Magnesium Hydroxide-coated Nanoscale Zero-Valent Iron for Nitrate Removal under Different Conditions

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水酸化マグネシウムで被覆したナノスケールゼロ価鉄の異なる条件下での硝酸イオン除去性能に関する研究

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Abstract

The short lifespan of nZVI has always posed a challenge despite its high nitrate removal efficiency. To address this issue, a coating technology was employed to fabricate magnesium hydroxide on the surface of nZVI, resulting in improved nitrate removal efficiency and extended service life. In this study, nZVI@$Mg(OH)_2$ was synthesized and its performance in nitrate removal was examined under various conditions. The findings indicate that the optimal practical conditions for nZVI@$Mg(OH)_2$ are as follows: an initial nitrate concentration of 200 mg/L, a Mg/Al ratio of 0.8, a dosage of 3.0 g/L, pH maintained at 7, and a temperature of 35℃. Under these conditions, the nZVI@$Mg(OH)_2$ exhibited impressive nitrate removal capabilities, capable of eliminating up to 207 mg/L of nitrate with a removal rate of 100%. It is noteworthy that the nitrate removal efficiency is directly proportional to the dosage and temperature, while inversely proportional to the increase in solution pH and initial nitrate concentration. These factors should be carefully considered when applying nZVI@$Mg(OH)_2$ for nitrate removal processes.

Contents

Chapter 1: Introduction

1.1 Background

In 2023, the world's population has reached 7.9 billion [1]. With the acceleration of global urbanization and population growth, urban areas face greater challenges in sewage management. High population density and limited infrastructure result in inadequate wastewater treatment facilities, leaving a significant amount of wastewater untreated. Untreated wastewater can cause groundwater contamination.

In China, despite the collection and transportation of sewage to wastewater treatment plants (WTPs), the removal ratio of reactive nitrogen remains below 30% due to the absence of tertiary treatment in these facilities [2]. The swift urbanization process in China has led to a substantial increase in the urban population [3], exerting immense pressure on resources and the urban environment. Many urban areas in China commonly experience WTP effluents that do not meet the required standards [3], suggesting that the urbanization process often prioritizes development at the expense of the environment [3]. However, the human and environmental costs associated with this approach are already unacceptably high in many places [3]. The contamination of groundwater with nitrate (NO_3^-) poses a significant threat to human health [4, 8]. Approximately 5% of ingested nitrate is converted by bacteria in the digestive system into nitrite, which then forms harmful substances such as N-nitrosamines and N-nitrosamides that can damage DNA [5, 8]. Elevated levels of nitrate in drinking water are frequently linked to birth defects and cancers, which have been extensively studied in epidemiological research, particularly in rural agricultural areas that rely on shallow groundwater for domestic water supplies [6, 8]. Nitrate concentrations exceeding the maximum contaminant level established by the World Health Organization are relatively common in certain regions, especially in emerging developing countries [6, 7, 8]. Consequently, the removal of nitrate is of utmost importance in wastewater treatment.

1.2 Nitrate

Nitrate is a chemical compound that consists of one nitrogen atom and three oxygen atoms, with the chemical formula NO_3^-. It is classified as an inorganic ion and possesses high solubility in water. In the environment, nitrates occur naturally, primarily as a result of nitrogen cycling within soil and water systems. They can be formed through the oxidation of ammonia or the reduction of nitrite.

Apart from their natural presence, nitrates can also be produced through human activities, including agriculture, industrial processes, and the use of nitrogen-based fertilizers. Excessive fertilizer uses and improper agricultural practices can lead to the accumulation of nitrates in soil and water bodies. When these nitrates are washed into waterways, they contribute to water pollution, particularly in the form of excessive nutrient levels, which can cause eutrophication. High levels of nitrates in drinking water can also pose health risks, particularly for infants, as nitrates can be converted into nitrites, which can disrupt the oxygen-carrying capacity of red blood cells.

On a positive note, nitrates find various industrial applications. They are used in the production of explosives, dyes, and certain medications. In food preservation, nitrates are commonly used as additives to prevent bacterial growth, especially in cured meats. However, there is ongoing debate and research concerning the potential health effects of consuming nitrates through processed foods

Understanding the sources, effects, and regulation of nitrates is crucial for managing their environmental impact, ensuring water quality, and striking a balance between the benefits and risks associated with their utilization in different industries. Monitoring of nitrate levels in various environments and effective nitrate removal method are necessary for the sustainable and responsible use of this important chemical compound.

1.3 Nanoscale Zero-valent Iron (NZVI) & Magnesium Hydroxide Coated Nanoscale Zero-valent Iron

Nanoscale zero-valent iron (nZVI) refers to iron particles that have been reduced to the zero-valent state and possess nanoscale dimensions, typically ranging from 1 to 100 nanometers. This unique form of iron exhibits exceptional reactivity and a high surface area-to-volume ratio, making it highly effective in various applications.

In environmental remediation, nZVI is widely used for treating contaminated groundwater and soil. It can efficiently degrade and transform a broad range of pollutants. When nZVI particles come into contact with these contaminants, they initiate redox reactions by donating electrons, leading to the breakdown of pollutants into less harmful forms.

The small size and large surface area of nZVI particles enable increased contact with contaminants, enhancing their remediation efficiency. Additionally, their ability to easily penetrate porous media, such as soil and groundwater, allows for effective distribution in contaminated areas. nZVI can be introduced into the subsurface using various delivery methods, including direct injection, injection wells, or permeable reactive barriers.

It is important to consider factors like particle stability, mobility, and potential ecological impacts when using nZVI. Environmental conditions, such as pH, temperature, and the presence of other substances, can affect the behavior and efficacy of nZVI.

In recent years, the use of nanoscale zero-valent iron (nZVI) has emerged as a prominent area of research for the remediation of nitrate pollution. The main products resulting from this removal process are ammonium, as depicted in Figure 1-1.

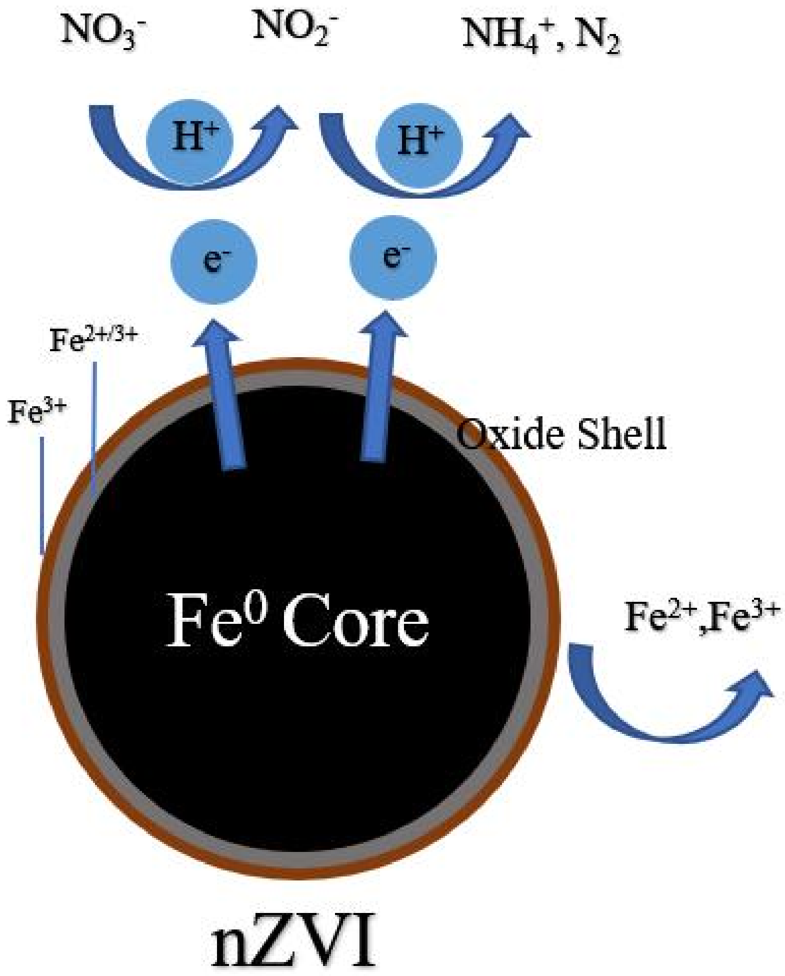


Fig. 1-1 The schematic images of nZVI main mechanisms

Representative reactions participate in this nitrate reduction process are shown below [9,19,20]:

$$Fe^0 + NO_3^- + 2H^+ \rightarrow Fe^{2+} + H_2O + NO_2^- \quad \text{(Eq. 1-1)}$$

$$3Fe^0 + NO_2^- + 8H^+ \rightarrow 3Fe^{2+} + 2H_2O + NH_4^+ \quad \text{(Eq. 1-2)}$$

$$3Fe^0 + 2NO_2^- + 8H^+ \rightarrow 3Fe^{2+} + 4H_2O + N_2(g) \quad \text{(Eq. 1-3)}$$

$$5Fe^0 + 2NO_3^- + 6H_2O \rightarrow 5Fe^{2+} + 12OH^- + N_2(g) \quad \text{(Eq. 1-4)}$$

Upon reaction with water or H^+ ions, nitrate is sequentially transformed to nitrogen with the intermediate products being nitrite and ammonium ions [20].

However, there are some drawbacks for nZVI application. One of the main challenges with nZVI is the tendency of the particles to agglomerate or clump together. This reduces their overall surface area and diminishes their reactivity, making it less efficient in contaminant removal. Agglomeration can occur due to various factors such as high concentrations, pH conditions, and the presence of certain ions or organic matter in the environment.

Another limitation is that the reactivity of nZVI particles may decline due to surface passivation or oxidation. This loss of reactivity reduces their effectiveness in contaminant removal and may require additional applications or replacement to sustain the desired remediation efficiency. To solve these problems, researchers have tried to use modified nZVI such as Bimetallic Fe^0 and Coated Fe^0.

Magnesium hydroxide coated nanoscale zero-valent iron is one of the modified forms of nZVI that have great potential applicability in water treatment applications. The utilization of magnesium hydroxide-coated nanoscale zero-valent iron demonstrated improved performance across various aspects of the particles' behavior in aqueous environments [10]. Increasing the Mg/Fe coating ratio resulted in a smaller average particle size compared to bare nZVI [10]. This reduction in size contributed to an anti-aggregation effect, promoting the stability of the coated nZVI particles [10]. In contrast, bare nZVI particles tend to aggregate more readily [10].

Furthermore, the coated nZVI exhibited enhanced stability when suspended in aqueous solutions compared to bare nZVI [10]. Additionally, the iron core of the synthesized NZVI was adequately protected from aqueous corrosion after the optimal modification with $Mg(OH)_2$, corresponding to leachates with lower iron oxides, indicating the enhanced reactive longevity of the modified composites [10].

These enhanced features of the coated NZVI nanocomposites could lead to great potential applicability toward sustainable effectiveness in water treatment applications [10].

1.4 Research objectives

Due to rapid population growth and the accelerated pace of industrialization, many water bodies and environments have been adversely affected by a variety of pollutants, resulting in severe environmental problems. Among these pollutants, nitrate poses a significant challenge due to its resistance to conventional removal methods. Nanoscale zero-valent iron (nZVI) has been developed as a potential solution for nitrate removal. However, nZVI is not without its drawbacks, such as issues with particle agglomeration and corrosion.

In contrast, magnesium hydroxide exhibits unique properties that make it an ideal coating material for nZVI when compared to other coating substances. These characteristics include low cost, high surface area, non-magnetization, non-toxicity, and low solubility constant [11]. These attributes make $Mg(OH)_2$ a promising choice for coating nZVI, enhancing its performance and addressing the limitations associated with uncoated nZVI.

The objective of this research is to identify the optimal conditions for nitrate removal using magnesium hydroxide coated nZVI. By exploring the potential of this novel composite material, the aim is to overcome the challenges associated with nitrate removal and improve the efficiency of the remediation process. By finding the ideal conditions for the application of magnesium hydroxide-coated nZVI, this research seeks to contribute to the development of more effective and sustainable strategies for nitrate removal from water bodies and the environment.

Chapter 2: Materials and method

2.1 Chemical materials

The following chemical reagents and materials were used: Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_20$), Magnesium Chloride Hexahydrate ($MgCl_2 \cdot 6H_2O$), Sodium borohydride ($NaBH_4$), Potassium Nitrate (KNO_3), Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Nitrogen gas was purged all prepared solutions for de-oxygenation. All chemicals were applied as delivered without further purification.

Ferric chloride hexahydrate and sodium borohydride were used for the synthesis of nZVI, magnesium chloride hexahydrate, sodium hydroxide and sodium borohydride were used for the synthesis of magnesium coated nZVI, potassium nitrate was used for the preparation of nitrate solution, and hydrochloric acid and sodium hydroxide were used for the adjustment of solution pH.

2.2 Synthesis of nZVI and magnesium hydroxide coated nZVI

2.2.1 The synthesis of nZVI

Chemical reduction methodology was considered to synthesize the nanoscale zero-valent iron particles, using ferric chloride and sodium borohydride as precursor and reductant respectively, following this reaction equation [10, 12, 13]:

$$2FeCl_3 + 6NaBH_4 + 18H_2O \rightarrow 2Fe^0 + 21H_2 + 6B(OH)_3 + 6NaCl \quad \textbf{(Eq.2-1)}$$

A total of 100 mL of the $NaBH_4$ solution (22 g/L) was added drop by drop into a four-neck flask containing 200 mL of the ferric chloride solution (25 g/L), with a flow rate of 10 mL/min. The mixing of the synthesis solutions was done mechanically at 400 rpm. Throughout the injection process and an additional 5 minutes for aging, the solutions were kept in a water bath at 30℃. To prevent oxidation and ensure uninterrupted progress, nitrogen bubbling was employed.

After the synthesis, the particles were collected using a vacuum filtration system. They were washed multiple times with DDIW (Deionized Distilled Water). For a visual representation of the nZVI synthesis system, please refer to Figure 2-1.

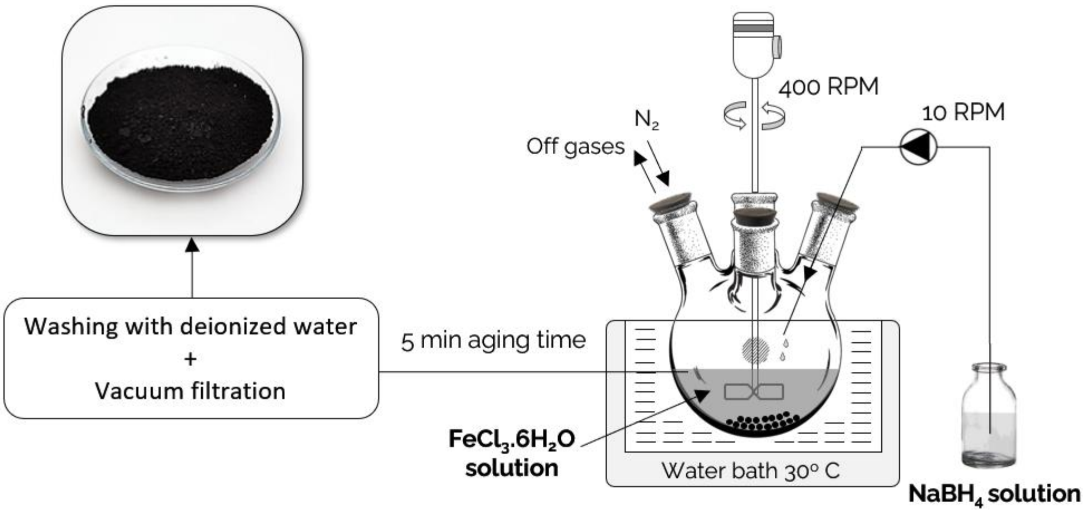


Fig. 2-1 The schematic images of nZVI synthesis system

2.2.2 The synthesis of magnesium hydroxide coated nZVI

The synthesis of the iron-magnesium nanocomposite involved the hydrothermal precipitation of $Mg(OH)_2$ onto the surface of nZVI in an alkaline medium (NaOH) [10, 14, 15]. To maintain a desired OH^- /Mg^{2+} molar ratio of 2, the Mg/ethanol and NaOH/ethanol solutions concentrations were carefully controlled. Additionally, various Mg/Fe mass coating ratios were achieved by adjusting the added volumes of the magnesium and hydroxide solutions.

The entire coating process took place under ultrasonication at a temperature of 50°C. Once the process was completed, the final composite product was separated using a vacuum filtration method.

For a visual representation of the magnesium hydroxide coated nZVI synthesis system, please refer to Figure 2-2.

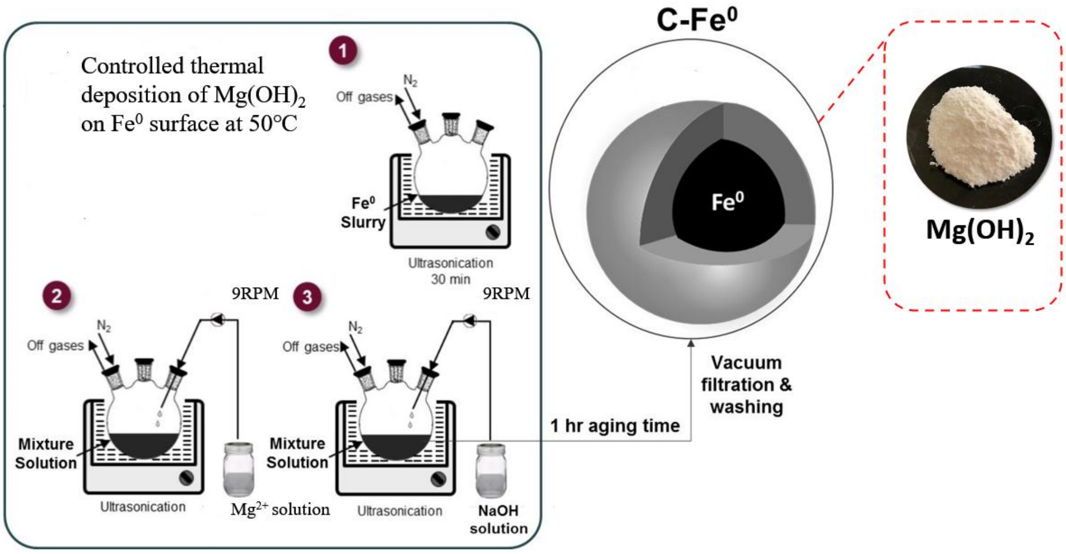


Fig. 2-2 The schematic images of magnesium hydroxide coated nZVI synthesis

2.3 Batch experiment

For batch experiment, take 101.1g of KNO_3 and dissolve it in 1000 ml of deionized water (DIW) while stirring with a magnetic stirrer. Once the solution becomes clear and transparent, adjust the pH of the solution to 7. This process will yield a nitrate solution with a concentration of 1000 mg/L for sample solution. Samples after experimental treatment were taken through a syringe filter, and nitrate concentrations in the samples were measured by UV-Vis spectrophotometer (DR 3900, HACH Co., USA).

In order to investigate the optimum conditions, this research studied the effect of different conditions for magnesium hydroxide coated nZVI to remove nitrate through batch experiments. The experimental procedures are as figure 2-3.

Nitrate was considered as the indicator for the reactivity influence of the synthesized materials towards adsorption and reduction mechanisms, respectively. Removal efficiency of the synthesized iron-magnesium nanocomposites towards nitrate was calculated as a function of initial (C_o) and final (C_f) concentrations, using the following formula [10]:

$$Removal\ Efficiency(\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad \textbf{(Eq.2-2)}$$

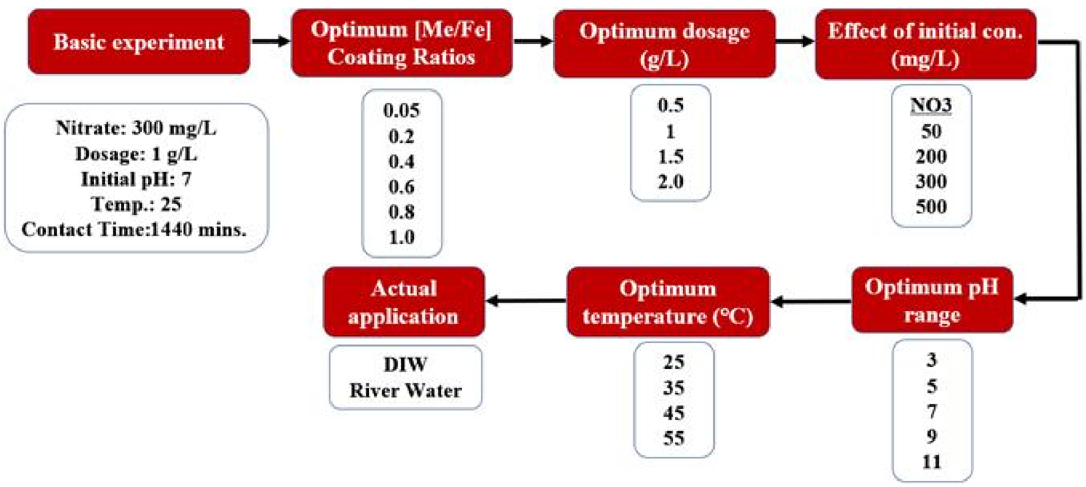


Fig. 2-3 The experimental procedure flow chart of batch experiment

Chapter 3: Results and discussion

3.1 Optimum [Me/Fe] Coating Ratios

The Fe^0 nanoparticles were coated with $Mg(OH)_2$ shell to overcome the drawbacks of Fe^0. In this regard, the particles coated with different coating ratios (0.05, 0.2, 0.4, 0.6, 0.8, 1.0) to demonstrate the optimum coating ratio of Mg to Fe^0.

Previous research has demonstrated that magnesium hydroxide coated nanoscale zero-valent iron exhibits higher crystallinity compared to bare nZVI, resulting in a lower dissolution rate [16]. As a result, the Fe^0 core remains preserved for a longer period, thereby enhancing the availability of integrated electrons in reduction processes [16].

As depicted in Figure 3-1, the nitrate removal efficiency of coated nZVI is significantly higher at low coating ratios within 120 minutes compared to high coating ratios. However, at 1440 minutes, the high coating ratio sample exhibits noticeably superior removal efficiency compared to the low coating ratio sample, maintaining a favorable decreasing trend. The high coating ratio of Mg/Fe^0 may lead to a slower electron emission speed, resulting in relatively inferior short reaction time performance compared to low coating ratio Mg/Fe^0 or bare Fe^0. Nevertheless, Figure 3-1 illustrates the excellent long reaction time performance of high coating ratio Mg/Fe^0.

Considering the efficiency and cost factors, a coating ratio of 0.8 has been selected as the optimal choice for subsequent experiments, as it outperforms a coating ratio of 1.0 and offers slightly lower costs.

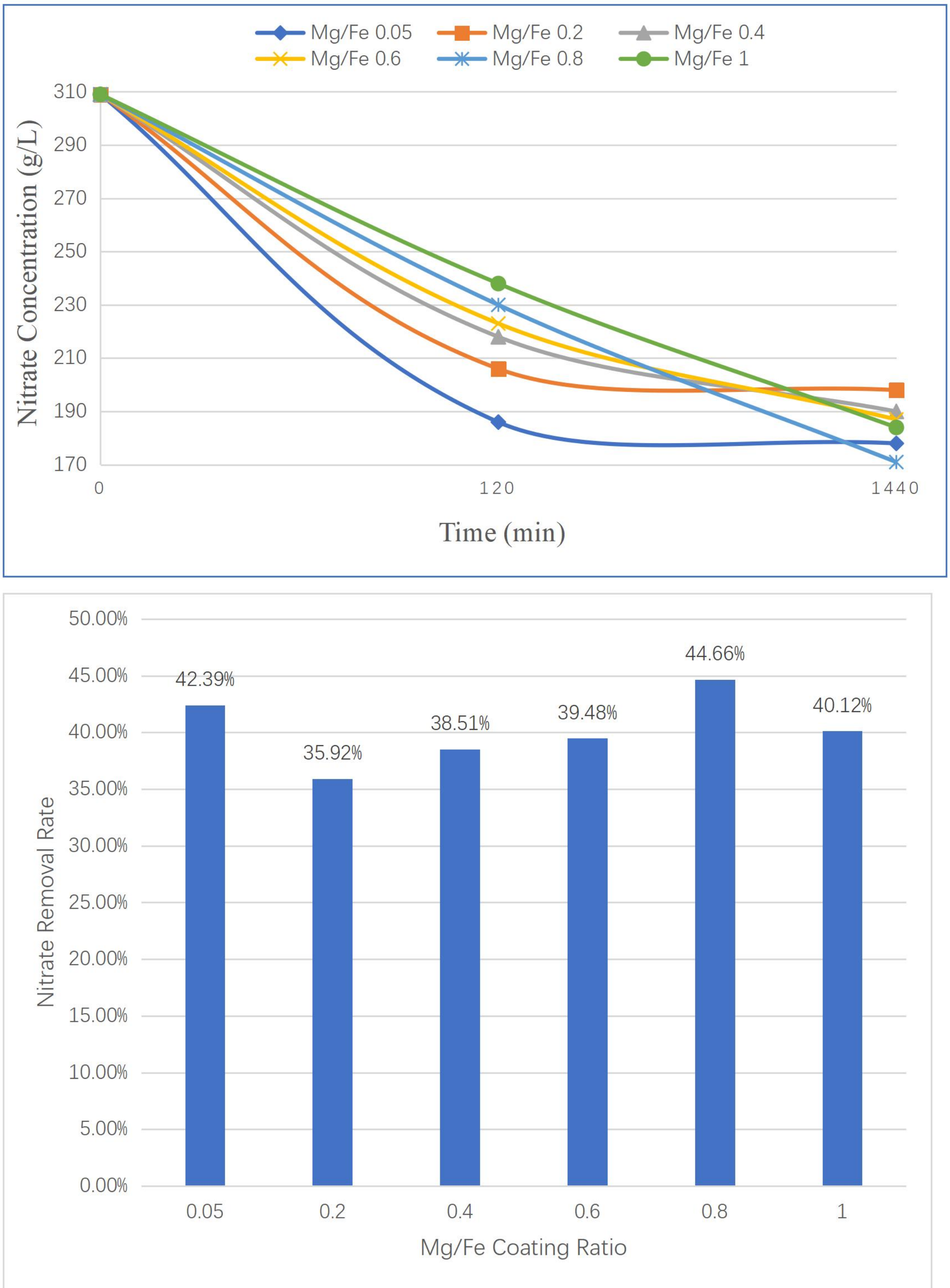
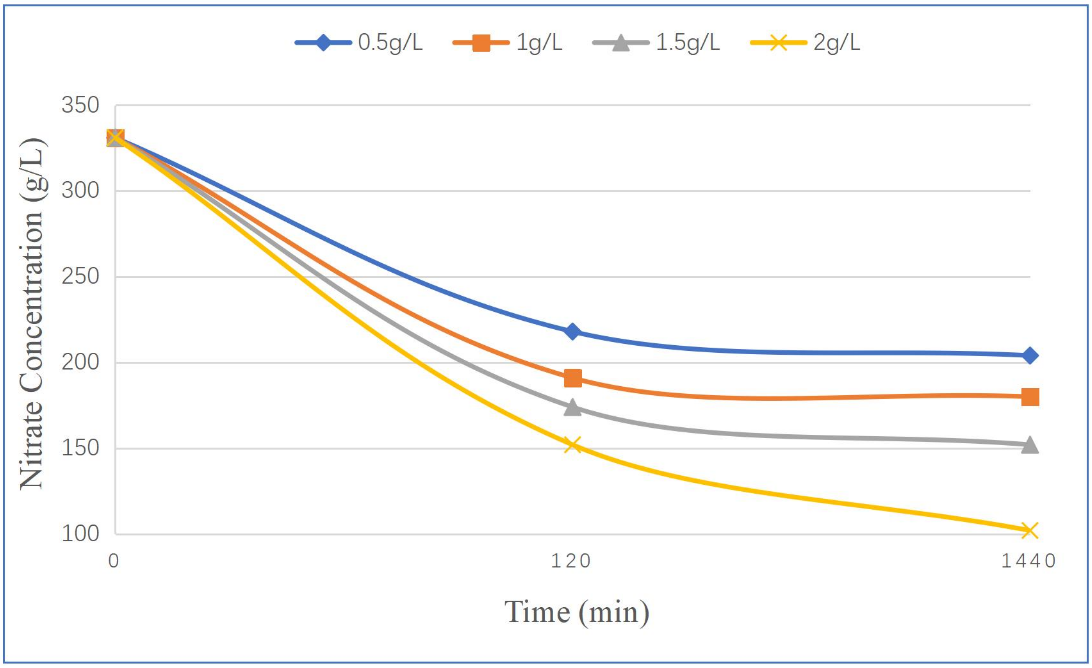


Fig. 3-1 nitrate removal efficiency of nZVI@Mg$(OH)_2$ under different Mg/Fe coating ratio

3.2 Optimum dosage

To determine the optimal dosage and assess the effect of higher dosages on nitrate removal efficiency, various amounts of magnesium hydroxide $Mg(OH)_2$ coated Fe^0 particles were tested. The dosages tested included 0.5g/L, 1g/L, 1.5g/L, and 2.0g/L. This experimentation aimed to identify the most effective dosage for nitrate removal and to confirm whether increasing the dosage enhances the efficiency of nitrate removal. When the coated Fe^0 nanoparticles were dosed from 0.5 to 2 g/L, the nitrate removal efficiency gradually increased, implying that 2g/L was the optimal dosage of coated Fe^0 nanoparticles for increasing removal rate. A dosage of 2.0 g/L has been selected as the optimal choice for subsequent experiments. More nZVI@$Mg(OH)_2$ particles in the solution provided more iron surface-active sites thus increasing the removal amount and removal rate [21].

Once all the optimum conditions have been determined, the dosage will be progressively increased in order to completely remove the nitrate by the end of the experiments.



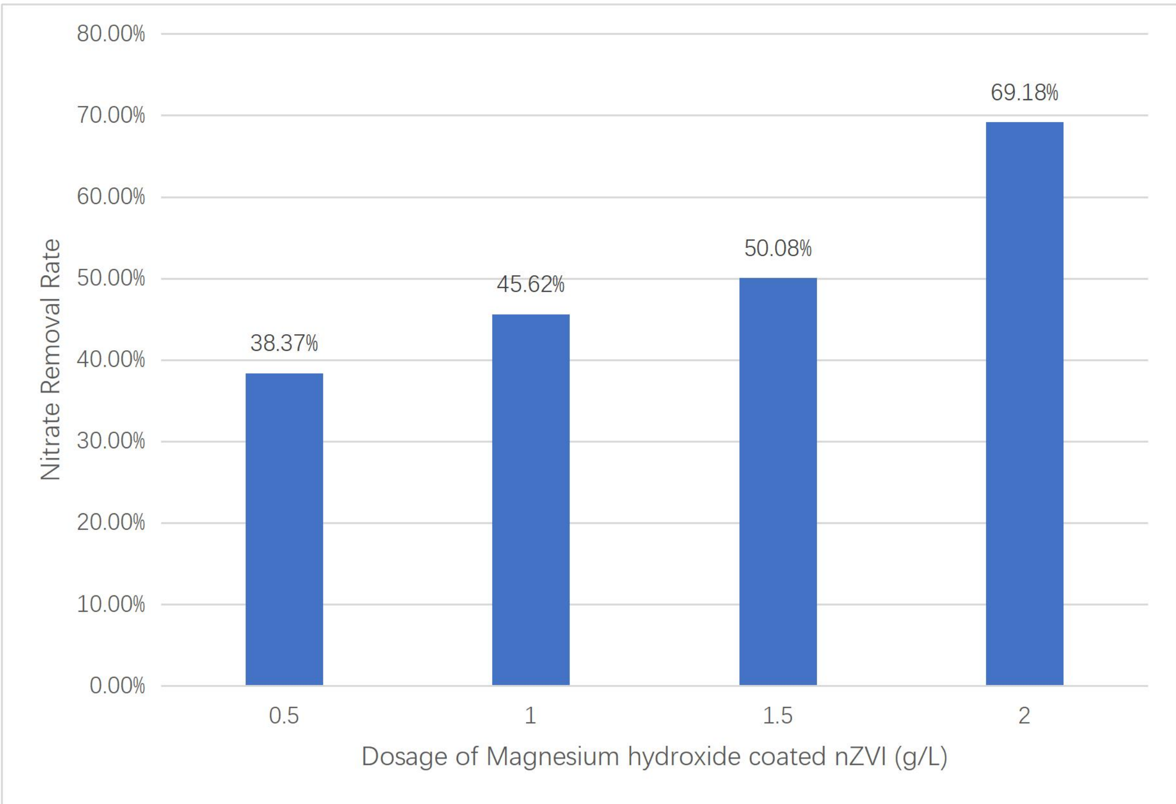
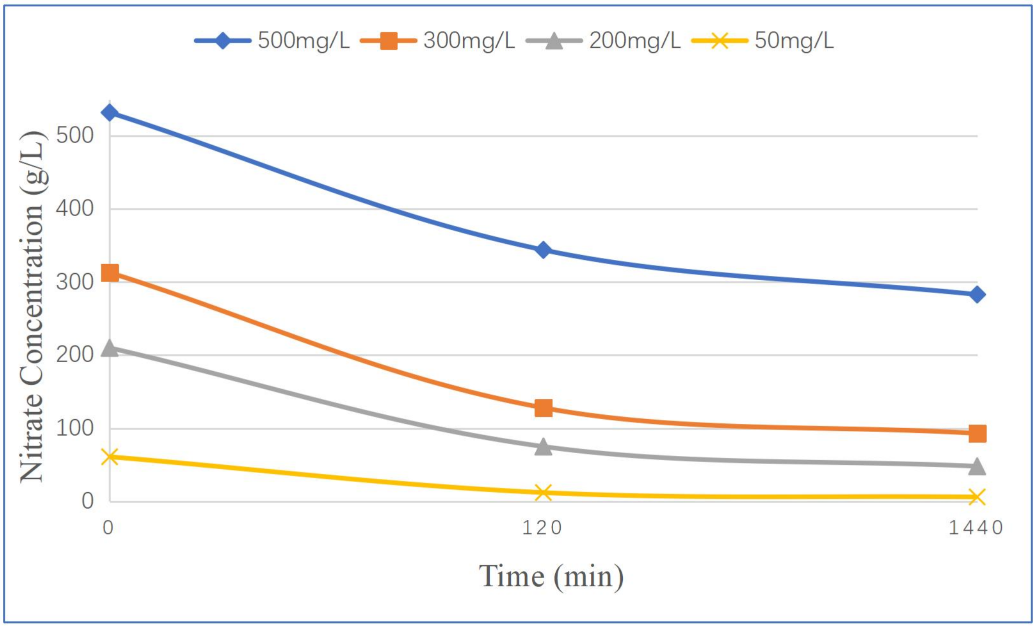


Fig. 3-2 nitrate removal efficiency of nZVI@$Mg(OH)_2$ under different dosage

3.3 Effect of initial concentration

The effect of varying nitrate initial concentrations within the range of 50-500 mg/L was investigated, and the results are presented in Figure 3-3. It is evident from the graph that the removal ratio gradually decreases with an increase in the nitrate initial concentration. This observation can be considered as high concentration nitrate solutions require more surface-active sites, and a certain amount of $Mg(OH)_2$ coated Fe^0 nanoparticles had limited removal capacity, which leaded to a decrease in removal ratio [17,18]. Conversely, the removal amount increases as the initial concentration rises. This is because a higher concentration of nitrate enables a more efficient utilization of the surface-active sites on the $Mg(OH)_2$ coated Fe^0 nanoparticles, thereby increasing the removal amount [17,18, 21].

In subsequent experiments, 200mg/L was selected as the initial concentration to clearly express the difference in removal efficiency. Although 50mg/L is easier to achieve complete removal, low nitrate concentration might increase the error when evaluating other optimal conditions.



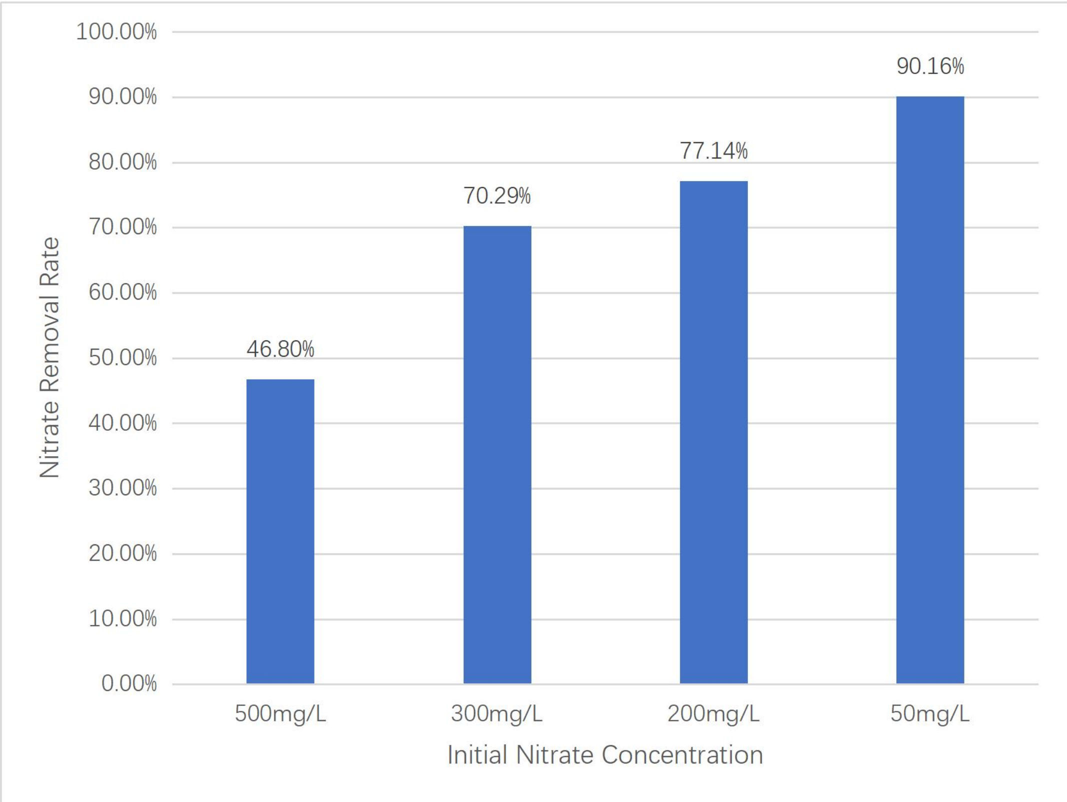
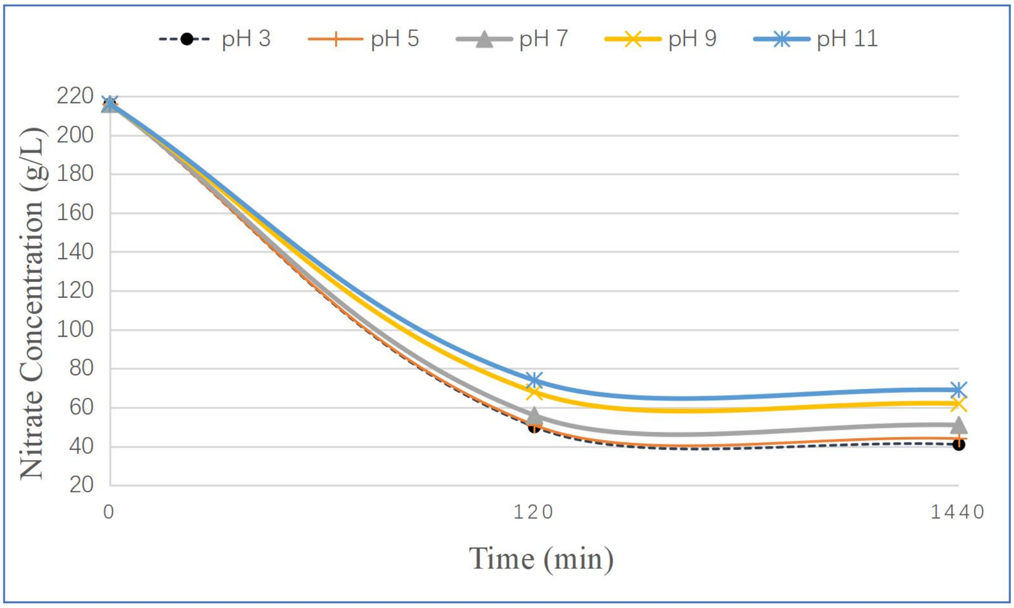


Fig. 3-3 nitrate removal efficiency of nZVI@$Mg(OH)_2$ under different initial nitrate concentration

3.4 Optimum pH range

The pH of solution is an important factor that affects the removal of nitrate. Therefore, the removal rate of nitrate by nZVI@$Mg(OH)_2$ at pH 3–11 was studied. It can be seen in Fig. 3-4 that the removal ratio of nitrate by nZVI@$Mg(OH)_2$ reaches the maximum value at pH = 3, both the removal ratio and removal amount show a downward trend with the increase of pH. This can be explained by that it is more favorable to $Mg(OH)_2$ shell on the nZVI surface dissolve under acidic conditions, and the occurrence of the dissolution reaction is conducive to the activation of the nZVI reaction performance, low pH might accelerate the of electron emission process of nZVI@$Mg(OH)_2$ [18].



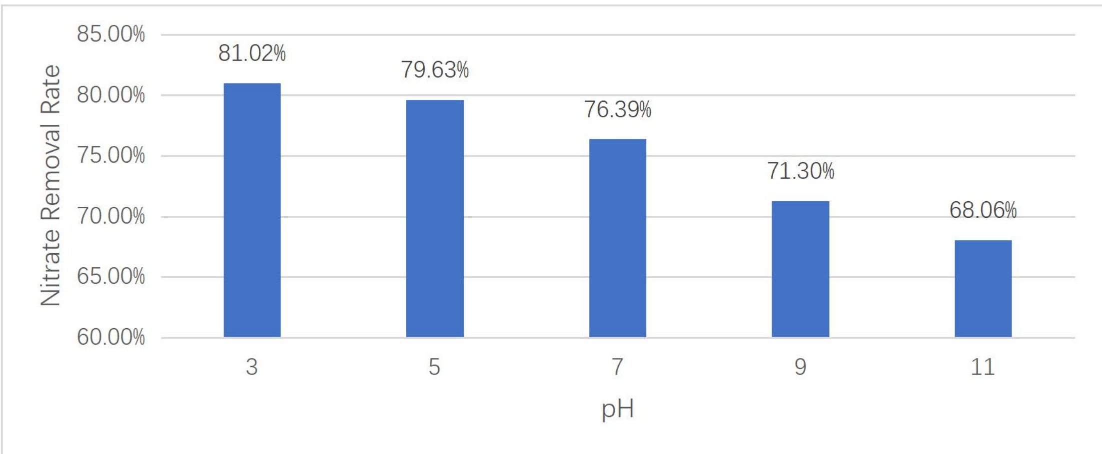


Fig. 3-4 nitrate removal efficiency of nZVI@$Mg(OH)_2$ under different pH

3.5 Optimum temperature (°C)

The effect of varying temperature within the range of 25-55°C was investigated, and the findings are presented in Figure 3-5. The graph clearly illustrates that as temperature increases, the removal ratio also increases, which aligns well with previous research [22]. Elevated reaction temperatures facilitate the movement of nitrate molecules towards the surface of nZVI particles, while also providing the necessary energy to overcome the activation energy barrier [22]. However, it should be noted that excessively high temperatures can accelerate the oxidation of nZVI nanoparticles, thereby reducing their reactivity [20]. To ensure the preservation of the iron core and minimize aqueous corrosion, the NZVI particles were effectively protected by $Mg(OH)_2$ modification. This resulted in lower levels of iron oxides in the leachates, indicating improved reactive longevity of the modified composites under high-temperature conditions [10]. In subsequent experiments, a temperature of 35°C was chosen to better simulate practical applications.

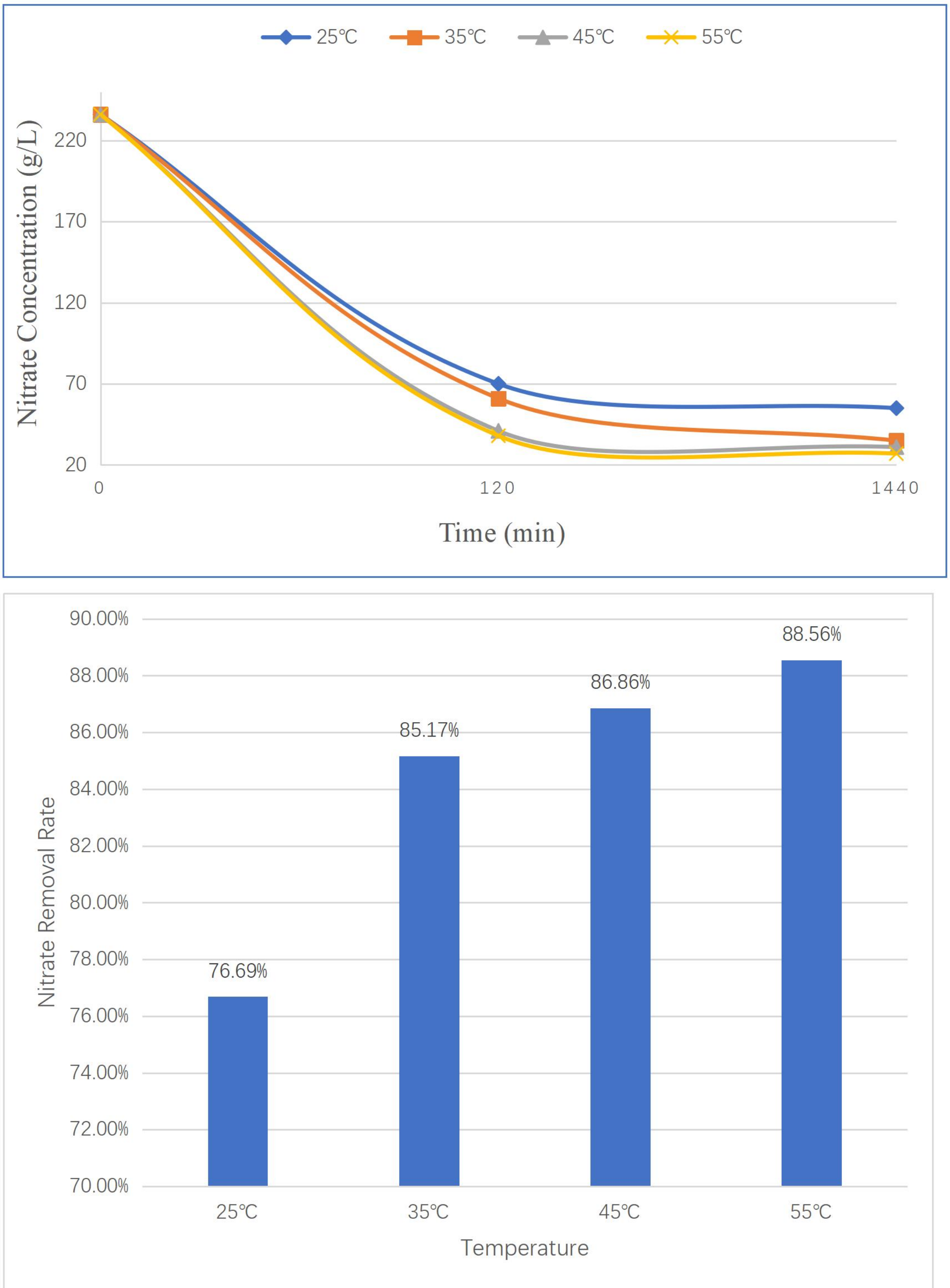


Fig. 3-5 nitrate removal efficiency of nZVI@$Mg(OH)_2$ under different temperature

3.6 River water application

To validate the practical application efficacy and long-term performance of nZVI@$Mg(OH)_2$, a 28-day experiment utilized the optimal conditions determined in previous steps was proceed to remove nitrate from both deionized water and river water. The outcomes are depicted in Figure 3-6. Notably, the final removal rate for river water reached 88.33%, which was comparable to that of deionized water. The removal capacity primarily peaked on the first day, and the nitrate concentration remained stable throughout the 28-day period, indicating the stability of nZVI@$Mg(OH)_2$. To achieve a complete removal rate of 100%, the dosage was increased to 2.5g/L and 3.0g/L. As shown in the figure 3-7, the 100% removal rate was successfully attained at a dosage of 3.0g/L.

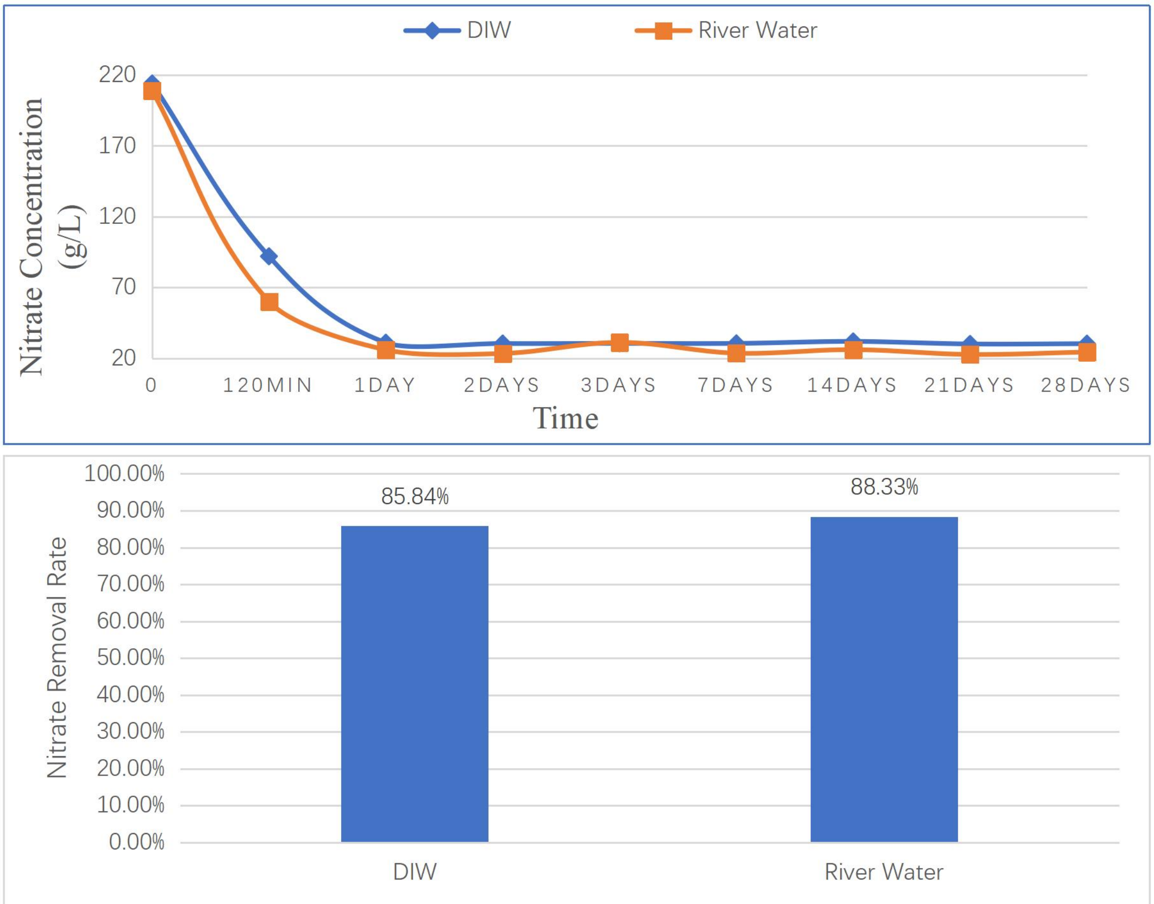


Fig. 3-6 nitrate removal efficiency of nZVI@$Mg(OH)_2$ under optimum condition in deionized water and river water

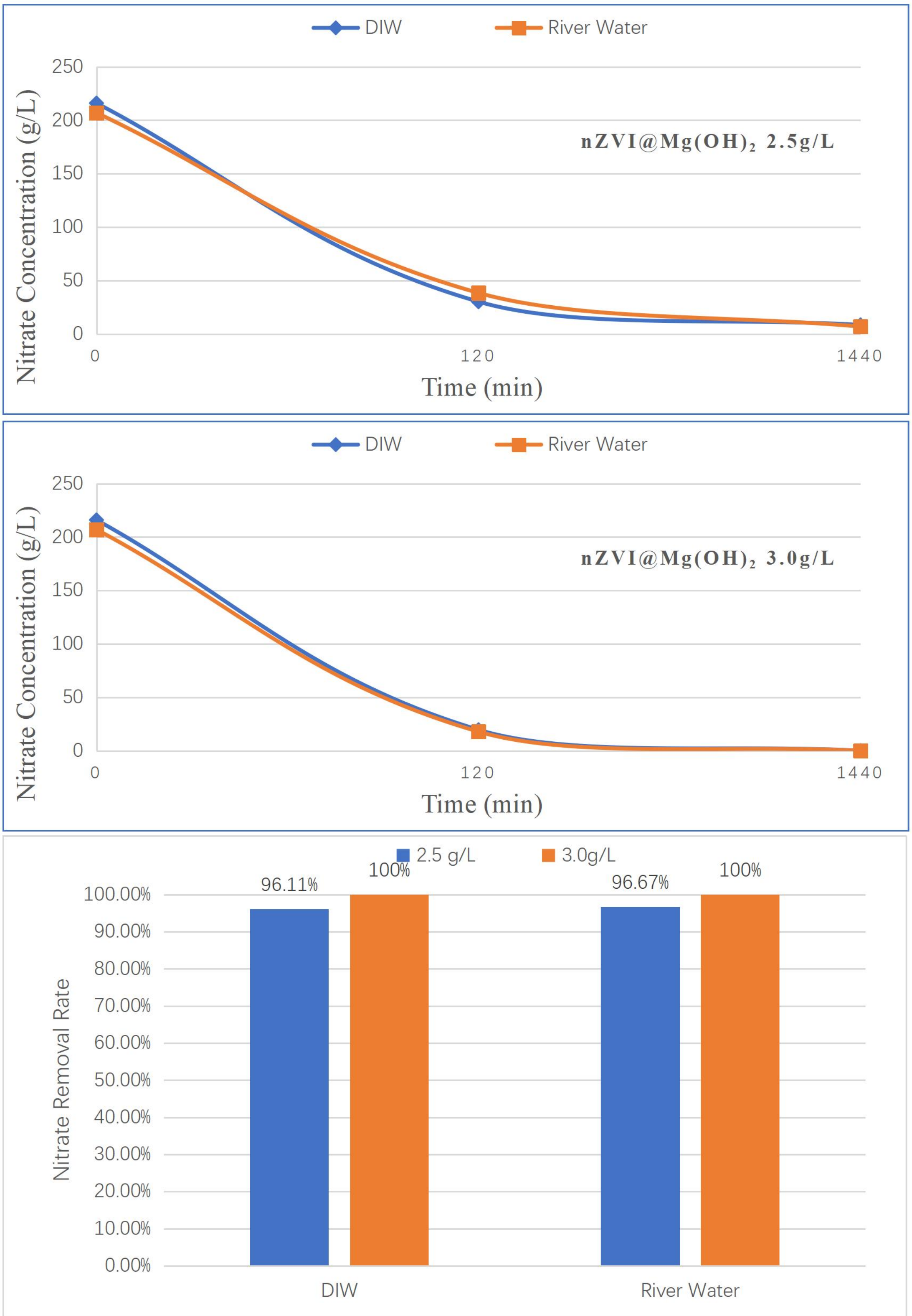


Fig. 3-7 nitrate removal efficiency of nZVI@$Mg(OH)_2$ in deionized water and river water under optimum conditions and with doses of 2.5g/L and 3.0g/L

Chapter 4: Conclusion

4.1 Optimum conditions for nitrate removal using nZVI@Mg(OH)$_2$ & Effect of different conditions

1). For an initial nitrate concentration of 200 mg/L, the optimum practical conditions for nZVI@Mg(OH)$_2$ are as follows: a Mg/Fe^0 ratio of 0.8, a dosage of 3.0 g/L, pH maintained at 7, and a temperature of 35°C.

2). A high coating ratio of Mg-Fe^0 lead to a slower emission speed of electrons, resulting in poor short-term performance compared to low coating ratio Mg-Fe^0 or bare Fe^0. Nevertheless, the long-term performance of high coating ratio Mg-Fe^0 remains excellent. The crystallinity of nZVI@Mg(OH)$_2$ is higher than bare nZVI, resulting in a reduced dissolution rate and enhanced reactive longevity. Taking into account efficiency and cost considerations, a coating ratio of 0.8 has been identified as the optimal choice.

3). As the dosage of coated Fe^0 nanoparticles increased from 0.5 to 3 g/L, the efficiency of nitrate removal showed a gradual improvement, eventually reaching 100% removal, indicating that 3.0 g/L was the optimal dosage for enhancing the removal rate using coated Fe0 nanoparticles. Therefore, a dosage of 3.0 g/L has been identified as the optimal choice for a sample solution with an initial nitrate concentration of 200 mg/L. The presence of more nZVI@Mg(OH)$_2$ particles in the solution resulted in an increased number of iron surface-active sites, leading to a higher removal amount and removal rate.

4). With an increase in the initial concentration of nitrate, the removal ratio exhibits a gradual decrease. It can be considered that high concentration nitrate solutions require more surface-active sites, and a certain amount of nZVI@Mg(OH)$_2$ nanoparticles had limited removal capacity, which leaded to a decrease in removal ratio. However, in contrast, the removal amount shows an increase as the initial concentration rises. This phenomenon occurs due to the higher concentration of nitrate facilitating more efficient utilization of the surface-active sites on the nZVI@$Mg(OH)_2$ nanoparticles, thereby leading to an increased removal amount.

5). As temperature increases, the removal ratio also increases. Elevated reaction temperatures facilitate the movement of nitrate molecules towards the surface of nZVI particles, while also providing the necessary energy to overcome the activation energy barrier. Coated nZVI has great improvement in reactive longevity under high-temperature conditions because of minimizing aqueous corrosion.

6). Both the removal ratio and removal amount show a downward trend with the increase of pH. This can be explained by that it is more favorable to $Mg(OH)_2$ shell on the nZVI surface to dissolve under acidic conditions, and the occurrence of the dissolution reaction is conducive to the activation of the nZVI reaction performance.

7). The practical application efficacy and long-term performance of nZVI@$Mg(OH)_2$ was verified within a 28-day experiment utilized the optimal conditions.

4.2 Future suggestion

The primary focus of this research is to determine the optimal conditions for nitrate removal using nZVI@$Mg(OH)_2$ and investigate their effects. If further research is to be conducted in the future, it is suggested to explore the following aspects:

1). Cost reduction of material production: Investigate methods to reduce the production cost of nZVI@$Mg(OH)_2$ materials, such as exploring alternative synthesis routes or optimizing the manufacturing process.

2). Development of a continuous system: Establish a continuous system to assess the long-term performance of the material. This will enable studying its effectiveness and stability over an extended period under realistic operating conditions.

3). Practical application and scale-up: Explore opportunities to apply the nZVI@$Mg(OH)_2$ material in practical settings. Expand the laboratory-scale experiments to larger-scale applications and evaluate its performance under real-world conditions. This will provide valuable insights into the feasibility and efficiency of implementing the material on a larger scale.

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