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Experimental Investigation for Nitrate Reduction Using Iron Powder in Porous Media

Haruka Shimada, Kazuya Inoue, Ikko Ihara, Katsutoshi Suzuki and Tsutomu Tanaka
Graduate School of Agricultural Science, Kobe University, Japan

ABSTRACT: This paper assessed the potential of iron powder as a nitrate reduction and retardation material in porous media. Under saturated and unsaturated flow conditions, column experiments were conducted in silica sand with a mixture of two kinds of iron powders. Experimental breakthrough curves were analyzed using temporal moments not only to estimate the retardation factor and the degradation rate but to quantify mass recovery fractions associated with nitrate and ammonium ions. The results showed the increase of the amount of iron powder resulted in the increase of the degradation rates and the retardation factor estimates. Moreover, the production of ammonium occurred by nitrate reduction was confirmed. A mixture of iron powder with soil has a potential to reduce the concentration of nitrate by the reduction of nitrate to ammonium and to retard a nitrate.

Keywords: Nitrate, Reduction, Iron Powder, Column Experiments

1. INTRODUCTION

Excessive nitrate concentrations in groundwater are related to land use activities including pastoral farming market gardening, application and leaching of nitrogenous fertilizers and industrial and sewage waste disposal [1]. Overloading agricultural soils with nitrogen leads to rising nitrate concentration in groundwater, while enhancing crop growth by the application of nitrogen gives economic benefits in many parts of the world. Protection of groundwater from nitrate contamination is an often overlooked health concern. The immediate health concern is the reduction of nitrate to nitrite in the digestive tract by nitrate-reducing bacteria. Nitrite is readily absorbed into the blood where it combines with the hemoglobin that carries oxygen, leading to the form of methemoglobin, which is unable to transport oxygen, and the physical stress. When severe enough, nitrate poisoning is life threatening because of suffocation, which is called methemoglobinemia, or blue baby syndrome, in infants [2], [3]. Nitrate released to the environment can also increase eutrophication levels in rivers or lakes.

In general, nitrate can readily be transported beneath the soil zone without ion exchange or adsorption to soil surface. Therefore, high concentration of nitrates can be found in shallow groundwater systems, especially in sandy aquifers [4],[5]. There has been developed many processes for removing nitrate from water, including biological denitrification, separation with ion exchange or reverse osmosis and reduction by chemical reductants [6]. However, almost all treatment processes are performed after groundwater extraction by wells or drains, which is the primary technology to treat contaminated groundwater [7], and have a markedly different property from the reduction of nitrate concentrations at a source in a contaminated site. In addition, at a vast contaminated site groundwater extraction might be ineffective [8]. This ineffectiveness has been led to the development of alternative and unique approaches towards groundwater cleanup [9]-[11].

At present, reduction of nitrate using zero-valent iron (Fe^0 or ZVI) is a highly exergonic reaction and is expected to be an alternative for nitrate removal from water [6]. ZVI has been used to remediate contaminated groundwaters by placing large quantities of granular metal to act as a permeable barrier [12]. Although nitrate reduction using ZVI is a rapid reaction if the solution pH remains within an acidic range [13], the formation of passivating scales on the ZVI over time may limit its long-term reduction potential since nitrate reduction by ZVI is a corrosive process. Previous work has demonstrated the ability for ZVI to reduce nitrate in batch experiments, with nearly stoichiometric recovery of nitrogen as ammonium [14],[15]. However, only a few studies have been reported the reduction of nitrate in column experiments [16].

The present work is aiming to evaluate the reduction of nitrate and nitrate transformation to ammonium ions by ZVI in columns where a sandy soil is homogeneously mixed with ZVI and to quantify the retardation of nitrate onto ZVI surfaces. Temporal moment approaches are applied to estimate the retardation factor and the degradation constant based on the experimental breakthrough curves (BTCs) in columns. Specifically, the effect of the weight ratio of ZVI to sandy soils on the degree of the retardation and degradation of nitrate is of concern to explore the possible use of ZVI in a field.

2. MATERIALS AND METHODS

2.1 Materials

For column experiments, silica sand with a low uniformity coefficient of 1.25 was selected in order to simulate a sandy aquifer having a relatively high hydraulic conductivity. Silica sand of interest had 0.050 cm and 2.68 g/cm^3 of physical properties such as the mean particle size and the particle density, respectively. A ZVI powder in hand warmer and a commercial ZVI powder with a high reduction property were used to compare the degree of nitrate reduction and retardation and were referred to as Material 1 and Material 2, respectively.

2.2 Column experiments

In column experiments, ZVI powder of concern was mixed with soil in order to examine the relation between the amount of ZVI powder and the degree of reduction of nitrate. From the practical viewpoint, mixture ratios of ZVI powder were set to 0%, 7.5%, 15% and 30% by weight. These soils with ZVI powder were completely saturated before packing to avoid the entrance of air and were filled into the column, which had 30 cm in length and 5 cm in

Table 1 Experimental cases.

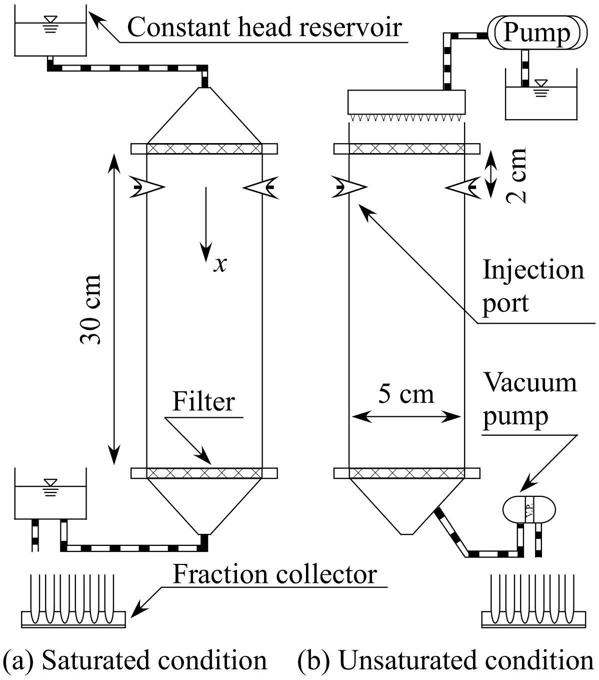
ZVI material	Mixture ratio of ZVI powder (%) *	Seepage velocity (cm/s) *	Volumetric water content (-)	Moisture condition
None (Sand only)				
	0	0.010, 0.037	0.41	Saturated
	0	0.053	0.30	Unsaturated
Material 1				
	7.5, 15, 30	0.010, 0.037	0.41	Saturated
	7.5, 15, 30	0.053	0.30	Unsaturated
Material 2				
	7.5, 15, 30	0.010, 0.037	0.41	Saturated
	7.5, 15, 30	0.053	0.30	Unsaturated

*All combinations of these factors were treated in column experiments.

diameter in increments of 2.5 cm. Each layer was compacted to adjust the dry density prior to filling the next layer. The porosity was able to be estimated in each experiment indirectly from the measurements of the particle density and the dry soil bulk density, resulting in approximately 0.41 of the porosity in flow field for both materials. In Fig. 1, the detailed column design is illustrated. Also, experimental cases are listed in Table 1.

After packing, as shown in Fig. 1(a), water was applied to the column up to a specific level controlled by constant head reservoirs at the top and bottom of the saturated media, while maintaining the saturated condition of porous media. Steady saturated flow field was established in the column when fluctuations in the observed drainage rate from the bottom reservoir became negligible. A volume of 40 cm^3 KNO_3 solution under saturated condition was applied to the top of the column to produce a pulse input with an initial concentration of 1.5×10^{-4} g/cm^3 of NO_3-N. Prescribed solute source condition was designed to clarify the transient concentrations of NO_3-N and to effectively provide the parameter identification relevant to solute transport using temporal moment approaches, which will be stated in the following subsection. Pore water samples at the end of the column were taken at specific intervals using a fraction collector. Nitrate ion in the pore water samples was analyzed by capillary electrophoresis (G1600A, Agilent technologies, USA). The basic anion buffer and a fused silica capillary with 104 cm in length and 50 μm internal diameter were obtained from Agilent technologies. The temperature controlled cartridge for fused silica was set at 15 °C. The concentration of ammonium ion was determined by the indophenol blue method using a spectrophotometer (HACH, DR-4000).

To investigate the impact of water content on the nitrate behavior, column experiments under unsaturated conditions were carried out in a similar manner but a different pulse volume of 20 cm^3 due to the difference of volumetric water content. As shown in Fig. 1(b) in unsaturated experiments, instead of constant head reservoir, suction was applied using a vacuum pump at the bottom of the column to keep the moisture content inside the column uniform while water was sprinkled over the top of the medium until the outflow from the bottom of the column equaled the volume of the water input. Prior to an application of solute pulse, samples were adjusted to steady state water flow condition.



(a) Saturated condition (b) Unsaturated condition

Fig. 1 Schematic diagram of experimental column system.

2.3 Temporal moment analysis

A sorbing and degradable chemical moving through a homogeneous medium at a steady and uniform flow rate is considered. Assuming linear, equilibrium sorption and first-order kinetic degradation for the solute, the governing transport equation can be written as

$$R\frac{\partial c}{\partial t} = \alpha_L v_p \frac{\partial^2 c}{\partial x^2} - v_p \frac{\partial c}{\partial x} - \lambda c \qquad (1)$$

where c is the concentration of solute, x is the coordinate, t is the time, R is the retardation factor estimate, v_p is the average pore water velocity, α_L is the dispersivity, and λ is the degradation rate [17].

Temporal moment analysis is convenient to use, as there is no need to solve the transport model in real time and degrees of spreading and asymmetry [18]. The n-th order temporal moments are defined as

$$M_n = \int_0^\infty t^n c(x,t)dt \tag{2}$$

The nomalized temporal moments μ_n at a location x, are defined as

$$\mu_n = \frac{M_n}{M_0} = \frac{\int_0^\infty t^n c(x,t)dt}{\int_0^\infty c(x,t)dt} \tag{3}$$

Equations (2) and (3) are used to obtain experimental temporal moments from concentration BTCs. Das and Kluitenberg [17] derived theoretical first temporal moment using Laplace formation of Eq. (1). By setting the experimentally determined moments equal to the theoretical moments, we can estimate the dispersivity and the retardation factor [19].

$$\alpha_L = \frac{\xi_p}{2} \frac{\mu_2}{\mu_1^2} \tag{4}$$

$$R = \frac{(\mu_1 - 0.5t_0)\sqrt{v_p^2 + 4\alpha_L v_p \lambda}}{x} \tag{5}$$

where ξ_p is the distance between the source and the observation location and t_0 is the pulse duration. In all experiments, t_0 was set to 30 seconds.

The mass fraction of solute that is collected in the effluent during column experiment is summed up to provide an estimate of the mass recovery fraction (MRF) [17].

$$\text{MRF} = \frac{\int_0^\infty Q(L,t)c(L,t)dt}{\int_0^\infty Q(0,t)c(0,t)dt} \tag{6}$$

where Q is the volumetric flow rates and L is the length of the soil column. MRF allows to obtain the degradation rate [17].

$$\lambda = \frac{1}{\mu_1} \ln\left(\frac{1}{\text{MRF}}\right) \tag{7}$$

3 RESULTS AND DISCUSSION

3.1 Effect of ZVI powder on nitrate retardation

Representative BTCs under different mixture ratios of ZVI powder as a function of pore volume for Materials 1 and 2 are shown in Fig. 2 and Fig. 3, respectively. Pore volume is calculated as

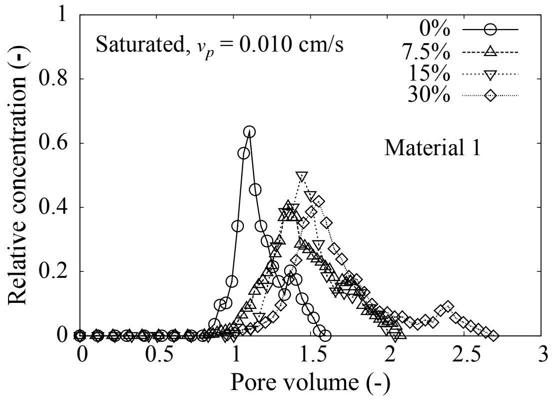


Fig. 2 Representative BTCs for different mixture ratios of ZVI powder in hand warmer under saturated condition.

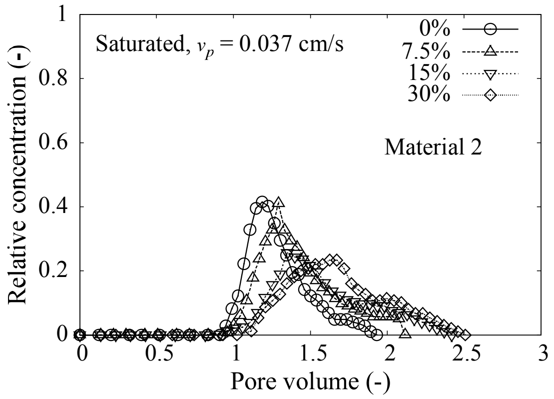


Fig. 3 Representative BTCs for different mixture ratios of commercial ZVI powder under saturated condition.

$$\text{Pore volume} = \frac{q_w t}{\theta L} = \frac{v_p t}{L} \tag{8}$$

where q_w is the water flux and θ is the volumetric water content. When solutes travel without the adsorption onto the soil particle, or the retardation, the pore volume becomes the unity.

As shown in Fig. 2 and Fig. 3, observed BTCs exhibit the shift of the peak concentration at the corresponding pore volume toward a larger pore volume with the increase of the amount of ZVI powder. A slight tailing of the BTCs, which shows an asymmetric shape and extends longer with the increase of the pore volume, can also be seen in Fig. 2 and Fig. 3, except for the case of 0% of the mixture ratio. These results imply that as for the influence of a mixture of ZVI powder and soil in a practical situation, degradation of nitrate concentration is expected due to the reaction of nitrate with ZVI powder as a travel time of nitrate from ground surface to groundwater becomes longer. Thus, for

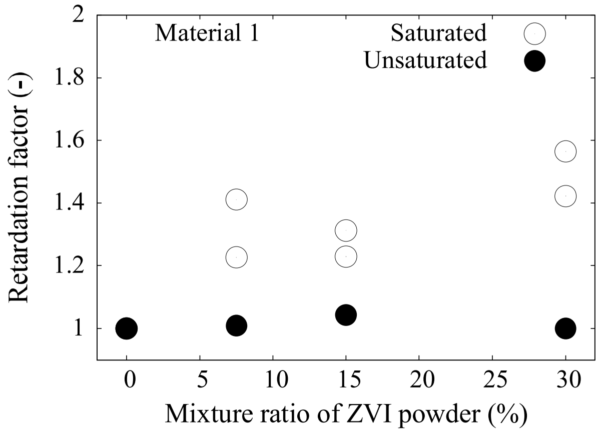


Fig. 4 Relation between the mixture ratio of ZVI powder in hand warmer and the retardation factor estimates.

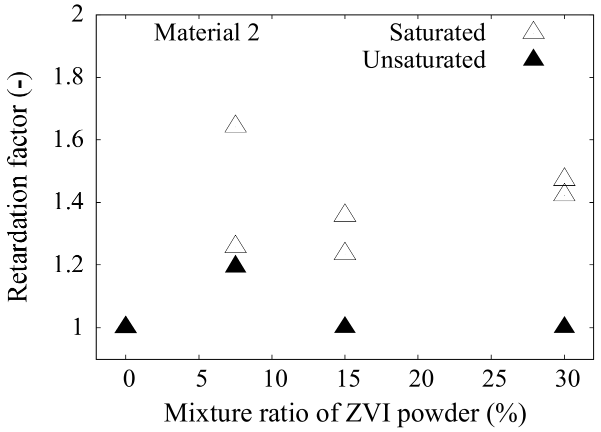


Fig. 5 Relation between the mixture ratio of commercial ZVI powder and the retardation factor estimates.

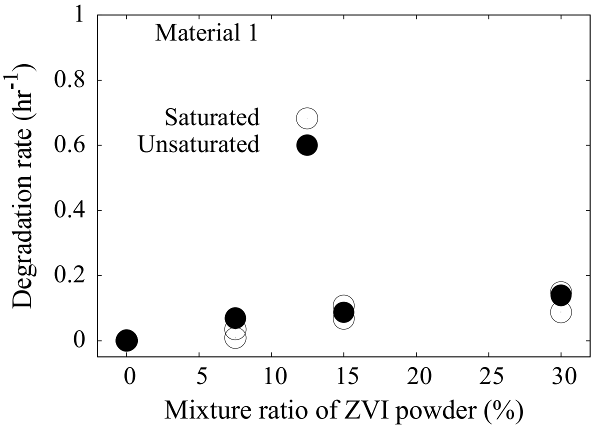


Fig. 6 Relation between the mixture ratio of ZVI powder in hand warmer and the degradation rate.

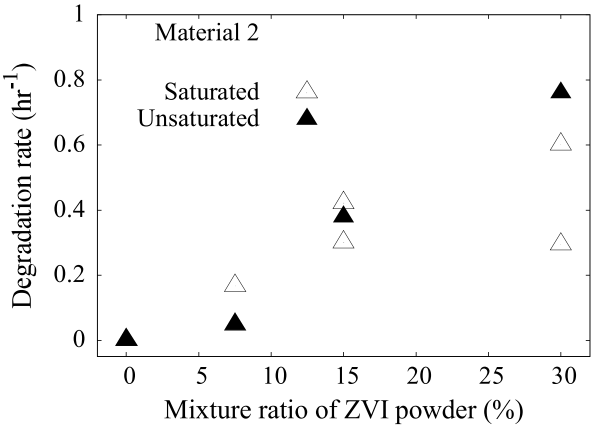


Fig. 7 Relation between the mixture ratio of commercial ZVI powder and the degradation rate.

the purpose of the retardation of nitrate, the use of ZVI powder might be effective in soils.

In order to quantify the degree of adsorption of nitrate onto ZVI powder, the retardation factor is employed as a measure and is estimated based on Eq. (5). The relation between the mixture ratio of ZVI powder and the retardation factor estimates for Materials 1 and 2 are shown in Fig. 4 and Fig. 5, respectively. As a whole, the retardation factor estimates are within the range of approximately 1.3 to 1.6 under saturated condition. Some kind of sorption of nitrate to ZVI powder may occur associated with the mixture of ZVI powder with soil. On the other hand, under unsaturated condition, the retardation factor estimates range from approximately 1.0 up to 1.2, indicating that the degree of adsorption under unsaturated condition is lower than that under saturated condition. This is because a less water content and a higher pore velocity may lead to decrease the course of transport under unsaturated condition in comparison with solute pathways under saturated condition.

The values of retardation factor between two kinds of ZVI powder, as seen in Fig. 4 and Fig. 5, vary with a similar tendency. In addition, the retardation factor estimates for both materials are almost the same values corresponding to the same mixture ratio of ZVI powder. These results show that there is no difference in the degree of adsorption between two materials.

3.2 Effect of ZVI powder on nitrate reduction

To quantify the effect of ZVI powder on nitrate reduction during a transport, degradation rate estimates are calculated using Eq.(7) and are plotted as a function of mixture ratio of ZVI powder for Materials 1 and 2 in Fig. 6 and Fig. 7, respectively. Regardless of water content, the degradation rate increases as the amount of ZVI powder increases for both materials, suggesting that the increase of the amount of ZVI powder is expected to contribute nitrate reduction. As stated in the preceding subsection, under saturated condition, the opportunity of adsorption of nitrate to ZVI powder may occur due to the mixture of ZVI powder with soil and may enhance the nitrate reduction in the duration occurring adsorption phenomena. In contrast to the results of retardation factor estimates under saturated condition, as shown in Fig. 4 and Fig. 5, values of retardation factor are little change in the range of approximately 1.0 to 1.2 regardless of the mixture ratio of ZVI powder under unsaturated condition. However, the degradation rates exhibit a little difference between saturated and unsaturated

Table 2 MRF of each mixture ratio of ZVI powder.

Nitrogen species	Moisture condition	Mixture ratio of ZVI powder (%)	Material 1			Material 2		
		0	7.5	15	30	7.5	15	30
NO_3-N	Saturated	1.000	0.976	0.924	0.930	0.939	0.853	0.795
NH_4-N	Saturated	0.000	0.003	0.000	0.005	0.038	0.044	0.090
NO_3-N	Unsaturated	1.000	0.990	0.985	0.978	0.992	0.951	0.893
NH_4-N	Unsaturated	0.000	0.003	0.009	0.000	0.010	0.048	0.109

conditions at the same amount of ZVI powder as seen in Fig. 6 and Fig. 7. This may attribute to the presence of air under unsaturated condition, enhancing a prompt oxidation of ZVI powder, since corrosion process may induce the nitrate reduction [15].

As for the case of Material 1, the degradation rate estimates are in the range of approximately 0.09 hr^{-1} to 0.15 hr^{-1} in Fig. 6, when pH ranges from 7 to 9 in this study. The results are in good agreement with a previous study. Alowitz and Scherer [9] reported the degradation rate of approximately 0.13 hr^{-1} at pH 8. In the comparison with two kinds of ZVI powder, although the retardation factor estimates have similar values, the degradation rates hinge on the material of interest. In the case of Material 2 as shown in Fig. 7, the estimate of degradation rate at 7.5% of the mixture ratio is about 2 times larger than that of Material 1 in Fig. 6. At 30% of the mixture ratio, the degradation rate of Material 2 becomes about 4 times larger than that of Material 1. These results show that commercial ZVI powder is more effective than ZVI powder in hand warmer from the point of view of nitrate reduction.

3.3 Mass recovery fraction

In the process of nitrate reduction, the product of ammonium and relevant mass recovery are of important. Table 2 lists the MRFs for different mixture ratios of ZVI powder estimated from Eq. (6) in order to compare the total amount of NO_3-N leaching from the bottom of the column with the total amount of NH_4-N yielded by NO_3-N reduction. As for the results under saturated conditions, the mean values of two experimental cases having different seepage velocities are shown. The reaction of nitrate reduction can be described by Eq. (9) [16].

$$NO_3^- + 10H^+ + 4Fe^0 \rightarrow NH_4^+ + 3H_2O + 4Fe^{2+} \quad (9)$$

As seen in Table 2, the MRF of NO_3-N decreases with the increase of the mixture ratio of ZVI powder, resulting in the increase of the MRF of NH_4-N, particularly in Material 2. Interestingly, the loss of NO_3-N does not necessarily correspond to the production of NH_4-N, especially in the media mixed with Material 1. It appears that a part of nitrate or ammonium ion may strongly adsorb to ZVI powder and remain in the column, consequently leading to the unbalance of the total MRFs of NO_3-N and NH_4-N.

Moreover, the MRF of NH_4-N of Material 2 is about 10 times larger than that of Material 1 at the same mixture ratio, indicating the property of commercial ZVI powder in terms of nitrate reduction to ammonium. On the contrary to this, nitrate is slightly converted to ammonium by the reaction between nitrate and Material 1. Hence, single application of Material 1 becomes less effective in the nitrate degradation.

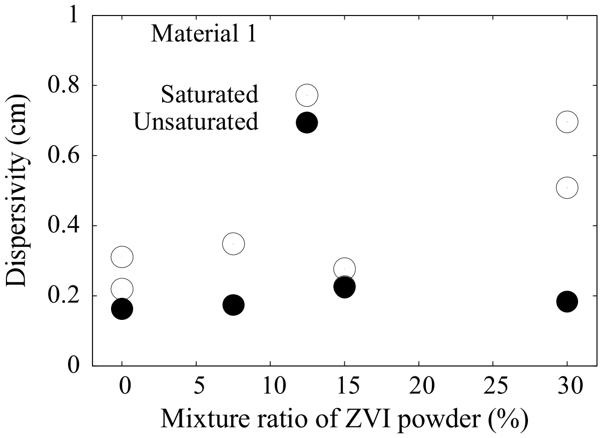


Fig. 8 Relation between the mixture ratio of ZVI powder in hand warmer and the dispersivity.

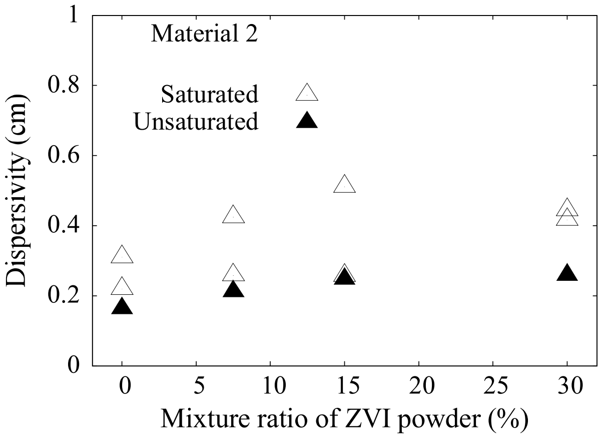


Fig. 9 Relation between the mixture ratio of commercial ZVI powder and the dispersivity.

3.4 Effect of ZVI powder on dispersivity

The spread of the nitrate in soils is also important in a field application of ZVI powder. The dispersivities of nitrate are also estimated from Eq. (4), and are shown as a function of mixture ratio of ZVI powder for Materials 1 and 2 in Fig. 8 and Fig. 9, respectively. As seen in Fig. 8 and Fig. 9, the longitudinal dispersivity estimates range from approximately 0.16 cm to 0.70 cm and slightly increase with increasing the mixture ratio of ZVI powder because of the influence of the mixture of ZVI powder and soil. The longitudinal dispersivity at maximum mixture ratio of ZVI powder is about 3 times larger than the case without ZVI in porous media. Therefore, the effect of the mixture of ZVI powders in field soils on nitrate dispersion may be relatively lower.

4 CONCLUSIONS

This paper assessed the potential of zero-valent iron (ZVI) powders as a nitrate reduction and retardation material in porous media. Under saturated and unsaturated flow conditions, column experiments were conducted in silica sand with a mixture of two kinds of ZVI powders. Experimental breakthrough curves were analyzed using temporal moments not only to estimate the retardation factor and the degradation rate but to quantify mass recovery fractions associated with nitrate and ammonium ions. The findings of this study are drawn as follows:

1) The retardation factor estimates under saturated condition were slightly larger than those under unsaturated condition regardless of the kinds of ZVI powders.
2) The increase of the amount of ZVI powder resulted in the increase of the degradation rate regardless of the water content. The degradation rates of commercial ZVI powder were larger than those of ZVI powder in hand warmer, indicating that commercial ZVI powder was more effective in the reduction of nitrate to ammonium.
3) According to the results of the mass recovery fraction, it was confirmed that ammonium was produced by reduction of nitrate in the presence of ZVI. The degree of production of ammonium increased with increasing the amount of ZVI powder, especially for commercial ZVI powder.
4) The longitudinal dispersivities slightly increased with increasing the mixture ratio of ZVI powder.

5 ACKNOWLEDGMENT

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Corresponding Author: Haruka Shimada