Reductive catalysis of novel TiO$_2$/Fe$^0$ composite under UV irradiation for nitrate removal from aqueous solution

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**Abstract**

Groundwater contaminated by nitrate has become a worldwide problem. Existing technologies for nitrate removal, including zero-valent iron reduction, can only transform nitrate ions to predominantly NH$_4^+$. As a result, many studies have concentrated on seeking a solution to convert nitrate to N$_2$. In this study, the efficiencies of nitrate removal from aqueous solution by single (TiO$_2$ and nano zero valent iron, nZVI), and composite (Nano-TiO$_2$–Fe$^0$ composite, NTFC) system under UV illumination were prepared. Among the three systems, both nZVI and NTFC can effectively remove nitrate. However, only NTFC can achieve satisfactory transformation of nitrate to N$_2$. Further investigation has proven that the composition of NTFC (TiO$_2$/nZVI ratio) greatly influences the conversion of nitrate to N$_2$, which can be attributed to the maintenance of high level of ferrous ions in the NTFC system due to its reducing condition.

**Keywords:** Nitrate, Zero-valent iron, TiO$_2$, Catalysis

**1. Introduction**

Contamination of groundwater by nitrate has become more and more serious in many countries because of the excessive use of fertilizer. Drinking water containing high concentration of nitrates can cause methemoglobinemia or blue baby syndrome in infants. Processes like ion exchange, reverse osmosis and dialysis have been applied for nitrate removal; however, these methods can only move nitrate from one phase to another or transform it to another form, mostly ammonia nitrogen rather than nitrogen, which creates another pollutant in the treated water. Besides the aforementioned treatment processes, chemical reduction by materials like nano zero-valent iron (nZVI) is another approach for nitrate removal from water [1]. As known, nZVI has been widely used in environmental remediation due to its strong reduction capacity. Studies have shown that electrons and ferrous ions are released into the aqueous solutions, through the oxidation on the nZVI surface, to reduce nitrate ions. Moreover, hydrogen generated in the reaction of nZVI can also remove nitrate ions from the aqueous solution. As a result, the availability of nZVI surface active sites is extremely important in nitrate removal [2,3]. However, due to the rapid oxidation of nZVI, metal oxide layer (e.g. Fe$_2$O$_3$, FeOOH, Fe$_3$O$_4$) will form on its surface, which handicaps the reactivity of the nZVI. The resulting retardation of hydrogen generation further reduces iron reaction with time. Normally, the reduction of nZVI was kept at low pH [1,4,5] to dissolve the metal oxide layer on the nZVI surface, which is not an economical operation.

Titanium oxide is a photocatalyst and a semiconductor. However, the recombination of electrons and holes lowers the photodegradation performance of TiO$_2$. If the electrons can be diverted away from the photocatalyst surface to avoid the recombination of electrons and holes, the reactivity of the catalyst can be maintained. In previous studies, substances which can trap electrons, such as Ag, Fe, Pt, Pd, Ru and Rh [6,7], have been added to suppress the recombination of electrons and holes in TiO$_2$. Ranjit and Viswanathan [8] further indicated that the amount of metals loaded on TiO$_2$ and the method of metallization had great impact on the photocatalytic reduction of nitrate. By using nano-scale titanium dioxide particles photodeposited by fine Ag clusters as catalyst (Ag/TiO$_2$) and formic acid as hole scavenger in photocatalytic reduction of nitrate, high rate of nitrate transformation (98%) and with nearly 100% of N$_2$ as final product were obtained when the size and morphology of Ag was well controlled [7]. In addition to monometal-loaded catalysts, bimetallic catalysts such as Ni–Cu/TiO$_2$ and Cu/MgTiO$_2$–TiO$_2$ have also demonstrated excellent photocatalytic reduction of nitrate [9,10].

Since the surface oxidation of nZVI has limited its widespread application on environmental remediation, studies have been conducted to improve the efficiency through material preparation or modification [11,12]. However, the final product of nitrate reduction by their nZVIs is mainly NH$_4^+$ other than N$_2$. This is the bottle neck of nitrate removal from wastewater.

In our previous study, it has been verified that a lab-prepared Nano-TiO$_2$–Fe$^0$ composite (NTFC) can simultaneously delayed the formation of the surface oxide layers on nZVI and the recombination of electrons and holes on TiO$_2$ [13]. It has also been demonstrated that ferrous ions can be released from the NTFC...
sustainability and a high concentration can be maintained for the duration of the reaction. In this study, nitrate removals by single system with TiO2 or nZVI and NTFC composite system were compared and the compositions of NTFC (TiO2/nZVI ratio) were manipulated to investigate its effect on the transformation of nitrate to N2.

2. Materials and methods

2.1. Materials

The particle sizes and specific surface areas of nZVI and NTFC particles synthesized in the lab were 20–30 nm and 141 m²/g and 40–70 nm and 164 m²/g, respectively. The synthetic wastewater samples contained 10 mg NO3⁻-N/L. The final pH values and oxidation reduction potentials (ORP) of synthetic samples ranged from 4.1 to 4.5 and 540 to 580 mV, respectively. All nano materials used in this study were synthesized in the laboratory by the methods described in our previous study [14]. Different amounts of 1% TiO2 sol were mixed with 2.3 ± 0.1 g nZVI to prepare NTFC of different nZVI/TiO2 ratio, as shown in Table 1.

2.2. Experiments

In each test, nano-scale particles of 0.01–0.25 g were put in the 30 mL of KNO3 aqueous solution containing 10 mg NO3⁻-N/L. The solution pH was then adjusted to desired values (3, 7 and 10) using H2SO4 (0.1, 1.0 N) and NaOH (0.1, 1.0 N). Acetate acid was used as buffer to control the pH during the reaction. To mix nitrate solution and nanoparticles completely, the vials were put in the mixer (Intelli-Mixer RM-2M) (Fig. 1). The enclosed reactor was equipped with the mixer and UV illuminator. UV light was generated by a cold cathode fluorescent lamp (CCFL) (1.8–1.9 mW/cm²). The enclosed reactor was operated at a uniform rotation rate (Intelli-Mixer RM-2M) (Fig. 1). The enclosed reactor was equipped with the mixer and UV illuminator. UV light was generated by a cold cathode fluorescent lamp (CCFL) (1.8–1.9 mW/cm²). The vials and reactor were kept oxygen-free by filling with argon gas.

2.3. Analysis

Samples withdrawn from the vials by syringes were filtrated through 0.2 µm (Millipore) filters. NO3⁻ and NO2⁻ were analyzed by ion chromatography (Dionex DX-120) using a Dionex IonPac AS12A column. The flow rate of the eluent (2.7 mM Na2CO3 and 0.3 mM NaHCO3) was set at 1.5 mL/min. NH4⁺ was analyzed by ion chromatography (Dionex ICS-1000) using a Dionex IonPac CS12A column. Twenty millimolar of methanesulfonic acid solution was used as the eluent with a flow rate of 1.0 mL/min. Each sample was analyzed in triplicate. Ferrous and ferric ions were analyzed with spectrophotometry (Hach DR4000). The amounts of oxygen gas and ferric ion produced were determined via mass balance of concentrations of NO3⁻, NO2⁻, NH4⁺, ferrous ions and total iron in the samples. Final pH and ORP of the reaction were recorded.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Amounts of 1% TiO2 sol mixed with nZVI (2.3 ± 0.1 g) to prepare NTFC of different ratio of nZVI and TiO2.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTFC ratio (TiO2:nZVI, wt:wt.)</td>
<td>TiO₂⁻ (mL)</td>
</tr>
<tr>
<td>1:2</td>
<td>150.0</td>
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<tr>
<td>1:5</td>
<td>50.00</td>
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<tr>
<td>1:10</td>
<td>25.00</td>
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<tr>
<td>1:13</td>
<td>18.75</td>
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<tr>
<td>1:20</td>
<td>12.50</td>
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</table>

Fig. 1. (a) The air-tight, oxygen-free UV reactor; and (b) the mixer.

3. Results and discussion

3.1. Nitrate removal by single and composite systems

Nitrate removal by the TiO2 or nZVI single system and NTFC composite system were conducted at 0.25 g/30 mL of catalyst for either single or composite system (TiO2:Fe0 = 1:10). Fig. 2 shows nitrate removals by TiO2, nZVI and NTFC systems at pH 3. Both nZVI and NTFC are efficient in nitrate removal. Almost 100% of nitrate was removed in 30 min in nZVI, and 95% removal was achieved in NTFC system. Less than 1% of nitrate were removed at the end of reaction (390 min) by TiO2.

Although TiO2 possesses both oxidative and reductive abilities under suitable light irradiation, the recombination of electron/hole on TiO2 has contributed to the poor nitrate removal. Sá et al. [15] have suggested that in removing nitrate from aqueous system, TiO2 can only assume a supplemental role in promoting the reaction. Without the presence of other materials to capture the electron, TiO2 is ineffective in nitrate removal. In addition, the variation of ORP during the reaction, as shown in Fig. 3, indicates that the TiO2 system was under oxidizing condition (300 to 500 mV), which is unfavorable to nitrate reduction. On the contrary, in both nZVI and NTFC system, the ORP dropped to less than −200 mV after 30 min of reaction, which benefits nitrate reduction, similar to the finding of Liao et al. [16].

Previous studies have shown that although nZVI can effectively remove nitrate, its final products contain mainly ammonia. The ultimate solution for nitrate removal is to convert it to nitrogen gas, which is the bottleneck that researchers are striving to breakthrough. The compositions of final products from the three single and composite systems are illustrated in Fig. 4. Significant

![Fig. 2. Nitrate removal by TiO2, nFe0 and NTFC systems at pH 3. (NO3⁻: 10 mg/L; TiO2, nFe0, NTFC (1:10): 0.25 g/30 mL.)](image-url)
difference in nitrate transformation was observed between nZVI and NTFC systems. As expected, in nZVI system, the majority of nitrate was converted to ammonia, with only 10% transformation to nitrogen gas, similar to the study of Choe et al. [17]. In contrast, around 40% of nitrate was converted to N2 in NTFC system. This can be explained by the following reasons. First, high concentration of ferrous ions is critical in nitrate conversion. To verify this hypothesis, the concentrations of ferrous ions in NTFC system were monitored over a period of 22 h. The result is shown in Fig. 5. Significant amount of ferrous ion was released with time, while the concentrations of ferric ions stayed very low. In addition, with the help of TiO2 catalysis, large amount of H2 were released to further promote the reduction of nitrate. Finally, as indicated in Fig. 3, the ORP of NTFC provided the suitable reducing condition for nitrate conversion by maintaining the continuous release of Fe2+ into the suspension [16].

3.2. Effect of TiO2/nZVI ratio on nitrate removal

In this experiment, NTFCs of five TiO2/nZVI ratio, namely, 1:2, 1:5, 1:10, 1:13, and 1:20, were prepared and used in the UV reactor to investigate the effect of NTFC composition on the transformation of nitrate to N2. The result, as seen in Fig. 6, shows that an optimal TiO2/nZVI ratio, namely, 1:10, is required to reach the maximum conversion of nitrate to N2.

When excessive amounts of TiO2 particles covered the active sites on the nZVI surface, such as TiO2:nZVI = 1:2, the release of ferrous ions was reduced. The insufficient amount of ferrous ions repressed the transformation of nitrate. On the other hand, when the amount of TiO2 was too low (TiO2:nZVI = 1:20), electrons generated in the system were insufficient to reduce nitrate as well as ferric ions to ferrous ions. Therefore, suitable TiO2/nZVI ratio in NTFC is necessary to maintain a high concentration of ferrous ion, which is critical in nitrate conversion as indicated in the previous session.

4. Conclusions

Both nZVI and NTFC can effectively remove nitrate; however, only NTFC can achieve satisfactory transformation of nitrate to N2. The NTFC system is in reducing condition (low ORP) and large amounts of ferrous ions can be maintained in the system. The composition of NTFC (TiO2/nZVI ratio) is critical in nitrate removal as
well as nitrate transformation to N₂. In our UV reactor, best performance is achieved by NTFC at 1:10 of TiO₂ to nZVI ratio.

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References