Catalytic Nitrate Removal in Continuous Bimetallic Cu−Pd/Nanoscale Zerovolta
ciron System

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ABSTRACT: In this study, we investigated catalytic nitrate removal using nanoscale zerovalent iron (NZVI) supported Cu−Pd bimetallic catalyst (Cu−Pd/NZVI) in a continuous reactor system. Control experiments showed that Cu, Pd, and a proper supply of H2 are essential for relatively sustainable nitrate (30 mg/L NO3−-N) reduction in continuous mode. When we optimized operational parameters to enhance removal efficiency and N2 selectivity, we finally achieved complete nitrate removal with 48% N2 selectivity at 9 h. During a longevity test (200 h reaction), excellent removal was observed (>91% in 24 h) with 42−60% N2 selectivity. However, removal gradually decreased to 13% in 200 h with increasing nitrite production. X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy analysis revealed that both the support (NZVI) and the Cu(0) oxidized after continuous denitrification. This indicated that loss of NZVI reductive capacity and the oxidation of Cu(0) to Cu(I) and Cu(II) deactivated nitrate removal during the continuous nitrate reduction by Cu−Pd/NZVI.

1. INTRODUCTION

Nitrate is an environmental pollutant frequently found in surface water and groundwater due to poorly treated domestic and industrial wastewater, and to excessive use of fertilizer during agricultural activities.1 Nitrate pollution not only causes eutrophication but is also hazardous to human health. It can cause methemoglobinemia, resulting in a decrease in the oxygen-carrying capacity of hemoglobin, and may be converted to carcinogenic N-nitroso compounds.2−5 Hence, many efforts have been made to develop removal and control technologies for the treatment of nitrate-contaminated wastewater and groundwater. Physical technologies such as adsorption and reverse osmosis can remove nitrate efficiently, but they also produce concentrated nitrate wastewater that needs further treatment and disposal. Biological denitrification, which is used in wastewater treatment plants, is a very slow process requiring huge infrastructure and multistage processes to meet effluent standards and regulations.

Recently, nitrate removal using bimetallic catalysts has captured much attention due to their higher removal efficiency, selectivity toward nontoxic products, requirement for relatively mild conditions, and easier operation compared to other physicochemical and biological technologies.6−10 To develop effective and selective bimetallic catalysts, a variety of materials have been used for catalytic nitrate removal to date. Among various promoter metals (e.g., Cu, Ni, Sn) and noble metals (e.g., Pd, Pt, Au, and Ru), the combination of copper and palladium (Cu−Pd) is known to be the most effective and selective combination for catalytic denitrification.1,2,7−11 In addition, various support materials (e.g., activated carbon, carbon nanotubes, and metal oxides) have been used to enhance catalytic denitrification.1,2,12−17 However, nanomaterials such as carbon nanotubes, alumina, and silica are still under scrutiny regarding their potential toxic effects on the natural environment and on human health.18−20 Furthermore, sophisticated and expensive techniques are required to separate and collect nanoparticles after they are used, creating another critical barrier to the practical application of bimetallic catalysts to treatment plants.

Some iron-based supports (e.g., magnetite, hematite, and nanoscale zerovalent iron (NZVI)) are known to be ecofriendly materials that can prevent the leaching of bimetal deposits on supports during catalytic-denitrification processes.1,8,21 Among such materials, NZVI has been extensively used for water and groundwater treatment in laboratory and field studies. This is due to its high capacity for reduction of diverse contaminants as well as to its easier and economical method of production than other iron oxides.22,23 In addition, NZVI possesses magnetic properties, leading to easy separation from suspension by magnetic force. For these reasons, NZVI has been used as a support for Cu−Pd bimetallic catalysts and showed enhanced catalytic denitrification in batch reactors.7,9 However, there is presently only limited knowledge about continuous catalytic denitrification by Cu−Pd/NZVI catalyst. Furthermore, most studies using other bimetallic catalysts in continuous reactor systems focused on the investigation of factors relevant to the material properties of the catalysts and the effect of these properties on the reactions. Therefore, it is timely to elucidate the effect of significant operational factors (H2 flow rate, hydraulic retention time (HRT), catalyst loading, and
The main goal of this study was to evaluate the catalytic nitrate removal in continuous mode using Cu–Pd catalyst supported by NZVI. The specific objectives of this study were (1) to determine the proper content of promoter and noble metals in Cu–Pd/ZVI catalyst for effective and continuous nitrate removal, (2) to investigate the effect of various operational factors on enhanced catalytic nitrate removal and N₂ selectivity, (3) to determine optimal conditions leading to the stable denitrification with high N₂ selectivity, and (4) to evaluate the longevity of Cu–Pd/NZVI catalyst for practical application.

2. MATERIALS AND METHODS

2.1. Chemicals. Ferric chloride hexahydrate (98%, Sigma-Aldrich Inc., USA) and sodium borohydride (98.0%, Samchun Pure Chemical Co., Korea) were used for NZVI synthesis. Copper(II) chloride dihydrate (97.5%, Samchun Pure Chemical Co., Korea) and disodium tetrachloropalladate (98% Sigma-Aldrich Inc., USA) were used as Cu and Pd precursor reagents, respectively. Nitrate stock solution was prepared using potassium nitrite (97.0%, Samchun Pure Chemical Co., Korea), and ammonium chloride (98.5%, Duksan Pure Chemical Co., Korea). Sodium bicarbonate (99.7%, Sigma-Aldrich Inc., USA) and sodium carbonate (99.5%, Sigma-Aldrich Inc., USA) were used to prepare eluent for nitrite and ammonium measurement. Deionized water (DIW) was obtained from an ultrapure water system (ELGA PURELAB Classic system) and purged with argon gas for 12 h to prepare deaerated deionized water (DDIW). The DDIW was used in all experiments in this study. MOPS buffer (3-morpholinos propane-1-sulfonic acid; ≥99.5%, Sigma) was used to control the pH in pH experiments.

2.2. Synthesis of Cu–Pd/NZVI Catalyst. NZVI was synthesized according to a widely known method. Briefly, 0.9 M NaBH₄ solution was prepared in 500 mL of DDIW and added dropwise to a 500 mL solution of FeCl₃·6H₂O (0.11 M), with continuous mixing, at room temperature. The stirring was continued for 30 min to remove H₂ gas released from NaBH₄. Synthesized NZVI was filtered using a membrane filter (0.2 μm, Advantech, Japan), washed three times with DDIW, and resuspended in 1 L of DDIW.

The copper precursor solution was prepared by adding an appropriate amount of copper(II) chloride dihydrate to DDIW (e.g., 0.1207 g in 125 mL of DDIW for 1.5% Cu loading). Similarly, Pd precursor solution was prepared by adding disodium tetrachloropalladate to DDIW (e.g., 0.041 g of disodium tetrachloropalladate to 250 mL for 0.5% Pd loading). The solutions of copper and palladium precursors were sequentially added dropwise into the NZVI suspension, and the resultant slurry was constantly mixed for 30 min each to reduce Cu(II) to Cu(0) and Pd(II) to Pd(0), by NZVI. The Cu–Pd/NZVI bimetallic catalyst was then filtered in an anaerobic chamber to maintain the catalyst reactivity. The filtered catalyst was dried by a freeze-dryer (Labconco Freezone 6 plus, USA) at −81 °C for 24 h and stored in the anaerobic chamber for further use. Catalysts with different loadings of Cu (0.5, 1, 1.5, and 2 wt %) and Pd (0.1, 0.3, 0.5, 1.5, and 2 wt %) were also prepared using the same method described above, except for the Cu and Pd contents. Cu–Pd/magnetite catalyst was also prepared using similar steps as described earlier. All the above-mentioned synthesis steps were performed under anaerobic conditions.

2.3. Continuous Reactor System and Experimental Procedures. All experiments for the continuous removal of nitrate by Cu–Pd/NZVI catalyst were conducted in a 500 mL glass reactor (200 mL effective volume for the catalytic denitrification). Our previous batch reactor was modified to create a continuous reactor by continuously introducing water containing nitrate through the inlet and discharging treated effluent from the outlet. A mixed cellulose–ester membrane filter (0.2 μm, Advantech Japan) was attached at the inlet and outlet of the reactor to avoid loss of catalyst during the reaction.

For continuous nitrate treatment, water solution containing 30 mg/L NO₃⁻-N (132.8 mg/L NO₃⁻) was prepared in a water-storage flask by adding an appropriate amount of KNO₃ to DIW. We intended to use a much higher concentration of nitrate than the maximum concentration of nitrate in drinking water (10 NO₃⁻-N mg/L) set by the World Health Organization. The nitrate-containing water was purified with argon gas overnight (and during the experiment) to remove dissolved oxygen, and then pumped to the reactor while maintaining the hydraulic retention time (HRT) at 60 min (unless otherwise specified). Hydrogen (H₂) gas was introduced into the reactor as redundant and to maintain anaerobic conditions inside the reactor as soon as the reactor attained a steady state discharge under constant stirring at 300 rpm.

Figure 1. Schematic diagram of continuous reactor system.
rpm (unless otherwise specified). Hydrogen gas from a gas cylinder was provided to the continuous reactor. The flow rate of H₂ was controlled by a gas flow meter (Dwyer Instruments, Inc. USA). A glass diffuser was used to provide a uniform distribution of H₂ bubble size during the catalytic nitrate removal (Figure 1). After 30 min of H₂ introduction, 0.2 g of catalyst (1 g/L) was added to the reactor (unless otherwise specified). Samples were collected using falcon tubes from the outlet at each sampling time, and immediately filtered using a syringe filter (0.2 µm, PTFE (Teflon) filter media, Whatman) to remove any metallic particles in the samples. A detailed schematic plan of the continuous reactor system is shown in Figure 1.

Control experiments were performed to check potential losses of nitrate not by catalysis (losses caused by additional reactions with NZVI, bimetals (Cu and Pd), and H₂) by comparing them according to their respective factors. To investigate the loss due to NZVI, experiments were performed with and without H₂ (50 mL/min) under controlled conditions (30 mg/L NO₃⁻−N, 60 min HRT, and 1 g/L NZVI loading). To investigate the losses by monometallic catalysts, experiments were performed using two catalysts (1.5% Cu–0% Pd/NZVI and 0% Cu–0.5% Pd/NZVI) under controlled conditions (30 mg/L NO₃⁻−N, 60 min HRT, 50 mL/min H₂, and 1 g/L catalyst loading). To investigate noncatalytic nitrate loss due to H₂ experiments were performed using 1.5% Cu–0.5% Pd/NZVI with and without H₂ (50 mL/min) under controlled conditions (30 mg/L NO₃⁻−N, 60 min HRT, and 1 g/L catalyst loading).

Continuous experiments were performed to investigate the effect of variation in metal (Cu and Pd) loading and H₂ supply on nitrate removal and byproduct selectivity. We evaluated four concentration of Cu (0.5, 1, 1.5, and 2%) with 0.5% Pd, and five concentrations of Pd (0.1, 0.3, 0.5, 1 and 2%) with 1.5% Cu. The other conditions were kept constant for all experiments (30 mg/L NO₃⁻−N, 60 min HRT, 1 g/L catalyst loading, and 50 mL/min H₂ supply). The effect of H₂ supply was examined at four different H₂ flow rates (10, 30, 50, and 100 mL/min) under controlled conditions (1.5% Cu–0.5% Pd/NZVI, 30 mg/L NO₃⁻−N, 60 min HRT, and 1 g/L catalyst loading).

Continuous kinetic experiments were also performed to investigate the effect of operational parameters (HRT, catalyst loading, and continuous operation) on nitrate removal. We evaluated three (20, 40, and 60 min) HRTs to investigate the effect of residence time on nitrate removal and byproduct selectivity. To investigate the proper amount of catalyst loading for optimal operation of nitrate removal, five catalyst loadings (0.1, 0.5, 1, 2, and 4 g/L) were tested. A longevity test to check the effect of continuous operation was also performed for 200 h under the optimal operational conditions obtained from the previous experiments (1.5% Cu–0.5% Pd/NZVI, 30 mL/min H₂ flow, 60 min HRT, 2 g/L catalyst loading, and 30 mg/L NO₃⁻−N).

2.4. Analytical Procedures. The concentrations of nitrate, nitrite, and ammonium were analyzed using an ion chromatography (IC; 883 basic IC plus, Metrohm, U.K.) equipped with a compact autosampler (863 Compact IC, Metrohm USA), anion column (Metrosep A Supp 4-250/40), and cation column (Metrosep C4-150/4.0). Eluents for anion analysis were prepared by mixing Na₂CO₃ (1.8 mM) and NaHCO₃ (1.7 mM) in DIW, and eluents for cation analysis were prepared by mixing HNO₃ (1.7 mM) in DIW. Exact amounts of samples (5 mL) collected from the reactor outlet were immediately filtered using a membrane filter (0.2 µm, PTFE filter media, Whatman) and analyzed by IC. The removal of nitrate (RNO₃⁻) and the selectivity toward byproduct (Sbyproduct) were calculated using the following equations.15

\[
R_{\text{NO}_3^-} (%) = \frac{[\text{NO}_3^- - \text{N}]_i - [\text{NO}_3^- - \text{N}]_f}{[\text{NO}_3^- - \text{N}]_i} \times 100
\]

\[
S_{\text{NO}_3^-} (%) = \frac{[\text{NO}_3^- - \text{N}]_f}{[\text{NO}_3^- - \text{N}]_i} \times 100
\]

\[
S_{\text{NH}_4^+} (%) = \frac{[\text{NH}_4^+ - \text{N}]_f}{[\text{NO}_3^- - \text{N}]_i} \times 100
\]

where subscripts "i" and "f" refer to initial and final concentrations, respectively. Other byproducts such as NO and N₂O are assumed to be negligible in this study. The specific nitrate loading is defined as the mass of nitrate introduced per unit mass of catalyst per unit of time (mg NO₃⁻−N/g cat/h), and it was calculated using the following equation.

\[
\text{specific nitrate loading} = \frac{V C_{\text{NO}_3^-}}{C_{\text{cat}}}
\]

where Q is the volumetric flow rate (L/h), CNO₃⁻ is the nitrate concentration (mg/L) in influent water, V is the volume of the reactor (L), H is the HRT (h) equal to V/Q, and Ccat is the catalyst concentration in the reactor (g/L). The specific nitrate removal of the continuous system is defined as "the maximum mass of nitrate that can be removed by unit mass of catalyst in unit time (mg of NO₃⁻−N/g cat/h)" and it was calculated by the following equation.

\[
\text{specific nitrate removal} = \frac{[\text{NO}_3^- - \text{N}]_i - [\text{NO}_3^- - \text{N}]_f}{H C_{\text{cat}}}
\]

The Cu–Pd/NZVI catalyst was identified by X-ray diffraction (XRD; RIGAKU, D/MAX-2500, 18 KW) with Cu KN radiation. A solid sample was obtained by filtration of the Cu–Pd/NZVI suspension, and then immediately dried using a freeze-dryer in a special cylinder which has a valve for a closed system for 24 h. After the drying was finished, the samples in the cylinder were transferred to the anaerobic chamber for sample preparation of XRD. Dried samples from before and after the reaction were carefully transferred to an XRD template. The samples on the XRD template were treated with 1:1 (v/v) glycerol solution to avoid surface oxidation, and scanned from 20 to 80° at a scan speed of 2° min⁻¹. XRD patterns of samples were analyzed by comparison with references in the Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data files (JADE 9, Materials Data Inc.).

DOI: 10.1021/acs.iecr.5b01127
Ind. Eng. Chem. Res. XXXX, XXX, XXX--XXX
Change in the morphological characteristics of Cu–Pd/NZVI catalyst before (fresh catalyst) and after the reaction (200 h) was investigated using a transmission electron microscope with energy-dispersive X-ray (TEM/EDX, Tecnai G2 F30 model, FEI Co.). The dried catalyst prepared for TEM analysis was dispersed in serum bottles containing ethanol, in the anaerobic chamber, and tightly capped for ultrasonication. After 5 min of sonication, several droplets of the suspension were put on carbon TEM grids in the anaerobic chamber. TEM samples were analyzed at an acceleration voltage of 300 kV.

An inductively coupled plasma mass spectrometer (ICP-MS; 7700S, Agilent) was used to quantify leaching of Fe, Cu, and Pd from the Cu–Pd/NZVI catalyst during the continuous removal of nitrate. Effluent samples collected at 9 and 200 h were immediately filtered using a membrane filter, treated with 10% HNO₃, and then analyzed using ICP-MS.

X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo VG Scientific) analysis was performed to investigate the oxidation state of Cu, Pd, and Fe on the catalyst surface. The Cu–Pd/NZVI catalyst for XPS analysis was collected using vacuum-filtering. The filtered catalyst was dried using the freeze-dryer at −81 °C for 24 h maintaining the anaerobic condition. The dried catalyst was then carefully packed onto XPS sampling templates, and then shifted to airtight vials containing ethanol to avoid oxidation of samples. All sample preparations were carried out within the anaerobic chamber.

3. RESULTS AND DISCUSSION

3.1. Control Experiments. Control experiments were performed to evaluate the role of NZVI in the continuous catalytic removal of nitrate, and to investigate the effects of Cu, Pd, and H₂ supply during the reaction (Figure 2). Rapid nitrate removal (85%) was observed in 1 h using NZVI alone in the absence of Cu, Pd, and H₂. NZVI reactivity continued to decrease to almost zero in 7 h. This indicates that NZVI alone cannot sustain stable nitrate removal in a continuous treatment system due to the loss of reactivity caused by passivation of Fe(0) to iron (hydr)oxides.¹²,3⁰–3² Nitrate removal by NZVI alone with 50 mL/min H₂ supply showed a trend similar to that with NZVI alone, indicating that H₂ supply did not significantly affect nitrate removal in the presence of NZVI alone. Monometallic catalysts (1.5% Cu/NZVI and 0.5% Pd/NZVI) with a supply of H₂ showed almost complete nitrate removal in 1 h. For Cu/NZVI, Cu(0) particles formed from Cu(II) by NZVI²⁸ removed more nitrate ([NO₃⁻ + Cu(0) → Cu(II)O + NO₂⁻] in 1 h than did NZVI alone. Regardless of the H₂ supply, the reactivity of the Cu/NZVI rapidly decreased as the reaction proceeded. This may be due to a lack of adsorption of H₂ to Cu sites, leading to insignificant nitrate removal after 1 h. For Pd/NZVI, the initial nitrate removal was higher than 93% (until 3 h), which is comparable to those of other controls (20–60%). This may be caused by the adsorption of H₂ to Pd sites. H₂ has been known to properly reduce iron oxides to Fe(0),³³ thus it could be possible to avoid rapid passivation of the NZVI surface during the continuous nitrate removal. It has been reported that H₂ adsorbed on Pd sites cannot reduce nitrate,³⁴,³⁵ thus NZVI, during its slow passivation to iron (hydr)oxide, reduces nitrate more than Cu/NZVI does. The reactivity of Cu–Pd/NZVI catalyst without H₂ supply was poor during continuous nitrate removal, indicating that the amount of H₂ produced from anaerobic corrosion of NZVI [Fe(0) + 2H₂O → Fe(II)O + 2OH⁻ + H₂] was not enough to activate Cu–Pd/NZVI catalyst for nitrate removal. To confirm this effect, we conducted a batch experiment without H₂ supply. The results from the batch experiment (Figure S1 in Supporting Information) showed complete nitrate removal in 10 min (without H₂ supply), which is in accordance with the results reported by Liu et al.⁹ Although experimental results reported in this study and those reported by Liu et al.⁹ showed successful nitrate removal by Cu–Pd/NZVI without H₂ supply in batches (for 1 h), our results obtained from continuous mode clearly showed the loss of its catalytic reactivity without a supply of H₂. Compared to the results from controls, complete nitrate removal was sustained by Cu–Pd/NZVI catalyst with H₂ flow within 9 h. This shows that the presence of three components (i.e., Cu, Pd, and H₂) is essential to achieve effective and stable nitrate removal by Cu–Pd/NZVI catalyst. It is well-known that nitrate can first be adsorbed on Cu sites, resulting in reduction of nitrate to nitrite with further reduction to ammonia or N₂ on Pd sites activated by H₂ supply.⁸,¹³ Based on the experimental results, complete nitrate removal by Cu–Pd/NZVI for 9 h may be achieved by the probable combined effort of (1) reactive NZVI at the initial stage of the reaction and (2) consecutive catalytic activation from Cu–Pd bimetallic sites during the whole reaction.

3.2. Effect of Cu, Pd, and H₂ Loadings. Figure 3 shows the nitrate (30 mg/L NO₃⁻−N) removal and byproduct production after 9 h of continuous reactor operation at four different Cu loadings (0.5, 1, 1.5, and 2%). The removal increased from 21% to more than 99% as Cu loading increased from 0 to 1.5%, although it slightly decreased (~97% removal) at 2% Cu loading. This indicates that more than 1% Cu is required to achieve stable and complete nitrate removal (for 9 h) by Cu–Pd/NZVI catalyst. Although effective nitrate removal (97–99%) was observed within 9 h in the range of 1–2% Cu loading, the production of nitrite and ammonium and selectivity of N₂ were different at each Cu loading. The highest nitrite production (13%) was observed at the highest Cu loading (2%). This result is similar to those from other studies.⁸,⁵⁶ According to the results from the controls, nitrate can be mostly reduced to nitrite by Cu(0) surface after 9 h. High Cu content could cover active Pd sites (0.5%), resulting in

![Figure 2. Control experiments: effects of Cu, Pd, and H₂ supply on nitrate removal.](image-url)
the loss of the active Pd sites needed for further nitrite reduction (i.e., leading to accumulation of nitrite) and causing a decrease in the number of H’s adsorbed on Pd sites (i.e., resulting in low production of ammonia). Therefore, an optimal experimental condition needs to be proposed to increase N2 selectivity. In this study, 1.5% Cu showed the highest N2 selectivity (33.3%) with almost complete nitrate removal. We selected 1.5% Cu loading to use in further optimization experiments.

Figure 4 shows nitrate removal and byproduct production after 9 h of continuous operation at five different Pd loadings (0, 0.1, 0.3, 0.5, 1.5, and 2 wt %). Removal increased from 17 to 100% as Pd loading increased from 0.1 to 0.5%, but slightly decreased to 96% at 2% Pd loading. The results show that Pd loading higher than 0.5% was required for effective and sustainable nitrate removal in continuous mode. Nitrite production was low (<6.5%) for Pd-loading greater than 0.5%, while increase of ammonium selectivity (59% to more than 80%) and decrease of nitrate removal (from 33% to more than 99%) were observed. The results showed that increased Pd loading can increase the number of active H’s adsorbed on Pd sites, leading to enhanced nitrite production, and ammonium selectivity. It is well-known that the N/H ratio is one of the most important factors controlling byproduct selectivity. A high N/H ratio usually leads to increased N2 selectivity, while ammonium selectivity can increase at low N/H ratio. High Pd loading can cause more adsorption of H on Pd sites, leading to bonding with N atoms to produce more ammonia. This can inhibit bonding between N atoms, resulting in low N2 selectivity. Based on its results for effective nitrate removal, high N2 selectivity, and expense of Pd and H2, we selected 0.5% Pd loading for further experiments.

Figure 5 shows nitrate removal and byproduct production after 9 h of continuous operation at four different H2 flow rates (10, 30, 50, and 100 mL/min). Removal increased from 7% to more than 99% when the H2 flow rate increased from 0 to 50 mL/min, and slightly decreased to 92% when the H2 supply was 100 mL/min. This indicates that an H2 supply greater than 30 mL/min was necessary to effectively remove nitrate in continuous mode. Nitrite production decreased from 45% to 6% as the H2 flow rate increased from 30 to 50 mL/min, but significantly increased to 44% at 100 mL/min H2 supply. When the supply of H2 is insufficient (0–30 mL/min), nitrite reduction to ammonium or N2 may be inhibited, resulting in the accumulation of nitrite. On the other hand, formation of OH− ions produced from rapid reduction of nitrite (NO2− + H → NO + OH−) by high H2 loading can inhibit the contact of nitrite ions with the Pd surface. This could result in the increase of nitrite production with a decrease of ammonium and N2 selectivity at 100 mL/min H2 flow rate. Although nitrite was not fully reduced at 30 mL/min, we selected the flow rate for the next experiments because of its cost effectiveness, low ammonium selectivity, and N2 selectivity similar to that at 50 mL/min.

3.3. Effect of Hydraulic Retention Time. Figure 6 shows nitrate removal and byproduct production after 9 h of continuous operation at three different HRTs (20, 40, and 60 min). Removal increased from 51 to 100% as HRT increased from 20 to 60 min. The increase in removal could be attributed to simultaneous changes in nitrate input and contact time for the reaction. To investigate the integrated effect of operational parameters (i.e., HRT, catalyst dosage, and initial nitrate loading), we adopted combined parameters, "specific nitrate loading equation (6) and specific nitrate removal equation (7)" for continuous catalytic nitrate removal. Specific nitrate loading could be significantly influenced by any changes in
HRT, initial nitrate loading, and catalyst dosage (green lines in Figures 5 and 6). The specific nitrate loading is similar to the food/microorganism (F/M) ratio, while specific removal is similar to the maximum specific substrate utilization rate used in the design and monitoring of biological treatment systems. An integrated data analysis showed that the specific nitrate removal for this system was 37.4 mg of NO$_3^-$-N/gcat/h, (2.67 mM NO$_3^-$-N/gcat/h, brown lines in Figures 5 and 6). The specific nitrate loading decreased from 90 to 30 mg of NO$_3^-$-N/gcat/h with the increase of HRT from 20 to 60 min (Figure 6). This indicates that the fixed amount of catalyst (1 g/L) at 60 min HRT received 3 times less specific nitrate loading than that at 20 min HRT. The catalyst at 60 min HRT can achieve complete nitrate removal (100%), while that at 20 min can remove only 51% of the nitrate. This is because higher HRTs present more chances for contact of nitrate with catalysts than do lower HRTs. It should be noted that specific nitrate loading and specific removal are of great industrial importance because they can be used to effectively operate continuous catalytic nitrate removal systems.

Figure 6 also shows that nitrite production decreased from 62 to 45% with the increase of HRT from 20 to 60 min, while ammonium selectivity increased from 12 to 45%. Nitrite could not have been properly reduced to final products (ammonium and N$_2$) at the HRTs of 20 and 40 min due to insufficient contact times with active Pd sites of the catalyst. Therefore, the decrease of nitrite production and increase of ammonium and N$_2$ selectivity can be observed at 60 min HRT. This result indicates that at least 60 min HRT is required for effective nitrate removal with higher N$_2$ selectivity in this continuous system.

3.4. Effect of Catalyst Loading and pH. Figure 7 shows nitrate removal and byproduct production after 9 h of continuous operation at five different catalyst loadings (0.1, 0.5, 1, 2, and 4 g/L). The removal efficiency increased from 20 to 100% when catalyst loading increased from 0.1 to $\geq$ 1 g/L. This result shows that a certain amount ($\geq$ 1 g/L) of catalyst is necessary for the complete denitrification of 30 mg/L NO$_3^-$-N, in continuous mode. The specific nitrate loading decreased from 300 to 7.5 mg of NO$_3^-$-N/gcat/h when catalyst loading increased from 0.1 to 4 g/L (green line in Figure 7). On the other hand, the specific nitrate removal was constant at 37.4 mg of NO$_3^-$-N/gcat/h as described in section 3.3 (brown lines in Figures 6 and 7). Therefore, the specific nitrate loading in the catalyst loading range $\geq$ 1 g/L was equal to, or smaller than, the specific nitrate removal, suggesting the effective and selective nitrate removal for this specific nitrate loading and removal relationship. It is important to mention that the specific nitrate removal or steady state rate by Cu−Pd/NZVI catalyst (2.67 mM NO$_3^-$-N/gcat/h) is 11.61 times higher than that reported by Matatov-Meytal and Sheintuch (0.23 mM NO$_3^-$-N/gcat/h) using Cu−Pd/ACC catalyst, while, it is 9.89 times higher.
than that reported by Prusse et al.\textsuperscript{6} using In−Pd/Al\textsubscript{2}O\textsubscript{3} catalyst, in continuous mode. The first-order steady state kinetic rate constant calculated for this system was 1.95 min\textsuperscript{−1}. However, such kinetic rate constants in steady state catalytic nitrate removal using continuous reactors could not be found in the literature, for comparison.

To elucidate the mass transfer limitation of H\textsubscript{2} in the Cu−Pd/NZVI reduction system, the reaction was performed at three different mixing speeds (i.e., 75, 150, and 300 rpm). The results (Supporting Information, Figure S4) show that >99% nitrate removal was achieved for 9 h at all mixing speeds and there was no mass transfer limitation during the reaction time. In order to further verify this, nitrate reduction rates were plotted as a function of initial catalyst loading (0.1, 0.5 and 1 g/L, Supporting Information, Figure S5). The results show that the reduction rate was linearly related to catalyst loading (R\textsuperscript{2} = 0.9896). Hence, the results from mixing speed and catalyst loading show that there is no mass transfer limitation of H\textsubscript{2} in this continuous flow system.

The selectivity toward ammonium, N\textsubscript{2}, and production of nitrite varied within the range of complete nitrate removal (≥1 g/L catalyst loading). The production of nitrite decreased from 46 to 4.8%, and ammonium selectivity increased from 26 to 73% as the catalyst loading increased from 1 to 4 g/L. At the same time, N\textsubscript{2} selectivity data resembled a volcanic shape, showing maximum selectivity (48%) at 2 g/L catalyst loading. We monitored the pH during the reaction which increased from 6.5 to 11 in all cases (low and high catalyst loading), indicating the pH was not a significant factor affecting the increase of ammonium selectivity during the catalyst loading. This behavior could be attributed to the increase of Pd sites by increased catalyst loading, consequently leading to the increase of Hads \[2\text{Pd}(0) + \text{H}_2 \rightarrow 2\text{Hads}^\text{−} + \text{Pd}(0)\]. Because the increase in catalyst loading under fixed nitrate and H\textsubscript{2} supplies increased H\textsubscript{ads}, the nitrite production decreased at high catalyst loadings. On the other hand, it has been reported that the fate of N atoms (from NO\textsubscript{2}− + H\textsubscript{ads} \rightarrow N) is dependent on the concentration of H\textsubscript{ads}. Therefore, the increase in H\textsubscript{ads} caused by the increase in catalyst loading could be equally useful for the recombination of N−H and N−N. As shown in Figure 7, ammonium and N\textsubscript{2} selectivities were very similar (i.e., 26.3 and 27% at 1 g/L, and 47 and 48% at 2 g/L, respectively). Further
increase in catalyst loading (to 4 g/L) produced an excessive amount of H_{ads} promoting recombination of N–H more than that of N=N. Consequently, ammonium selectivity further increased to 73%, and N\textsubscript{2} selectivity dropped by 23%. Although the total amount of Pd is the same, the N\textsubscript{2} and ammonium selectivities from this experiment (0.5% Pd x 2 g/L catalyst) are different from those of our previous experimental result showing 15% N\textsubscript{2} selectivity and 71% ammonium selectivity at the amount of Pd (1% Pd x 1 g/L catalyst). High catalyst loading (2 g/L) with low Pd content (0.5%) could make Pd sites more uniformly dispersed on the catalyst and in liquid phase without overlapping Cu by Pd, as compared to low catalyst loading (1 g/L) with high Pd content (1%). Therefore, the former one could have very similar N\textsubscript{2} and ammonium selectivities (48 and 47%) at the experimental condition.

During the previous experiments, it was normally observed that pH increased from 6.5 to around 11 during 9 h of reaction due to the NZVI corrosion and/or nitrite reduction to N\textsubscript{2} and NH\textsubscript{4}\textsuperscript{+} (2NO\textsubscript{3}\textsuperscript{-} + 6H\textsuperscript{+} + Pd(0) → Pd(0) + N\textsubscript{2} + 2OH\textsuperscript{-} + 2H\textsubscript{2}O and NO\textsubscript{2}\textsuperscript{-} + 6H\textsuperscript{+} + Pd(0) → Pd(0) + NH\textsubscript{4}\textsuperscript{+} + 2OH\textsuperscript{-})\textsuperscript{40}, which can dramatically increase the suspension pH. In order to investigate the effect of pH on nitrate reduction efficiency, we conducted an experiment at pH 7 (Figure 8). MOPS buffer (\textgreek{sigma} 99.5%, Sigma) was used to maintain the pH at 7. The experiment was conducted under an optimized condition obtained from previous experiments (i.e., 1.5% Cu–0.5% Pd/NZVI, 30 mL/min H\textsubscript{2} flow rate, 60 min HRT, and 2 g/L catalyst loading). About 99% removal of nitrate was observed in 13 h and a relatively stable nitrogen selectivity (∼50%) was observed during the reaction. However, nitrate reduction dramatically dropped to 10% in 33 h. It should be noted that dark black suspension of Cu–Pd/NZVI became a bit transparent suspension at 33 h, indicating that NZVI catalyst was dissolved out at neutral pH. Therefore, the drop in nitrate reduction was most probably due to lower remaining solid catalyst in the reactor. In order to avoid catalyst loss, the next experiment (durability test) was performed without pH control.

### 3.5. Durability of Catalyst for Long-Term Catalytic Nitrate Removal

Figure 9 shows nitrate removal and byproduct production during 200 h of continuous operation under the experimental conditions optimized in previous sections (i.e., 1.5% Cu–0.5% Pd/NZVI, 30 mL/min H\textsubscript{2} flow rate, 60 min HRT, and 2 g/L catalyst loading). High nitrate removal was sustained for 24 h and then decreased continuously. The catalytic removal of nitrate can be strongly influenced by oxidation of the initial NZVI, leaching of deposited bimetals, and aggregation of bimetals.\textsuperscript{9,12,17,41} Therefore, we carried out relevant experimental verifications to investigate the behavior of nitrate removal in continuous mode. First, we conducted XRD analysis (Figure 10) to investigate Fe-mineral phases after denitrification by Cu–Pd/NZVI. Figure 10a shows the well-ordered, narrow peaks of NZVI and Cu, while Pd was not detected due to content lower than those of Cu and NZVI.\textsuperscript{8} After 9 h of reaction time (Figure 10b), the NZVI peak started to vanish. After 100 and 200 h of reaction (Figure 10c,d), those peaks had disappeared, and peaks corresponding to magnetite (Fe\textsubscript{3}O\textsubscript{4}) emerged. The conversion of NZVI to magnetite in the diffractograms indicated that nitrate removal can occur both by direct denitrification by NZVI, and by Cu–Pd catalysis with H\textsubscript{2} in 9 h (also shown by control experiments, Figure 2). Further reduction of nitrate could have been carried out only by Cu–Pd catalysis in 200 h. To further check this hypothesis, 1.5% Cu–0.5% Pd/magnetite catalyst was prepared using the same procedures and tested for nitrate reduction (Supporting Information, Figure S3). It was found that Cu–Pd/magnetite catalyst started losing nitrate reduction activity after 5 h with low (∼20%) nitrogen selectivity, suggesting that nitrate reduction was probably carried out by Cu–Pd/magnetite only from around 9 to 200 h.

Second, we checked the leaching of metals from the catalyst by ICP-MS after the reaction. A negligible leaching of Cu (<0.075%) and Pd (<0.03%) metals was observed after 9 and 200 h, indicating no significant decrease in nitrate reduction by the metal leaching. We also performed XPS analysis to further investigate the change in valence states of Fe, Cu, and Pd, on fresh and spent Cu–Pd/NZVI catalysts (Figure 11). Figure 11a shows the narrow scans of Fe(2p\textsubscript{3/2}) on fresh catalyst. Peaks of Fe\textsubscript{0}, Fe\textsubscript{2+}, and Fe\textsubscript{3+} were identified at 706.4, 709.5, and 711.4 eV, respectively.\textsuperscript{30,42–44} The presence of Fe\textsubscript{2+} and Fe\textsuperscript{3+} could be due to the oxidation of NZVI during the installation of the template in the XPS instrument.\textsuperscript{30} After 200 h of reaction (Figure 11b), we observed that the peak was composed mostly of Fe\textsuperscript{2+}, confirming that NZVI was oxidized to iron (hydr)-oxides during nitrate removal. Figure 11c shows narrow scans of Cu(2p\textsubscript{3/2}) on the surface of spent catalyst. Two main peaks at 932 (Cu(0) or Cu\textsubscript{2}O) and 934.4 eV (CuO) were identified.\textsuperscript{45,46} It is hard to distinguish the binding energies of Cu(0) or Cu\textsubscript{2}O at 932 eV because their difference is only 0.1 eV.\textsuperscript{45} However, the peak at 934.4 eV can be clearly identified to CuO, indicating that Cu(0) or Cu\textsubscript{2}O were oxidized to CuO (NO\textsubscript{2}\textsuperscript{-} + 2Cu(0) → Cu\textsubscript{2}O + NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} + Cu\textsubscript{2}O → 2CuO + NO\textsubscript{3}\textsuperscript{-})\textsuperscript{8,26} during continuous nitrate removal by Cu–Pd/NZVI. Therefore, the oxidation of Cu could also have caused the decrease of nitrate removal observed in this study. However, Pd(3d\textsubscript{3/2} 335 eV) and Pd(3d\textsubscript{5/2} 340.5 eV) were observed in the form Pd(0) on the surface of spent catalyst. Two main peaks at 932 (Cu(0) or Cu\textsubscript{2}O) and 934.4 eV (CuO) were identified.\textsuperscript{45,46} It is hard to distinguish the binding energies of Cu(0) or Cu\textsubscript{2}O at 932 eV because their difference is only 0.1 eV.\textsuperscript{45} However, the peak at 934.4 eV can be clearly identified to CuO, indicating that Cu(0) or Cu\textsubscript{2}O were oxidized to CuO (NO\textsubscript{2}\textsuperscript{-} + 2Cu(0) → Cu\textsubscript{2}O + NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} + Cu\textsubscript{2}O → 2CuO + NO\textsubscript{3}\textsuperscript{-})\textsuperscript{8,26} during continuous nitrate removal by Cu–Pd/NZVI. Therefore, the oxidation of Cu could also have caused the decrease of nitrate removal observed in this study. However, Pd(3d\textsubscript{3/2} 335 eV) and Pd(3d\textsubscript{5/2} 340.5 eV) were observed in the form Pd(0) on the surface of spent catalyst (Figure 11d), showing that Pd was continuously rejuvenated on the catalyst surface by H\textsubscript{2}. The results from XRD and XPS revealed that the decrease of nitrate removal was due mainly to the oxidation of NZVI and Cu on the Cu–Pd/NZVI catalyst during continuous exposure to nitrate.

The selectivity toward N\textsubscript{2} and ammonium continuously decreased from 60 to 41%, and from 41 to 27%, respectively,
24 h, while production of nitrite increased from 0 to 34%. Later, stable production of nitrite and selectivity toward ammonium, and N₂, were observed throughout the 200 h of reaction (Figure 9). The increase of nitrite production in 24 h could be attributed to the change of structure and texture of the catalyst (due to the change in oxidation states of NZVI and Cu) during the catalytic reaction.41 It has been also reported that the size of Pd particles aggregated and grew during continuous nitrate reduction12,44 due probably to the change of support (oxidation of NZVI to iron oxide) and/or physical sintering. To investigate the morphological change in NZVI and the bimetals, TEM analysis was conducted before and after the reaction (9 and 200 h, Figure 12). A TEM image of fresh catalyst (Figure 12a) shows that tiny particles (1−5 nm) were well distributed over the spherical surface of NZVI. EDX analysis revealed that the tiny particles were Cu and Pd (Figure 12a-1). After 9 and 200 h of reaction, NZVI particles changed to rectangular shape and the size of the particles (see arrow) increased to 6−20 nm (Figure 12b,c). EDX analysis also verified that these were Cu and Pd particles (Figure 12b-1,c-1), confirming the presence of bigger Cu and Pd particles after the reaction. It has been reported that the change in the size of Pd particles can deteriorate N₂ selectivity by blocking Pd−H_ads12,36,44 Therefore, aggregation of Pd particles could suppress nitrite reduction to N₂ and/or ammonium on Pd sites, resulting in a gradual increase in nitrite. In addition, the increase of nitrite could be caused by the increase of OH⁻ on active Pd sites as the reduction of nitrite to N₂ or NH₄⁺ proceeds (2NO₂⁻ + 6H + Pd(0) → Pd(0) + N₂ + 2OH⁻ + 2H₂O and NO₂⁻ + 6H + Pd(0) → Pd(0) + NH₄⁺ + 2OH⁻). The accumulation of OH⁻ on Pd sites can inhibit the adsorption of nitrite due to the Coulombic repulsion between negative ions (OH⁻ and NO₂⁻), resulting in the decrease of nitrite reduction. After 24 h, the byproduct selectivity seemed to be stable due to the continuous denitrification on limited active sites during the deactivation of the Cu−Pd/NZVI catalyst.

4. CONCLUSION

NZVI is known as an ecofriendly, economic, and easy separable material; it can easily be applied to real wastewater and groundwater treatment and remediation sites. We also achieved an excellent nitrate removal (>91%) for 24 h with relatively higher N₂ selectivity (42−60%) while investigating the effect of significant factors (Cu and Pd loadings, H₂ supply, HRT, and catalyst loading). This result is much higher than those reported previously using similar bimetallic catalysts in batch systems.59 However, the removal efficiency dropped slowly to 13% in 200 h due to the oxidation of NZVI to magnetite, and
Cu(0) to Cu(I) and Cu(II). The results from this study suggest that Cu–Pd/NZVI is a highly reactive catalyst (steady state rate constant 2.67 mM NO$_3^-$/$\text{g}_{\text{cat}}$/h) as compared to other catalysts in the continuous system; however, further research work is needed to improve its stability and selectivity, especially enhanced reduction of NO$_2^-$ to N$_2$. The loss of catalyst due to NZVI dissolution at neutral pH indicated that the catalyst is likely less stable in acidic and neutral regimes. Some others have also investigated continuous nitrate removal by Cu–Pd bimetallic catalysts, however, most of those studies were focused on the effect of Cu/Pd ratios, metal precursors, and type of support materials. As demonstrated in this study, we first showed that catalytic nitrate reduction and byproduct selectivity can be significantly influenced by the most important operation factors. High nitrate removal and byproduct selectivity can be obtained by an optimization regime like that adopted in this study. Therefore, the experimental results obtained from this study can provide basic knowledge and background understanding helpful in the development of novel continuous catalytic denitration systems, and provide guidelines for system design, operation, scaling up, and management.

**ASSOCIATED CONTENT**

**Supporting Information** Additional figures of nitrate reduction by Cu–Pd/NZVI in continuous mode, particle size distribution of Cu–Pd/NZVI catalyst before and after the reaction, nitrate reduction by Cu–Pd/magnetite in continuous mode, effect of mixing speed on nitrate reduction, and effect of initial catalyst loading on nitrate reduction rate. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b01127.

** Figure 12.** TEM and EDX images of (a, a-1) fresh, (b, b-1) 9 h, and (c, c-1) 200 h catalysts.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research work was partially supported by GAIA Project 173-111-036 and another GAIA Project (RE201402059) funded by the Korean Ministry of Environment.


