

Catalytic reduction of nitrate in reverse osmosis concentrate by using Pd-Cu/activated carbon felt

Energy & Environment

2021, Vol. 32(1) 152–167

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DOI: 10.1177/0958305X20923115

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Abstract

The reverse osmosis concentrate generated during the water reuse process contains a high concentration of nitrate but a low amount of biodegradable organic carbon for heterotrophic denitrification. Catalytic reduction of nitrates using Pd-Cu is one of the most promising technologies to achieve complete removal of nitrate; however, the effect of a range of experimental factors on the nitrate removal rate and N₂ selectivity is still an ongoing concern. Two kinds of supporting materials, alumina and activated carbon felt, were used to immobilize the Pd-Cu catalyst. The alumina-based catalyst was used to establish reference conditions for further experiments, and the effect of pH control was evaluated for both supporting materials. It was observed that pH has a direct influence on the nitrate reduction rate as well as the N₂ selectivity. Nitrate reduction efficiency was low at acidic conditions while the highest N₂ selectivity was obtained at the acidic conditions. The optimal pH condition for Pd-Cu/activated carbon felt was determined as pH 4, showing the highest total nitrogen removal as N₂ gas. Finally, the feasibility of catalytic nitrate reduction for reverse osmosis concentrate was evaluated by investigating the effects of organic and inorganic components commonly present in reverse osmosis concentrate. The organic and inorganic components did not show a significant inhibitory effect on catalytic nitrate reduction, while a high concentration of salt significantly decreased the nitrate reduction rate as well as the N₂ selectivity. The filter type morphology of the Pd-Cu/activated carbon felt would be beneficial for field application compared to the conventional catalyst with powder form.

Keywords

Catalytic nitrate reduction, bimetallic catalyst, pH control, activated carbon felt, reverse osmosis concentrate

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Introduction

The global water situation involves significant contamination of water sources with nitrate pollutants as a consequence of increasing industrial activities, the use of nitrogen-based fertilizers in agricultural activities, and inappropriate disposal of wastewater.¹ The elimination of nitrate compounds from water sources has become an important challenge among researchers and experts due to their harmful effects on the environment and human health.^{2,3} In particular, they are a potential precursor of several types of cancer and they reduce the blood capacity to carry oxygen (called “blue baby syndrome”).⁴ At the same time, excessive nitrate ions in the environment produce anoxic or hypoxic conditions due to the massive growth of algae, destroying ecosystems, and having a negative impact on human well-being.⁵

During recent decades, nitrogen removal from wastewater sources has been the focus of research carried out using physicochemical technologies such as electro-dialysis, ion exchange, and reverse osmosis (RO).^{6–8} In particular, the RO process is the most widely applied technology for wastewater reuse. These technologies, however, separate nitrogen-based compounds from water while generating a brine or a concentrate, containing high concentrations of salt and non-biodegradable organic matter, thus necessitating further treatment prior to disposal. Heterotrophic denitrification is widely used as a method for removing nitrate, and is considered to be a very economical and effective nitrate removal method. However, the removal of nitrate by heterotrophic denitrification is not recommended for reverse osmosis concentrate (ROC) because most of the biologically degradable organic matter is consumed through the sewage treatment process.⁹ The necessity of an external carbon source and the risk of bacterial contamination thus make this method unsuitable for ROC treatment.^{10,11}

In this study, a catalytic denitrification process was considered as an alternative method to eliminate nitrate in ROC. The process involves the transfer of electrons from an electron-donating agent in order to reduce the nitrate contaminant with the help of a monometallic or bimetallic catalyst placed on the surface of a support material on which the reaction will occur.^{12,13} The active bimetallic sites with an optimal Pd-M ratio are required to carry out the reduction of nitrate to nitrite and monometallic Pd (or Pt) sites are needed to hydrogenate nitrites to the end-products. The reaction occurs within a short time and without bacterial contamination.

Numerous investigations have been performed to establish how the reaction proceeds and which experimental factors are determinants for the reaction.^{14,15} It has been reported that pH has a significant effect on the activity on the surface of the catalyst, and therefore the sub-byproducts formed during it. The surface of the catalyst will be covered with different species depending on the pH value: hydrogen species at low pH and hydroxide species at high pH. These compounds will lead to a drop in the activity due to the repulsion between the negative nitrate ions and the negatively charged metal surface. A drop in the activity has been reported for low pH values and for high pH values for all catalysts, but different effects are shown for each promoter metal (Cu, Sn, and In).^{16,17} Therefore, pH control during the reaction is crucial for an efficient catalytic reduction. Moreover, the testing under real-life environmental conditions to develop novel catalytic systems and successfully implementing them at water and wastewater treatment was suggested as further research work.¹⁴

Extensive research has also been performed to find the most effective supporting materials to enhance reduction and N₂ selectivity. The current state-of-art in catalytic reduction

processes are mainly composed of support materials in powder form; therefore, the achievement of complete reuse of water becomes hard to accomplish due to the subsequent powder separation process.^{12,14} Although complete elimination of nitrate has been achieved by using aluminum oxide (Al_2O_3), SiO_2 , pillared clays, or other materials,^{18–21} the main disadvantage of their application in real water treatment is their powder form and its complicated separation process after the treatment. Therefore, it is required to develop a support material in a filter form or other similar, that can be combined with existing water and wastewater treatment processes.

Carbon-based support materials show excellent performance due to their large available surface area and high dispersion of metal loading. Complete removal of nitrate and up to 80% selectivity towards nitrogen gas have been attained using carbon nanotubes.¹⁹ Activated carbon felt (ACF) is meanwhile an excellent adsorbent material, and its filter shape provides versatility for use in several application fields such as water treatment, air purification, and chemical recovery.^{22,23} ACF offers the advantages of a carbon-based material in a filter shape and therefore is appropriate to serve as a support material for catalytic reduction of nitrate as an additional filter treatment in real wastewater treatment, showing competitiveness when compared with other current powder form support materials.

The objectives of this study were to investigate the feasibility of ACF as a support material for catalytic reduction of nitrates and to evaluate the role of pH on the performance of catalytic nitrate reduction. We used a Pd-Cu bimetallic catalyst supported on alumina in order to find reference experimental conditions to be tested on a Pd-Cu bimetallic catalyst supported on ACF. The effects of pH on the nitrate reduction rate and N_2 selectivity were investigated using Pd-Cu/ACF. Finally, the inhibitory effect of the organic and inorganic components commonly present in ROC was investigated with simulated ROC in order to evaluate the applicability of the ROC.

Materials and methods

Materials

Precursor solutions of palladium and copper were prepared with palladium (II) chloride, 99.0%, and copper (II) chloride dehydrate 97.5%, respectively, purchased from Samchun Pure Chemical Co., Ltd $\gamma\text{-Al}_2\text{O}_3$ (99.0%, Kanto Chemical Co., Ltd) and ACF (HACF1500, HP Material Solutions, Inc.) were used as support materials. Sodium borohydride (98.0%, Samchun Pure Chemical Co., Ltd) was used to reduce the Pd-Cu catalyst. Stock solutions of nitrate, nitrite, and ammonium were prepared by using potassium nitrate (99.0%, Samchun Pure Chemical Co., Ltd), sodium nitrite (98.0%, Samchun Pure Chemical Co., Ltd), and ammonium chloride (98.5%, Samchun Pure Chemical Co., Ltd). An eluent solution for ion chromatography (IC) was prepared by using sodium carbonate ($\geq 99.5\%$, Sigma-Aldrich Inc., USA) and sodium bicarbonate ($\geq 99.7\%$, Sigma-Aldrich Inc., USA). High purity hydrogen (99.999%, Daesung Industrial Gases Co., Ltd) and high purity carbon dioxide gas (99.99%, Air Korea Co., Ltd) were used as an electron donor and pH controller, respectively. Deionized water was prepared by using a Cascada RO-Water Purification system (Pall Corporation). Stock solutions of inorganic constituents for simulated ROC were prepared individually by dissolving NaHCO_3 , Na_2SO_4 , $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$, KCl, NaNO_3 , $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, and NaH_2PO_4 in deionized water (all purchased from Sigma-Aldrich Inc., USA). Salinity and humic acid solutions were prepared using NaCl and humic acid sodium

salt, purchased from Sigma-Aldrich Inc., USA and Wako Pure Chemicals Inc., USA, respectively.

Catalyst preparation

Pd-Cu/Al₂O₃. Pure γ -Al₂O₃ was used as a support material for testing the pH effect on catalytic nitrate reduction due to its high surface area and excellent stability of metallic particles. The Pd-Cu bimetallic catalyst was prepared by a simple impregnation method; alumina previously dried at 100°C for 24 h was mixed with deionized water and sonicated for 10 min before the addition of the catalyst, where the concentration of each of the metallic solutions was adjusted to produce 0.5 wt.% Pd and 0.5 wt.% Cu. The mixed solution was continuously stirred at 150 rpm under room temperature conditions for 2 h and dried in an oven for 24 h at 100°C for complete removal of water. The dried catalyst was calcinated at 350°C for 2 h to coat the bimetallic catalyst on the surface of the support. The prepared catalyst was reduced by a dropwise addition of 0.01 mM NaBH₄ solution under continuous stirring at 700 rpm. The reduced catalyst was separated by centrifugation for 10 min at 4000 rpm, washed two times in an anaerobic chamber to remove residual chemical, and used immediately for the batch experiment.

Pd-Cu/ACF. The purchased ACF was washed two times with deionized water and dried in an oven at 100°C for 24 h before the addition of precursor solutions of palladium and copper by a simple impregnation method. The overall catalyst preparation procedure is similar to that for Pd-Cu/Al₂O₃. The concentration of both metals was chosen as 0.5 wt.% and 0.5 wt.%, respectively. The mixed solution was stirred continuously at 500 rpm for 2 h at 85°C, dried in an oven for 24 h at 100°C, and finally calcinated at 300°C for 2 h to coat the bimetallic particles on the surface of the carbon fibers. The prepared catalyst was used immediately for the batch experiment after reduction and washing.

Catalyst characterization

XRD analysis was performed by using a Bruker DE/D8 advanced diffractometer to identify the presence of each metal over the surface of the Pd-Cu/Al₂O₃. Samples were scanned between 10° and 90° at a scan speed of 16° per minute using 40 kV voltage and 40 mA current. The distribution and morphology of the Cu and Pd particles over the surface of alumina and ACF were identified by using a Hitachi SU8010 high-resolution field emission scanning electron microscope equipped with energy dispersive spectroscopy (SEM-EDS).

Nitrate reduction test procedure

Catalytic nitrate reduction experiments were performed in a 500 mL batch reactor equipped with a mechanical stirrer, an H₂ gas supply inlet, a CO₂ gas supply inlet, a sampling port, and a gas outlet connected with a 200 mL of H₂SO₄ container (10% v/v) to capture stripped ammonia gas produced during the reaction (see Figure 1). The reactor was filled with 400 mL of deionized water and constantly stirred while pure hydrogen was continuously introduced through a gas diffuser inside of the reactor to remove all oxygen and provide an anaerobic condition for the reaction. The dried Pd-Cu/Al₂O₃ or Pd-Cu/ACF of 0.5 g was prepared and used immediately for the experiment in the batch reactor. Once the bimetallic catalyst was introduced into the reactor, 10 mL of 4000 mg NO₃/L stock solution was

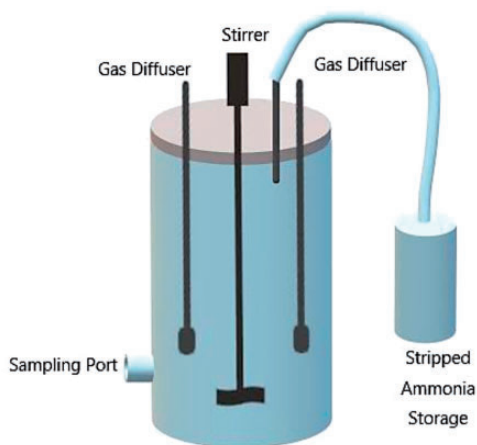


Figure 1. Scheme of the batch reactor used for experiments.

injected to initiate the reaction and obtain an initial concentration of 22 mg $\text{NO}_3\text{-N/L}$. All experiments were performed within 1.5 h and samples were taken at 1, 3, 5, 10, 15, 20, 30, 40, 60, and 90 min to evaluate the performance of the catalytic reaction.

Synthetic RO concentrate. It has been reported that RO concentrate components will differ according to the water source; however, it is possible to identify common organic and inorganic constituents. The main inorganic cations constituents are identified as K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , and the commonly found anions are Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} .²⁴ On the other hand, the RO concentrate commonly contains high concentrations of dissolved salts and recalcitrant organics, and it has been reported that biological treatments may be inhibited by the presence of high salinity due to the inhibition of microbial growth.^{25,26} Therefore, to investigate the inhibitory effect of organic, inorganic, and saline components, the performance of ACF/0.5%Pd-0.5%Cu was evaluated in the presence of each of these compounds individually.

The inorganic constituents stock solutions were individually prepared by dissolving NaHCO_3 , Na_2SO_4 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, KCl , NaNO_3 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and NaH_2PO_4 in deionized water to achieve concentrations of 400 mg/L alkalinity as CaCO_3 , 250 mg/L SO_4^{2-} , 100 mg/L Ca^{2+} , 70 mg/L K^+ , 30 mg/L TN, 20 mg/L Mg^{2+} , and 10 mg/L TP, respectively.²⁴ This solution was named ROC inorganic. Humic acid sodium salt was used as a surrogate of wastewater effluent organic matter in a concentration of 80 mg/L, and salinity concentration was prepared by dissolving NaCl into ultrapure water to achieve 490 mg/L of NaCl . Table 1 shows the four different combinations that were prepared to evaluate the effect of the RO concentrate constituents. Footnote c in the table indicates the used concentrations for each one of the constituents.

Analytical procedures

Nitrate and nitrite concentrations on aqueous media were measured by using an Ion Chromatograph (Dionex Aquion, Thermo Fisher Scientific Solutions Korea Ltd) equipped with an autosampler (Dionex AS-DV, Thermo Fisher Scientific Solutions Korea Ltd). Samples

Table 1. Prepared stock solutions for RO concentrate tests.

Solution	Salinity ^a	Humic acid ^b
ROC inorganic	–	–
ROC inorganic + NaCl	Yes	–
ROC inorganic + HA	–	Yes
ROC inorganic + NaCl + HA	Yes	Yes

^aSalinity: 490 mg/L NaCl.^bHumic acid: 80 mg/L humic acid.^cAll stock solutions have 400 mg/L alkalinity as CaCO₃, 250 mg/L SO₄²⁻, 100 mg/L Ca²⁺, 70 mg/L K⁺, 30 mg/L TN, 20 mg/L Mg²⁺, and 10 mg/L TP.

(3 mL) were removed from the batch reactor through a 5 mL disposable syringe and immediately filtered by using a disposable 0.45 μ m polyether sulfone syringe filter (Hyundai micro Co., Ltd). Two-milliliter of the taken sample was diluted and used to measure concentrations of nitrate, nitrite, and ammonia concentration using IC. In every sampling time, an additional 2 mL of H₂SO₄ storage ammonia solution was captured to measure the concentration of stripped ammonia generated during the catalytic performance. The total amount of ammonia calculated for each sampling time was the ammonia concentration in the aqueous media inside the reactor and the concentration in the ammonia storage. The removal of nitrate and the selectivity towards different nitrogen-based compounds were calculated as follows

$$\text{NO}_3^- \text{ Removal} = \frac{(\text{NO}_3^- - \text{N})_{\text{initial}} - (\text{NO}_3^- - \text{N})_{\text{final}}}{(\text{NO}_3^- - \text{N})_{\text{initial}}} \quad (1)$$

$$\text{NO}_2^- \text{ Selectivity} = \frac{(\text{NO}_2^- - \text{N})_{\text{final}}}{(\text{NO}_3^- - \text{N})_{\text{initial}} - (\text{NO}_3^- - \text{N})_{\text{final}}} \quad (2)$$

$$\text{NH}_4^+ \text{ Selectivity} = \frac{(\text{NH}_4^+ - \text{N})_{\text{final}}}{(\text{NO}_3^- - \text{N})_{\text{initial}} - (\text{NO}_3^- - \text{N})_{\text{final}}} \quad (3)$$

$$\text{N}_2 \text{ Selectivity} = 100\% - \text{NO}_2^- \text{ Selectivity} - \text{NH}_4^+ \text{ Selectivity} \quad (4)$$

Selectivity towards nitrogen gas was calculated by the difference in the selectivities of nitrite and ammonia calculated by mass balance (see equation (4)), assuming that the production of other nitrogen-based compounds such as NO and N₂O was negligible.

Results and discussion

Catalyst characterization

Pd-Cu/Al₂O₃. An XRD analysis was conducted to identify the crystalline structure of the prepared Pd-Cu/Al₂O₃ catalyst.

Tiny new peaks were detected at around 16° in the Pd-Cu/Al₂O₃ (see Figure 2) when compared with pure alumina; these new peaks are expected to be formed by the amount of metal addition of the precursor palladium stock solution since they increased when the

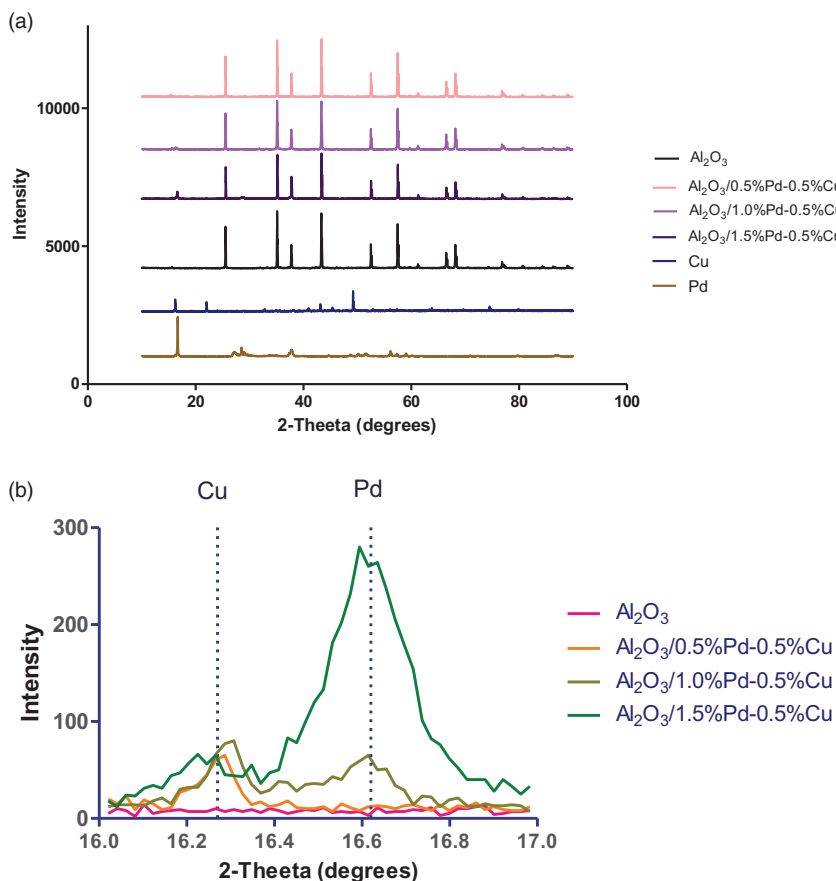


Figure 2. XRD analysis of Al₂O₃/Pd-Cu catalyst. (a) $2\theta = 10^\circ\text{--}90^\circ$ range, (b) $2\theta = 16^\circ\text{--}17^\circ$ range. Al₂O₃: aluminum oxide.

added palladium amount was higher. No relevant new peaks were detected around 50° by the presence of copper, likely due to the low Cu loading that was not sufficient to be detected in the XRD analysis, following the results reported by Jung et al.²⁷

SEM was used to investigate the morphological characteristics of the catalysts, showing that particles of both metals were well coated on the surface of alumina (see Figure 3). Besides agglomeration, it is possible to visualize bimetallic particles on the surface of the support material. An EDS analysis was performed to identify palladium and copper on the surface of the catalyst. Copper particles were well-detected in the EDS analysis, demonstrating that they were well coated on the surface of the support even though they were not well detected in the XRD analysis. Palladium particles have been reported to have better dispersion on the surface of the support material,²⁸ tending to form a higher concentration of metal, therefore explaining the higher peaks of Pd in the EDS analysis. Meanwhile, copper particles have been suggested to have small molecular size and are difficult to identify.²⁹

Pd-Cu/ACF. A SEM analysis was performed to analyze the morphology of the bimetallic particles over the surface of ACF. Both metal particles were well coated on the surface of

the catalyst, with a low degree of agglomeration when compared with Pd-Cu/Al₂O₃ (see Figure 4). The presence of palladium and copper was verified by the EDS analysis (Figure 4). The presence of palladium and copper was verified by the EDS analysis (Figure 4); however, the palladium particles were very prominent when compared to copper. As mentioned in the previous section, palladium particles have been reported to

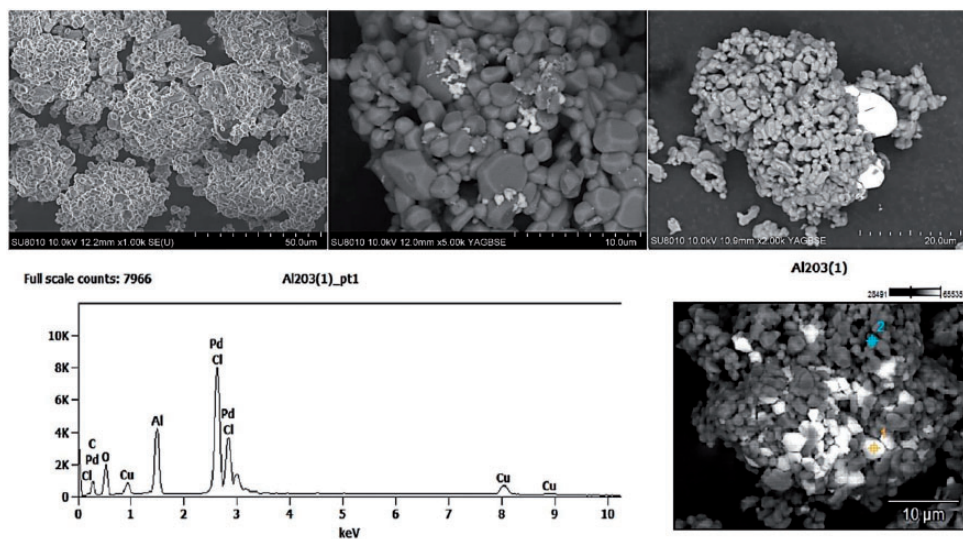


Figure 3. SEM-EDS analysis of Pd-Cu/Al₂O₃ (0.5%Pd-0.5%Cu). Al₂O₃: aluminum oxide.

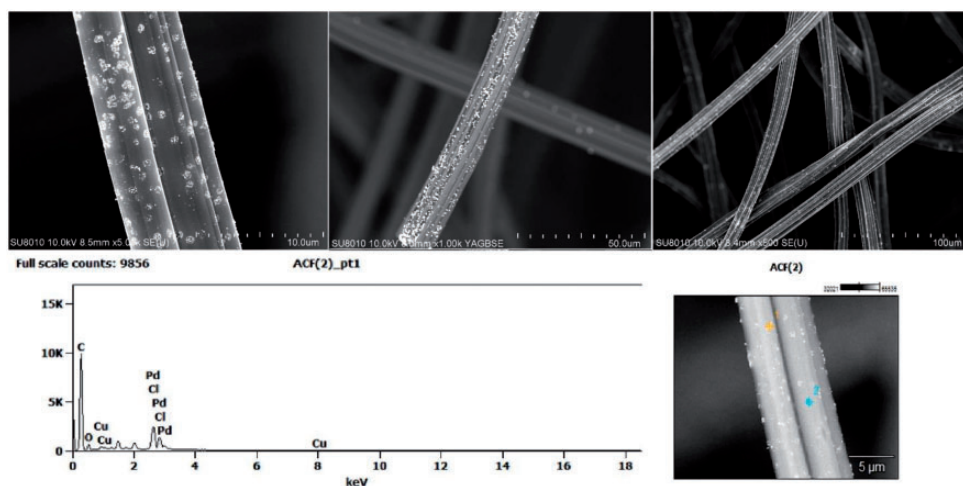


Figure 4. SEM-EDS analysis of Pd-Cu/ACF (0.5%Pd-0.5%Cu). ACF: activated carbon felt.

have a better dispersion on support materials, therefore explaining the big peaks on EDS analysis while copper has been difficult to identify.

An EDS mapping analysis was performed to visualize the composition and dispersion information of carbon, Pd, and Cu on the surface of the carbon fibers (see Figure 5), revealing that the presence of palladium metal particles was predominant and well dispersed while copper particles were not easily identifiable. As mentioned in the previous section, the addition of copper was not high enough to be detected in the EDS mapping.

Catalytic nitrate reduction by Pd-Cu/Al₂O₃

The effect of pH on the performance of nitrate reduction was investigated by using a Pd-Cu/Al₂O₃ (0.5%Pd-0.5%Cu) catalyst. The CO₂ was used as a buffering agent in order to achieve stable pH conditions during the entire reaction. Figure 6(a) presents the pH variation during the reaction with and without pH control. The pH increased rapidly during the reaction, and it reached above 9 when no carbon dioxide was supplied. On the other hand, a stable pH in the range of 4.5–5.0 was achieved when 40 mL/min of carbon dioxide was continuously supplied.

Figure 6(b) shows the nitrate reduction performance with and without pH control in terms of nitrate reduction efficiency (black circle), N₂ selectivity (bar graph), and the total percentage of nitrogen removed as N₂ gas (black triangle). The low nitrate reduction performance without pH control (only 39.9% of reduction) was observed, while almost

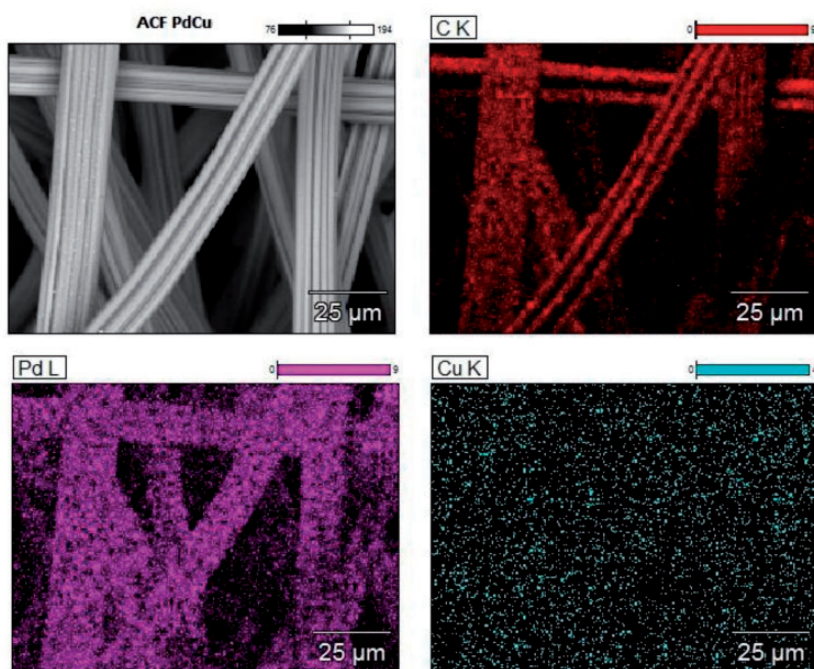


Figure 5. EDS mapping analysis of Pd-Cu/ACF (0.5%Pd-0.5%Cu). ACF: activated carbon felt.

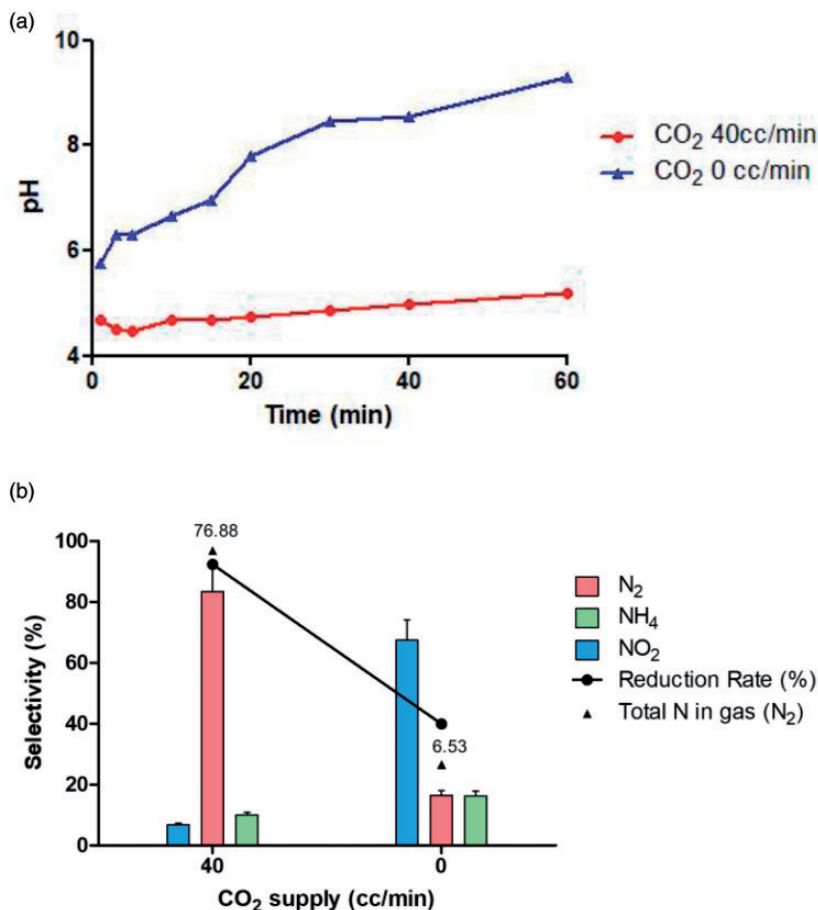


Figure 6. (a) pH variation during the reaction with and without pH control. (b) Nitrate reduction performance and N₂ selectivities of Pd-Cu/Al₂O₃ (0.5%Pd-0.5%Cu) catalyst with and without pH control (the reaction time was 60 min).

complete nitrate reduction (92.3%) was achieved when carbon dioxide was continuously supplied. A similar trend was also observed in the N₂ selectivity: 16.3% without pH control and 83.3% with pH control. If the nitrate reduction and the N₂ selectivity is considered together as the nitrogen mass basis, the total nitrogen converted as N₂ gas with and without pH control were 76.9% and 6.5%, respectively.

It has been reported that as the catalytic reaction proceeds, there is an increase in pH due to the formation of hydroxide species due to the hydrogenation of oxygen molecules during the reduction of nitrite over the surface of the catalyst.^{27,30} These OH⁻ concentrations can competitively be adsorbed on the active sites of catalyst, therefore inhibiting the adsorption of nitrate and nitrite and increasing the accumulation of nitrite or ammonia ions.^{12,27} Overall, the nitrogen removal efficiency was significantly increased by 11.8 times when carbon dioxide was used to control the pH on the reaction, reflecting the importance of pH control as the reaction proceeds due to the controlled production of hydroxide species on the active sites of the catalyst.

Catalytic nitrate reduction by Pd-Cu/ACF

Effect of pH on the performance of Pd-Cu/ACF catalyst. It was verified in the previous section that the pH condition was one of the main parameters determining the overall catalytic nitrate reduction performance. In order to find the optimal pH conditions for Pd-Cu/ACF catalyst, the initial pH was varied from 3 to 6 with pH control using CO₂. The same flow rate of H₂ and CO₂ achieved from Pd-Cu/Al₂O₃ (H₂ 30 cc/min, CO₂ 40 cc/min) was adopted in the experiment, and the initial pH was controlled by HCl and NaOH to be in the range of pH 3–6.

Figure 7(a) illustrates that pH is stable during the entire experiment, with a slight increase as a result of the reactions attributable to the adsorption of hydrogen and the reduction of nitrite on active sites. Figure 7(b) shows the nitrate reduction performance of the Pd-Cu/ACF (0.5%Pd-0.5%Cu) catalyst at different initial pH under H₂ 30 cc/min and CO₂ 40 cc/min flow. Overall, the nitrate reduction efficiency and N₂ selectivity showed a trade-off relationship. The nitrate reduction efficiency was low at an acidic condition, while increased reduction efficiency was observed at elevated pH. The highest nitrate reduction efficiency was 71.9% at pH 5, and the lowest was 40.8% at pH 3. On the other hand, the opposite trend was observed in terms of N₂ selectivity. The highest N₂ selectivity was 87.3% at pH 3, while the lowest N₂ selectivity of 20.9% was achieved at pH 6.

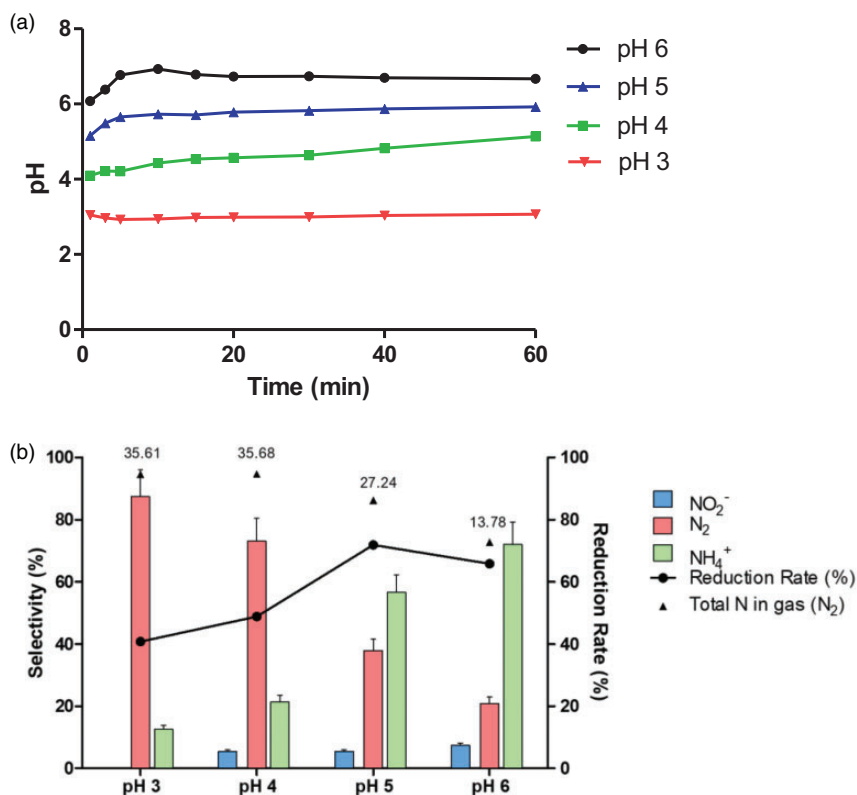


Figure 7. (a) pH variation during the reaction (H₂ 30 mL/min, CO₂ 40 mL/min). (b) Nitrate reduction performance and N₂ selectivities of Pd-Cu/ACF (0.5%Pd-0.5%Cu) catalyst with different initial pH (the reaction time was 60 min).

In order to evaluate the overall nitrogen removal performance, we calculated the removal amount of nitrogen as N_2 gas, and this is presented in Figure 7(b) as a black triangle. At acidic conditions, pH 3 and 4, showed similar values, 35.61% and 35.68%, which are much higher than elevated pH conditions. The removal amounts of nitrogen as N_2 gas at pH 5 and 6 were 27.2% and 13.8%, respectively. As the pH established for the reaction was higher, it is likely that active sites of the catalyst may have been inhibited with the presence of hydroxide species.^{12,27} This explains the increase in the selectivity towards NH_4 and the continuous decrease in the selectivity towards N_2 , which is consistent with the results obtained in the previous section from the pH effect experiment.

Performance of Pd-Cu/ACF catalyst on a synthetic RO concentrate. As mentioned in the introduction, the catalytic nitrate reduction process was considered for the RO concentrate treatment with a high concentration of nitrate and low biodegradable organic matter, which are difficult conditions for biological denitrification. Moreover, the RO concentrate contained a higher concentration of ionic species because the ionic species in the water were retained in the concentrate stream. However, the results obtained in the previous sections were for the case where the nitrate solution was prepared with deionized water; it is therefore necessary to investigate the effect of the water matrix on the catalytic nitrate reduction.

Figure 8 shows the nitrate reduction performance of Pd-Cu/ACF in the presence of four different solutions (see Table 1), the components of which have been reported to be present in RO concentrated brines.²⁴ RO concentrate commonly contains high concentrations of dissolved salts and organic components. In this study, we investigated the effect of each of those components in the nitrate reduction performance individually. In all experimental cases, the reference pH to start the reaction was fixed at 4, considering the optimal conditions obtained in the previous section.

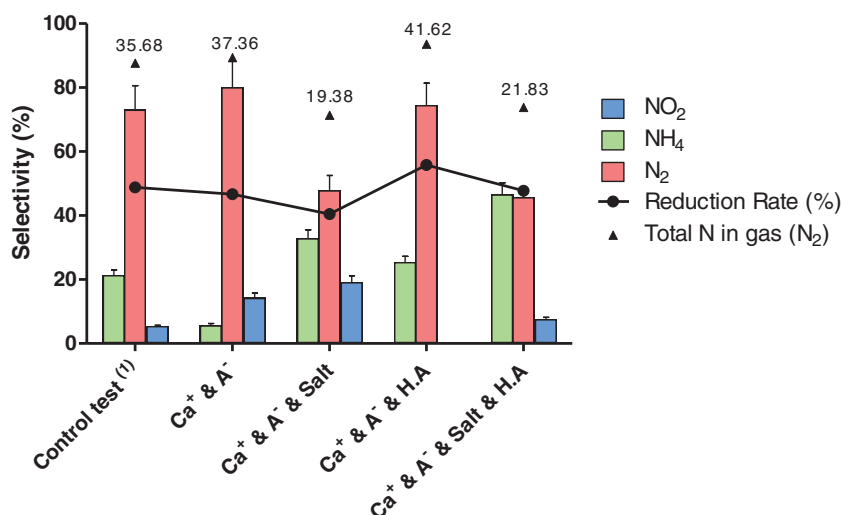


Figure 8. Nitrate reduction performance over different synthetic RO concentrate components by using ACF/0.5%Pd-0.5%Cu. The reaction time was 90 min. ^aThe control test refers to the pH 4 performance obtained in Figure 7.

The nitrate reduction efficiency, N_2 selectivity, and total nitrogen removed as N_2 gas in the control test were 48.8%, 73.1%, and 35.7%, respectively. The addition of ROC inorganics (Ca^{+} and A^{-} in the graph) did not have a significant change in the catalytic nitrate reduction. The nitrate reduction efficiency slightly decreased while the N_2 selectivity increased; thus 37.4% of total nitrogen removed as N_2 gas could be achieved. On the other hand, the addition of salt (490 mg/L) showed a significant inhibitory effect on catalytic nitrate reduction. N_2 selectivity decreased to 47.9%, and increased ammonia production (32.9%) was observed. Due to the lower N_2 selectivity, the total nitrogen removed as N_2 gas was decreased to 19.4%, which is almost half that of the control test.

The effect of humic acid was also investigated by adding humic acid (80 mg/L) in both cases of ROC only and ROC and salt. In general, the addition of humic acid did not show an inhibitory effect on the catalytic nitrate reduction. The nitrate reduction efficiency increased compared to the case without humic acid. For example, the nitrate reduction efficiency was 46.7% for ROC, but it was increased to 55.8% with humic acid. A similar trend was observed in the presence of salt (40.5%–47.7%). A slight change in the selectivity could be observed as well. The total nitrogen removed as N_2 gas was calculated as indicated in Figure 8 and a slight increase of the value in the presence of humic acid. The highest nitrogen removal was achieved in the case of ROC + HA as 41.6%.

It has been reported that humic acid has a small enhancement effect on microbial growth for nitrate reduction³¹ as well as for catalytic nitrate reduction because it acts as an electron donor for the reduction of NO_3 ,^{32,33} consistent with our results. This also explains the observation of the highest performance in the presence of humic acid when compared to other solutions composed only of inorganic constituents or in the presence of salt. On the other hand, it has been widely reported that high saline concentrations have an inhibitory effect on biological nitrate reduction³⁴ as well as on catalytic nitrate reduction and also due to the preferential sorption of Cl^{-} or its accumulation over the active sites of the catalyst.³⁵ This explains the diminishing reduction performance (40.46%) in the presence of saline concentrations.

Conclusions

Effective catalytic nitrate reduction was achieved by using the bimetallic Pd-Cu catalyst. SEM-EDS analysis confirmed a sound distribution of Pd-Cu bi-metallic particles over the surface of both alumina and ACF support materials. The alumina-based catalyst showed very high total nitrogen removal as N_2 gas (76.9%) owing to the almost complete reduction of nitrate (92.3%) and high N_2 selectivity (83.3%) in the presence of pH control by CO_2 , counteracting the value of 6.5% observed in the absence of pH control, indicating the importance of pH control in the catalytic reaction.

The effect of pH on the performance of the Pd-Cu/ACF catalyst was investigated with pH control in the range of pH 3–6. Nitrate reduction efficiency and N_2 selectivity showed a trade-off relationship. Nitrate reduction efficiency was low at acidic conditions while the highest N_2 selectivity was obtained at the acidic conditions. The optimal pH condition was determined as pH 4, showing the highest total nitrogen removal as N_2 gas (35.7%).

The inhibitory effect of ROC components on the catalytic nitrate reduction was investigated using Pd-Cu/ACF. In general, ROC inorganics did not show a significant effect on the performance. But, the presence of humic acid showed a slight enhancement effect on the catalytic reduction while salinity showed an inhibitory effect in the reduction rate as well as

N₂ selectivity. This finding indicated that the catalytic nitrate reduction would be promising for ROC concentrate management since the ROC inorganic and organic matter did not inhibit the overall performance of Pd-Cu/ACF on the nitrate reduction toward nitrogen gas.

Overall, the Pd-Cu/ACF was successfully prepared, and the reactivity was characterized. Moreover, the inhibitory effect of the water chemistry of ROC was discussed. The filter type morphology of the developed Pd-Cu/ACF would be beneficial for field application when compared to the conventional catalyst with powder form. However, further research must be performed to develop the continuous denitrification system using a filter type catalyst to demonstrate the real application scenario as a filtration system.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The authors disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This study was supported by the Advanced Research Project funded by the SeoulTech (Seoul National University of Science and Technology).

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