Research Article

Effects of Initial Nitrate Concentrations and Photocatalyst Dosages on Ammonium Ion in Synthetic Wastewater Treated by Photocatalytic Reduction

Orawan Rojviroon¹, Sanya Sirivithayapakorn¹, Thammasak Rojviroon², and Chalermraj Wantawin¹

¹Department of Environmental Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand
²Division of Environmental Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, Thailand

Correspondence should be addressed to Sanya Sirivithayapakorn; fengsys@ku.ac.th

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Ammonium (NH₄⁺) is an undesirable by-product of photocatalytic nitrate (NO₃⁻) reduction since it is harmful to aquatic life once it converts into ammonia (NH₃). This research investigated the removal efficiency of NO₃⁻ and for the first time quantified the relationships of initial nitrate concentrations ([NO₃⁻]₀) and photocatalyst dosages on the remaining ammonium (NH₄⁺) in synthetic wastewater using photocatalytic reduction process with either nanoparticle titanium dioxide (TiO₂) or 1.0%Ag-TiO₂ under Ultraviolet A (UVA). The experiments were systematically carried out under various combinations of [NO₃⁻]₀ (10, 25, 50, 80, and 100 mg-N/L) and photocatalyst dosages (0.1, 0.5, 1.0, and 2.0 g). The NO₃⁻ removal efficiency of both photocatalysts was 98.96-99.98%, and the catalytic selectivity products were nitrogen gas (N₂), nitrite (NO₂⁻), and NH₄⁺. Of the two photocatalysts under comparable experimental conditions, 1.0%Ag-TiO₂ provided better NO₃⁻ removal efficiency. For both photocatalysts, the remaining NH₄⁺ was predominantly determined by [NO₃⁻]₀; higher [NO₃⁻]₀ led to higher NH₄⁺. Multiple linear regression analysis confirmed the dominant role of [NO₃⁻]₀ in the remaining NH₄⁺. The photocatalyst dosage could play an essential role in limiting NH₄⁺ in the treated wastewater, with large variation in [NO₃⁻]₀ from different sources.

1. Introduction

Photocatalytic reduction is an effective technology for removal of nitrate (NO₃⁻) in wastewater. The major disadvantage of this process is the ammonium (NH₄⁺), an undesirable by-product, remaining at the end. Many researchers studied NO₃⁻ removal efficiency and the NO₂⁻ conversion selectivity [1–3]. There are also studies on the influencing factors on the remaining NH₄⁺, which investigated the relationships between remaining NH₄⁺ and those influencing factors in the process.

Previous studies demonstrated that high efficiency nitrate removal by photocatalytic reduction with low remaining [NH₄⁺] could be achieved by silver- (Ag-) doped TiO₂ nanoparticles under high-performance light sources (i.e., high-pressure Hg lamps and xenon lamps) [4–6]. However, those light sources have disadvantages that include high energy consumption, potential human health hazard, and generating high heat [7, 8]. For those reasons, the UVA light bulb is chosen for this process because it overcomes those disadvantages and is powerful enough for this process [9–11].

The influencing factors of the photocatalytic selectivity of NO₃⁻ conversion include initial nitrate concentration ([NO₃⁻]₀), light source intensity, type of photocatalyst, type of dopant, and quantity of photocatalyst dosage [4, 12, 13]. Evidence shows that manipulating the photocatalytic selectivity of photocatalytic reduction helps limit environmentally harmful compounds, particularly NH₄⁺ [14, 15]. NH₄⁺ is
harmful to aquatic life once in the natural waterways where it converts into ammonia (NH₃). According to the United States Environmental Protection Agency (US EPA), the upper safety limit of total ammonia nitrogen (NH₃-N) is 17 mg-N/L (1-hour average) and 1.9 mg-N/L (30-day rolling average) at pH 7.0 and 20°C for acute and chronic criteria, respectively [16]. The reported total ammonia concentrations in treated wastewater from photocatalytic reduction vary between 0.07 and 57.8 mg-N/L [4, 17–22].

Doping of silver (Ag⁺) on photocatalysts, especially TiO₂, to improve the photocatalytic performance was a common practice. Previous studies applied 0.1%-7.0% Ag⁺ loading on TiO₂ photocatalysts and found that 1% Ag⁺ was the most optimum dose to enhance the photocatalytic NO₃⁻ reduction activity [23–25].

This research investigated the effects of initial nitrate concentrations ([NO₃⁻]₀) and photocatalyst dosages on NO₃⁻ removal efficiency in synthetic wastewater using photocatalytic reduction. The experiments were carried out under various [NO₃⁻]₀ (10, 25, 50, 80, and 100 mg-N/L) and photocatalyst dosages (0.1, 0.5, 1.0, and 2.0 g) under UVA irradiation as light source for photocatalytic nitrate reduction. The experimental photocatalysts were TiO₂ and 1.0%Ag-TiO₂ nanoparticle as photocatalysts [21]. The catalytic selectivity of NO₃⁻ conversion was also determined, and the actual concentrations of NH₃ under different experimental NO₃⁻ removal conditions were compared. Multiple linear regression was performed to characterize the relationship between the remaining NH₃ and [NO₃⁻]₀ and photocatalyst dosages. Essentially, the novelty of this research lies in the use of TiO₂ nanopowder as photocatalyst, as opposed to commercial-grade TiO₂. By comparison, TiO₂ nanopowder possesses larger surface area for adsorption and reaction. Another research novelty is the systematical use of various [NO₃⁻]₀ and photocatalyst dosages, unlike previous researches which experimented with specific [NO₃⁻]₀ and photocatalyst dosages.

2. Materials and Methodology

2.1. Ag-TiO₂ Photocatalyst Preparation and Characteristics

In this research, 1.0%Ag-TiO₂ photocatalyst was prepared by composite colloid deposition under alkaline condition, following Doudrick et al. [4, 9] with minor modifications. In the experiment, 12 g of TiO₂ nanopowder was dispersed in 500 mL deionized water and purged with nitrogen gas (N₂) for 30 min to remove O₂. After degassing, 8 mL of methanol was added and stirred prior to adding NaOH to adjust pH of the mixture to 12-13. Afterward, 1.0%AgNO₃ (w/v; Fluka) was added and stirred in the dark for 30 min before irradiation with UVA (800 µW/cm²) for 1 h at room temperature.

The mixture was then centrifuged at 200 rpm for 2 min to settle the powder, and the supernatant was discarded. Deionized water was added to wash the powder. It was then stirred and centrifuged. The process was repeated until the mixture pH was 7. The washed powder was oven dried at 103°C for 24 h and calcined at 450°C for 1 h for Ag-TiO₂ photocatalyst in the form of dried light purple powder.

The experimental TiO₂ nanopowder was of 15 nm in particle size and 99.5% anatase crystalline phase (US Research Nanomaterials, Inc., USA). The composition and specific surface area of dose photocatalysts were characterized by transmission electron microscopy (TEM, JEM-1400 TEM instrument) and X-ray fluorescence spectrometer (XRF; Bruker model S8 Tiger), Brunauer, Emmett and Teller (BET) analyzer (BELSORP-max Bel Japan Inc.).

2.2. Photocatalytic Reduction for NO₃⁻ Removal

The photocatalytic reduction to remove nitrate (NO₃⁻) was carried out using TiO₂ and Ag-TiO₂ photocatalysts in 125 mL cylindrical borosilicate glass photoreactor. Figure 1 illustrates the schematic of experimental photocatalytic reduction for NO₃⁻ removal. Synthetic NO₃⁻ wastewater of variable initial nitrate concentrations was prepared by dissolving potassium nitrate (KNO₃ > 99%, Fluka) in deionized water. The initial nitrate concentration ([NO₃⁻]₀) varied between 10, 25, 50, 80, and 100 mg-N/L.

The photoreactor was filled with 100 mL synthetic wastewater of varying [NO₃⁻]₀ and 58 mM of formic acid (FA) as hole scavenger, with the mixture pH ranging from 2.28 to 2.42. TiO₂ and Ag-TiO₂ photocatalysts of varying dosages were independently added into the photoreactor. The photocatalyst dosage was varied from 0.1, 0.5, 1.0, and 2.0 g. The photoreactor condition was anaerobic by purging with N₂ for 30 min to remove dissolved oxygen (DO) in the synthetic wastewater.

Prior to UVA irradiation, samples were drawn for initial measurement of pH, DO, [NH₃], [NO₂], and [NO₃]. The samples were subsequently irradiated with two UVA light bulbs (300 W, Osram) for 6 h. The UVA light bulbs were located on either side of the photoreactor vessel at a distance of 20 cm. The UVA intensity in the photoreactor vessel was 800 µW/cm² on average. The concentrations of NO₃⁻ and by-products ([NO₂] and [NH₃]) relative to reaction time were periodically measured throughout the experiment, while pH and DO were measured at the beginning and at termination (at 360 min). The concentrations of NO₃⁻, NO₂, and NH₃ in the synthesis wastewater were determined using ion chromatography instrument with chemical suppression (Metrohm 882 Compact IC Plus). Nitrogen gas (N₂) was calculated by the mass balance of nitrogen of the photocatalytic reduction process.

To verify the experiment, photocatalytic reduction was also carried out under three control conditions: (1) in the absence of photocatalyst but with UVA irradiation; (2) with Ag-TiO₂ photocatalyst of varying dosages but without UVA irradiation; and (3) with TiO₂ photocatalysts of varying dosages but without UVA irradiation. The measured [NO₃⁻], [NO₂], and [NH₃] of photocatalytic reduction using Ag-TiO₂ and TiO₂ photocatalysts irradiated with UVA were subsequently compared against the controls.

2.3. Selectivity of Photocatalytic Reduction for NO₃⁻ Removal

The NO₃⁻ removal efficiency of photocatalytic reduction (η) and the catalytic selectivity (S) of NO₃⁻ into NH₃, NO₂, and N₂ (denoted by SₙH₃, SₙO₂, and SₙN) [21, 26] are
mathematically expressed in the following equations.

\[ \eta = \left( \frac{[\text{NO}_3^-]_0 - [\text{NO}_3^-]_t}{[\text{NO}_3^-]_0} \right) \times 100, \]  
(1)
\[ \%S_{\text{NO}_3^-} = \left( \frac{[\text{NO}_3^-]_0 - [\text{NO}_3^-]_t}{[\text{NO}_3^-]_0} \right) \times 100, \]  
(2)
\[ \%S_{\text{NH}_4^+} = \left( \frac{[\text{NH}_4^+]_0 - [\text{NH}_4^+]_t}{[\text{NH}_4^+]_0} \right) \times 100, \]  
(3)
\[ \%S_{\text{N}_2} = \left( \frac{[\text{NO}_3^-]_0 - [\text{NO}_3^-]_t - [\text{NO}_2^-]_t - [\text{NH}_4^+]_t}{[\text{NO}_3^-]_0 - [\text{NO}_3^-]_0} \right) \times 100, \]  
(4)

where \([X]_0\) is the initial concentration of \(X\) and \([X]_t\) is the concentration of \(X\) at time \(t\).

3. Results and Discussion

3.1. Ag-TiO₂ Nanopowder Photocatalyst Characteristics. The results of transmission electron microscopy were used to examine the particle size and morphology of Ag nanoparticles on TiO₂ as well as the lattice information of both photocatalysts investigated by XRF. In comparison, the TEM image of nano-TiO₂ and nano-Ag-TiO₂ photocatalysts (Figure 2) showed a similar particle size and morphology with average particle size (in diameter) of approximately 15 nm (as the result of the average TiO₂ particle size before Ag doping). The results of the TEM analysis were not clearly distinguishable in terms of particle size and morphology although it was reported that Ag doping would slightly decrease the particle size of the larger TiO₂ powders [27].

The XRF patterns of TiO₂ and 1.0%Ag-TiO₂ nanopowder photocatalysts showed strong peaks of Ti, as shown in Figure 3. The XRF pattern of 1.0%Ag-TiO₂ photocatalyst indicated that Ag⁺ dopant was effectively doped onto TiO₂ which is the same with the theoretical adding. The Ag dopant in Ag-TiO₂ phase was 0.99% for theoretical doping of 1.0% (Table 1). It was confirmed that Ag was effectively deposited on the surface of TiO₂ nanopowder. Specifically, Ag⁺ ions were adsorbed onto the crystal structure of TiO₂ and subsequently formed Ag-TiO₂ [28, 29].

The BET specific surface areas of TiO₂ and 1.0%Ag-TiO₂ nanopowder photocatalysts were 1.164 × 10² and 1.124 × 10² m²/g, and the corresponding pore volumes were 4.727 × 10⁻² and 3.951 × 10⁻² m³/g. It was found that the specific surface area and pore volume of Ag-TiO₂ were decreased after doping. The findings were consistent with previous studies which doped TiO₂ nanopowder photocatalysts with varying dopants [4, 30, 31].

The slightly decreased BET surface areas and pore volume were due to the interference of Ag dopant on the formation of anatase crystallization [32, 33], and a marked influence on the microstructures was exhibited by calcination temperature [34]. However, the advantage of metal doping on semiconductor particles, Ag-TiO₂, was the prevention of recombination between electron and hole by trapping the electron on the metal surface resulting in increasing the lifetime of electron in conduction band, thus enhancing the efficiency of photocatalytic nitrate reduction [34].

3.2. NO₃⁻ Removal Using Photocatalytic Reduction. The NO₃⁻ removal efficiency (\(\eta\)) of photocatalytic reduction using TiO₂ and 1.0%Ag-TiO₂ photocatalysts under variable initial NO₃⁻ concentrations ([NO₃⁻]₀, 10, 25, 80, and 100 mg-N/L) and TiO₂ and 1.0%Ag-TiO₂ dosages (0.1, 0.5, 1.0, and 2.0 g) was determined by equation (1). The NO₃⁻ removal efficiency of TiO₂ and 1.0%Ag-TiO₂ photocatalysts was 98.96-99.98%. The NO₃⁻ removal efficiency increased with the increase in photocatalyst dosage as the surface area for adsorption and reaction increased.

The ammonium ion selectivity (\(S_{\text{NH}_4^+}\)) and actual ammonium ion concentration ([NH₄⁺]₀) of photocatalytic reduction under various [NO₃⁻]₀ using TiO₂ and 1.0%Ag-TiO₂ photocatalysts. The NO₃⁻ removal efficiency of TiO₂ and 1.0%Ag-TiO₂ photocatalysts was 98.96-99.98%. The NO₃⁻ removal efficiency increased with the increase in photocatalyst dosage as the surface area for adsorption and reaction increased.

The ammonium ion selectivity (\(S_{\text{NH}_4^+}\)) and actual ammonium ion concentration ([NH₄⁺]₀) increased with the increase in photocatalyst dosage for both TiO₂ and 1.0% Ag-TiO₂ photocatalysts. In addition, the initial nitrate concentration and [NH₄⁺]₀ were positively correlated. In other words, low [NO₃⁻]₀ resulted in low [NH₄⁺]₀ and vice versa. Moreover,
[NH₄]⁺ of 1.0% Ag-TiO₂ photocatalyst was higher than that of TiO₂ photocatalyst under all experimental conditions.

The NO₃⁻ reduction in photocatalytic process was a stepwise mechanism. When the photoinduced electrons (e⁻) in valence band were excited onto conduction band, holes (h⁺) appeared at valence band. This process was called electron-hole pairs photogeneration [32] (equation (5)). The photogenerated holes consumed HCOO⁻, and CO₂ was generated [35] (equation (6)). The CO₂⁻ is a strong reducing agent to reduce NO₂⁻ to either NH₄⁺ or N₂ (equations (7)–(12)), in which nitrite (NO₂⁻) was an intermediate product. The results of NO₂⁻, NH₄⁺, and N₂ in percent named the selectivity of NO₃⁻ reduction.

\[
\text{TiO}_2 + h^+ \rightarrow e^- + h^+ \quad (5)
\]

\[
\text{HCOO}^- + h^+ \rightarrow H^+ + CO_2^- \quad (6)
\]

\[
\text{NO}_3^- + 2H^+ + 2e^- \rightarrow \text{NO}_2^- + H_2O \quad (7)
\]

\[
2\text{NO}_3^- + 12H^+ + 10CO_2^- \rightarrow N_2 + 6H_2O + 10CO_2 \quad (8)
\]

\[
\text{NO}_3^- + 10H^+ + 8CO_2^- \rightarrow \text{NH}_4^+ + 3H_2O + 8CO_2 \quad (9)
\]

\[
\text{NO}_2^- + 8H^+ + 6CO_2^- \rightarrow \text{NH}_4^+ + 2H_2O + 6CO_2 \quad (10)
\]

\[
2\text{NO}_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6CO_2 \quad (11)
\]

\[
\text{NO}_3^- + 10H_2O + 8e^- \rightarrow \text{NH}_4^+ + 3H_2O \quad (12)
\]

In the nitrate reduction experiments, 58 mmol of formic acid (FA) was used as a hole scavenger to improve the photocatalytic reduction reaction, while the pH of the solution increased from 2.28–2.42 to 2.41–5.5 due to the consumption of formic acid in the reaction and the generation of [NH₄]⁺. In addition, the highly efficient conversion of NO₂⁻ to N₂ was also related to the initial acidity of the solution [36]. This was probably due to the specific absorption properties of NO₃⁻ and NO₂⁻ in varying pH solutions. Considering that the point of zero charge of the TiO₂ was 6.25 [37], in acidic solution, TiO₂ surface accumulated a net positive charge due to the increasing fraction of TiOH₂⁺ sites on the surface and NO₂⁻ could be quickly adsorbed.

Figure 4 compares the nitrate concentrations of photocatalytic reduction under various [NO₃⁻]₀ and photocatalytic dosages (TiO₂ and 1.0%Ag-TiO₂) from the start to end. In Figure 4, the NO₃⁻ removal was positively correlated with photocatalyst dosage due to the surface area effect, independent of photocatalyst type. Although at termination there were not much differences in final NO₃⁻ removal efficiencies, the NO₃⁻ removal rates of 1.0%Ag-TiO₂ photocatalyst were faster than those of TiO₂ photocatalyst for the comparable conditions. The faster removal rate of photocatalytic reduction activity was attributable to Ag⁺ doping [33, 38]. The loading of TiO₂ with Ag⁺ reduced the difference between
energy levels of the valence and conduction bands, resulting in the extension of light absorption wavelength into the visible light region. Ag⁺ also acted as a trap site for excited electrons, giving rise to electron-hole separation. In addition, Ag⁺ doping enhanced charge transport, prolonged the life-time of electron-hole pairs, and reduced the charge recombination [39–42]. As a result, Ag⁺ could be adopted for photocatalytic reduction process to improve NO₃⁻ removal.

Figure 5 illustrates the catalytic selectivity (%) of photocatalytic reduction using TiO₂ and 1.0%Ag-TiO₂ photocatalysts in which NO₃⁻ was transformed into NO₂⁻, NH₄⁺, and N₂. The results showed that overall N₂ accounted for the largest proportion of NO₃⁻ by-products, followed by NH₄⁺ and NO₂⁻.

In Figure 5, the photocatalyst types (TiO₂ and 1.0%Ag-TiO₂) and dosage played a role in the selectivity of the photocatalytic reduction scheme. This showed that the Ag dopant enhanced the photocatalytic reduction activity, and both the activity and [NH₄⁺] increased with 1.0%Ag-TiO₂ dosage increase. However, 1.0%Ag-TiO₂ photocatalyst dosage beyond 0.1 g (i.e., 0.5, 1.0, and 2.0 g) contributed to [NH₄⁺] in the treated wastewater exceeding that of TiO₂ photocatalyst (Table 2). NH₄⁺ is harmful to aquatic life once in the natural waterways where it converts into NH₃.

The initial nitrate concentrations also played a role in [NH₄⁺] in the treated wastewater, independent of photocatalyst type (TiO₂ and 1.0%Ag-TiO₂). Specifically, higher [NO₃⁻]₀ resulted in higher [NH₄⁺]. Given 0.1 g of either TiO₂ or 1.0%Ag-TiO₂ photocatalyst, [NH₄⁺] was 1.96–16.09 mg-N/L, independent of [NO₃⁻]₀. Assuming complete NH₄⁺-to-NH₃ conversion, these were equivalent to 1.96–16.09 mg-N/L total ammonia nitrogen (NH₃-N), which is below 17 mg-N/L NH₃-N of the US EPA [16]. Meanwhile, the nitrate concentrations of the three control conditions (i.e., the controls) remained unchanged at the end of the experiment.

In Figure 5, the catalytic selectivity of NO₃⁻ into NO₂⁻ could also be observed. The remaining nitrite concentrations ([NO₂⁻]) were negligible as NO₂⁻ was converted into NH₄⁺ and N₂ during the photocatalytic reduction process [43].

To comparatively investigate the effect of initial nitrate concentration and photocatalyst dosage on the concentration of ammonium ion, the relationships between [NH₄⁺] and [NO₃⁻]₀ and photocatalyst dosage (TiO₂ and 1.0%Ag-TiO₂) were established by using statistical multiple linear regression. [NH₄⁺] and photocatalyst dosage are denoted by Y, X₁, and X₂, respectively. The multiple linear regression was expressed in equation (13), and Table 3 tabulates the regression results.

\[
Y = b + \beta_1 X_1 + \beta_2 X_2 + \cdots + \epsilon, \quad (13)
\]

where b is the linear regression constant, \(\beta\) is the linear regression coefficient, and \(\epsilon\) is the error constant.

In Table 3, \(\beta\) of the initial nitrate concentration ([NO₃⁻]₀) was, respectively, 0.925 and 0.838 for TiO₂ and 1.0%Ag-TiO₂ photocatalysts (p < 0.001), indicating that [NO₃⁻]₀ played the dominant role in NO₃⁻ removal efficiency and the remaining NH₄⁺. Meanwhile, \(\beta\) of photocatalyst dosage was 0.407 and 0.288 for 1.0%Ag-TiO₂ and TiO₂ photocatalysts, suggesting that the photocatalyst dosage had considerably less effect on the remaining NH₄⁺.

In reality, [NO₃⁻]₀ varies from area to area. Given diverse [NO₃⁻]₀, it is operationally practical to vary the

### Table 1: Composition of TiO₂ and 1.0%Ag-TiO₂ photocatalysts.

| Photocatalyst | TiO₂ | Ag | SiO₂ | P₂O₅ | Nb₂O₅ | Other | BET surface area (m²/g) | Pore volume (m³/g) |
|---------------|------|----|------|------|-------|-------|------------------------|------------------|
| TiO₂          | 96.8 | —  | 0.44 | 0.15 | 0.11  | 2.50  | 1.164 × 10⁶          | 4.727 × 10⁻²     |
| 1.0%Ag-TiO₂   | 96.1 | 0.99| 0.40 | 0.17 | 0.11  | 2.23  | 1.124 × 10⁶          | 3.951 × 10⁻²     |

### Table 2: NO₃⁻ removal efficiency, [NO₃⁻]₀, %S₉⁻, and [NH₄⁺]₄ of photocatalytic reduction using TiO₂ and 1.0%Ag-TiO₂ photocatalysts at termination.

| Photocatalyst | [NO₃⁻]₀ (mg-N/L) | Dosage (g) | NO₃⁻ removal (%) | %S₉⁻ | [NH₄⁺]₄ (mg-N/L) | pH |
|---------------|-----------------|------------|------------------|------|-----------------|----|
| TiO₂          | 10              | 0.1-2.0    | 98.96-99.48      | 25.81-34.00 | 2.55-3.38      | 2.41-2.84 |
| 25            |                |            | 99.35-99.92      | 20.53-36.5  | 5.10-9.12      | 2.54-3.11 |
| 50            |                |            | 99.84-99.92      | 9.53-26.40   | 4.76-13.18     | 2.80-3.61 |
| 80            |                |            | 99.85-99.98      | 16.35-25.55  | 13.06-20.43    | 2.9-3.28  |
| 100           |                |            | 99.90-99.95      | 17.13-22.56  | 17.12-22.55    | 2.93-3.3 |
| 1.0%Ag-TiO₂   | 10              | 0.1-2.0    | 99.60-99.62      | 19.71-64.09  | 1.96-6.38      | 2.50-2.51 |
| 25            |                |            | 99.30-99.84      | 17.59-44.81  | 4.39-11.19     | 2.52-2.64 |
| 50            |                |            | 99.78-99.90      | 14.97-45.98  | 7.47-22.97     | 2.73-3.03 |
| 80            |                |            | 99.85-99.94      | 19.20-38.15  | 15.33-30.50    | 3.00-4.02 |
| 100           |                |            | 99.82-99.96      | 16.12-38.10  | 16.09-38.10    | 3.06-5.50  |

Note: %S₉⁻ is NH₄⁺ selectivity (%), [NH₄⁺]₄ is actual [NH₄⁺], and pH is pH at the end.
photocatalyst dosage in the photocatalytic reduction scheme. Based on the experimental results, 0.1 g of Ag-TiO$_2$ photocatalyst is advisable due to efficient removal of NO$_3^-$ (Figure 3).

To facilitate estimation of the remaining [NH$_4^+$] in treated wastewater using photocatalytic reduction, the multiregression prediction equations of the theoretical remaining ammonium ion ([NH$_4^+$]$_T$), as a function of [NO$_3^-$]$_0$ and photocatalyst dosage, are expressed in equations (14) and (15), respectively.

The prediction equation for TiO$_2$ photocatalyst is

$$[\text{NH}_4^+]_T = -1.489 + 0.185[\text{NO}_3^-]_0 + 2.698\text{dosage.} \quad (14)$$

The prediction equation for 1.0%Ag-TiO$_2$ photocatalyst is

$$[\text{NH}_4^+]_T = -3.744 + 0.274[\text{NO}_3^-]_0 + 6.064\text{dosage.} \quad (15)$$

The relationships between [NH$_4^+$]$_T$, [NO$_3^-$], and photocatalyst dosage, as shown in equations (7) and (8), could be further applied to estimate the remaining [NH$_4^+$] under various [NO$_3^-$]$_0$ and photocatalyst dosages.

4. Conclusion

This research investigated the NO$_3^-$ removal efficiency of photocatalytic reduction process under various [NO$_3^-$]$_0$ (10,
25, 50, 80, and 100 mg-N/L) and photocatalyst dosages (0.1, 0.5, 1.0, and 2.0 g) using nanoparticle TiO$_2$ and 1.0%Ag-TiO$_2$ photocatalysts under UVA. The NO$_3^-$ removal efficiency of both photocatalysts under experimental [NO$_3^-$]$_0$ and photocatalyst dosages was between 98.96 and 99.98%. The catalytic selectivity products were NH$_4^+$, NO$_2^-$, and N$_2$, with N$_2$ accounting for a significant proportion of the selectivity. The doping of TiO$_2$ with Ag$^+$ improved the removal efficiency of NO$_3^-$. It was found that [NO$_3^-$]$_0$ played a more important role in the remaining NH$_4^+$ than the photocatalyst dosage. Specifically, higher [NO$_3^-$]$_0$ led to higher [NH$_4^+$] in the treated wastewater. Multiple linear regression analysis confirmed the dominant role of [NO$_3^-$]$_0$ in the remaining NH$_4^+$.

**Data Availability**

The analysis data used to support the findings of this study are included within the supplementary information file(s).

**Conflicts of Interest**

The author(s) declare(s) that they have no conflicts of interest.
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References

[1] N. Tong, Y. Wang, Y. Liu et al., "Pd/SnNiO/NaTaO3:La for photocatalytic ammonia synthesis by reduction of NO3− with formic acid in aqueous solution," Journal of Catalysis, vol. 361, pp. 303–312, 2018.

[2] Y. A. Shaban, A. A. El Maradny, and R. K. Al Farawati, “Photocatalytic reduction of nitrate in seawater using C/TiO2 nanoparticles,” Journal of Photochemistry and Photobiology A: Chemistry, vol. 328, pp. 114–121, 2016.

[3] D. Sun, W. Yang, L. Zhou, W. Sun, Q. Li, and J. K. Shang, “The selective deposition of silver nanoparticles onto {0 0 1} facets of TiO2 nanocrystals with co-exposed {0 0 1} facets, and their enhanced photocatalytic reduction of aqueous nitrate under simulated solar illumination,” Applied Catalysis B: Environmental, vol. 182, pp. 85–93, 2016.

[4] K. Doudrick, T. Yang, K. Hristovski, and P. Westerhoff, “Photocatalytic nitrate reduction in water: managing the hole scavenger and reaction by-product selectivity,” Applied Catalysis B: Environmental, vol. 136-137, pp. 40–47, 2013.

[5] R. Lucchetti, L. Onotri, L. Clarizia et al., “Removal of nitrate and simultaneous hydrogen generation through photocatalytic reforming of glycerol over "in situ" prepared zero-valent nanocopper/P25,” Applied Catalysis B: Environmental, vol. 202, pp. 539–549, 2017.

[6] E. Bahadori, A. Tripodi, G. Ramis, and I. Rossetti, “Semi-batch photocatalytic reduction of nitrates: role of process conditions and co-catalysts,” ChemCatChem, vol. 11, no. 18, pp. 4642–4652, 2019.

[7] Z. W. Lipsky and G. K. German, “Ultraviolet light degrades the mechanical and structural properties of human stratum corneum,” Journal of the Mechanical Behavior of Biomedical Materials, vol. 100, article 103391, 2019.

[8] T. F. Anderson, “Artificial light sources,” Dermatologic Clinics, vol. 4, no. 2, pp. 203–215, 1986.

[9] T. Rojiviroon and S. Sirivithayapakorn, “E. coliBacteriostatic action using TiO2Photocatalytic reactions,” International Journal of Photoenergy, vol. 2018, 12 pages, 2018.

[10] T. Rojiviroon, O. Rojiviroon, and S. Sirivithayapakorn, “Photocatalytic decolourisation of dyes using TiO2thin film photocatalysts,” Surface Engineering, vol. 32, no. 8, pp. 562–569, 2016.

[11] M. Long, J. Wang, H. Zhuang, Y. Zhang, H. Wu, and J. Zhang, "Performance and mechanism of standard nano-TiO2 (P-25) in photocatalytic disinfection of foodborne microorganisms – Salmonella typhimurium and Listeria monocytogenes," Food Control, vol. 39, pp. 68–74, 2014.

[12] J. Yuan, E. Wang, Y. Chen, W. Yang, J. Yao, and Y. Cao, "Doping mode, band structure and photocatalytic mechanism of B–N-codoped TiO2," Applied Surface Science, vol. 257, no. 16, pp. 7335–7342, 2011.

[13] K. Nakata and A. Fujishima, "TiO2 photocatalysis: design and applications," Journal of Photochemistry and Photobiology C: Photochemistry Reviews, vol. 13, no. 3, pp. 169–189, 2012.

[14] F. Zhang, R. Jin, J. Chen et al., “High photocatalytic activity and selectivity for nitrogen in nitrate reduction on Ag/TiO2 catal.
[30] N. T. Minh and B.-K. Lee, “Feasibility of silver doped TiO$_2$-glass fiber photocatalyst under visible irradiation as an indoor air germicide,” *International Journal of Environmental Research and Public Health*, vol. 11, pp. 3271–3288, 2014.

[31] L. Lu, G. Wang, Z. Xiong et al., “Enhanced photocatalytic activity under visible light by the synergistic effects of plasmonics and Ti$^{3+}$-doping at the Ag/TiO$_2$- heterojunction,” *Ceramics International*, vol. 46, no. 8, pp. 10667–10677, 2020.

[32] A. Herissan, J. Meichtry, H. Remita, C. Colbeau-Justin, and M. Litter, “Reduction of nitrate by heterogeneous photocatalysis over pure andradiolytically modified TiO$_2$ samples in the presence of formic acid,” *Catalysis Today*, vol. 281, 2016.

[33] L. Elsellami, F. Dappozze, A. Houas, and C. Guillard, “Effect of Ag$^{+}$ reduction on the photocatalytic activity of Ag-doped TiO$_2$,” *Superlattices and Microstructures*, vol. 109, pp. 511–518, 2017.

[34] X. F. Lei, X. X. Xue, and H. Yang, “Preparation and characterization of Ag-doped TiO$_2$ nanomaterials and their photocatalytic reduction of Cr(VI) under visible light,” *Applied Surface Science*, vol. 321, pp. 396–403, 2014.

[35] D. Zhang, B. Wang, X. Gong, Z. Yang, and Y. Liu, “Selective reduction of nitrate to nitrogen gas by novel Cu$_3$O-Cu$_4$@Fe$_3$ composite combined with HCOOH under UV radiation,” *Chemical Engineering Journal*, vol. 359, pp. 1195–1204, 2019.

[36] W. Gao, R. Jin, J. Chen et al., “Titania-supported bimetallic catalysts for photocatalytic reduction of nitrate,” *Catalysis Today*, vol. 90, no. 3–4, pp. 331–336, 2004.

[37] F. Zhang, Y. Pi, J. Cui, Y. Yang, X. Zhang, and N. Guan, “Unexpected selective photocatalytic reduction of nitrite to nitrogen on silver-doped titanium dioxide,” *The Journal of Physical Chemistry C*, vol. 111, no. 9, pp. 3756–3761, 2007.

[38] S. Parastar, S. Nasseri, S. H. Borji et al., “Application of Ag-doped TiO$_2$ nanoparticle prepared by photodeposition method for nitrate photocatalytic removal from aqueous solutions,” *Desalination and Water Treatment*, vol. 51, no. 37-39, pp. 7137–7144, 2013.

[39] J. Huang, L. Ding, Y. Xi et al., “Efficient silver modification of TiO$_2$ nanotubes with enhanced photocatalytic activity,” *Solid State Sciences*, vol. 80, pp. 116–122, 2018.

[40] R. Qian, H. Zong, J. Schneider et al., “Charge carrier trapping, recombination and transfer during TiO$_2$ photocatalysis: an overview,” *Catalysis Today*, vol. 335, 2018.

[41] S. Buda, S. Shafei, S. A. Rashid, H. Jaafar, and N. F. M. Sharif, “Enhanced visible light absorption and reduced charge recombination in AgNP plasmonic photoelectrochemical cell,” *Results in Physics*, vol. 7, pp. 2311–2316, 2017.

[42] B. Xin, L. Jing, Z. Ren, B. Wang, and H. Fu, “Effects of simultaneously doped and deposited Ag on the photocatalytic activity and surface states of TiO$_2$,” *The Journal of Physical Chemistry B*, vol. 109, no. 7, pp. 2805–2809, 2005.

[43] G. Tokazhanov, E. Ramazanova, S. Hamid, S. Bae, and W. Lee, “Advances in the catalytic reduction of nitrate by metallic catalysts for high efficiency and N$_2$ selectivity: a review,” *Chemical Engineering Journal*, vol. 384, p. 123252, 2020.