Elimination of nitrate in secondary effluent of wastewater treatment plants by Fe⁰ and Pd-Cu/diatomite

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ABSTRACT

Because total nitrogen (TN), in which nitrate (NO₃⁻) is dominant in the effluent of most wastewater treatment plants, cannot meet the requirement of Chinese wastewater discharge standard (<15 mg/L), NO₃⁻ elimination has attracted considerable attention. In this research, the novel diatomite-supported palladium-copper catalyst (Pd-Cu/diatomite) with zero-valent iron (Fe⁰) was tried to use for catalytic reduction of nitrate in wastewater. Firstly, specific operational conditions (such as mass ratio of Pd:Cu, catalyst amounts, reaction time and pH of solution) were optimized for nitrate reduction in artificial solution. Secondly, the selected optimal conditions were further employed for nitrate elimination of real effluent of a wastewater treatment plant in Beijing, China. Results showed that 67% of nitrate removal and 62% of N₂ selectivity could be obtained under the following conditions: 5 g/L Fe⁰, 3:1 mass ratio (Pd:Cu), 4 g/L catalyst, 2 h reaction time and pH 4.3. Finally, the mechanism of catalytic nitrate reduction was also proposed.

Key words | chemical catalytic reduction, nitrate removal, Pd-Cu/diatomite, wastewater treatment

INTRODUCTION

Contamination of nitrate in water resources has become a severe environmental problem. Excess nitrate in water can cause water pollution (such as river eutrophication and water quality deterioration). On the other hand, nitrate can also be reduced to nitrite, which poses several health threats to humans, such as liver damage and even cancer (Hosseini et al. 2011). Nitrate in wastewater mainly comes from agricultural activities, domestic and industrial sewage (Hwang et al. 2010). With aggravation of water pollution, efficient technologies for nitrate elimination have attracted much attention.

Among the existing technologies for nitrate removal, physico-chemical denitrification, biological and chemical reductions have been widely used (Kim et al. 2013). However, physico-chemical methods like ion exchange, reverse osmosis and electrodialysis, require frequent regeneration of the medium and further treatment for the secondary waste produced (Soares et al. 2008). Biological denitrification can achieve high nitrate removal. However, this process is complex and requires monitoring of the carbon source (Subramanyan et al. 2010). To date, chemical catalytic reduction of nitrate has been regarded as one of the promising techniques to reduce nitrate in wastewater.

Vorlop & Tacke (1989) proposed the new method of catalytic reduction to reduce nitrate in water. Since then, this potential technology has been gradually accepted by researchers. In previous research, H₂ and organic acids (e.g. HCOOH) were employed as a reductant for catalytic nitrate reduction. However, the potential risk of explosion, low solubility of H₂ in aqueous media, difficulty in operational conditions and potential health problems limit

Studies indicate that nitrate removal with bimetallic catalysts are better than those with monometallic ones. A noble metal (such as Pd, Pt, Ir) and a promoter metal (such as Cu, Ag, In) are usually chosen as the active components to coat on different supports (Soares et al. 2011) and it has been proven that Pd-Cu is much more efficient (Aristizábal et al. 2014). In addition to the active components, the supports also play an important role in nitrate reduction. Therefore, different types of materials (such as CeO₂, TiO₂, SnO₂, ZrO₂, membrane, activated carbon) used as the supports have been tested for the reduction of nitrate. However, satisfactory catalytic performance could not be obtained (Yun et al. 2016).

Diatomite has attracted considerable research attention due to its special properties. Diatomite primarily consists of SiO₂, which guarantees better chemical properties and thermal stability. Additionally, diatomite also possesses a unique porous structure, which can be used as a very adsorbent material for wastewater treatment (Zhu et al. 2014).

On the other hand, appropriate reductants should also be selected. Using only zero-valent iron (Fe⁰) on nitrate reduction has been intensively studied to date. However, the nitrate removal of this system mainly depends on low pH and undesirable ammonia is the predominant by-product (Huang & Zhang 2004).

Based on the aforementioned, Fe⁰ and Pd-Cu/diatomite were innovatively used for nitrate reduction. Controlled reaction conditions (Pd:Cu mass ratio, reaction time and pH) were firstly studied, and then the mechanism of catalytic nitrate reduction was proposed.

MATERIALS AND METHODS

Materials

Diatomite with a specific surface area of 285 m²/g and a mean particle diameter of 62 nm was used as the support. The chemicals used in this research were as follows: sodium nitrate (NaNO₃), cupric chloride dihydrate (CuCl₂·2H₂O), palladium chloride (PdCl₂), hydrochloric acid (HCl), iron powder (<0.07 nm, >98%). All chemicals were of analytical grade.

Catalyst preparation

A wet impregnation method was adopted to obtain Pd-Cu/diatomite catalyst (Saada et al. 2015). PdCl₂ and CuCl₂·2H₂O were used as metal precursors to obtain the desired amount of metals coated on diatomite. Five grams of the catalyst was prepared as follows: (1) PdCl₂ (0.5 g) and CuCl₂·2H₂O (0.3 g) solution were added into the diatomite (4.8 g) suspension solution and continuously stirred for 10 min (400 rpm); (2) the above mixed solution (400 mL) was dried in a vacuum oven at 100 °C for 24 h; (3) the dried mixture was heated at 350 °C for 2 h in order to coat the metals on the surface of the diatomite; (4) a certain volume of NaBH₄ solution was added dropwise to the mixture with vigorous agitation to load Pd and Cu elements on diatomite; (5) Pd-Cu/diatomite catalyst was separated using a centrifuge (5,000 rpm, 10 min per cycle); (6) the prepared catalyst was washed twice with deionized water and dried in a vacuum oven at 60 °C for 24 h.

Catalyst characterization

The specific surface area of the catalyst was determined by a Brunauer-Emmett-Teller (BET) surface area analyzer (F-Sorb X400, Gold APP Instruments Corporation, China). The morphology of diatomite and Pd-Cu/diatomite were analyzed by electron microscopy (SEM, JSM-35C, Japan) and elemental information of the catalyst was obtained with energy dispersive spectroscopy (EDS) in conjunction with SEM. The samples were also characterized by X-ray diffraction analysis (XRD-6000, Rigaku, Japan). Fourier transform infrared spectroscopy (FTIR) spectra of the samples were analyzed by an FTIR spectrometer (Tensor 27, Bruker).

Experimental design

Artificial solution (20 mg/L NaNO₃) was firstly prepared for optimization experiments of operational conditions. The optimum operational conditions were chosen under different operational conditions including Pd:Cu mass ratio, reaction time, catalyst amount and pH value of solution.
Then, the real treated wastewater was used for the feasibility tests under the optimum operational condition. Water samples were collected from the secondary effluent of a municipal wastewater treatment plant in Beijing, China.

All experiments were performed in necked flasks with a total volume of 150 mL. One hundred mL of NaNO₃ solution or wastewater was added to each flask with 0.5 g of Fe⁰. All flasks were placed in an electronic oscillator stirring under 250 rpm at room temperature.

**Laboratory analyses**

Samples were collected periodically to determine nitrate, nitrite and ammonium concentrations in accordance with standard methods. Nitrate removal and catalytic selectivity to N₂ were calculated as:

\[
\text{Nitrate removal} \ (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)
\]

\[
\text{Catalytic selectivity to } N_2 \ (\%) = \frac{C_{N_2}}{C_0 - C_t} \times 100\% \quad (2)
\]

where \(C_0\) is the initial concentration of nitrate in solution (mg/L), \(C_t\) is the nitrate concentration (mg/L) at time \(t\) (min) and \(C_{N_2}\) is the amount of N₂ produced (mg/L).

**RESULTS AND DISCUSSION**

**Optimization of operational condition**

**Pd:Cu mass ratio**

Pd:Cu mass ratio can significantly affect nitrate reduction (Yoshinaga et al. 2002). In Figure 1, nitrate conversion and N₂ selectivity reached 67 and 61% at a Pd:Cu mass ratio of 3:1 and then remained stable. When only Pd was coated on diatomite, removal efficiency and N₂ selectivity both decreased. However, the catalytic performance improved with the addition of Cu because of the synergistic effect of Pd and Cu, which implied that Cu could be used as a second metal to promote catalytic reduction of nitrate (Aristizábal et al. 2011). Additionally, the catalytic reaction mainly occurred at the Pd active site. Therefore, when Cu was overloaded (\(m_{Cu} > m_{Pd}\)), nitrate conversion and N₂ selectivity both decreased due to the decreased active site of Pd (Deganello et al. 2000).

By-products were analyzed after catalytic reduction. Results indicated that the removed nitrate was mostly converted to N₂, whilst ammonium and nitrite were only minor parts under the optimal Pd:Cu mass ratio (3:1). EDS analysis shown in Figure 2(a) indicates that Pd and Cu were both detected on diatomite and the mass ratio was nearly 3:1. Figure 2(b) shows that diatomite presents cribriform, which is the porous material that may adsorb more nitrate in water and indirectly improve catalytic performance. For the Pd-Cu/diatomite catalyst, an XRD pattern (see Figure 2(c)) shows no distinguished characteristic peaks of Pd, Cu, which may be due to the homogeneous dispersion of Pd and Cu on diatomite. FTIR spectra of diatomite and Pd-Cu/diatomite are shown in Figure 2(d). The absorption peaks at 476, 793 and 1,093 cm⁻¹ in the spectra strongly imply the existence of the silica framework in the diatomite (Pal & De 2002). The peak at 1,630 cm⁻¹ is due to the H-O-H bending modes of surface-adsorbed water molecules. The peak between 3,429 and 3,446 cm⁻¹ may result from the Si-O-H group (Sun et al. 2003). It is obvious that diatomite and Pd-Cu/diatomite present a similar spectra, which means that after loading of Pd and Cu on diatomite, the chemical structure and composition of diatomite seldom changed.
Catalyst amount

According to Figure 3, it is obvious that the catalytic performance can be greatly affected by the catalyst amount (Gao et al. 2004). A better catalytic performance (68% of nitrate conversion and 62% of N$_2$ selectivity) could be obtained with 0.4 g of catalyst. By-product analysis indicated that N$_2$ was the dominant by-product with the dosages in the range of 0.35–0.5 g. Hence, 0.4 g was the optimum dosage. The reason may be due to the fact that the catalytic capacity of the bimetal rose with the increase of catalyst amount, thereby promoting the catalytic process and efficiently reducing the nitrate in solution. On the other hand, increasing the catalyst amount could provide numerous active sites, therefore enhancing the catalytic process (Chen et al. 2005).

Reaction time

Reaction time is also critical for this catalytic process (Hoerold et al. 1993). As described in Figure 4, nitrate conversion and N$_2$ selectivity both rose dramatically with an increase in reaction time. N$_2$ tended to be the dominant by-product after 105 min. According to the data, 120 min was chosen as the optimal time. Results indicated that sufficient contact time between the catalyst and the solution was necessary for nitrate removal, which could significantly improve nitrate reduction (Gao et al. 2004).
Figure 5 shows that nitrate conversion decreased with a further increase in pH, reaching the peak (93%) at 2.2 of pH. However, N₂ selectivity rose dramatically with increasing pH and reached the summit (62%) at 4.3 of pH, then showed a downward trend. Therefore, 4.3 was the optimal pH for this catalytic reaction.

Data indicated that pH greatly influenced the catalytic performance, which has been proven by the previous study (Chen et al. 2003). This finding was due to the association between the heterogeneous catalytic reduction reaction and active sites on catalytic surface (Fan et al. 2011), where active H took part in the reaction. A certain concentration of H⁺ could deter Fe⁰ from oxidizing, which could significantly influence the catalytic performance (Chen et al. 2003). Additionally, H⁺ concentration also determined the variety of by-products, which has been proven by the results shown above. pH values of solution were tested after reaction, which mildly increased, but still remained in the range of 7–9, meeting the requirements of the Chinese discharge standard of pollutants for municipal wastewater treatment plant (GB18918-2002).

**Application tests**

Based on the experiments on Pd:Cu mass ratio, catalyst amount, reaction time and pH value, optimal conditions were set (0.5 g Fe⁰, 100 mL water samples, 3:1 Pd:Cu mass ratio, 0.4 g catalyst, 2 h reaction time and pH 4.1). The properties of wastewater adopted in this study were listed as below: concentration of NO₃⁻N: 12.6 mg/L, NO₂⁻N: 0.15 mg/L, TN: 16.2 mg/L, NH₄⁺-N: 1.4 mg/L and pH: 6.5. The results are shown in Table 1.

Based on the results analyzed above, 64% of nitrate removal efficiency and 60% of N₂ selectivity were reached.

According to the related research, the catalytic performance under the catalysis of different Pd-Cu catalysts (e.g. CeO₂, TiO₂, MnO₂, Al₂O₃, SiO₂) with H₂ remained lower, the
nitrate removal ranging from 20 to 40%, while the N₂ selectivity ranged from 15 to 70% (Soares et al. 2014). It is clear to see that the Fe₀ and Pd-Cu/diatomite showed a better catalytic performance.

Additionally, it is obvious that after treatment by catalytic reduction, the effluent total nitrogen (TN) concentration greatly reduced to 11.2 mg/L (<15 mg/L). Indicators in Table 1 all meet the requirements of the Chinese discharge standard of pollutants for municipal wastewater treatment plants (GB18918-2002) without further treatment for the by-products produced. However, the nitrate removal in wastewater maintained lower than that of the experiments using NaNO₃ as water sample. The main reason for that may be due to the influence of the ions (e.g. HCO₃⁻, SO₄²⁻) in wastewater (Lemaignen et al. 2002). For the effluent after catalytic process, the physical properties of the wastewater were also analyzed. Iron ion (mainly Fe²⁺) could be detected because of the addition of Fe₀. Therefore, flocculation processes should be followed to remove Fe²⁺ for wastewater reuse and reclamation.

**Mechanism**

Many studies have been conducted on nitrate reduction with the reductant H₂ and different kinds of bimetallic catalysts. In our research, instead of H₂, Fe₀ with the catalyst (Pd-Cu/diatomite) was used for the catalytic reduction of nitrate. The nitrate reduction mechanism is depicted as a conceptual model in Figure 6.

The catalytic reduction of nitrate has been regarded as a typical heterogeneous catalysis process. In this redox process, Fe₀ mainly served as the electron donor (see Equation (3)) and H⁺ in solution could bond with the electrons from Fe₀ to transform H, which could be activated to active H (H°) on bimetallic active sites (Huang et al. 1998). H° is involved in the deoxidization reaction to reduce nitrate, following with several intermediate products, including NO₂⁻, NO and NH (Pintar et al. 1996). The main reaction equations are listed as below:

\[ \text{Fe}_0 - 2e^- \Leftrightarrow \text{Fe}^{2+}, \quad \phi^{\theta}_{\text{Fe}_0/\text{Fe}^{2+}} = 0.44 \text{ V}, \]  
\[ \text{NO}_3^- + 2e^- + 2H^+ \Leftrightarrow \text{NO}_2^- + 3\text{H}_2\text{O}; \quad \phi^{\theta}_{\text{NO}_3^-/\text{NO}_2^-} = +0.83 \text{ V}, \]  
\[ \text{NO}_2^- + 6e^- + 8\text{H}^+ \Leftrightarrow \text{NH}_4^+ + 2\text{H}_2\text{O}; \quad \phi^{\theta}_{\text{NO}_2^-/\text{NH}_4^+} = +0.89 \text{ V}, \]  
\[ 2\text{NO}_2^- + 10e^- + 12\text{H}^+ \Leftrightarrow \text{N}_2 + 6\text{H}_2\text{O}; \quad \phi^{\theta}_{2\text{NO}_2^-/\text{N}_2} = +1.52 \text{ V}. \]

The standard electrode potential formula is \( E^\theta = \phi^{\theta(\text{oxidiser})} - \phi^{\theta(\text{reductant})} \). The standard electrode potentials (E°) of NO₃⁻ to NO₂⁻ to NH₄⁺ and NO₂⁻ to N₂ by Fe₀ are 1.27, 1.35 and 1.96, respectively (>0.2 V). In

Table 1 | Results of the application tests
<table>
<thead>
<tr>
<th>Effluent</th>
<th>pH after the reaction</th>
<th>NO₃⁻ N (mg/L)</th>
<th>NH₄⁻ N (mg/L)</th>
<th>NO₂⁻ N (mg/L)</th>
<th>TN (mg/L)</th>
<th>Removal (%)</th>
<th>Catalytic selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.1</td>
<td>4.6</td>
<td>4.5</td>
<td>0.2</td>
<td>11.2</td>
<td>64</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 6 | Conceptual model of catalytic nitrate reduction.
theory, reactions could spontaneously occur under the condition of $E^\theta > 0.2 \text{ V}$ (Wang 2013). Thus, it is theoretically feasible to use $\text{Fe}^0$ for nitrate removal.

Based on the experiments and related literature, $\text{H}^+$ concentration in solution is also another critical factor for nitrate reduction. As demonstrated in Figure 6, when $\text{H}^+$ was sufficient in solution, the catalytic process may follow paths 1 and 2, and then more ammonium could be obtained, dominating the products that have been proved by the data in Figure 5. Actually, $\text{N}_2$ is the harmless gas, which is the desirable product. Therefore, appropriate $\text{H}^+$ concentration in solution could be controlled by adjusting pH to make this catalytic reaction follow path 1 and lower the occurrence of path 2. Additionally, appropriate supported materials could also boost the nitrate removal and transformation to $\text{N}_2$ (Aristizábal et al. 2011).

The bi-metals $\text{Pd}$ and $\text{Cu}$ coated on diatomite are also crucial in catalytic reduction. On the one hand, it is generally believed that metallic copper, as a promoting metal, could reduce nitrate by producing cupric oxide (CuO) or cuprous oxide (Cu$_2$O) and then be regenerated by hydrogens adsorbed on Pd active site, as shown in Figure 7 (Zhao et al. 2014).

However, based on the results, we assume that Pd played the leading role in catalytic nitrate reduction, strengthening the electron transformation from $\text{Fe}^0$ to $\text{H}^+$ in solution, forming active $\text{H}$ and promoting $\text{NO}_3^-$ conversion to $\text{N}_2$, as shown in Figure 8.

### Kinetic modeling

Different initial nitrate concentrations (100, 50, 40, 30 and 20 mg/L) were set to study the kinetics of catalytic reduction of nitrate by $\text{Fe}^0$ with $\text{Pd-Cu/diatomite catalyst}$. The reaction can be described by the first-order and zero-order reaction as given below (Pintar et al. 1996).

The first-order equation:

\[
\nu = -\frac{d[\text{NO}_3^-]}{dt} = k_{\text{obs}}[\text{NO}_3^-] \tag{7}
\]

and then the following equation can be obtained:

\[
\ln \frac{[\text{NO}_3^-]_0}{[\text{NO}_3^-]} = k_{\text{obs}} t \tag{8}
\]

The zero-order equation:

\[
\nu = -\frac{d[\text{NO}_3^-]}{dt} = k_{\text{obs}} \tag{9}
\]

the equation can be transformed:

\[
[\text{NO}_3^-] = -k_{\text{obs}} t \tag{10}
\]

where $\nu$ is the rate of reaction (mg/(L·min)); $[\text{NO}_3^-]$ is nitrate concentration at time $t$ (mg/L), $[\text{NO}_3^-]_0$ is the initial concentration of nitrate (mg/L), $k_{\text{obs}}$ is the reaction rate constant.

The results in Table 2 indicate that the correlation coefficients ($R^2$) obtained from the first-order equations were in the range of 0.9983–0.9995, while $R^2$ of zero-order equations ranged from 0.8775 to 0.9144. Therefore, it is obvious to
conclude that the modeling providing the best correlation with the experiments was the first-order equation, which could better explain the kinetic research of nitrate reduction by Fe\(^0\) and Pd-Cu/diatomite. On the other hand, data implied that \(k_{\text{obs}}\) gradually reduced with the increase of the nitrate concentration in solution.

### CONCLUSIONS

The results in this research implied that better nitrate removal performance could be obtained with a synergistic effect of Fe\(^0\) and Pd-Cu/diatomite. Sixty-seven per cent nitrate removal and 62\% \(N_2\) selectivity were reached under the optimum operational conditions: 5 g/L Fe\(^0\), 3:1 Pd-Cu mass ratio, 4 g/L Pd-Cu/diatomite catalyst, 2 h reaction time and 4.3 pH. The study on the mechanism of catalytic reduction revealed that the catalytic reaction is a process of stepwise deoxidization. Pd and Cu loaded on the diatomite are crucial to the catalytic performance and Pd played a leading role. The kinetic modeling research indicated that the first-order equation could be employed to better describe the catalytic reduction of nitrate by Fe\(^0\) and Pd-Cu/diatomite.

### ACKNOWLEDGEMENTS

This research was supported by the Academic Cooperation Project between University of Science and Technology Beijing and National Taipei University of Technology. Grant agreement No. TW201603.

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First received 6 July 2016; accepted in revised form 11 October 2016. Available online 17 December 2016

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