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Study about the effect of nanoscale zero valent Aluminum(nZVA) with nanoscale zero valent Iron(nZVI) on the performance of nitrate removal

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大気海洋環境システム学専攻修士論文

Study about the effect of nanoscale zero valent Aluminum(nZVA) with nanoscale zero valent Iron(nZVI) on the performance of nitrate removal

～硝酸塩除去の性能に及ぼす nZVA と nZVI の影響に関する研究～

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Abstract

As a material with high nitrate removal efficiency, the short lifetime of nZVI has always been a problem. Nano-zero-valent aluminum (nZVA) is fabricated on the surface of nZVI by coating technology, which can improve the nitrate removal efficiency and service life of nZVI. In this study, Fe/Al bimetals were prepared by different methods and their nitrate removal performance under different conditions was investigated. The results show that adding filtration in the synthesis step has the best performance under the conditions of Fe:Al ratio 100:33, pH=5, and initial nitrate concentration of 400mg/L, which can remove up to 220mg/L of nitrate, and the removal rate reaches up 57.7%. The removal efficiency of nitrate is proportional to the proportion of Al in the material and inversely proportional to the increase of solution pH. Through the characterization of the material, it was found that this material can not only remove nitrate by chemical degradation, but also remove nitrate from water by adsorption.

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Chapter 1: Introduction

1.1 Background

As of January 2022, the world's population has exceeded 7.82 billion [1], and the world population is expected to increase to 8.45 billion by 2025 [3]. But of these populations, about 10% (735 million) are still in poverty [2]. For these people, the most feasible and sustainable way to get rid of the interference of poverty is to break through and develop productive forces. With the world's growing focus on sustainable development, natural resource planners have focused their attention on the vulnerabilities that arise from the availability and use of water resources. Population growth, food self-sufficiency, industrial development, water pollution and climate change, these five factors are the biggest obstacles to the development of water resources [3]. Among them, water pollution is a topic that researchers are very concerned about, because thousands of people around the world live in the shadow of water pollution every day.

However, natural water was contaminated by industrial wastewater with rapid industrialization until now. And it is difficult to secure the safety water resources in all over the world.

In China, water shortage is one of the most difficult problems restricting rapid urbanization [5]. There are even different constraints in different regions, but no matter how they change, the common point is the pollution of water resources.

In northern China, which is dominated by agriculture and heavy industry, water scarcity occurs mainly through the cycle of water pollution. In agriculture, large-scale agricultural planting uses a large amount of chemical fertilizers. After the crops absorb a part, the remaining part is diluted with irrigation water and

washed to the ground, causing pollution of groundwater. In heavy industry, especially the petroleum industry, a large amount of natural water is poured into the oil layer in order to obtain oil, which directly causes a large amount of organic pollutants and heavy metal ions to enter the water body, causing water pollution [4].

In China's eastern coastal areas, where urbanization is relatively high, it has even evolved into a common constraint on urban development. Because of the rapid urbanization of the eastern coastal cities, there is a huge demand for water, especially on construction sites. At the same time, the demand for such a large amount of water resources is also superimposed on the demand for domestic water. In order to meet the demand for water resources, people need to exploit a large amount of groundwater resources, causing the groundwater level to drop or even deplete, and changes in groundwater lead to Due to the change of geological structure, pollutants such as heavy metal ions in the soil and in the process of urbanization enter the groundwater, which has a great resistance to ecological restoration [5].

As the examples mentioned above, when these groundwaters are enriched with too many pollutants, especially nitrogen and phosphorus, and then return to the surface water, it will cause serious surface water pollution, the most famous of which is the eutrophication of water bodies. This will lead to widespread extinction of aquatic organisms in eutrophic water bodies and rapid decline in water quality, which will have a huge impact on humans and the environment [6].Therefore, nitrates must be removed before being discharged into nature.

1.2 Nitrate

1.2.1 The summary of nitrate

Nitrate exists in large amounts in nature, the main source is the formation of nitrogen-fixing bacteria, or the nitrogen and oxygen in the air are directly converted into nitrogen oxides under the high temperature of lightning, dissolved in rainwater to form nitric acid, and reacted with minerals on the ground to form nitrates [7]. As one of the most common salts in nature, nitrate is sometimes used by humans as a food additive, mainly as a preservative in cheese products and cured meats (eg, sausage, ham) [7]. Most of the time, nitrate exists in nature as a solid in the form of inorganic substances, but if nitrate enters the liquid environment on a large scale, the situation changes dramatically. First of all, due to the enrichment of nitrogen and phosphorus nutrients in the water body, the rapid reproduction of algae and other plankton causes the dissolved oxygen content in the water body to decrease, resulting in the decline or even extinction of plants, aquatic organisms and fish [6]. And if the human body ingests too much nitrate, it can also cause adverse reactions, including cancer and poor reproduction [7]. Ingested nitrates undergo endogenous nitridation to form nitroso compounds (NOCs); most NOCs are carcinogens and teratogens. Therefore, NOCs formed after ingestion of nitrates in drinking water and dietary sources may contribute to cancer, birth defects, or other adverse health effects [8][9].

1.2.2 The current method of removing (collecting) nitrate

a) Chemical denitrification [10][11][12]

Chemical denitrification refers to the use of chemical methods to denitrify nitrates with metal elements, thereby removing them from water bodies.The reaction equation is as follows**(Eq. 1-1)(Eq. 1-2)(Eq. 1-3)(Eq. 1-4)**.

$3NO_3^- + 8Fe(OH)_2 + 6H_2O \rightarrow NH_3 + 8Fe(OH)_3 + OH^-$ **(Eq. 1-1)**[11]

$3NO_3^- + 2A1 + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3$ **(Eq. 1-2)** [12]

$NO_2^- + 2A1 + 5H_2O \rightarrow NH_3 + 2Al(OH)_3 + OH^-$ **(Eq. 1-3)**[12]

$2NO_2^- + 2A1 + 4H_2O \rightarrow N_2 + 2Al(OH)_3 + 2OH^-$ **(Eq. 1-4)**[12]

b) Reverse osmosis for denitrification [10][13][14][34]

Reverse osmosis membrane made of cellulose acetate, polyamide and composite materials, and the solution containing nitrate is injected into the reverse osmosis tank at a pressure of 300 to 1500 psi, which can reverse the normal osmotic flow of water and realize the separation and enrichment of nitrate. effect. However, the production cost of reverse osmosis membrane is high, and it is easy to scale, compact and deteriorate due to factors such as pollutant deposition and pH change.

c) Denitrification using a membrane bioreactor [10][31]

Nitrate-removing microorganisms are cultured in a submerged heterotrophic membrane bioreactor (MBR) and grown on the MBR. By passing the nitrate-containing water stream, the nitrate will diffuse through the pores of the membrane, and denitrification will occur on the shell side. However, this method is only suitable for nitrate solutions with lower concentrations, and the death of microorganisms will happen when the nitrate concentration is too high.

d) Adsorption [15]

Selecting the right material to remove specific types of anions is important to achieve optimal removal rates, especially with mineral-based and/or

surface-modified sorbents, through the selection of suitable materials for adsorption of different anions and cations.

1.3 Zero Valet Iron (ZVI) and Nanoscale Zero Valent Iron (NZVI)

For the remediation of nitrate pollution, nano-zero valent iron (nZVI) has become a research hotspot in recent years. nZVI is a nanomaterial that can release electrons in its core and form adsorbed oxides and hydroxides on the surface[17][30][41]. This feature can be used for the removal of nitrates, because the removal of nitrates mainly relies on free electrons[16][37], and its degradation products are mainly Ammonium, as shown in **Fig 1-1**.

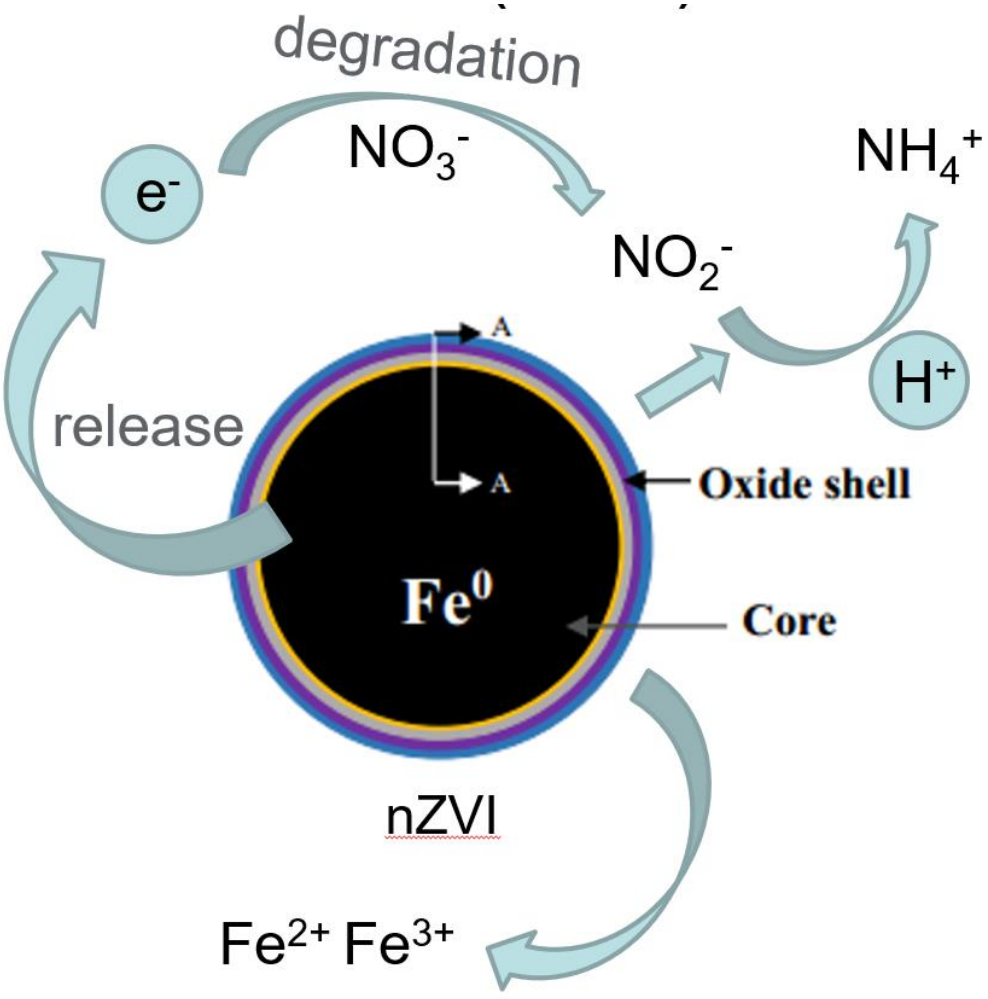


Fig. 1-1 The schematic images of ZVI (NZVI) main mechanisms

To improve the removal ability, bimetallic NZVI also has been investigated. Bimetallic NZVI are made by iron (NZVI) along with a noble metal such as platinum (Pt), palladium (Pd)[33], copper (Cu)[35][36][38][39] and metal oxide(eg. $Al(OH)_3$)[32]. This noble metal serves the role as a catalyst and increases a rate of reduction[40]. And also bimetallic particle serves more active site compare with bare NZVI. The structure of bimetallic NZVI ($Fe/Al(OH)_3$) is shown **Fig. 1-2**.

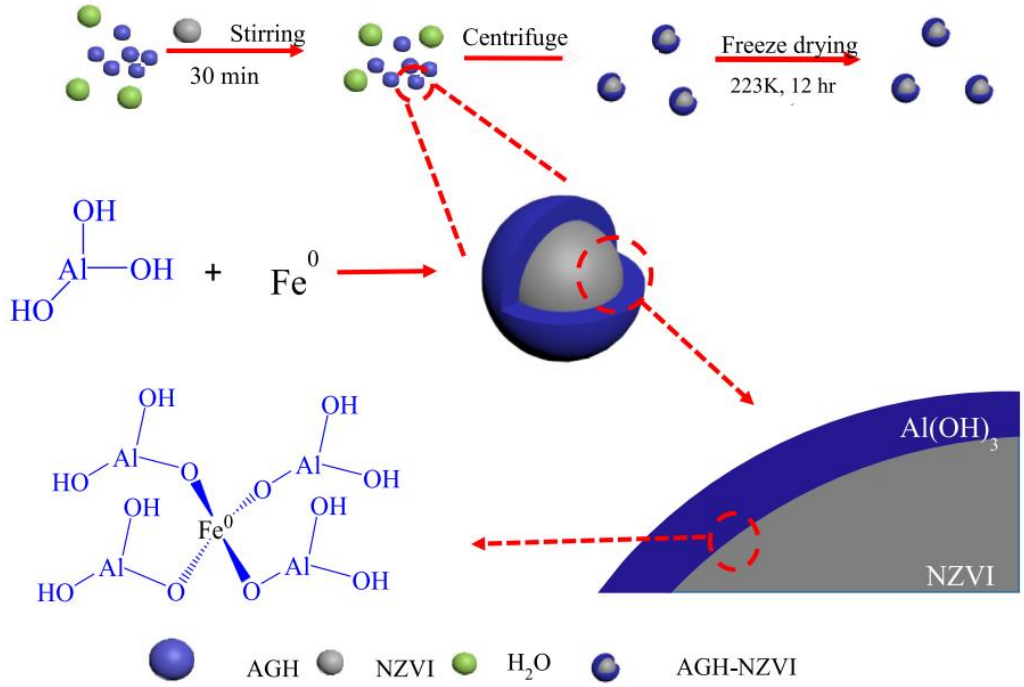


Fig. 1-2 Schematic illustration of the synthesis procedure for aluminum hydroxide gel-coated nanoscale zero-valent iron(AHG@NZVI) composites[28]

1.4 Previous study of removing nitrate by using iron materials

Check out the previous studies on the removal of nitrate by nZVI, summarized as follows:

Yun Zhang et al. [18] prepared nanoscale zero-valent iron (NZVI/PILC) supported on pillared clay and used for nitrate removal to improve efficiency. Good dispersion of NZVI particles (approximately 30-70 nm) in the clay phase was observed and compared with commercially available iron powder and NZVI with the same amount of iron[42]. The results show that NZVI/PILC can completely remove nitrate within 120 min. This efficiency is not only much higher than that of NZVI alone (62.3%), but also better than the sum of the reduction of NZVI plus the adsorption of PILC (9.19%) (71.5%).

Jayanga et al. [19] investigated the effectiveness of nano-zero valent iron (nZVI) in the removal of nitrate from drinking water groundwater under aerobic conditions. nZVI was synthesized under aerobic conditions and batch experiments were performed using artificial nitrate (150 mg/L) contaminated water samples. The results confirmed that at an optimal nZVI dose of 1 g/L and an optimal contact time of 30 minutes, 80% nitrate removal could be achieved with a residual nitrate level of approximately 30 mg/L (50 mg/L as nitrate))[43].

Jingqi Zhang et al. [20] studied the kinetics and mechanism of removal of nitrate, copper ions and hexavalent chromium from Al-Fe alloy particles composed of 20% Fe in a batch reactor. The effects of pollutant interactions and the initial pH of the solution were investigated, and the alloy particles before and after the reaction were characterized by X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy. Studies have shown that Al-Fe alloys have the potential

to remediate groundwater.

After induction, the main findings of nZVI removal of nitrate were found, which are summarized as follows:

1). nZVI can effectively remove nitrate in solution, and the removal effect is better under acidic conditions.

2). The removal of nitrate by nZVI is mainly by releasing free electrons, reducing nitrate to nitrite, and then reducing it to ammonium.

3). The service life of nZVI is limited, and the service time of nZVI can be extended by means of bimetallic system or coating technology.

4). The micron-scale aluminum can promote the removal of nitrate by nZVI..

1.5 Zero Valet Aluminum (ZVA) and Nanoscale Zero Valent Aluminum (NZVA)

Metal aluminum is the most abundant metal element in the earth's crust, and most of the time exists in the form of compounds [23], as shown in **Fig. 1-3**. When elemental aluminum is exposed to air, the surface will oxidize rapidly and react with oxygen to form a dense oxide film [29]. Therefore, most scholars do research on the properties of micron-scale aluminum or aluminum oxides and hydroxides[22][23], and few people have studied nano-zero-valent aluminum [26]. But in fact, nano-zero-valent aluminum is a very potential material, the oxidation activity of aluminum is 1.66V, and the oxidation activity of iron is 0.44V, so when metal aluminum and metal iron are in contact, a DC battery will be formed [21] [24].

Fenglian fu et al.[24] studied micron-scale Al-Fe bialloy and found that by combining the two metals, its surface area was greatly increased, and the removal rate of trivalent chromium and hexavalent chromium was greatly improved.

Hsing-lung et al. [25] also studied micron-sized Al-Fe bi-alloys and found that bimetallic particles can promote the Fenton reaction of ZVI and increase the electron release rate of Fe.

With so much research proving the viability of aluminum-iron alloys, is it possible to combine nanoscale iron with aluminum, to synthesize a material that has a better lifetime?

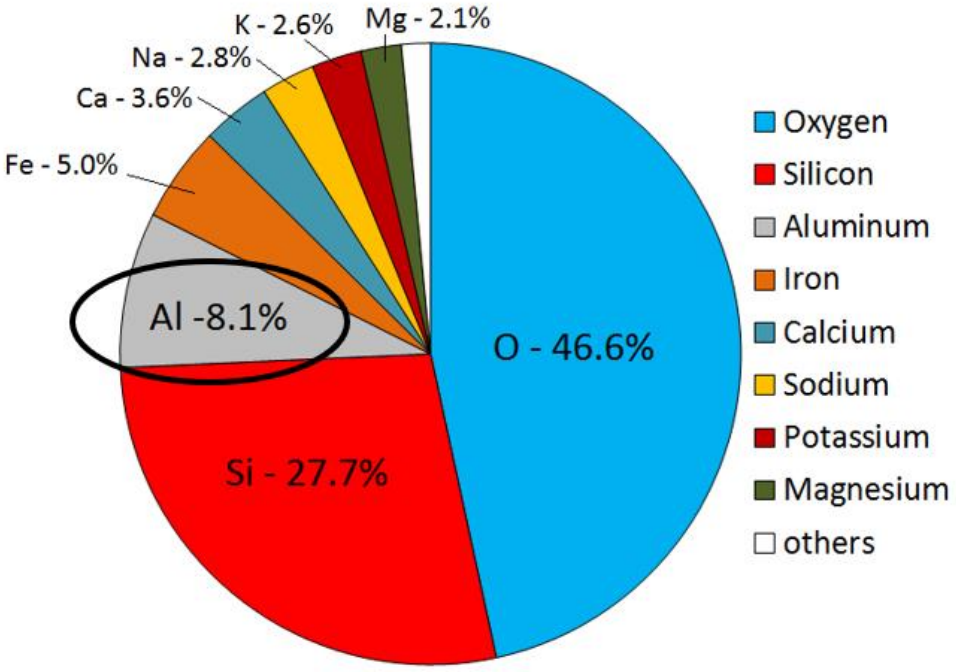


Fig 1.3 Distribution of element content in the earth's crust, with aluminum content ranking fourth (8.1%)

1.6 The problem findings and research objectives

1.6.1 The problem findings

By summarizing 1.1 to 1.5, we can roughly summarize the following questions:

1). Due to the recent rapid population growth, too many people will face the issue of safe water.

2). Due to the rapid development of industrialization, many water environments are damaged by various pollutants, causing serious environmental problems such as eutrophication, animal death, etc.

3). Nitrate, as one of the pollutants, has the characteristics of being very difficult to remove from the water body.

4). So far, several techniques for nitrate removal have been developed, but they all have corresponding disadvantages.

5). As a high-quality material for nitrate removal, nZVI has not been effectively solved for its lifetime.

1.6.2 The research objectives

According to the problems summarized above, the main research goals or problems to be overcome in this paper can be determined:

1). This study needs to find a method that can smoothly synthesize nano-zero-valent aluminum (nZVA). There have been enough studies on nZVI, but few studies have explored nZVA-related issues.

2). This study also needs to find a method that can smoothly synthesize the

nZVA/nZVI bimetallic system.

3). This research needs to study and improve the synthesis method of the nZVA/nZVI bimetallic system, and find the most suitable synthesis conditions and application conditions for this material.

1.7 Framework

The overall structure of this study takes the form of four chapters, including this introductory chapter. Chapter 1 introduces the current status of water resources in the world, the status of the main pollutant nitrate, the current status of nitrate removal and nZVI and nZVA. Chapter 2 presents the exploration of the successful synthesis of nZVI and nZVA, as well as some properties of the two materials. Chapter 3 presents the investigation of methods that can successfully combine the two materials, as well as the investigation of the properties of the nZVA/nZVI bimetallic system. Chapter 4 summarizes the whole research and summarizes the new findings of this research.

Chapter 2: Synthesis and Properties of NZVA and NZVI

2.1 Chemical materials

The following chemical reagents and materials were used: Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_20$), Hydrated Aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$), Aluminum Chloralhydrate ($AlCl_3$), Sodium borohydride ($NaBH_4$), Sodium nitrate ($NaNO_3$), 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 and sodium borohydride were used for the synthesis of nZVI, aluminum chloride, aluminum sulfate and sodium borohydride were used for the synthesis of nZVA, sodium 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 NZVA and NZVI

2.2.1 The synthesis of NZVI

NZVI was synthesized following this chemical reaction **(Eq. 2-1)**

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

Precursor 1 was prepared by dissolving 21.0 g of $NaBH_4$ in 1,200 mL of deoxygenated deionized water (DIW). Precursor 2 was prepared by dissolving 50.0 g of $FeCl_3 \cdot 6H_2O$ in 1,200 mL of DIW in a separate flask. Then precursor 1 was added to precursor 2 using a peristaltic pump at a rate of 16 mL/min. with vigorous stirring at 400 rpm under nitrogen condition at constant temperature of 25 ± 0.5 °C using a water bath. The synthesis was conducted in 5 L four-neck glass flask and left 5 min. for aging to complete the reaction [17]. **Fig. 2-1** shows that the schematic images of synthesis system NZVI.

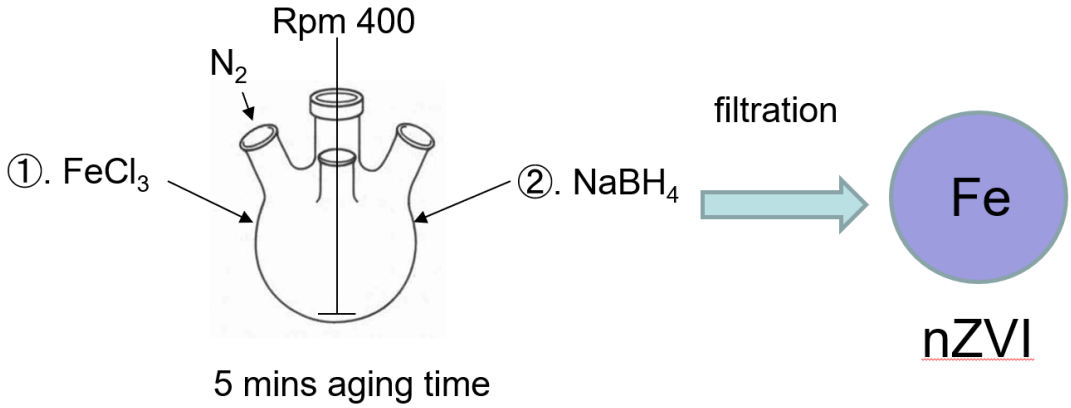


Fig. 2-1 The schematic images of iron based material synthesis system

2.2.2 The synthesis of NZVA

To prepare 1 g of nZVA, 12.8 g of aluminum sulfate was dissolved in deionized water (DIW) to make precursor 1, and 4.28 g of sodium borohydride was dissolved in deionized water (DIW) to make precursor 2. Precursor 1 and precursor 2 were stirred on a magnetic stirrer for one and a half minutes until the solution was clear, and nitrogen gas was introduced into precursors 1 and 2 for ten minutes to ensure an anaerobic environment. After the anaerobic environment is complete, add Precursor 1 to the four-necked glass flask via a funnel, then add Precursor 1 to the flask at a rate of 16 mL/min using a peristaltic pump at a constant temperature of 25 ± 0.5 ℃ using a water bath Stir vigorously at 400 rpm under nitrogen. When the sodium borohydride solution was completely added to the flask, the reaction was continued for five minutes, and then the solution was suction filtered to obtain nZVA solid, as shown in **Fig. 2-2**.

Besides aluminum sulfate, different compounds (eg. $AlCl_3$) were also used as the aluminum source of nZVA during the experiment. However, when $AlCl_3$ was used as the aluminum source, the synthesis experiment did not go well. When $NaBH_4$ was added to the $AlCl_3$ solution, no solid matter appeared in the flask even after stirring for more than half an hour. This shows that the sulfate radical can promote the synthesis of nZVA and is helpful for the synthesis of nZVA.

Combined with the research of other scholars [25], the equation for the synthesis of nZVA using aluminum sulfate as the aluminum source can be obtained **(Eq. 2-2)**

$$2Al(SO_4)_3 + 12NaBH_4 + 36H_2O \rightarrow$$

$$4Al^0 + 42H_2 + 12B(OH)_3 + 6\ Na_2SO_4 \qquad \textbf{(Eq. 2-2)}$$

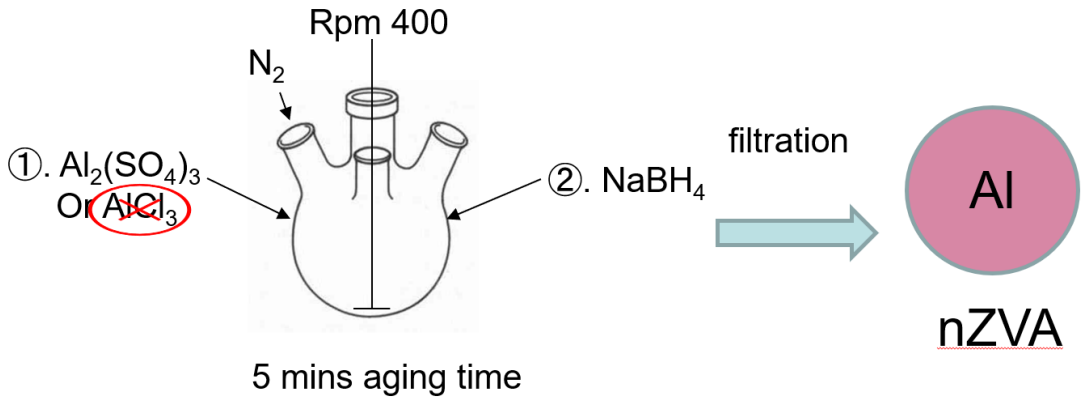


Fig. 2-2 The schematic images of nZVA synthesis

2.3 Batch experiment

2.3.1 The procedure of batch experiment

For batch experiments, weigh 0.164g NaNO3, dissolve it in 400ml deionized water (DIW) under magnetic stirring, adjust the pH of the solution to 7 after the solution is clear and transparent, and divide it into two groups. oxygen environment. In this way, a nitrate solution of 300 mg/L can be obtained. 0.2 g of nZVI and nZVA were synthesized as described in Sections 2.2.1 and 2.2.2, respectively, added to the pre-prepared nitrate solution, and the experiment was carried out on a magnetic stirrer for two hours.

Samples were taken through a syringe filter at 0, 10, 30, 60, 120 minutes, and nitrate concentrations in the samples were measured by UV-Vis spectrophotometer (DR 3900, HACH Co., USA).

2.3.2 Result and discussion

Fig. 2-3 shows the effect of synthetic nZVI and nZVA on nitrate removal. In the batch experiment, the nitrate concentration in the nZVI group reached equilibrium at 10 minutes, dropping from 278 mg/L to 136 mg/L. After two hours, the nitrate concentration in the solution was 133 mg/L. The nitrate removal amount reached 145mg/L, and the nitrate removal rate reached 52.1%. The nitrate concentration in the nZVA group also reached equilibrium at 10 minutes, dropping from 278 mg/L to 267 mg/L, and two hours later, the nitrate concentration in the solution was 265 mg/L. The nitrate removal amount reached 13mg/L, and the nitrate removal rate reached 4.7%.

In batch experiments, nitrate removal and removal rate were calculated by the following equations **(Eq. 2-3) (Eq. 2-4)**:

$$C_{ra} = C_I - C_{2h} \quad \textbf{(Eq. 2-3)}$$

$$C_r = (C_I - C_{2h}) / C_I * 100\% \quad \textbf{(Eq. 2-4)}$$

where C_{ra} is the amount of nitrate removed, C_I is the initial concentration of nitrate solution, C_{2h} is the nitrate concentration after the two-hour batch experiment, and C_r is the nitrate removal rate.

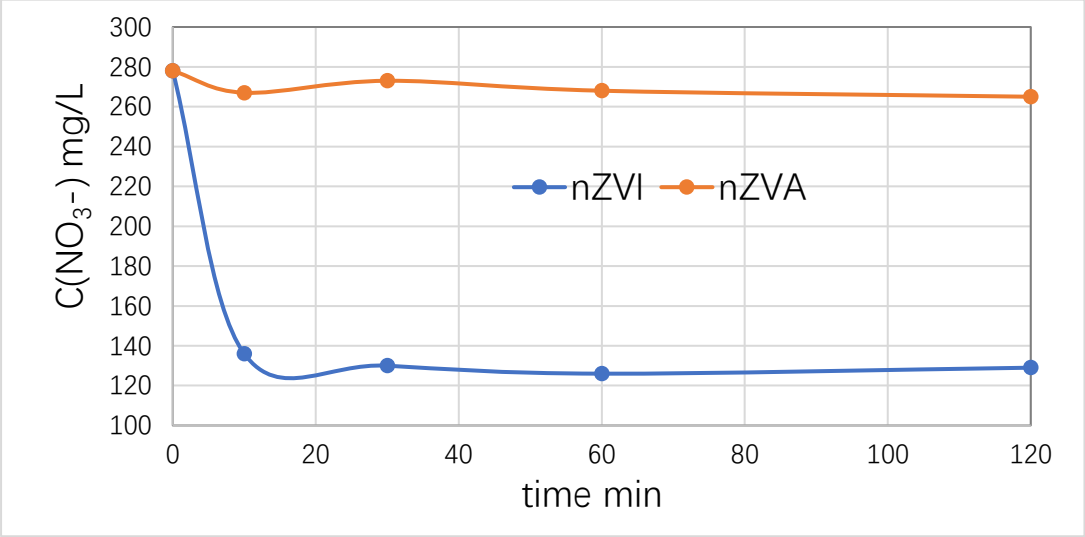


Fig. 2-3 Batch experiment of nitrate removal of nZVI and nZVA

2.4 Characterization of NZVA and NZVI

2.4.1 Instrumental analysis

Compositions of the iron products were analyzed by XRD (TTR, Rigaku, Tokyo, Japan). Samples were analyzed using Cu Ka radiation (λ = 1.5418 Å) with a scan rate of 2˚ min-1 and scanning range between 3˚ and 90˚. The surface morphologies of synthesized particles were obtained on TEM (JEM-ARM 200F, JEOL Co., Japan). The surface morphology and chemical elemental mapping images were obtained by using SEM-EDS (JSM-6060 LA/VI, JEOL Co., Japan). The particle size of synthesized particles was estimated by laser diffraction particle size analyzer (SALD-2300, Shimadzu Co., Japan).

2.4.2 Characteristics of NZVI and NZVA

According to the laser diffraction particle size analyzer results, the average particle size of NZVI was 38 nm.

The composition of synthesized particles was observed by analyzing the XRD pattern. **Fig. 2-4** shows that nZVI and nZVA. **Fig. 2-4 (a)** shows a main peak of intensity at 44.8˚, 2θ indicating the presence of zero valent iron in the synthesized nanoscale iron materials. **Fig. 2-4 (b)** shows a main peak of intensity at 42.5˚ and 65.4˚, 2θ indicating the presence of zero valent Aluminum in the synthesized nanoscale Aluminum materials.

Fig. 2-5 shows the SEM images of nZVI and nZVA. The SEM images of nZVI (**Fig. 2-5 a**) shows that most of the nZVI have irregular shapes, with many thorn-like protrusions around the periphery. The distribution of oxygen is looser than that of iron, which indicates that the surface of nZVI is mostly iron, but at the same time it is partially oxidized. The SEM images of nZVA (**Fig. 2-5 b**) shows that nZVA has obvious edges, all nZVA are blocky. And from the distribution of oxygen and aluminum elements, it can be found that compared with nZVI, there are more

oxygen elements on the surface of nZVA, indicating that the degree of surface oxidation of nZVA is higher.

The Fig. 2-6 shows the TEM images of nZVI and nZVA. The TEM results of nZVI (**Fig. 2-6 a**) shows that the particle size of the synthesized nZVI is about 40-100 nm, there is an oxide film on the surface, and they have a chain structure. But at the same time, the nZVI particles exist independently, which helps to increase the surface area of nZVI and increase the contact area of nZVI with the solution. The TEM results of nZVI (**Fig. 2-6 b**) shows that most of the nZVA particles are connected together by an oxide film, forming a Bulk structure (as shown in the yellow circle, the large yellow circle is a Bulk structure, 6 nZVA particles are wrapped inside). Most of the nZVA particles have a particle size of 20-40 nm, and the particle size of the bulk structure is 60-120 nm. This oxide film provides a lot of adsorption spots for nZVA, which increases the surface area, which is why nZVA has excellent performance in phosphate removal.

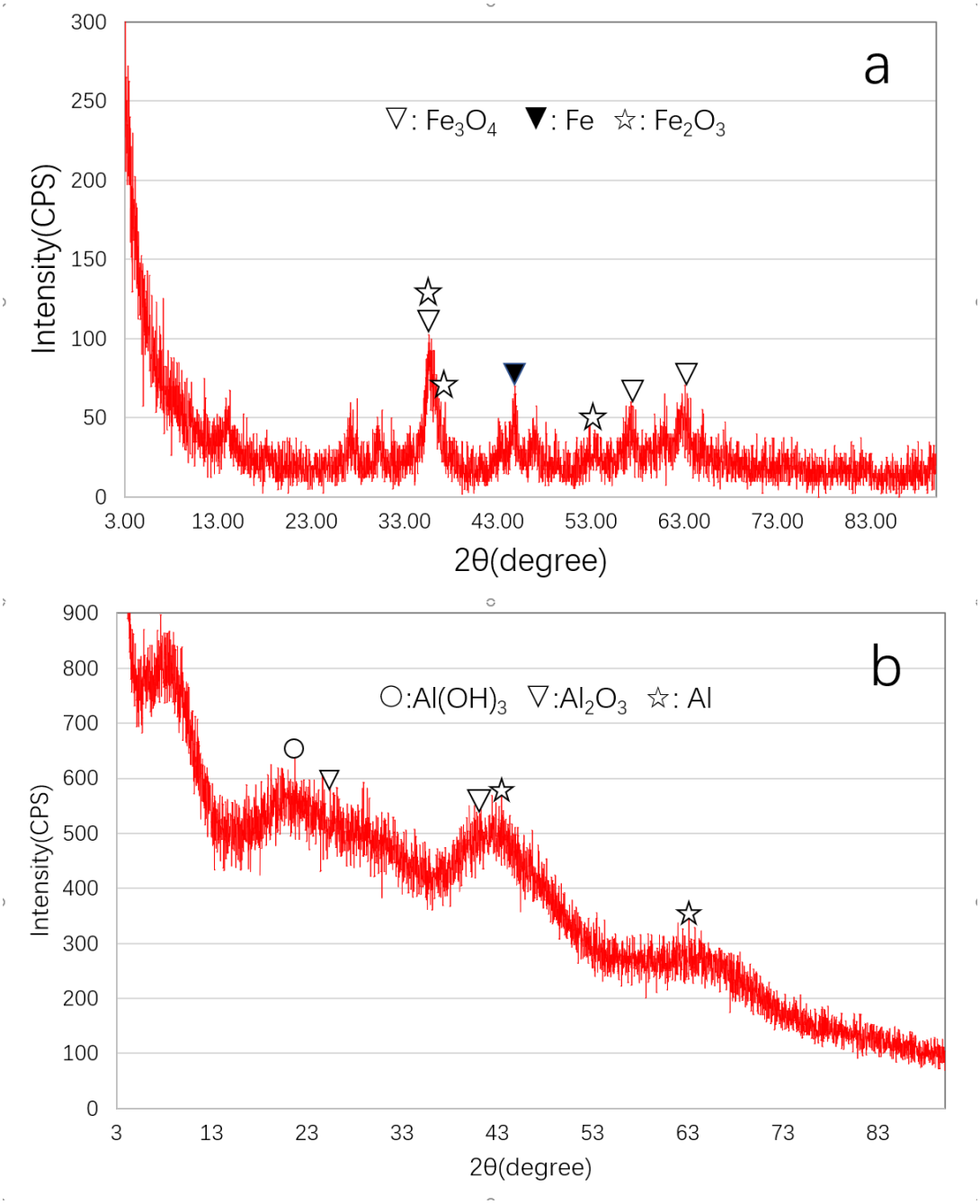


Fig. 2-4 XRD images of a) Fresh nZVI, b) Fresh nZVA

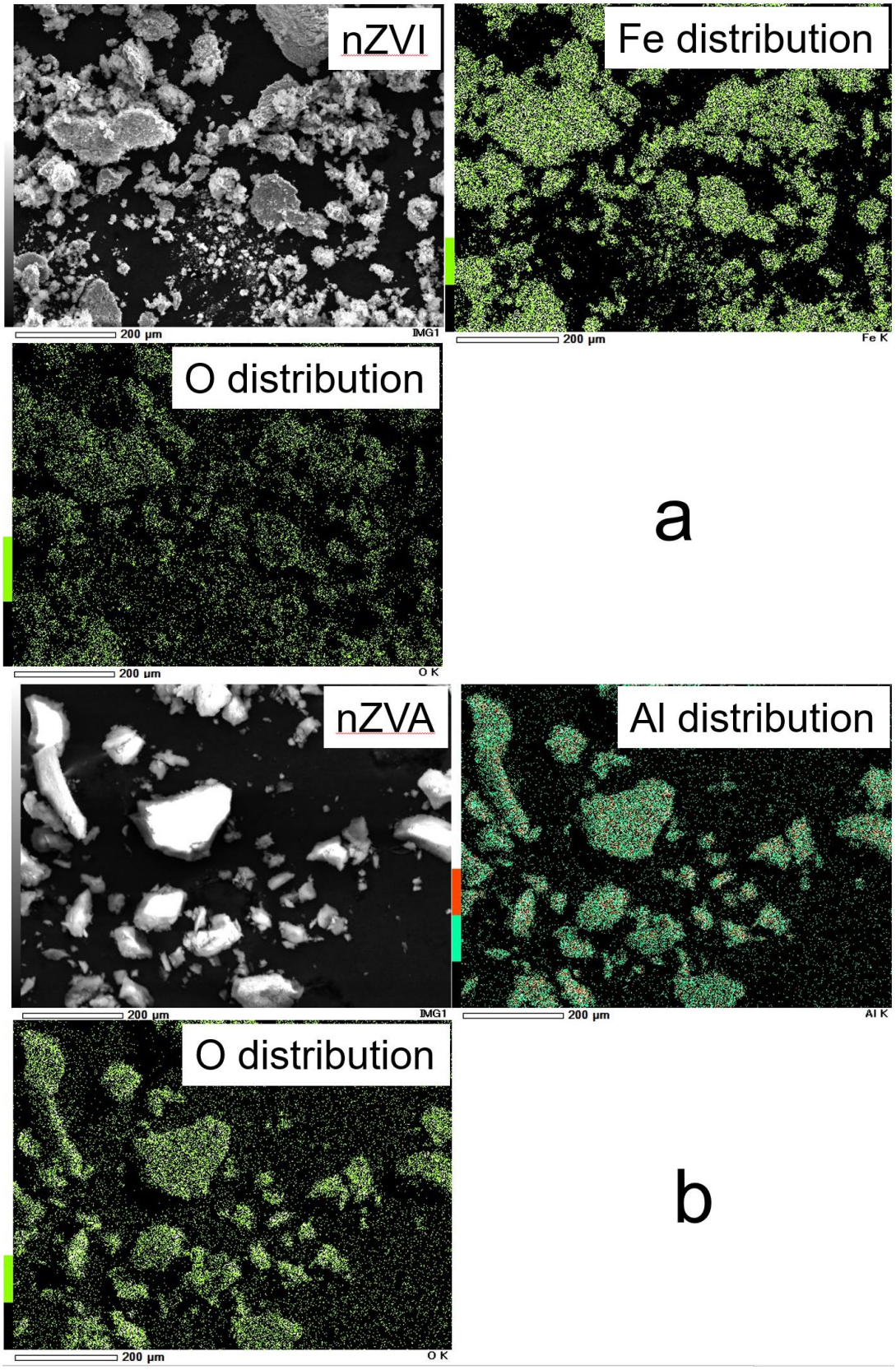


Fig. 2-5 SEM images of a) Fresh nZVI, b) Fresh nZVA

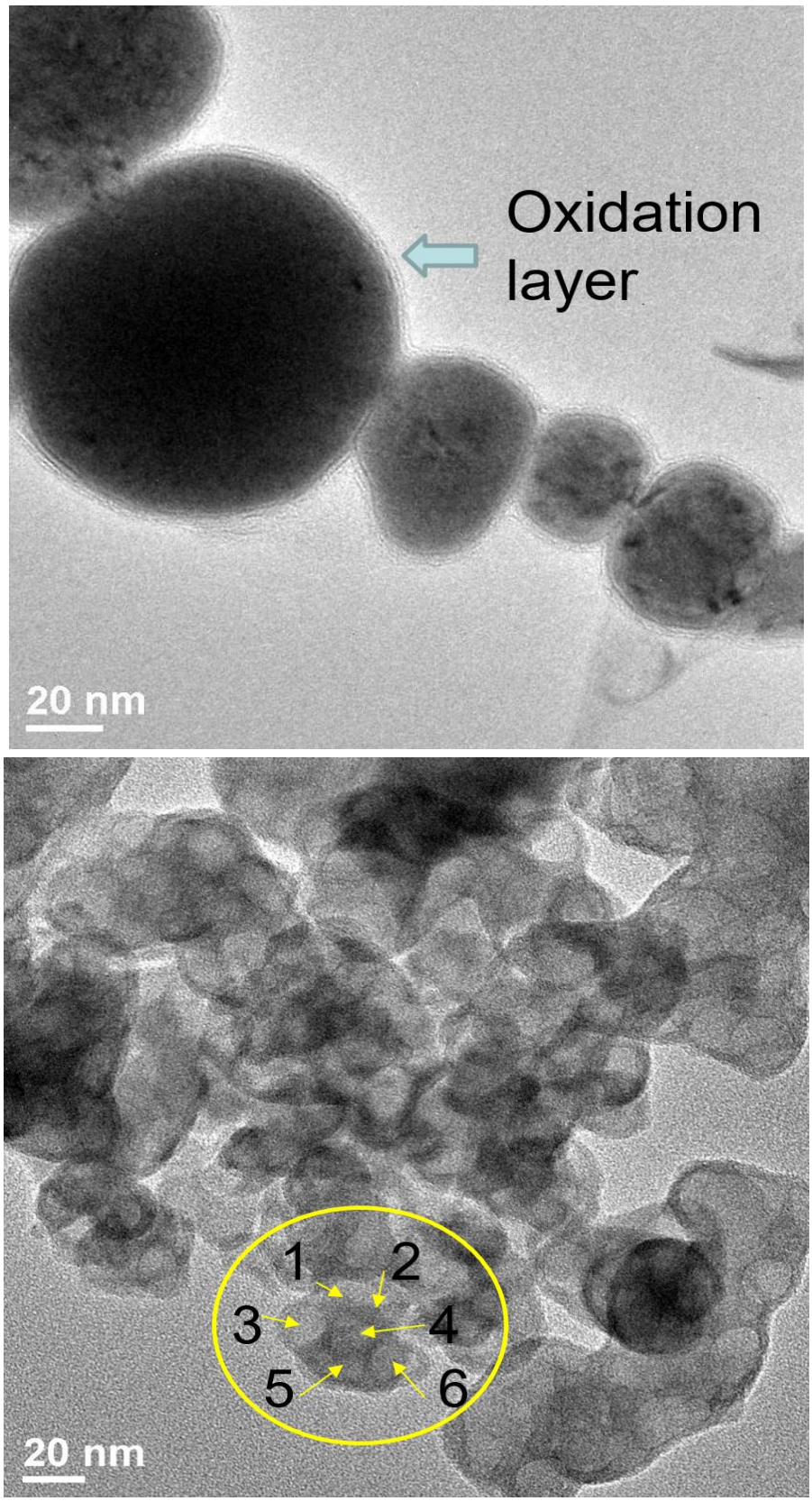


Fig. 2-6 TEM images of a) Fresh nZVI, b) Fresh nZVA

2.5 Chapter conclusion

1). Through these two preparation methods, nZVA and nZVI were successfully synthesized.

2). Sulfate can promote the synthesis of nZVA.

3). The nZVI particles are mainly chain-like, independent structures, and the surface is covered with an oxide film. The nZVA particles are mainly bulk structures, several nZVA particles are wrapped together by an oxide film.

4). nZVI has a good removal efficiency on nitrate, and the removal amount is about 140mg/L.

5). nZVA has no significant effect on nitrate removal. For a 300 mg/L nitrate solution, only about 15 mg/L of nitrate can be removed

Chapter 3: Synthesis and Optimization of NZVI/NZVA Bimetallic System

3.1 Chemical materials

The following chemical reagents and materials were used: Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_20$), Hydrated Aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$), Sodium borohydride ($NaBH_4$), Sodium nitrate ($NaNO_3$), 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.

3.2 Synthesis of NZVA/NZVI Bimetallic System

3.2.1 Synthesis of Al coated with nZVI

Al coated with nZVI was prepared by two different methods.

The first method is to generate nZVA anaerobic in a round-bottomed flask according to the method in Section 2.2. After 5min of aging time, $FeCl_3$ solution is added through the funnel, and the $NaBH_4$ solution is pumped at a speed of 16 mL/min with a peristaltic pump, and the $NaBH_4$ solution is waited for. After all the solution was added to the round-bottomed flask, the reaction was carried out for 5 mins, and filtered with suction to obtain Al coated with nZVI (without filtration). As shown in **Fig. 3-1 a**.

The second method is to generate nZVA anaerobic in the round-bottomed flask according to the method in Chapter 2.2. After 5min of aging time, suction filtration

is completed. After the suction filtration is completed, the nZVA particles are added back to the round-bottomed flask, and the $FeCl_3$ solution is added with a funnel at the same time. , pump the $NaBH_4$ solution at a speed of 16 mL/min with a peristaltic pump, wait for all the $NaBH_4$ solution to be added to the round-bottomed flask, react for 5 mins, filter with suction, and Al coated with nZVI (with filtration). As shown in **Fig. 3-1 b**.

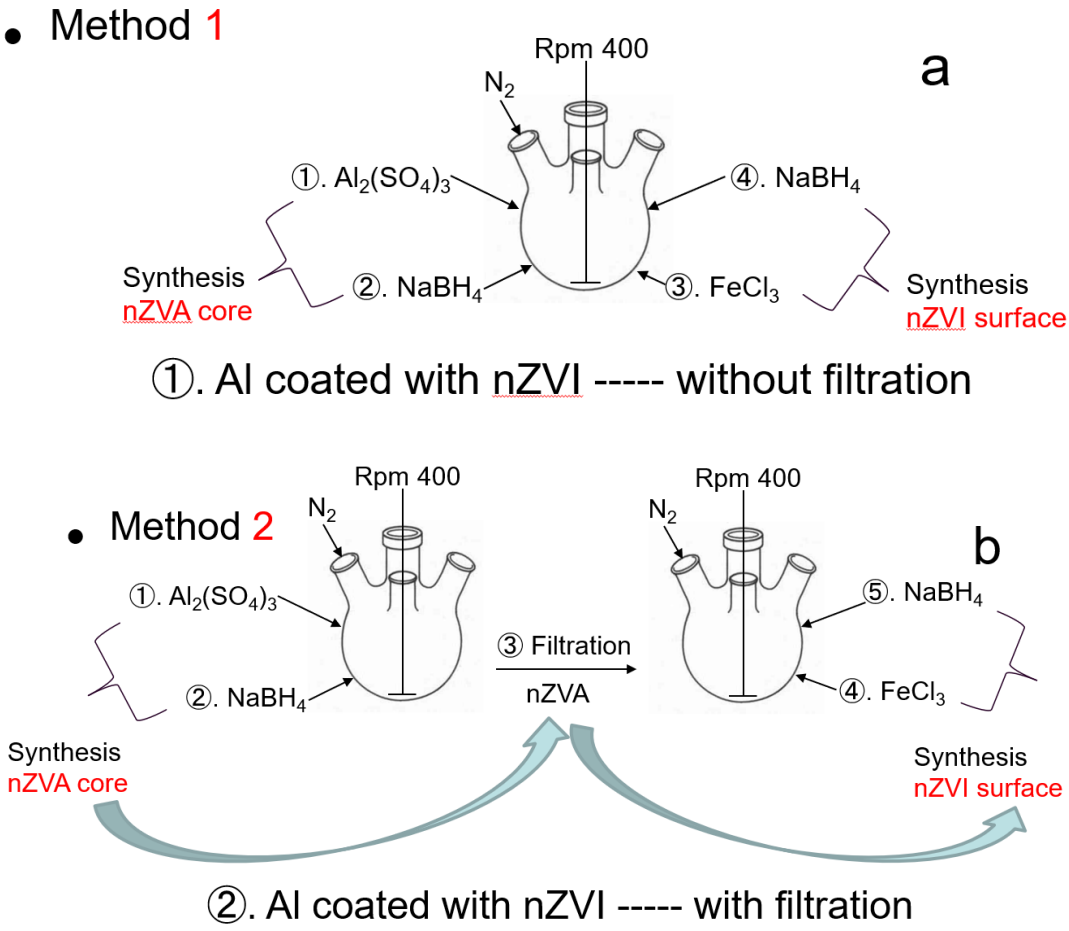


Fig. 3-1 Synthesis method of Al coated with nZVI a). without filtration, b). with filtration

3.2.2 Synthesis of Fe0 coated with nZVA

Fe coated with nZVA was prepared by two different methods.

The first method is to generate nZVI anaerobic in a round-bottomed flask according to the method in Section 2.2. After 5min of aging time, $Al_2(SO_4)_3$ solution is added through the funnel, and the $NaBH_4$ solution is pumped with a peristaltic pump at a speed of 16 mL/min. After the $NaBH_4$ solution was all added to the round-bottomed flask, the reaction was carried out for 5 mins, and suction filtered to obtain Fe coated with nZVA (without filtration). As shown in **Fig. 3-2 a**.

The second method is to generate nZVI anaerobic in the round-bottomed flask according to the method in chapter 2.2. After 5min of aging time, suction filtration is completed. After the suction filtration is completed, the nZVI particles are re-added to the round-bottomed flask, and $Al_2 (SO_4)_3$ solution, the $NaBH_4$ solution was pumped with a peristaltic pump at a speed of 16 mL/min. After all the $NaBH_4$ solution was added to the round-bottomed flask, the reaction was performed for 5 mins, suction filtration, and Fe coated with nZVA (with filtration). As shown in **Fig. 3-2 b**.

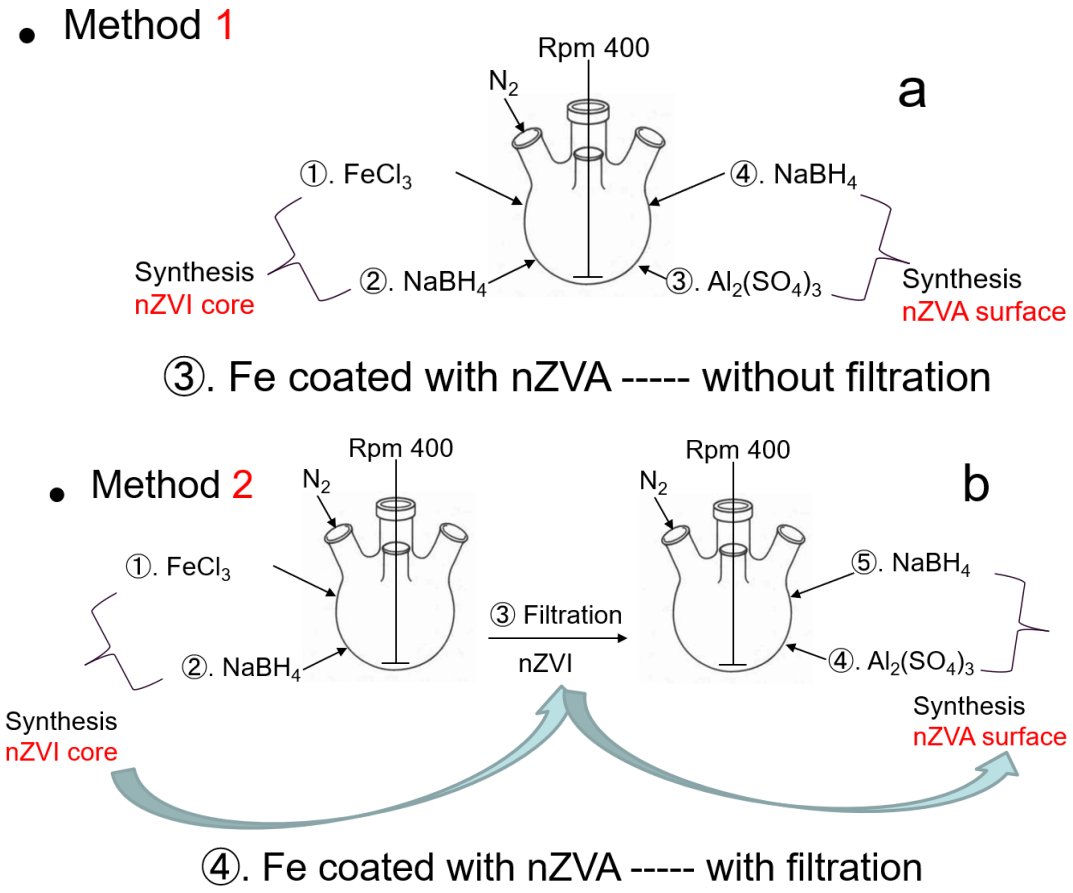


Fig. 3-2 Synthesis method of Fe coated with nZVA a). without filtration, b). with filtration

3.3 Optimization and the procedure of batch experiment

Prepare 200 ml of 300 mg/L nitrate solution as described in Section 2.3, add 0.2 g of the four materials synthesized according to Section 3.2, and conduct a 2-hour batch experiment under magnetic stirring. Samples were taken through a syringe filter at 0, 10, 30, 60, 120 minutes, and nitrate concentrations in the samples were measured by UV-Vis spectrophotometer (DR 3900, HACH Co., USA).

The best method for synthesizing Fe/Al bimetals was determined by the above experiments, at 25°C; nitrate concentration of 300 mg/L; mass dose of 1 g/L; and initial pH of 7. Different Fe:Al ratios, initial pH of the solution, and initial nitrate concentration of the solution were changed to explore the optimal conditions for Fe/Al bimetallic nitrate removal.

3.4 Result and discussion

3.4.1 Synthesis method optimization

Fig. 3-3 shows the removal of nitrate by Fe/Al bimetals synthesized by different methods. For Al core without filtration, nitrate removal peaked at 30 minutes, with a removal rate of 30 mg/L and a removal rate of 10.8%. For Al core with filtration, nitrate removal peaked at 120 min, with a removal rate of 135 mg/L and a removal rate of 48.7%, as shown in **Fig. 3-3 a**.

For Fe core without filtration, nitrate removal peaked at 120 minutes, with a removal rate of 138 mg/L and a removal rate of 49.6%. For Fe core with filtration, nitrate removal peaked at 120 min, with a removal rate of 150 mg/L and a removal rate of 53.9%, as shown in **Fig. 3-3 b**.

From these results, the materials synthesized with the addition of the filtration step have better nitrate removal effects than those without the addition of the filtration step, and the removal effect is better when nZVI is used as the core than when nZVA is used as the core. This could be caused by:

1). When nZVI is used as the core, the nZVA coating on the surface forms an oxide layer, which isolates the contact between nZVI and air and reduces the oxidation of nZVI.

2). Metal Al and metal Fe form a DC battery, and Fe^{3+} and Fe^{2+} are reduced to Fe^{0}[21][27].

3). The outer layer of nZVA coating on the surface forms $Al(OH)_3$ gel, which has an adsorption effect on nitrate [28]. This can be proved by the absorption peak of nitrate in **Fig. 3-7**.

Therefore, selecting the method that nZVI as the core, nZVA as the coating, and adding a filtration step during the synthesis process can obtain Fe/Al bimetallic materials with the best nitrate removal efficiency.

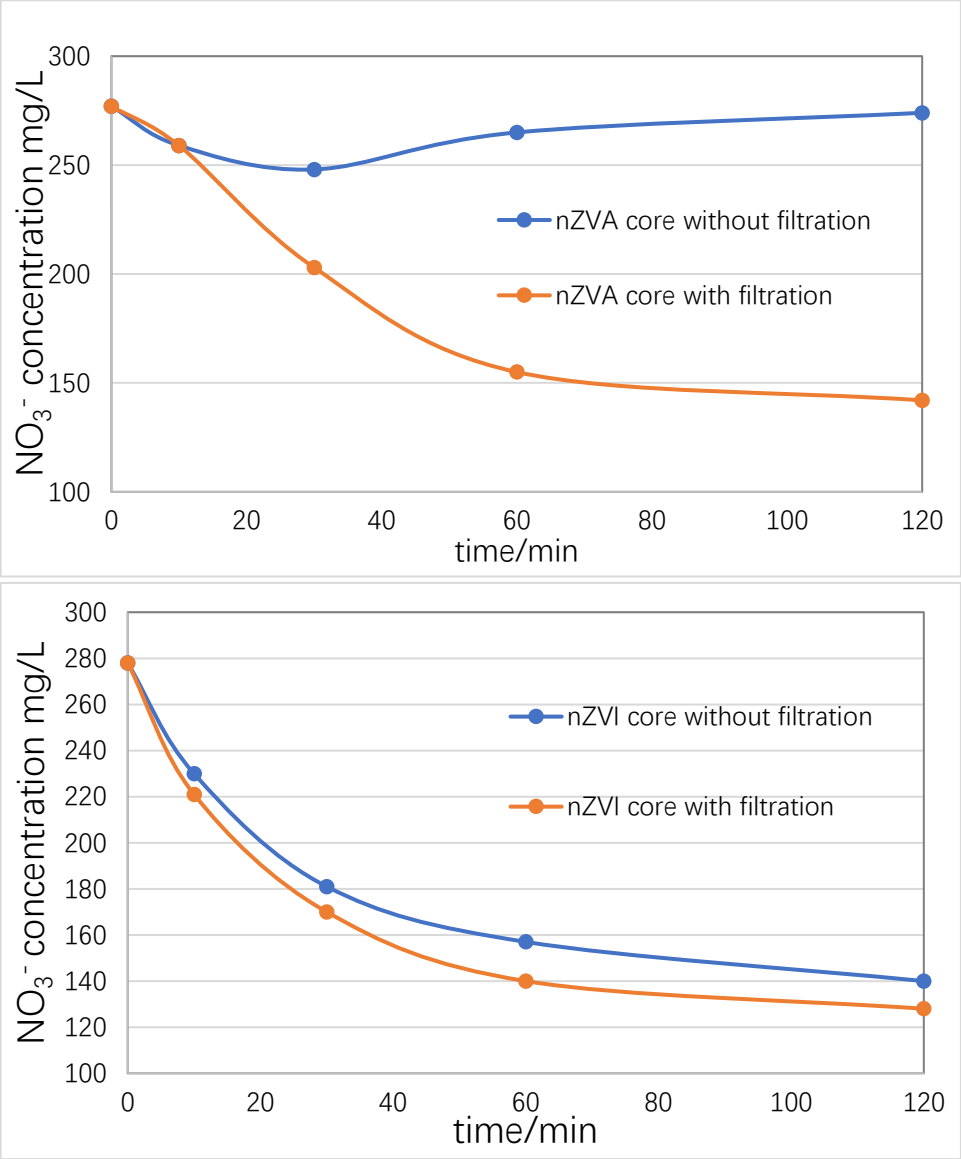


Fig. 3-3 Nitrate removal efficiency by different material synthesized by different method a). Al coated with nZVI, b). Fe coated with nZVA

3.4.2 Effect of Fe:Al ratio, initial pH, initial nitrate concentration

Fig. 3-4 shows the research on the nitrate removal efficiency of Fe coated with nZVA in batch experiments under different conditions, in which **Fig. 3-4 a), b), c)** are the change curves of solution nitrate concentration, **Fig. 3-4 b), d), f)** are the corresponding converted nitrate removal rates. The formulas for the nitrate removal amount and the nitrate removal rate refer to **(Eq. 2-3) (Eq. 2-4)**.

As the Fe:Al ratio increases, the nitrate removal also increases, reaching a maximum value of 49.35% when the Fe:Al ratio is 100:85, but at the same time, the Fe:Al ratio is 100:33, 100 :67, the nitrate removal rate at 1:1 has no big difference, and there is not much difference with the ratio of 100:85. Considering the economic factor, the Fe:Al ratio of 100:33 is considered to be the best ratio of Fe/Al bimetallic. best ratio. As shown in **Fig. 3-4 b)**.

To verify this result, the samples were analyzed by SEM and XRD. SEM results show that, different from pure nZVI and pure nZVA, the outermost layer of Fe/Al bimetal has a flocculent structure, and the surface of the core of nZVI is wrapped by metal aluminum, and then connected by an oxide layer to form such a structure. As shown in Fig. 3-5.

When the Fe:Al ratio is 100:85, compared with the fresh sample (**Fig. 3-6 a)**), there is no Fe0 in the used sample, and XRD can no longer detect the intensity peaks of Fe and Al, such as **Fig. 3-6 b)**. When the Fe:Al ratio is 1:1, the intensity peaks of Fe and Al can still be found in the sample after the batch experiment, as shown in **Fig. 3.6 d)**, but compared with the fresh sample before the reaction, the peak intensity dropped, as shown in **Fig. 3-6 c)**. This shows that with the increase of Fe:Al ratio, the use time of nZVI is enhanced, and it also shows that nZVA does promote the removal of nitrate by nZVI.

Fig. 3-4 c), d) show the removal amount and removal rate of bimetals to nitrate at different pH. When pH=5, the maximum removal rate is 172 mg/L and the maximum removal rate is 57.7%. The results showed that with the increase of pH,

the removal rate of nitrate by bimetals decreased, and acidic conditions seemed to be effective conditions for nitrate removal. This result is in good agreement with previous studies on nitrate removal by nZVI [18][20]. This can be explained by the nZVI equation for nitrate removal at different pH **(Eq. 3-1) (Eq. 3-2) (Eq. 3-3) (Eq. 3-4)**, which is also confirmed in reverse results of other studies.

$$Fe^0 + NO_3^- + 2H^+ \rightarrow Fe^{2+} + H_2O + NO_2^- \quad \textbf{(Eq. 3-1)}$$

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

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

$$5Fe^0 + 2NO_3^- + 6H_2O \rightarrow 5Fe^{2+} + N_2(g) + 12OH^- \quad \textbf{(Eq. 3-4)}$$

Fig. 3-4 e), f) show the effect of different initial nitrate concentrations on nitrate removal. When the initial nitrate concentration is 400 mg/L, the maximum removal amount is 220 mg/L, and the removal rate is 53%. The results showed that with the increase of the initial nitrate concentration, the removal of nitrate also increased, but the removal rate of nitrate has been decreasing. This may be because the rate of electron release from nZVI limits the progress of the reaction.

The FTIR spectra (**Fig. 3-7**) were used to identify the functional groups present in Fe coated with nZVA(Fe:Al ratio 100:85 and 1:1). The band around 3,417 cm^{-1} is attributed to -OH vibration in H_2O molecules, indicating that some hydroxyl groups existed on the surface of the nZVI sample. The band at 1,643 cm^{-1} is ascribed to the absorption of water. The band at 1350 cm^{-1} Belongs to nitrate. The band at 1016 cm^{-1} is the characteristic band for hydroxyl groups in ferric hydroxide. The band in 588 cm^{-1} belongs to magnetite/iron oxides. The band in 535 cm^{-1} is due to the asymmetric stretching vibration of Al-O-Al. This result confirms that this material not only can remove nitrate by chemical way, but also has the ability to absorb nitrate from nitrate solution.

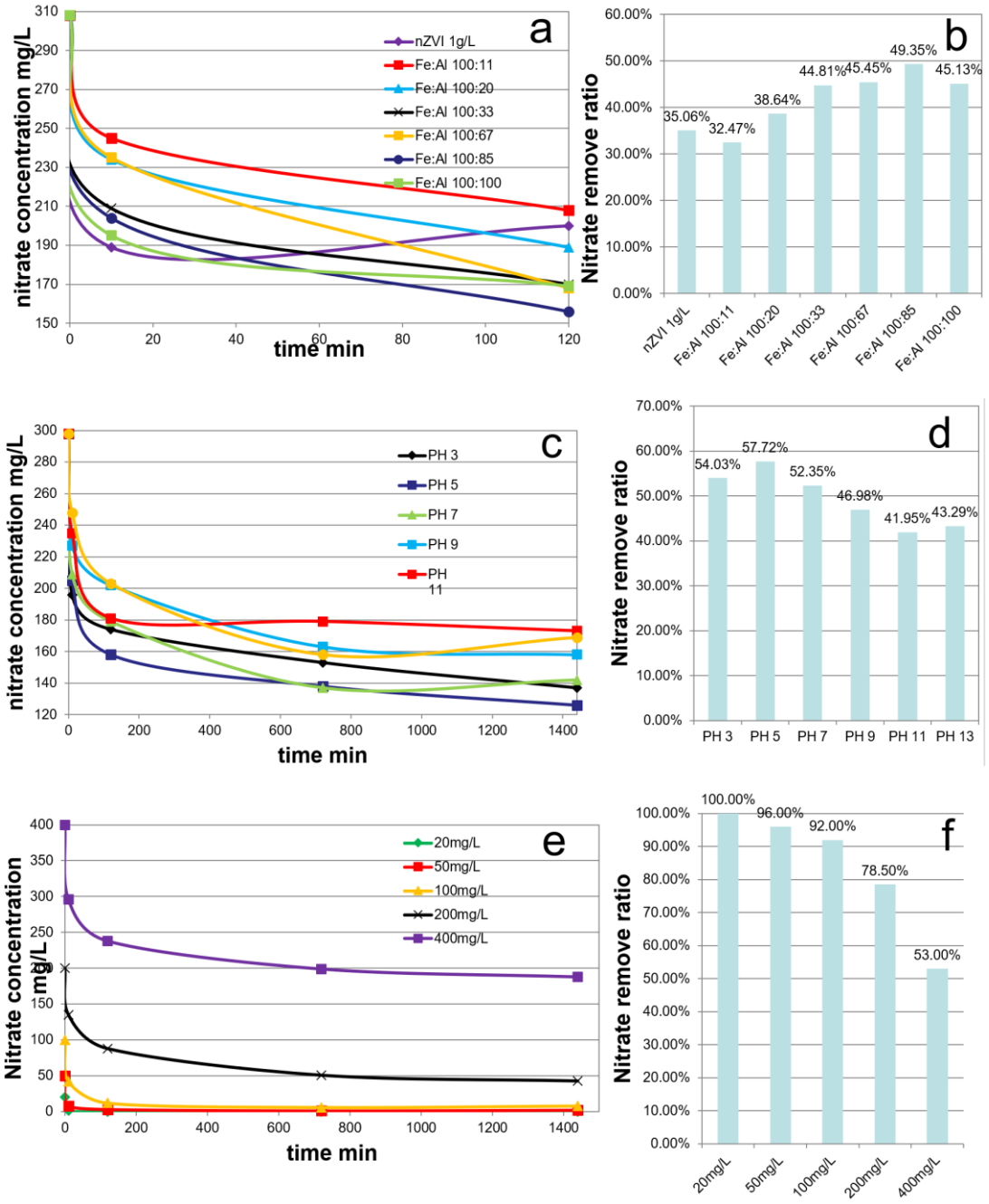


Fig. 3-4 nitrate removal efficiency of Fe coated with nZVA under different

a). Fe:Al ratio, c). pH, e). initial nitrate concentration and their nitrate removal ratio

b). Fe:Al ratio, d). pH, f). initial nitrate concentration

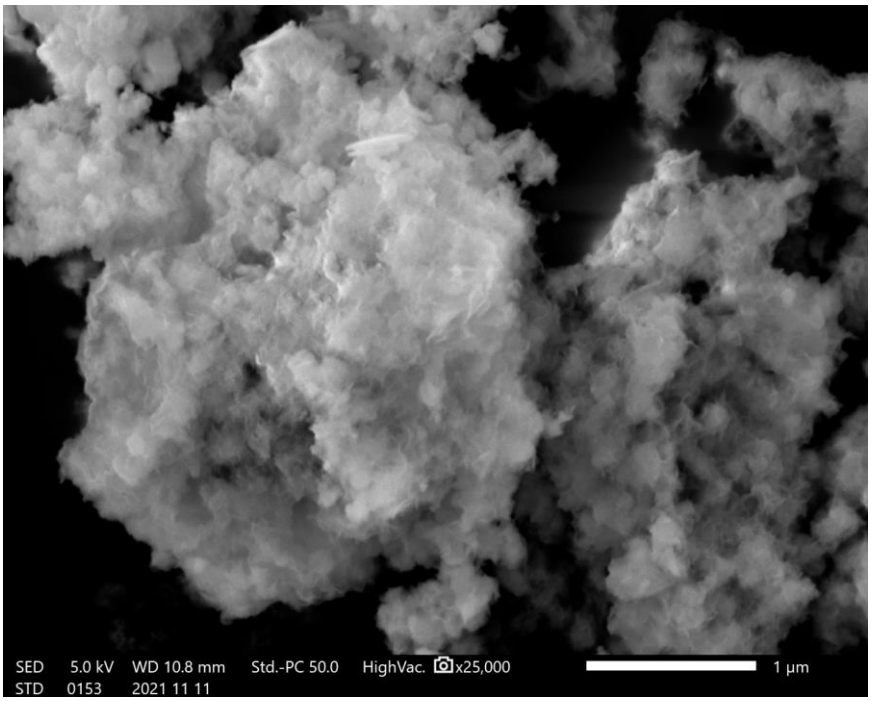
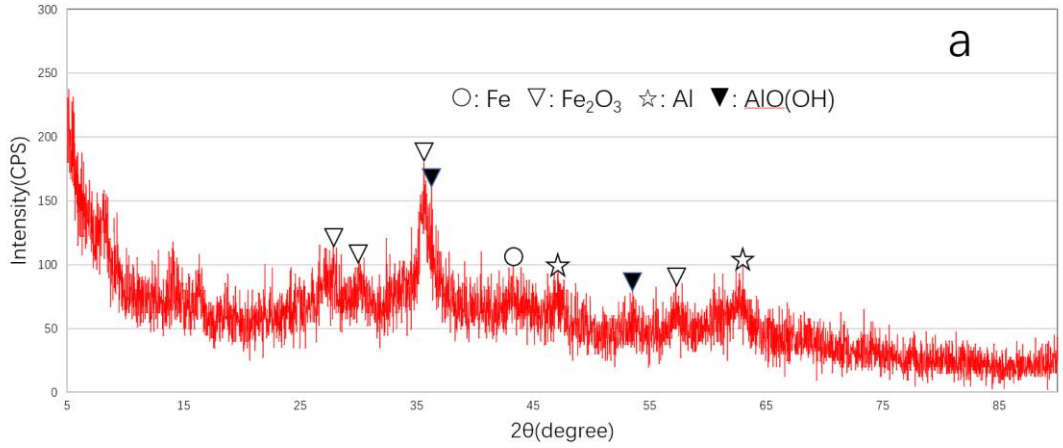
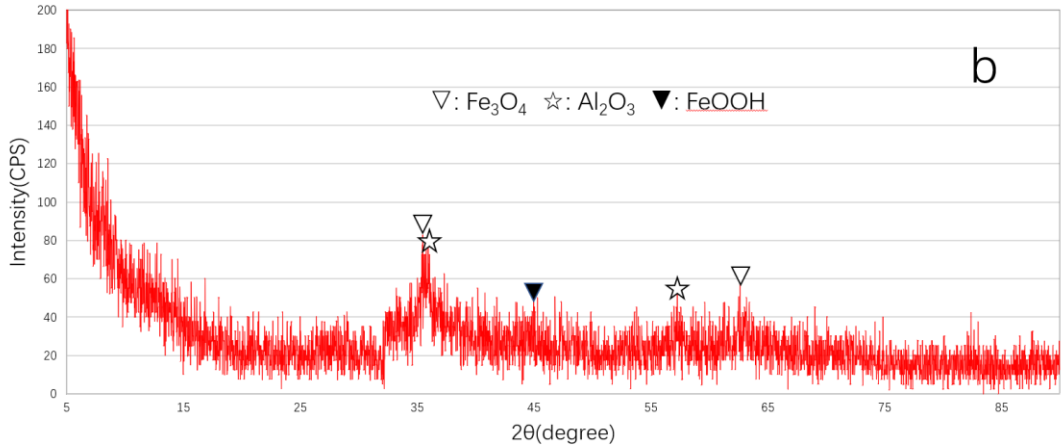
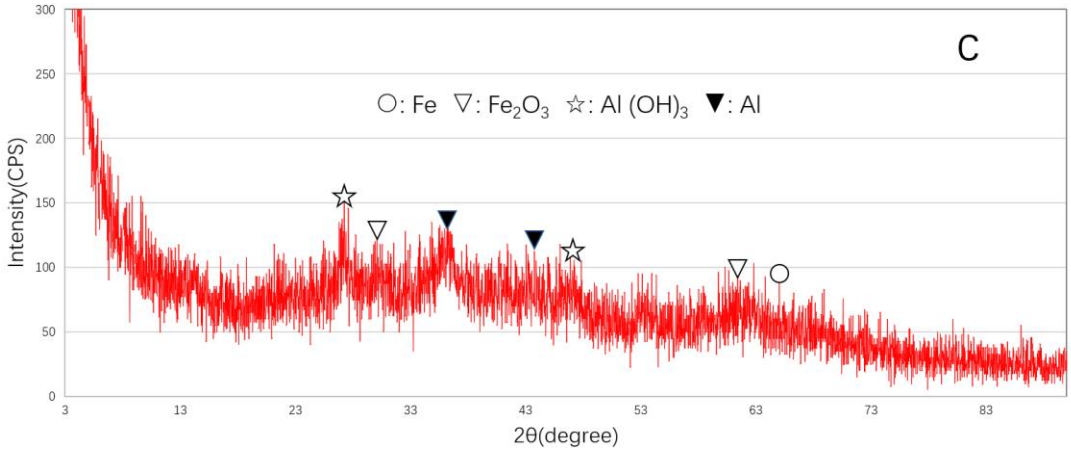


Fig. 3-5 SEM image of Fe coated with nZVA, Fe:Al ratio 100:67


a
○: Fe ▽: Fe2O3 ☆: Al ▼: AlO(OH)
Intensity(CPS)
2θ(degree)


b
▽: Fe3O4 ☆: Al2O3 ▼: FeOOH
Intensity(CPS)
2θ(degree)


c
○: Fe ▽: Fe2O3 ☆: Al (OH)3 ▼: Al
Intensity(CPS)
2θ(degree)

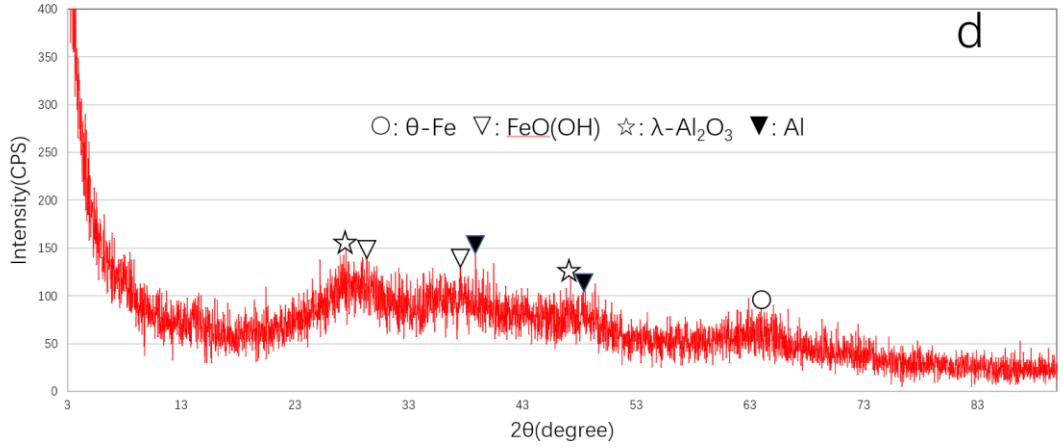
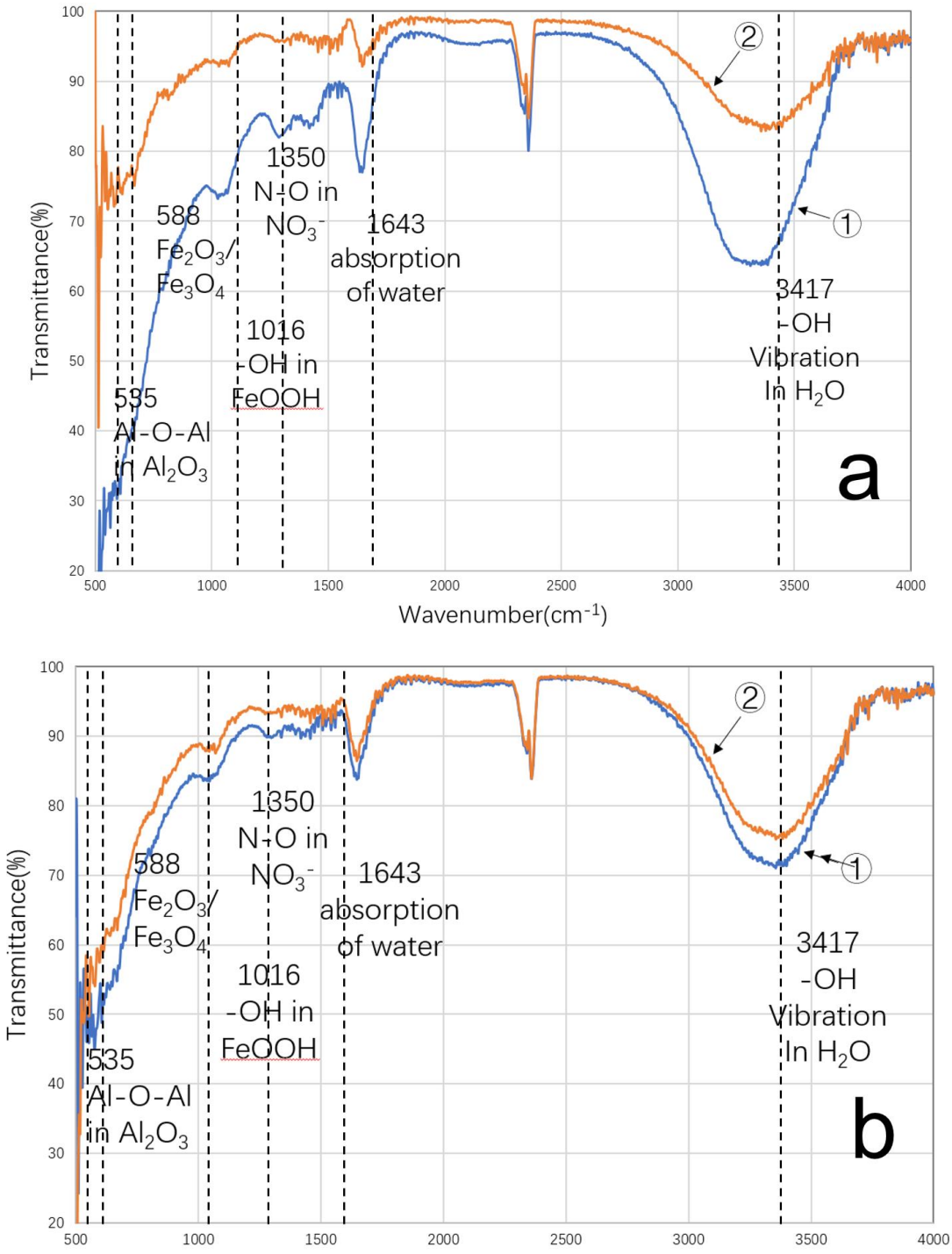

d
○: θ-Fe ▽: FeO(OH) ☆: λ-Al2O3 ▼: Al
Intensity(CPS)
2θ(degree)

Fig. 3-6 XRD result of Fe coated with nZVA:

a). Fe:Al 100:85 Fresh sample, b). Fe:Al 100:85 Spent sample

c). Fe:Al 100:100 Fresh sample, d). Fe:Al 100:100 Spent sample



3.5 Chapter conclusion

1). A mathod to synthesis nZVI/nZVA bimetallic system is found and proved feasible.

2). Adding a filtration step during synthesis step helps improving nitrate removal rate.

3). Fe:Al ratio 100:85, PH5, initial nitrate concentration 400 mg/L is the best condition for Fe coated with nZVA, which has a nitrate removal amount of 138 mg/L, 178mg/L and 225 mg/L.

4). With the increase of nZVA ratio, the longevity of nZVI improved.

5). This material could also absorb nitrate from nitrate solution, the band in 1350 cm-1 could approve that.

Chapter 4: Conclusion

4.1 Chapter 2: Synthesis and Properties of NZVA and NZVI

1). Through these two preparation methods, nZVA and nZVI were successfully synthesized.

2). Sulfate can promote the synthesis of nZVA.

3). The nZVI particles are mainly chain-like, independent structures, and the surface is covered with an oxide film. The nZVA particles are mainly bulk structures, several nZVA particles are wrapped together by an oxide film.

4). nZVI has a good removal efficiency on nitrate, and the removal amount is about 140mg/L.

5). nZVA has no significant effect on nitrate removal. For a 300 mg/L nitrate solution, only about 15 mg/L of nitrate can be removed

4.2 Chapter 3: Synthesis and Optimization of NZVI/NZVA Bimetallic System

1). A method to synthesis nZVI/nZVA bimetallic system is found and proved feasible.

2). Adding a filtration step during synthesis step helps improving nitrate removal rate.

3). Fe:Al ratio 100:85, PH5, initial nitrate concentration 400 mg/L is the best condition for Fe coated with nZVA, which has a nitrate removal amount of 138 mg/L, 178mg/L and 225 mg/L.

4). With the increase of nZVA ratio, the longevity of nZVI improved.

5). This material could also absorb nitrate from nitrate solution, the band in 1350 cm-1 could approve that.

4.3 Future suggestion

This research mainly focuses on the synthesis of nano-zero-valent aluminum and Fe/Al bimetals and studies their properties. If you want to carry out further research in the future, you can start from the following aspects:

1). Reduce the production cost of materials

2). Make a continuous system to study the performance of this material for a long time

3). Try to apply this material to practical occasions and expand the laboratory scale to the application scale

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