The Effect of Aging nZVI on Removal of Nitrate

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The effect of aging nZVI on removal of nitrate

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Abstract: *This study aimed to assess the effect of the aging period on the efficiency of nanoscale zero valent iron (nZVI) for nitrate removal from water. A series of batch tests to evaluate changing in the efficiency of nZVI for nitrate removal over a range of aging time (0-90 days) under different storing conditions such as temperature, air condition, and solvent has been investigated. The effect of temperature ranged from 5℃ to 20℃, the air condition of atmospheric air and nitrogen gas, the solvent in water, 50% volume ratio of ethanol and ethanol was studied. Scanning electron microscopy (SEM) was used to investigate the changes in the physicochemical properties of again nZVI. The results proved that lower temperature, atmospheric air, and ethanol were the best storage conditions to keep the high efficiency of aging nZVI.*

Keywords: nanoscale zero-valent iron(nZVI), aging, nitrate

1. INTRODUCTION

According to the United Nations data on world population trends, the total population is expected to exceed 8 billion by 2025 [1]. The total population is projected to continue to grow after 2050 and will increasingly produce more. As a result, Humanity's output will continue to increase, and environmental pollution from their excessive disposal will further increase. Nitrate is considered as a hazardous contaminant in the drinking water. When large amounts of nitrate flow into lakes and marshes, they will cause eutrophication problems there. Not only the natural environment, but human health also gets bad influences such as oxygen deficiency disease [2]. In addition, nitrate transforms into nitrite which increases toxicity level, resulting in blue baby syndrome, liver damage, cancer and so on [3]. In order to prevent them, World Health Organization (WHO) allowed concentration of nitrate is under 50 mg NO_3^-/L [4]. Therefore, it must be efficiently and effectively treated. The removal methods of nitrate in wastewater contain the ion exchange [5], chemical [6], biological denitrification [7], and electrocatalysis [8]. However, most of these methods are relatively high cost because of potential side effects on water quality [9]. Therefore, many researchers need to study more low-cost treatment method.

Nanoscale zero-valent iron (nZVI) has been the research attention from so many researchers in wastewater treatment and environmental applications over the last two decades. The nZVI has some advantages such as ts low dosage, high reactivity, easy operation and high-cost effectiveness [10]. However, it has mainly two disadvantages. Firstly, rapidly tend to aggregate due to the strong attraction between the particles. Q. Zhang et al. [11] said the attraction leads to increase the particle size which results in reducing the available surface area and hence affect the reactivity towards the targeted contaminants. The second one is highly reactive material and rapidly reacts with the surrounding media such as water and oxygen, which lose their effectiveness [12]. To solve these concerns, the nZVI was added some modifications such as polymerization [13], bimetallic catalyzation [14], [15], sulfidation [16], biochar-supporting [17], and so on. Due to these modifications of nZVI, the performance of nZVI dramatically improved. For example, Giorgio Vilardi et al. [18] obtained a Cu–Fe0 nanoparticles loading of 0.5 g L-1, which corresponds to a molar ratio Cu–Fe0/NO3- = 5 achieved the maximum removal efficiency at 2hr which was about 73%. Such positive effect was applied for other contaminants such as Cr(VI) [19]. However, it wasn't studied about the effect between aging time and removal efficiency for nZVI in detail.

In usual, most nZVI was used for the experimental work as soon as it was synthesized, so the aging time was 0hr. In the past studies, Dan Lv et al. [20] stored nZVI and sulfide-modified nZVI (S-nZVI) for up to 12 days and investigated these performances for Cr(VI) removal. They showed that the removal efficiency about nZVI was less than 40% after 12 days aging. However, it hasn't been studied the performance of nZVI for other contaminants removal when stored for more than 1 month.

The objectives of this research were to investigate the change of nZVI in removal efficiency when stored at different temperatures, air conditions, and conditions within a solvent for a specific period. Besides, it was also investigated to characterize the aging nZVI by Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2. MATERIALS AND METHODS

2.1. Materials

The following were used for synthesizing nZVI; Sodium borohydride (>98.0%, Sigma-Aldrich Inc., USA) and ferric chloride hexahydrate (99%, Junsei Chemical Co., Japan). Sodium nitrate (99%, Junsei Chemical Co., Japan) was used for nitrate solution. Deionized water (DIW) and ethanol were used for solvents when nZVI particles were stored. Nitrogen gas was used for deoxygenating the DIW and ethanol, and nitrate solution.

2.2. Synthesis of nZVI (Fe^0)

nZVI was synthesized in the laboratory by the chemical reduction method as shown in Fig.1 [21]. The reaction was followed it [12]:

$2FeCl_3 \cdot 6H_2O + 6NaBH_4 + 18H_2O \rightarrow 2Fe^0 + 21H_2 + 6B(OH)_3 + 6NaCl$ (1)

In detail, to synthesize 1 gram of nZVI particles, it was followed; 2.2 grams of sodium borohydride was dissolved by 100mL of deoxygenated water (DW) which had been bubbled with nitrogen gas for 10 min and 5.0 grams of ferric chloride hexahydrate was dissolved by 200mL of DW. These solutions were magnetically stirred for more than 10min to make the chemicals completely dissolved. After the two solutions prepared, the ferric chloride hexahydrate solution was added to the four-neck flask, and the sodium borohydride solution was decanted into the ferric solution by using a peristaltic pump with a flow rate of 20mL min^{-1} under nitrogen gas injected. After adding the borohydride solution, the mixture of the solutions was agitated under nitrogen gas injected via a mechanical mixer at 400rpm and at 30℃ for 5min to ensure the complete reduction of ferric. The synthesized nZVI was immediately collected and filtered by using a vacuum filtration system and washed by DW 3 times.

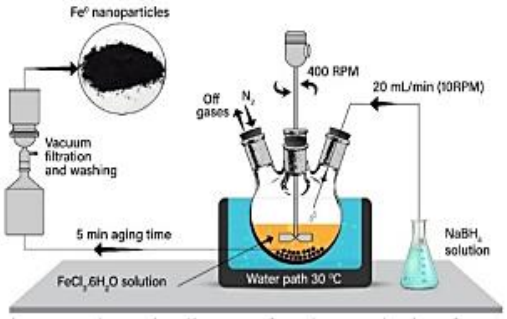

Fig. 1. Schematic diagram for the synthesis of nZVI.

2.3. Aging nZVI and batch experiments

After synthesizing nZVI, it was divided into 10mL plastic tube and stored under each condition. In nitrogen condition, the nitrogen gas was injected into 10mL plastic tube and nZVI was preserved in it at 20℃. For storage in solution, each solvent was bubbled with nitrogen gas sufficiently in advance. After that, nZVI was stored in 10mL plastic tube with each solvent at 20℃.

Batch testing was performed using temperature, air, and solvent parameters. For temperature, the synthesized nZVI was stored at 20°C, 5°C, and -5°C under atmospheric conditions. In air, nZVI was stored under air and nitrogen gas conditions at 20°C. Finally, in solvent, nZVI was stored in an ethanol solution with a DIW, ethanol, volume ratio of 0.5 at 20°C. Here, each solvent was previously anoxic with nitrogen gas. Each nZVI was stored for 0 days, 1 week, 2 weeks, 3 weeks, 1 month, 2 months, and 3 months. After those periods of storage, batch tests were performed. The conditions for the batch tests were as follows: initial concentration of nitrate was 300 mg/L, volume of nitrate solution was 200 mL, dose of nZVI was 0.25 g, stirring speed was 1500 rpm, stirring was 3 hours, temperature was 25°C, anoxic conditions, and neutral conditions. After stirring, 2 mL liquid sample was taken by a plastic syringe and filtered by 0.45 μm filter and kept in 2 mL sampling tube for further analysis.

2.4. Analytical instruments

The residual concentration of nitrate after the treatment was measured by UV-vis spectrophotometer (DR 3900, Hach Co., USA). Scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM-EDS, JSM-IT700HR, JEOL, Japan) was used to investigate the surface morphology, size and particle dispersion of nZVI , aging nZVI, and nZVI reacted with nitrate.

2.5. Assessment of nZVI reactivity

The performance of all nZVI particles was assessed by calculating the final removal efficiency (RE) using the following equation [22]:

$RE\ (\%) = (C_i - C_f) * 100 / C_i$ (2)

Where C_i and C_f represent nitrate initial and final concentrations(mg/L), respectively.

2.6. Mechanism of nitrate removal by nZVI

Due to the past research, it was revealed that the mechanism of nitrate removal by nZVI was reduction process [23]. Nitrate reduction by nZVI is regarded as a spontaneous process under acidic conditions and followed the equation [24]:

$NO_3^- + 4Fe^0 + 10H^+ \rightarrow NH_4^+ + 4Fe^{2+} + 3H_2O$ (3)

In eq (3), Khalil et al [25] further explained the nitrate reduction process. Firstly, nitrate is reduced to nitrite. Then, nitrite is consumed inside reactions which occurs to produce ammonia with a reduced content of nitrogen with the following equations:

$NO_3^- + 4Fe^0 + 2\ H^+ \rightarrow Fe^{2+} + H_2O + NO_2^-$ (4)

$NO_2^- + 3Fe^0 + 8\ H^+ \rightarrow NH_4^+ + 3Fe^{2+} + 2H_2O$ (5)

$NO_3^- + 4Fe^0 + 10H^+ \rightarrow NH_4^+ + 4Fe^{2+} + 3H_2O$ (6)

$NO_2^- + 3Fe^0 + 8\ H^+ \rightarrow N_2 + 3Fe^{2+} + 4H_2O$ (7)

From these equations, the production of nitrite and ammonia and nitrogen is regarded to be present in insignificant amount [25].

3. RESULTS AND DISCUSSION

3.1. Characterizations of nZVI, aging nZVI, and nZVI reacted with nitrate

SEM-EDS was used for characterizing nZVI materials. The SEM-EDS results of fresh nZVI were shown in Fig. 2. Fig. 2a showed chain like structures. However, more detailed morphologies could not be seen at this resolution, so observations were made at a resolution of 0.2μm (Fig.2b). From Fig. 2b, not only chain-like structures but also spherical structures were observed. The particles were approximately 50 nm in diameter and was almost same conditions in the past papers [26], [27]. Fig. 2c and 2d, EDS mapping shows oxygen and iron atoms throughout. Comparing the Fig. 2a and 2b, iron atoms are mapped more than oxygen atoms. To further analyze this, EDS spectra and elemental percentages were shown in Fig. 3 and Table 1. In Fig. 3, iron was detected higher intensity than oxygen. In addition, Table. 1 showed both ratios of iron were much higher than that of oxygen. It is thought the oxidation wasn't proceeded.

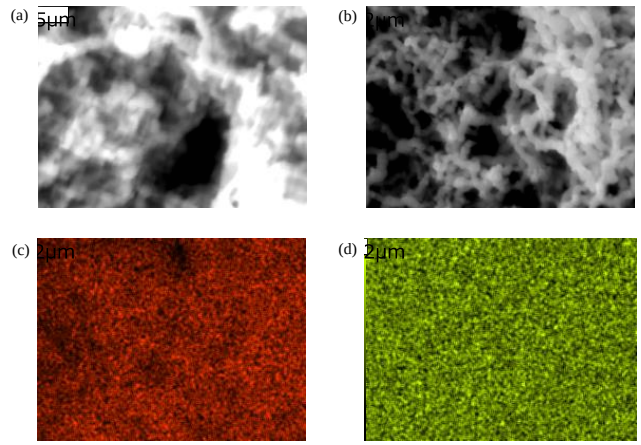

Fig. 2. SEM images with (a) resolution of 0.5µm and (b) resolution of 0.2µm and EDS images with (c) O-K and (d) Fe-K of fresh nZVI.

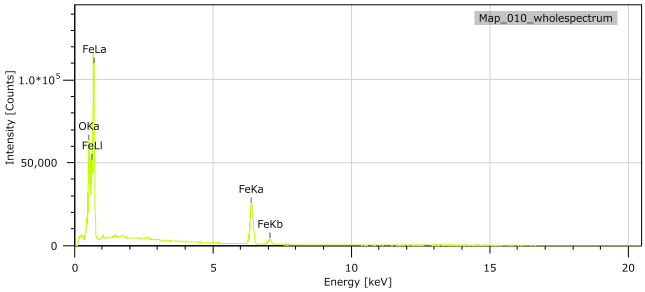

Fig.3. EDS spectra of fresh nZVI.

Table.1. The mass and atom ratio of fresh nZVI.

Element	Line	Mass ratio(%)	Atom ratio(%)
O	K	5.21	16.1
Fe	K	94.79	83.9

Fig. 4a and 4b showed images with a resolution of 0.5 µm and 0.2 µm, respectively. Both images showed spherical and chain-like structures, but in Fig. 4b, the nZVI particles were found to be approximately 200 nm in diameter. The diameter was approximately 4 times larger than that of fresh nZVI. It might be due to the formation of a passivation shell which caused less reactivity with nitrate reduction [28].On the other hand, Fig. 4c and 4d showed the EDS images with O-K and Fe-K respectively. Compared to Fig. 2c, the mapping volume of oxygen was increased in Fig. 4c. Clearly, the mapping of iron atoms decreased compared to Fig. 2d. The detailed data was shown in Fig. 5 and Table. 2. In Fig. 5, the intensity of iron was lower than that in Fig. 4. On the other hand, it was found the reverse result about that of oxygen. As a basis, table showed both ratios of oxygen were increased more than 3 times compared to Table. 1. It would be due to that the reaction between iron and oxygen was undergone during the storing time.

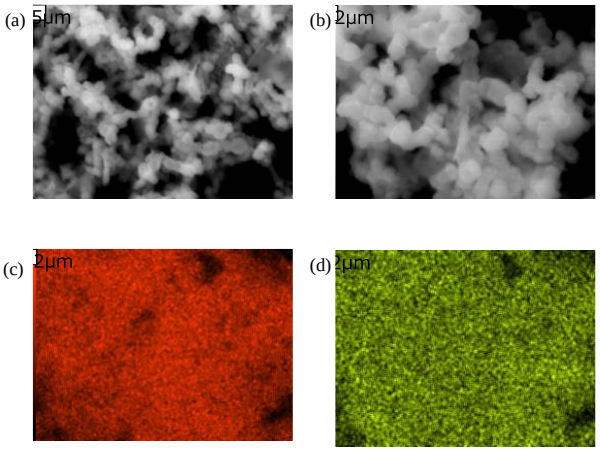

Fig.4. SEM images with (a) resolution of 0.5µm and (b) resolution of 0.2µm and EDS images with (c) O-K and (d) Fe-K of Fig.3. EDS spectra of aging nZVI at 5°C for 3 months.

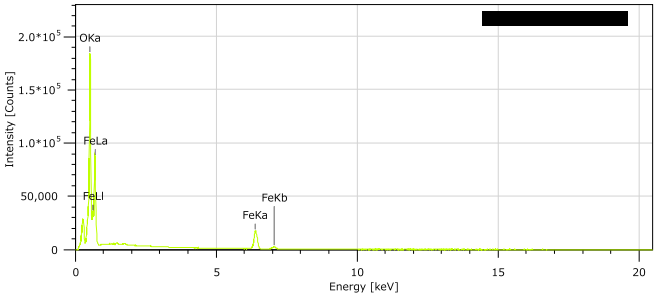

Fig. 5. EDS spectra of Fig.3. EDS spectra of aging nZVI at 5°C for 3 months.

Table. 2. The mass and atom ratio of aging nZVI at 5°C for 3 months.

Element	Line	Mass ratio(%)	Atom ratio(%)
O	K	21.45	48.8
Fe	K	78.55	51.2

Fig. 6a and 6b showed images with a resolution of 1.0 µm and 0.5 µm of aging nZVI at 5°C for 3 months reacted with nitrate, respectively. In both images, spherical and chain-like structures were not seen at all. It was attributed to the reaction with nitrate. The cotton-like objects in the two images are thought to be nZVI reacting with nitrate to become ferric or ferrous. On the other hand, Fig. 6c and 6d showed the EDS images with O-K and Fe-K of aging nZVI at 5°C for 3 months reacted with nitrate, respectively. The mapped amounts of both iron and oxygen atoms were clearly reduced from before the reaction with nitrate. The detailed data for the EDS data was shown in Fig. 7 and Table.3. In Fig. 7, the intensity of oxygen was higher than that of iron, however, it was lower than that of oxygen in Fig. 5. As shown in Table. 3, both ratios of oxygen were slightly decreased compared to those in Table. 2.

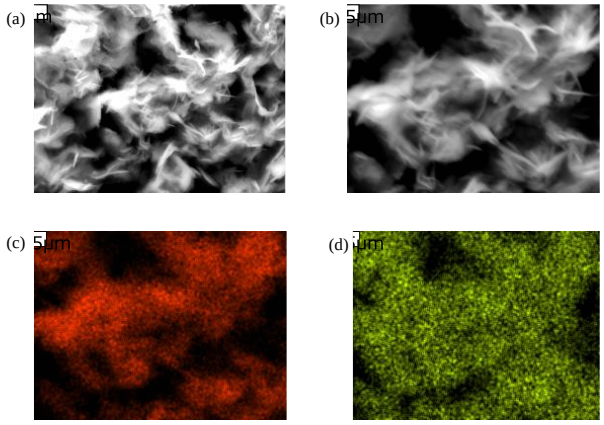

Fig. 6. SEM images with (a) resolution of 1.0μm and (b) resolution of 0.5μm and EDS images with (c) O-K and (d) Fe-K of Fig.3. EDS spectra of aging nZVI at 5℃ for 3 months reacted with nitrate.

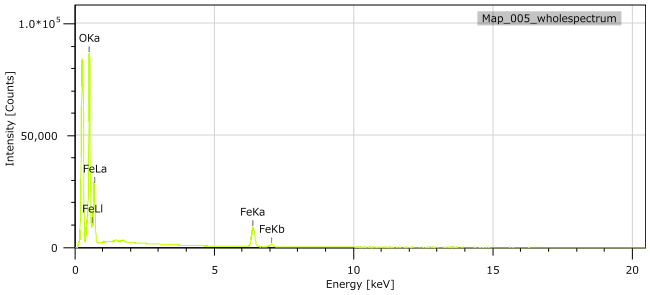

Fig. 7. EDS spectra of Fig.3. EDS spectra of aging nZVI at 5℃ for 3 months reacted with nitrate.

Table. 3. The mass and atom ratio of aging nZVI at 5℃ for 3 months reacted with nitrate.

Element	Line	Mass ratio(%)	Atom ratio(%)
O	K	20.65	47.59
Fe	K	79.35	52.41

3.2. The effect of temperature on storage of nZVI

Temperature is one of the most important parameters to determine that influences the corrosion of nZVI. Fig. 8 shows the changes of the removal efficiency (RE) of nZVI on aging time. As shown in Fig. 8, the RE hasn't changed for 3 months at -5℃ so much. It was nearly 70%. On the other hand, at 5℃ and 20℃, both REs were tendency to decrease compared to that at -5℃. In 2 months and 3 months, the RE of 5℃ and 20℃ would include experimental error, they have nothing to do with that tendency. This trend may have occurred because the lower temperatures slowed the rate of corrosion of iron. Filip et al. [29] found nZVI reaction with water under anaerobic conditions at 80 °C was considerably accelerated, which the rate was nearly one order-of-magnitude higher than that at 25 °C. It was under water and anaerobic conditions but found that higher temperature affected the reaction rate. On the contrary, it would be shower than that at 25 °C if the temperature had been lower than 25 °C. Therefore, lower temperature affects aging nZVI better than higher one.

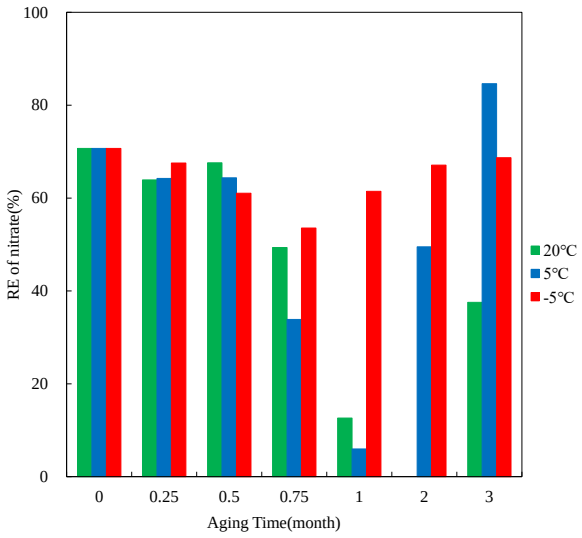

Fig. 8. The effect of temperature on nZVI storing (Batch test conditions; 300mg/l of nitrate, 200mL of volume, 0.25g of nZVI dosage, 25℃ of temperature, 1500rpm of mixing speed, 3h of reaction time, neutral pH, and anoxic condition).

3.3. The effect of air condition on storage of nZVI

In this section, it was investigated to determine the effect of air condition on storage of nZVI. As shown in Fig. 9, the air condition was tend to decrease the RE and it was 0% at 2 months storage. On the other hand, nitrogen gas part was rapidly decreased from 0 day to 0.25 months. In 0.75 months and 1 month, they would contain the experimental error, therefore, they have nothing to do with that tendency. In 2 months and 3 months, these REs weren't different so much. From these results, the nitrogen condition made nZVI aged earlier than air condition. Wang et al. [30] suggested that dry condition is better than humid condition for the storage of nZVI in view of the oxidation process. In this research, when it was stored in 10mL plastic tube, the air wasn't humid and the tube was closed by the cap, so it's thought that the oxidation was more slowly undergone in the tube.

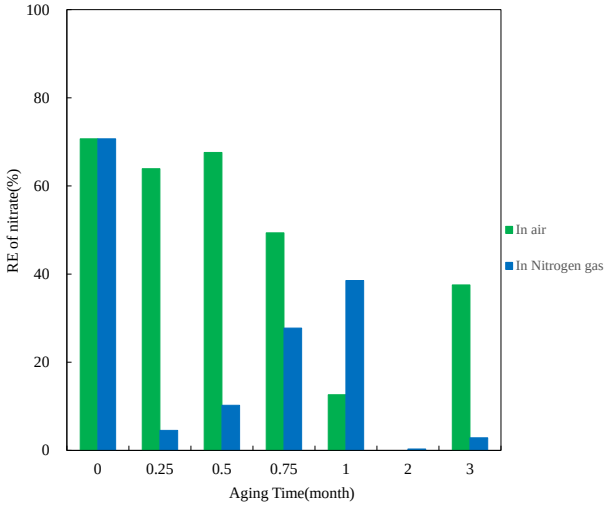

Fig. 9. The effect of air condition on nZVI storing (Batch test conditions; 300mg/l of nitrate, 200mL of volume, 0.25g of nZVI dosage, 25℃ of temperature,

1500rpm of mixing speed, 3h of reaction time, neutral pH, and anoxic condition).

3.4. The effect of solvents on storage of nZVI

In this part, the effect of solvents on storage of nZVI was investigated because nZVI easily reacted with solvent such as water, [31]. As shown in Fig. 10, water condition was the earliest to reach almost 0% of RE in all conditions. It would be due to the reaction with water. Through this reaction, ferrous iron was produced [32], and it's thought that the reaction consumes nZVI and decreases the reactivity on nitrate removal. Here, the 0.75 months and 2 months data of 50%-ethanol would include the experimental error, so they have nothing to do with that tendency. In 50%-ethanol, the RE was gradually decreased but the rate of aging wasn't faster than that of water. It would be due to that the effect of water was weaken by the same volume of ethanol. In ethanol, RE was relatively highest by 1 month of all solvents except to 0.5 months. The RE would have the experimental error. This solvent also tended to decrease RE gradually, but the rate wasn't faster than that of 50%-ethanol. Ponder et al. [33] found that ethanol could prevent nZVI from oxidation. In addition, Korgel et al. [34] mentioned that nanoparticles aggregation was more easily formed with increased solvent polarity. ethanol is lower polarity than water. Due to the lower polarity, aggregation of nZVI by ethanol was slower than that of water. Therefore, ethanol would be the best solvent to store nZVI.

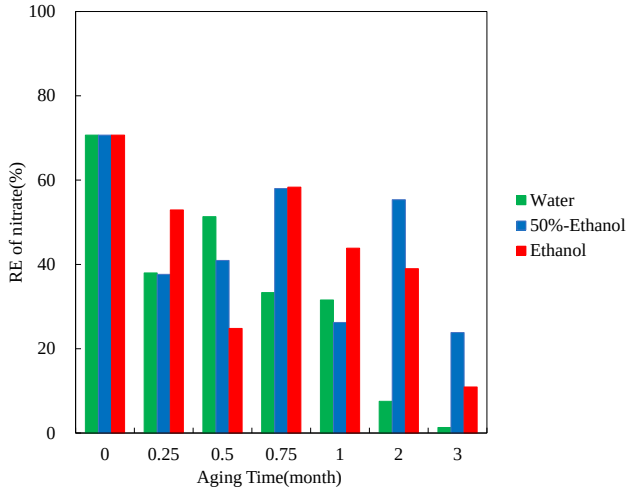

Fig. 10. The effect of solvents on nZVI storing (Batch test conditions; 300mg/l of nitrate, 200mL of volume, 0.25g of nZVI dosage, 25℃ of temperature, 1500rpm of mixing speed, 3h of reaction time, neutral pH, and anoxic condition).

4. CONCLUSIONS

In this research, there were mainly 3 parameters: temperature, air condition, and solvent. From these parameter experiments, it was found that lower temperature, air condition, and ethanol were the best for aging nZVI. Through this research, it would be better to keep nZVI for a long time. The challenge with this study is that experimental errors were observed in the data, and the effect of long-term storage of nZVI modified by sulfurization or other means is uncertain. By resolving these issues, it's thought that it is expected to make new discoveries.

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