loading order of Fe and Pd affected the activity and selectivity of DOW 3N-Fe/Pd.
- Nitrate removal (>95%) using DOW 3N-Fe/Pd was obtained at near-neutral pH.
- N_2 selectivity of 71.0% was obtained at pH 8.67 without addition of reductant H_2.

GRAPHICAL ABSTRACT
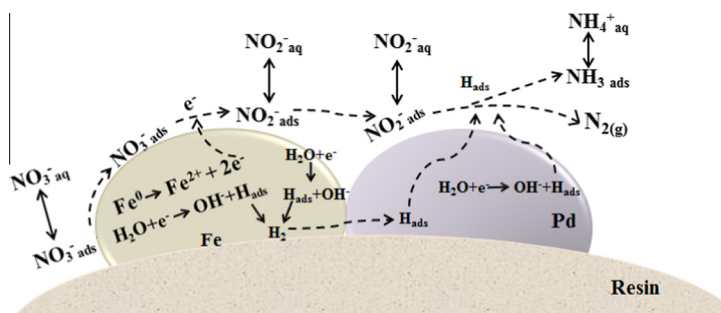
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ABSTRACT

Nano zero valent iron (nZVI) has emerged as a promising water treatment technology for reduction of contaminants. Unfortunately, for nitrate reduction by nZVI, near 100% of nitrate was converted to undesired ammonia (NH_3) and not to nontoxic nitrogen (N_2). In this study, supported bimetallic Fe–Pd nanoparticles were prepared by loading Fe and Pd on chelating resin (DOW 3N) by two different methods. The effect of the preparation method, solution pH and Pd loading on the reactivity and selectivity of Fe–Pd composites for nitrate removal was investigated at near-neutral pH in unbuffered solution. The results suggest that DOW 3N-Fe/Pd, which was prepared by loading Pd firstly and then Fe on DOW 3N, showed a remarkable nitrate removal (>95%). The selectivity to N_2 was increased with the increase of Pd content and solution pH; the N_2 selectivity of 69.2% was obtained at pH 6.75 using DOW 3N-Fe/Pd with 8 wt.% Pd–8 wt.% Fe. The high selectivity to N_2 benefited from the closer contact distance between Pd and Fe on the surface of DOW 3N-Fe/Pd and low intraparticle diffusion resistance.

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1. Introduction

Excess NO_3^- in drinking water is a potentially harmful contaminant because it may cause adverse health effects to humans, such as blue-baby syndrome (methemoglobinemia) and cancer. The World Health Organization has set the maximum contaminant level for nitrate at 10 mg N L^{-1} in drinking water. Diverse technologies have been developed to treat the water contaminated by NO_3^-. Ideally, NO_3^- should be selectively reduced to N_2 without further reduction to NH_4^+. Biological denitrification, catalytic hydrogenation and photocatalytic reduction have been reported as the promising technologies for selectively reducing nitrate to nontoxic N_2. However, these technologies suffer from sludge generation or massive addition of chemicals such as H_2 and oxalic acid [1,2].

Nano zero valent iron (nZVI) has been intensively studied for reductive removal of nitrate from water [3–6]. However, nZVI

particles tend to agglomerate into large particles, leading to a lower removal efficiency and reactivity. Moreover, nitrate was mainly reduced into undesired ammonium as the primary end product [7,8]. So, several strategies had been developed to enhance nitrate reduction by nZVI, including (1) immobilization of nZVI on support materials [9,10] and (2) deposition of other metals such as Cu, Ni, Pd, onto nZVI surfaces [11–13]. Even though these approaches resulted in significant increases in the reduction of NO_3^-, the N_2 yields remained low without pH control. An optimum N_2 selectivity of 30% was obtained in alkaline solution (pH = 7.5–8.5) using the ZVI deposited bimetallic Pd and Cu [13]. Although it is reported that nitrate could be converted into nitrogen gas with maximum 66% selectivity by the stabilized nZVI with carboxymethyl cellulose at pH 7–7.5 with buffer solution, only 40% of nitrate was reduced without the addition of a buffer [14]. However, pH control with buffer solution is inconvenient and not practical. In addition, nitrate removal by adsorption of reactive iron hydroxides formed during the reduction was not considered in these studies, which had a significant contribution to nitrate removal [15]. Therefore, an effective method is required to remove nitrate by nZVI with high N_2 selectivity in near-neutral pH without buffer solution.

The support can have an indirect effect on activity and selectivity by influencing the density, size, morphology of metallic nanoparticles. Recently, we reported that the nZVI immobilized onto the chelating resin (DOWEX™ M4195) had a high removal efficiency for nitrate [16]; however, the main problem was that undesired ammonium was the primary end product at a yield of >82%. Numerous studies had demonstrated that the iron-based bimetallic particles could degrade contaminants faster than monometallic ZVI particles [17,18]. In general, Pd was more catalytic active than the other metals (Ni, Pt or Cu) [12,19] and had been proved to be the most selective for nitrite reduction [10]. In the present work, bimetallic Fe/Pd nanoparticles were immobilized in DOWEX™ M4195 for nitrate reduction with a high N_2 selectivity without buffered solution. The overall objective of this study is to investigate the effect of methods of preparation of supported nanoparticles, solution pH and Pd loading on the denitrification rate and N_2 selectivity, and to acquire further insights into the underlying nitrate reduction mechanism.

2. Materials and methods

2.1. Materials

DOWEX™ M4195 (DOW 3N) was purchased from Sigma–Aldrich. The physicochemical properties of DOW 3N was shown in Table S1. The resin is composed of a polystyrene cross-linked with divinyl benzene backbone and bis (2-pyridylmethyl) amine functional groups. Prior to use, the resin was extracted with ethanol in a Soxlet apparatus for 8 h, and then washed by 4 wt.% hydrochloric acid and 4 wt.% sodium hydroxide. All chemicals including ferric sulfate ($Fe_2(SO_4)_3$), palladium chloride ($PdCl_2$), ethyl alcohol, sodium borohydride ($NaBH_4$), sodium nitrate ($NaNO_3$) were of analytical grade and purchased from Nanjing Chemical Reagent Co. Ltd., China.

2.2. Preparation of supported nanoparticles

The typical synthesized procedure in the present study is depicted as follows: 1 g DOW 3N resin was added into 500 mL Fe^{3+} solution containing 2–3 g L^{-1} of Fe^{3+} and shaken for 24 h at 30 °C. Then, the resin spheres were added into 125 mL of 150–650 mg L^{-1} Pd^{2+} solution and shaken for 10 h at 30 °C. Afterwards,

the resin spheres were reduced by 100 mL 2% $NaBH_4$ solution with constant stirring for 2 h at 20 °C under the N_2 atmosphere. The obtained product was called DOW 3N-Fe/Pd. Another method to prepare the supported bimetallic nanoparticles called DOW 3N-Fe/Pd-R was to load Pd firstly and then Fe. One gram of DOW 3N resin was added into 125 mL 650 mg L^{-1} Pd^{2+} solution and shaken for 10 h at 30 °C. Then the resin spheres were added into 500 mL Fe^{3+} solution containing 3 g L^{-1} of Fe^{3+} and shaken for 10 h at 30 °C. Finally, the resin spheres loaded with Pd and Fe were reduced by $NaBH_4$ using the same method with DOW 3N-Fe/Pd.

The amount of Fe and Pd loaded onto the DOW 3N was calculated by determining the initial and final concentrations of the preparation solution using an atomic absorption spectrophotometer (AA-6300C). In all cases, the Fe loading was approximately 80 ± 5 mg g^{-1} by changing the initial Fe^{3+} solution.

2.3. Characterization

The X-ray diffraction (XRD) analysis was performed by X-ray diffractometer (ARL X'TRA, Switzerland). High-resolution transmission electron microscope (HR-TEM) analyses were performed using electron microscope (JEM-2100, Japan). The Fe and Pd distribution in resin was observed by scanning electron microscope–energy dispersive spectrometer (SEM–EDS) (S-3400N II, Japan). The surface chemistry of NZVI was analyzed by X-ray photoelectron spectroscopy (XPS) (PHI5000 VersaProbe, Japan).

2.4. Batch experiments

All the batch experiments were carried out in three-neck flask at 25 °C. A certain amount of composites with various Pd loadings (2–8% in mass) were added to 500 mL of 20 mg N L^{-1} nitrate solution stirred with a mechanical stirrer, in which the content of Fe was kept at about 160 mg L^{-1}. Nitrate solution was deoxygenated by a N_2 stream. The initial solution pH was adjusted by HCl (1.0 mol L^{-1}) or NaOH (1.0 mol L^{-1}). At specific time intervals, samples were withdrawn with the aid of a syringe to analyze the concentration of nitrate, nitrite and ammonia in the solution after filtering it through a 0.22 μm membrane filter. Control experiments without the reductant were also performed at the same conditions. All solutions were prepared using ultrapure water produced by a Millipore-Q system (Millipore Synergy, USA).

As previous studies, N_2 selectivity could be calculated from the balance of nitrogen products analyzed in solution [20,21]. In this study, the off-gas from the reactor was absorbed in acidic solution for analyzing gas phase ammonia, which might has been produced when the solution pH was alkaline. Nitrate and nitrite adsorbed on the composites were detected after being washed using 5 mmol L^{-1} NaOH. Nitrate and nitrite were analyzed by ion chromatography (Dionex 1000, USA) with an AS11-HC guard column using 15 mmol L^{-1} KOH solution as mobile phase at a flow rate of 1.0 mL min^{-1}. Ammonium was determined by a UV–Vis spectrophotometer (UV 2450, Shimadzu, Japan) with the light absorption at 697 nm using salicylic acid spectrophotometry. The solution pH was determined by a pH meter (FE20, Mettler Toledo, Switzerland).

Nitrate removal ($R_{nitrate}$), nitrate conversion ($C_{nitrate}$) and the selectivity of each product ($S_{nitrite}$, $S_{ammonia}$, and $S_{nitrogen}$) were calculated as follows:

$$R_{nitrate}(\%) = \frac{[NO_3^-]_i - [NO_3^-]_f}{[NO_3^-]_i} \times 100 \tag{1}$$

$$C_{nitrate}(\%) = \frac{[NO_3^-]_i - [NO_3^-]_f - [NO_3^-]_a}{[NO_3^-]_i} \times 100 \tag{2}$$