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Effect of phosphate rock on denitrification in a nitrate-polluted groundwater remediation system

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ABSTRACT

This study was conducted to evaluate the performance of phosphate rock for the promotion of denitrification in groundwater remediation. The results showed that phosphate rock can release phosphorus in the leaching experiment and thus has potential to provide phosphorus for denitrifying bacteria growth. In column experiments, the nitrate removal efficiency of columns containing 1,500 and 750 g of phosphate rock was over 97% at 20 ± 2°C, and the nitrite concentrations were lower than 0.5 mg NO_2-N/L. However, the nitrate removal efficiency in columns containing 500 and 0 g of phosphate rock was lower than 90%, and nitrite accumulation was observed. Additionally, the nitrate concentration in effluent increased evidently when the influent flow rate was increased from 2.6 to 3.6 mL/min. Nevertheless, nitrate removal efficiency of columns containing 1,500 and 750 g of phosphate rock was higher than that of columns containing 500 and 0 g of phosphate rock. These findings indicated that phosphate rock was applicable as a phosphorus source for nitrate-polluted groundwater remediation.

Keywords: Groundwater; Nitrate; Biological denitrification; Phosphate rock

1. Introduction

Nitrate concentrations in groundwater have increased in many locations in the world. Potential sources of nitrate in groundwater include agricultural fertilizers, animal waste disposal, and improper disposal of industrial effluent [1,2]. Long-term drinking of nitrate-contaminated water may cause some health problems, such as methemoglobinemia and some cancers [3,4]. Consequently, the World Health Organization (WHO) set a threshold of 11.3 mg NO_3-N/L for drinking water to prevent negative effects [5].

Conventional methods for nitrate removal from contaminated groundwater include ion exchange, reverse osmosis, electrodialysis, and chemical reduction [6–9]. These methods have been proven effective for nitrate removal from groundwater. Biological denitrification is receiving considerable attention for removing nitrate from groundwater because of its

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high efficiency, moderate cost, and environmental soundness. In previous studies, denitrification-based processes have generally been limited to *ex situ* treatment in bioreactors, which are costly and complicated to operate [10,11]. *In situ* treatment system has recently become the focus of groundwater treatment and some researchers have investigated the use of permeable reactive barriers (PRBs) as a means of removing nitrate from flowing groundwater [12,13]. The denitrification efficiency of PRBs is influenced by dissolved oxygen (DO), temperature, organic carbon, and phosphorus [14–16]. In previous studies, considerable attention has focused on carbon sources, and the feasibility of using ethanol, molasses, and sawdust as carbon sources have been reported to stimulate microbial denitrification [17–19]. However, less attention has been directed toward phosphorus sources, although phosphorus is one of the major essential microbial nutrients for biological growth and development. De Vet et al. [20] found that microbial growth rates were limited at less than 100 μg PO_4-P/L and virtually stopped at less than 10 μg PO_4-P/L. Hunter [15] found that phosphorous concentrations can be correlated with nitrate reduction and that nitrate can be reduced completely when the level of available phosphorous is sufficient. Furthermore, the movement of phosphate through phosphate retention soils is significantly slower than that of nitrate [21], causing low levels of phosphorus in groundwater. Thus denitrification could be limited in underlying aquifers. Therefore, considering supplemental phosphorus sources is important when designing denitrifying barriers for treating nitrate-polluted groundwater. Synthetic phosphate-P sources, such as KH_2PO_4, have generally been used to stimulate microbial denitrification [22]. However, these sources are costly and require sophisticated process control when using in groundwater remediation systems. Accordingly, a great deal of attention has recently been focused on natural solid phosphorus sources. Hong et al. [23] found that nitrate removal efficiency can be enhanced by wheat rice stone (WRS) because WRS can leach trace elements and phosphorous to promote bacterial growth.

Phosphate rock originates mainly from igneous or sedimentary rock sources and consists of calcium phosphate. Extensive studies on the potential and actual effectiveness of phosphate rock as source of phosphorus mainly focus on commercial phosphate fertilizers and elemental phosphorus. However, few studies investigated the use of phosphate rock as a phosphorus source to enhance denitrification efficiency. In view of the potentially high phosphorus content, phosphate rock may be a suitable phosphorus source for denitrifying bacteria to stimulate denitrification in nitrate-polluted groundwater remediation.

In this study, to evaluate the effects of denitrification supported by phosphate rock and to identify the appropriate solid phosphorus source for groundwater remediation, the phosphorus release capability and performance of phosphate rock for the promotion of denitrification were investigated in laboratory denitrifying columns.

2. Materials and methods

2.1. Chemicals

Chemicals used in this study were of analytical reagent grade. Phosphate rock, obtained from Yunnan Province (China) and ground to grains of 2.0–4.0 mm, was selected as potential phosphorus sources. Washed zeolite (2.0–4.0 mm) was used as an inert material to fill the columns. The densities of phosphate rock and zeolite were 2.55 and 2.40 g/cm^3, respectively.

Phosphate rock and zeolite were washed, air-dried, and ground to a homogeneous fine powder, and then their elemental composition were analyzed by X-ray fluorescence spectrometry (S4-Explorer, Bruker, Germany). The elemental composition of phosphate rock is given in Table 1. The phosphorous content of zeolite is 0.09%, significantly lower than that of phosphate rock zeolite (13.6%).

According to previous findings [24], biodegradable plastic (BP) was selected as a potential carbon source for denitrifying bacteria. BP (φ2.0 × 5.0 mm), which was composed of 60% starch and 30% polypropylene, was obtained from Zhaohe Ecological Technology Company (China) and was analyzed for elemental composition using an elemental analyzer (Elementar Vario MACRO, Elementar Analysensysteme GmbH, Germany). Elemental analysis indicated that the total carbon and nitrogen contents of BP were 43.91% and 0.08%, respectively.

2.2. Groundwater

In this study, groundwater used in the column experiments was pumped from China University of Geosciences (Beijing). The composition of raw

Table 1
Elemental composition of phosphate rock

O	Ca	P	F	Fe	Si	Other elements
43.9%	34.1%	13.6%	3.57%	1.43%	1.26%	2.14%

groundwater is given in Table 2. Before use, groundwater was amended with an appropriate mass of $NaNO_3$ to achieve a nitrate concentration of 50 mg NO_3-N/L. The pH in prepared synthetic groundwater was 7.0–8.0. Seed sludge was obtained from Tsinghua University Wastewater Treatment Plant, Beijing, in which the suspended solids and volatile suspended solids were 7,300 and 5,110 mg/L, respectively.

2.3. Leaching experiments

Leaching experiments were conducted to determine the phosphorus released from phosphate rock. Phosphate rock was washed with distilled water and air-dried completely. Then, 100 g of phosphate rock was added to a 2,500 mL Erlenmeyer flask and then sterilized in an autoclave (YX-208D, Huatai, China) for 15 min (120℃). After sterilization, 2,000 mL of distilled water were added to the flasks and stirred slowly by 100r/min with a magnetic stirrer (H01-1C, Shanghai Meiyingpu, China). The flask was sealed with glass stopper, and the experiments were performed at 25℃. The supernatant was taken at the desired time interval (0.25–36 h) from the flask and were analyzed for pH and TP.

2.4. Batch adsorption experiments

To determine the influence of packing materials on the nitrogenous species in column experiments, batch adsorption experiments were conducted by adding 100 g of phosphate rock, 100 g of zeolite, and 100 g of BP to three 2,500 mL Erlenmeyer flasks. The flasks were then sterilized in an autoclave for 15 min (120℃). Afterwards, 1,500 mL of solutions containing 50 mg NO_3-N/L, 20 mg NH_4-N/L, and 10 mg NO_2-N/L were added to the flasks. Each flask was then sealed with a glass stopper, and the experiments were conducted at 25℃. The supernatant was taken at the desired time interval (0.25–36 h). The samples were analyzed for nitrate (NO_3-N), nitrite (NO_2-N), and ammonium (NH_4-N).

The adsorption of packing materials on TP in column experiments was ignored because natural zeolite showed poor phosphorus adsorption capacity [25,26].

2.5. Column experiments

Four PVC columns (10.0 cm in internal diameter, 50.0 cm in length) were used (Fig. 1). Each column has three sampling ports spaced along the length of the columns. The ports were installed at 17 cm (P_1), 32 cm (P_2), and 47 cm (P_3) from the base of the columns.

The three columns were filled with a mixture of zeolite, phosphate rock, and BP, containing 600 g of BP + 500 g of phosphate rock + 2,500 g of zeolite, 600 g of BP + 750 g of phosphate rock + 2,250 g of zeolite, and 600 g of BP + 1,500 g of phosphate rock + 1,500 g of zeolite, whereas the control column was filled with the mixture of zeolite (3,000 g) and BP (600 g), with no phosphate rock added. These packing materials were immersed in 2,000 mL of sludge for 24 h, mixed homogeneously, and then packed in each column. Quartz sand (1.0–2.0 mm) was placed at both ends of the column to hold the packing materials. Each column was sealed to create anaerobic conditions and then covered with an opaque material to prevent light exposure.

A polyethylene tank (25 L) served as the synthetic groundwater storage tank. The synthetic groundwater containing 50 mg NO_3-N/L was pumped upward into the columns using a four-channel peristaltic pump (LEAD-2, Baoding Longer Precision Pump Co., Ltd, China) through Tygon laboratory tubing. Similarly, Tygon laboratory tubing was used to carry effluent away from the top of the columns for disposal.

The column experiments were operated for 100 d and were divided into four periods according to the different experimental conditions. In the first period, the column experiments were conducted at 20 ± 2℃ for 30 d, and the influent flow rate was 2.0 mL/min. In the second period, the temperature increased to 25 ± 2℃, the influent flow rate was 2.0 mL/min, and the experiments were operated for 39 d. Thereafter, the influent flow rate was gradually increased to 2.6 and then to 3.6 mL/min. Samples were collected from the effluent line to analyze pH, oxidative redox potential (ORP), DO, NO_3-N, NO_2-N, NH_4-N, and TP.

2.6. Analytical methods

pH was measured by a pH meter (UB-7, Denver Instrument, USA). ORP was measured by an ORP meter (ORPTestr 10, OAKTON, USA). DO was

Table 2
Composition of raw groundwater used for the column study (mg/L)

NO_3-N	NO_2-N	NH_4-N	TP	HCO_3	SO_4	Cl	Ca	Mg	K	Na
2.5	0	0.16	0.03	39.6	50.8	31.5	38.6	15.9	2.75	23.5

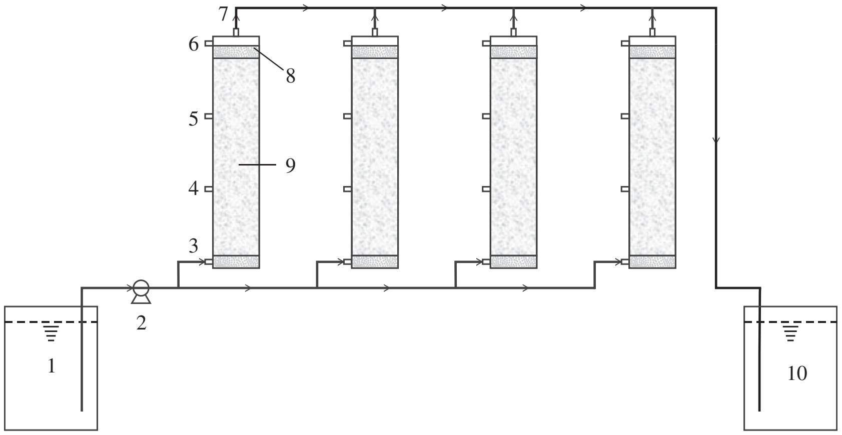

Fig. 1. Schematic of the column experiments setup. (1) Reservoir, (2) peristaltic pump, (3) inlet, (4) sampling port (P_1), (5) sampling port (P_2), (6) sampling port (P_3), (7) outlet, (8) quartz sand, (9) packing materials, and (10) collecting tank.

measured by a DO meter (DO 110, Eutech Instruments, Singapore). Nitrate, nitrite, ammonium, and TP were analyzed using a spectrophotometer (DR 5000, HACH, USA) according to the Water and Wastewater Monitoring Analysis Method [27]. Before analysis, all samples were filtered using 0.45 μm membrane filters.

3. Results and discussion

3.1. Phosphorous concentrations leached from phosphate rock

The leaching experiment was performed to simulate the migration and leaching behavior of the phosphorous from phosphate rock. Fig. 2 shows that TP was rapidly released from phosphate rock in the first 6 h and more slowly continued until an apparent equilibrium was reached. In particular, the leached TP increases rapidly from the beginning of the experiments and reached 8.0 mg/L at 6 h. Afterwards, the TP remained constant until the end of the experiments. Two distinct phases of release appeared. The rapid phase indicates that the high release rate of TP will supply phosphorus for denitrifying bacteria in a short period. By contrast, the slow phase indicates that the slow TP release will supply phosphorus to denitrifying bacteria for a longer period.

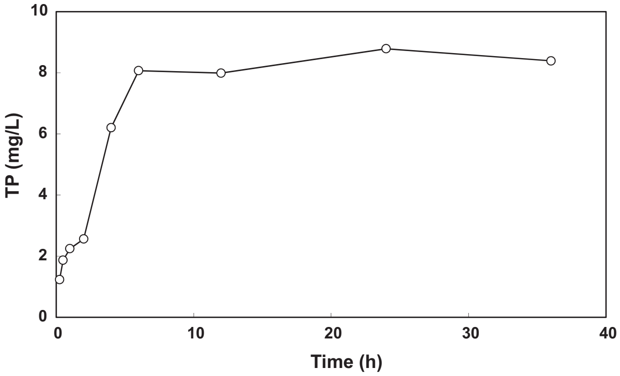

Fig. 2. TP leached from phosphate rock over time in leaching experiments. Phosphate rock dosage: 100 g; distilled water volume: 2,000 mL; temperature: 25℃.

These results indicate that phosphate rock has the potential to provide phosphorus for denitrifying bacteria growth. Furthermore, phosphate rock can provide increasing phosphorus when micro-organisms are present [28]. Consequently, phosphate rock can provide phosphorous for denitrifying bacteria when used as a phosphorus source for *in situ* nitrate-polluted groundwater remediation. Value of pH in the flask remained neutral with a range between 7.0 and 7.5. The neutral pH is beneficial for the development of denitrifying bacteria in future applications.

3.2. Batch adsorption experiments

Fig. 3 presents the results of the adsorption experiments. The percentage adsorption (%) was calculated using the following equation:

$$\%\ \text{Adsorption} = (C_0 - C_f)100/C_0 \tag{1}$$

where C_0 and C_f are the concentrations of the nitrogen compounds in the initial and final solutions, respectively.

As shown in Fig. 3(A) and (B), the percentage adsorptions of NO_3-N and NO_2-N were lower than

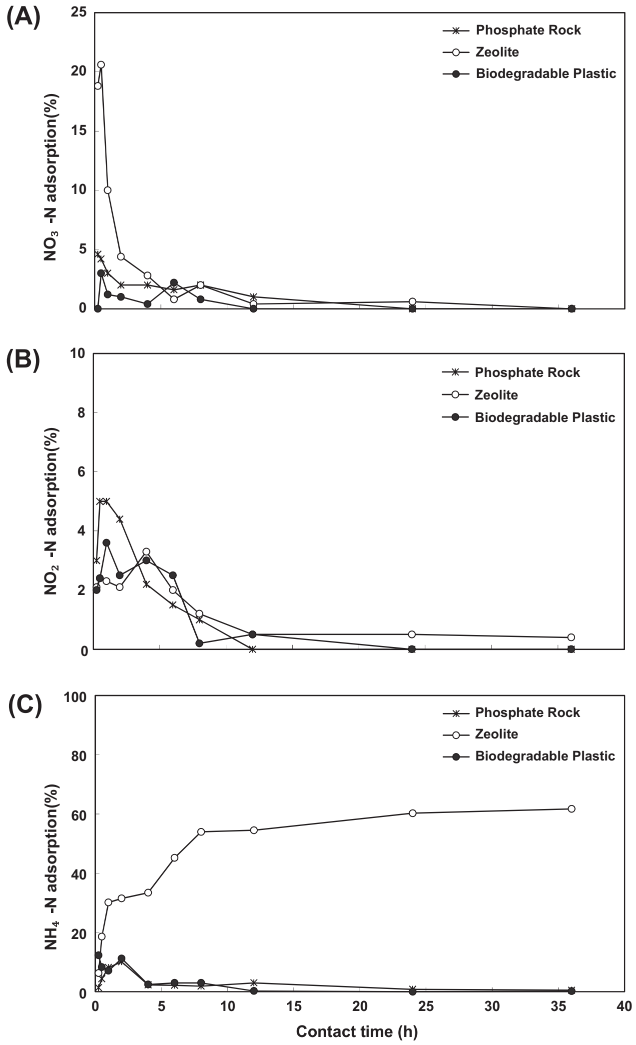

Fig. 3. NO_3-N, NO_2-N, and NH_4-N adsorption from synthetic solutions. Initial concentrations: 50 mg NO_3-N/L, 20 mg NH_4-N/L, 10 mg NO_2-N/L. Temperature: 25℃.

3% when the adsorption equilibrium occurred after 8 h, indicating that the influences of adsorptions of nitrate and nitrite by phosphate rock, zeolite, and BP on denitrification in column experiments can be neglected. Moreover, the adsorption of NH_4-N by phosphate rock and BP were lower than 3% after 4 h and lower than 1% or showed no adsorption at the end of the experiments. Conversely, zeolite had an evident adsorption of NH_4-N (Fig. 3(C)). A higher adsorption rate is observed in the first 1 h, and the percentage adsorption of NH_4-N was 30%. Thereafter, the adsorption rate became slow and the adsorption percentage of NH_4-N was 54% when adsorption equilibrium occurred at 8 h. After 8 h, the adsorption percentage of NH_4-N was slightly changed, indicating that the NH_4-N capacity of zeolite attained saturation.

As a result, the adsorption of phosphate rock, zeolite, and BP for NO_3-N and NO_2-N in column experiments was low. Moreover, the phosphate rock and BP did not absorb NH_4-N. Meanwhile, the adsorption of NH_4-N by zeolite may result in the removal of some NH_4-N by adsorption in column experiments at the initial time.

3.3. Column experiments

3.3.1. Environmental parameters in the columns

Denitrification is a biochemical reaction and can be influenced by many environmental factors. The pH in the columns remained neutral, fluctuating with values between 6.0 and 7.5, and no apparent differences were observed among the columns. The high denitrification rates depend on the anaerobic circumstances of the constructed system. In this study, ORP was measured as an overall redox parameter to indicate the reduction conditions of the column, and the ORP in effluent remained between −130 and −260 mV throughout the experiments. DO in the influent was approximately 7.0 mg/L, but was rapidly consumed in each column after the beginning of the experiments. After 9 d, the values fluctuated between 1.5 and 0.9 mg/L. Consequently, the neutral pH, low ORP, and rapid consumption of DO indicated that anoxic conditions were favorable for denitrification in each column.

3.3.2. Performance of the columns at different temperature

To investigate the influence of phosphate rock on denitrification at different temperatures, column experiments were conducted at 20 ± 2℃ and 25 ± 2℃, respectively.

3.3.2.1. Nitrate removal. The nitrate concentration in the effluent from the four columns is shown in Fig. 4(A). The nitrate removal efficiency varied with the amount of phosphate rock added. When the temperature was 20 ± 2℃, the nitrate concentrations in the effluent evidently decreased from the initial 50 mg NO_3-N/L to below 1.0 mg NO_3-N/L in 5 d for all columns. Thereafter, the nitrate concentrations in the effluent from the columns containing 1,500 and 750 g of phosphate rock was lower than 1.5 mg NO_3-N/L, and the nitrate removal efficiency was over 97%. Meanwhile, the nitrate concentrations in the effluent from the columns containing 500 and 0 g of phosphate rock increased rapidly from the fifth day, with the maximum values of 5.21 and 7.78 mg NO_3-N/L, respectively, and the nitrate removal efficiencies were 89% and 84%, respectively. Therefore, the columns containing 1,500 and 750 g of phosphate rock showed

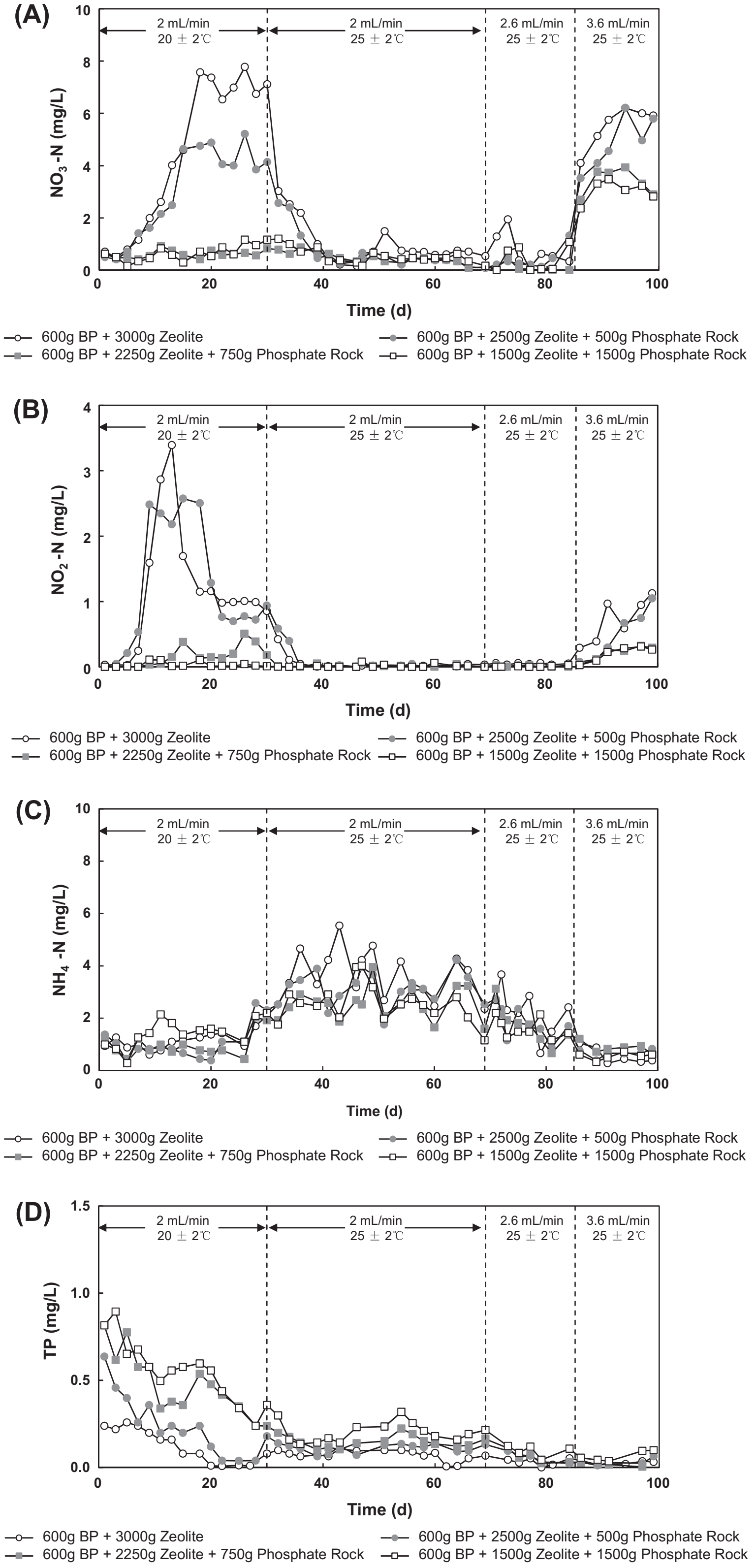

Fig. 4. Change in NO_3-N, NO_2-N, NH_4-N, and TP in column effluents. The concentration of the feed water for the column was 50 mg NO_3-N/L.

higher nitrate removal efficiency than the columns containing 500 and 0 g of phosphate rock. The possible reason for this difference is that the phosphorus concentrations in the columns containing 1,500 and 750 g of phosphate rock were high and can support denitrification completely.

After 30 d, the temperature increased from 20 ± 2 to 25 ± 2℃ to investigate the effects of phosphate rock on denitrification at high temperature, and complete nitrate reduction (>98%) was achieved in columns containing 1,500 and 750 g of phosphate rock. Additionally, the nitrate removal efficiency of columns containing 500 and 0 g of phosphate rock was considerably increased when compared with that at 20 ± 2℃, resulting in a nitrate concentration in the effluent lower than 2.0 mg NO_3-N/L after 39 d (Fig. 4(A)). The most likely reason for this is that a suitable temperature for denitrifying micro-organism can improve denitrification rate. Thus, when ambient temperature increased from 20 to 25℃, denitrification rate improved and the effluent NO_3-N decreased. The capacity of columns containing 500 and 0 g of phosphate rock for removing nitrate may cause the addition of phosphate rock into the aquifer to be unnecessary. Notably, the temperature (25 ± 2℃) is not the representative of shallow groundwater temperature, which is usually below 20℃ [29,30]. Consequently, phosphate rock should be added to *in situ* groundwater remediation for the enhancement of denitrification.

3.3.2.2. Accumulation of nitrite and ammonium. Nitrite, the intermediate product of nitrate reduction, is undesirable because it is more toxic to human health than nitrate. Accordingly, its conversion would present concern during denitrification, as the WHO maximum contaminant level for nitrate is 11.3 mg NO_3-N/L whereas that for nitrite is 0.03 mg NO_2-N/L.

From Fig. 4(B), the nitrite significantly accumulated in the columns containing 500 and 0 g of phosphate rock when the experiment temperature was 20 ± 2℃, with the maximum concentrations of 2.575 and 3.392 mg NO_2-N/L, respectively, significantly higher than 0.03 mg NO_2-N/L, which is the maximum permissible concentration set by the WHO. By contrast, the nitrite concentrations in the effluent from the columns containing 750 and 1,500 g of phosphate rock were less than 0.5 mg NO_2-N/L or were undetected in this period. The nitrite accumulation was attributed to the incomplete reduction of nitrate caused by some factors, such as organic carbon supply, the phosphate concentration, temperature, and oxygen content [14,15,31,32]. In this study, it can be reasonably inferred that the deficiency of available phosphorus in the columns containing 500 and 0 g phosphate rock may have been the leading factor contributing to nitrite accumulation. Chang et al. [33] found that phosphate concentration significantly affected the accumulation of nitrite. Hunter [15] also reported that nitrite accumulated when the phosphorus was insufficient.

From these results, it can be concluded that phosphorus have an important significance for denitrification, and the availability of phosphorus did not limit the denitrification process in the columns containing 750 and 1,500 g of phosphate rock in the experiments.

Likewise, ammonium production was observed in four columns. As shown in Fig. 4(C), no apparent differences were observed among the columns, with concentrations of 0.272–2.575 mg NH_4-N/L being observed when the experiment temperature was 20 ± 2℃. The formation of ammonium suggested that dissimilatory nitrate reduction to ammonia (DNRA) occurred. DNRA is a further anaerobic reduction reaction that competes with denitrification and converts nitrate to ammonium rather than N_2 [34]. Consequently, DNRA is seen as a counterproductive process in denitrification studies. Ammonium production was also observed when using wheat straw, sawdust, and BP as carbon sources in column experiments [24].

After 30 d, the temperature was increased from 20 ± 2 to 25 ± 2℃. The nitrite concentration in the effluent was less than 0.1 mg NO_2-N/L or undetected when steady-state conditions were achieved for all columns. It can be concluded that the influence of phosphorus on denitrification weakens when the temperature increased from 20 ± 2 to 25 ± 2℃.

Furthermore, the concentration of ammonium increased to a maximum value of 5.535 mg NH_4-N/L 43 d after the temperature increased to 25 ± 2℃, which occurred because higher temperature in synthetic groundwater favored DNRA over denitrification under anaerobic conditions, which finally caused ammonium accumulation [35].

3.3.2.3. TP in effluent. As shown in Fig. 4(D), the TP concentrations in the effluent from columns containing 1,500 and 750 g of phosphate rock were higher than that in the effluents from columns containing 500 and 0 g of phosphate rock, with the maximum TP concentration of 0.894 mg/L. This result conformed to the findings that the columns containing 1,500 and 750 g of phosphate rock showed higher nitrate removal efficiency than the columns containing 500 and 0 g of phosphate rock. These results indicated that the availability of phosphorous in columns containing 1,500 and 750 g of phosphate rock did not limit the denitrification process. However, the phosphorous in columns containing 500 and 0 g of phosphate rock were insufficient for denitrification. Kruithof et al. [36] found that denitrification was incomplete when the phosphorous levels were lower than 0.2 mg/L. Moreover, the nitrate removal efficiency had no apparent differences among the columns containing 1,500 and 750 g of phosphate rock. Consequently, the amount of phosphate rock added should be appropriate for in-situ groundwater remediation, and nitrate cannot be reduced completely if the phosphate rock added was insufficient. However, excessive phosphate rock may result in higher phosphorous in the groundwater.

3.3.3. Performance of the columns at different influent flow rate

After 69 d, the influent flow rate was increased from 2.0 to 2.6 mL/min and then to 3.6 mL/min to investigate the effects of phosphate rock on denitrification at different influent flow rates. As shown in Fig. 4(A), complete nitrate reduction was achieved at 2.6 mL/min, and the effluent nitrate concentrations of each column were low, ranging from 0.12 to 1.94 mg NO_3-N/L (0 g of phosphate rock), 0.21 to 1.32 mg NO_3-N/L (500 g of phosphate rock), 0 to 0.46 mg NO_3-N/L (750 g of phosphate rock), and 0 to 1.08 mg NO_3-N/L (1,500 g of phosphate rock). Meanwhile, little nitrite accumulation occurred in each column, with values between 0.034 and 0.057 mg NO_2-N/L (0 g of phosphate rock), 0 and 0.027 mg NO_2-N/L (500 g of phosphate rock), 0 and 0.027 mg NO_2-N/L (750 g of phosphate rock), and 0 and 0.023 mg NO_2-N/L (1,500 g of phosphate rock). Thereafter, the influent flow rate was increased to 3.6 mL/min at 85 d, and nitrate breakthrough occurred, with the maximum nitrate concentration in the effluent being 6.21 mg NO_3-N/L (0 g of phosphate rock), 6.21 mg NO_3-N/L (500 g of phosphate rock), 3.93 mg NO_3-N/L (750 g of phosphate rock), and 3.06 mg NO_3-N/L (1,500 g of phosphate rock). Moreover, nitrite accumulation was observed and reached a maximum of 1.127 mg NO_2-N/L (0 g of phosphate rock), 1.048 mg NO_2-N/L (500 g of phosphate rock), 0.291 mg NO_2-N/L (750 g of phosphate rock), and 0.265 mg NO_2-N/L (1,500 g of phosphate rock). These findings indicated that nitrate breakthrough occurred, and nitrite accumulated when the influent flow rate was increased to 3.6 mL/min. However, nitrate removal efficiency of columns containing 1,500 and 750 g of phosphate rock was better than the columns containing 500 and 0 g of phosphate rock. Thus, phosphate rock was applicable for further use as a phosphorus source for *in situ* nitrate-polluted groundwater remediation.

3.3.4. Influence of column depth on denitrification

The columns were designed with three sampling ports spaced evenly along the length of columns. Fig. 5(A) shows the profile of nitrate and nitrite for columns 66 d after steady-state conditions were achieved. The profile along the column revealed that nitrate was gradually diminished from 50 mg NO_3-N/L in the inlet to 1.08 and 2.28 mg NO_3-N/L in sampling ports P_1 (i.e. within the first 17 cm of the columns) of columns containing 1,500 and 750 g of phosphate rock, significantly far lower than 11.3 mg NO_3-N/L—the maximum permissible concentration set by the WHO. However, the nitrate concentrations in columns containing 500 and 0 g of phosphate rock in P_1 were 11.69 and 12.96 mg NO_3-N/L, respectively. The nitrate concentrations continue to decrease along the columns to 0.29 and 0.17 mg NO_3-N/L in sampling ports P_2 for columns containing 1,500 and 750 g of phosphate rock, respectively, and complete denitrification (>99%) was achieved. Meanwhile, the nitrate concentrations in sampling port P_2 for columns containing 500 and 0 g of phosphate rock were considerably decreased when compared with the nitrate concentrations in sampling ports P_1, with values of 1.94 and 2.94 mg NO_3-N/L. As shown in Fig. 5(A), no significant difference was observed in the nitrate concentrations in sampling ports P_2 and P_3 for all columns. These results indicate that nitrate in columns containing 1,500 and 750 g of phosphate rock were being depleted at a shorter distance than in columns containing 500 and 0 g of phosphate rock.

Fig. 5(B) presents the relationship between the nitrite concentration and column depth. Minimal nitrite accumulation occurred in the effluent from the column containing 1,500 g of phosphate rock in sampling port P_1, with a value of 0.04 mg NO_2-N/L. Nitrite accumulated evidently in the effluent from the column containing 750 g of phosphate rock in sampling port P_1, with a value of 0.42 mg NO_2-N/L. Conversely, the nitrite accumulated significantly in the effluent from columns containing 500 and 0 g of phosphate rock in sampling port P_1, with values of 0.524 and 0.527 mg NO_2-N/L, respectively. In sampling port P_2, no evident change was observed in the nitrite concentrations in the effluent from the column containing 1,500 g of phosphate rock when compared with that in sampling port P_1. However, the nitrite concentrations in the effluent from the column containing 750 g of phosphate rock was 0.042 mg NO_2-N/L, significantly lower than that in sampling port P_1. The nitrite concentrations in the effluent from columns containing 500 and 0 g of phosphate rock were evidently lower than that in sampling port P_1, with values of 0.068 and 0.091 mg NO_2-N/L, respectively. In sampling port

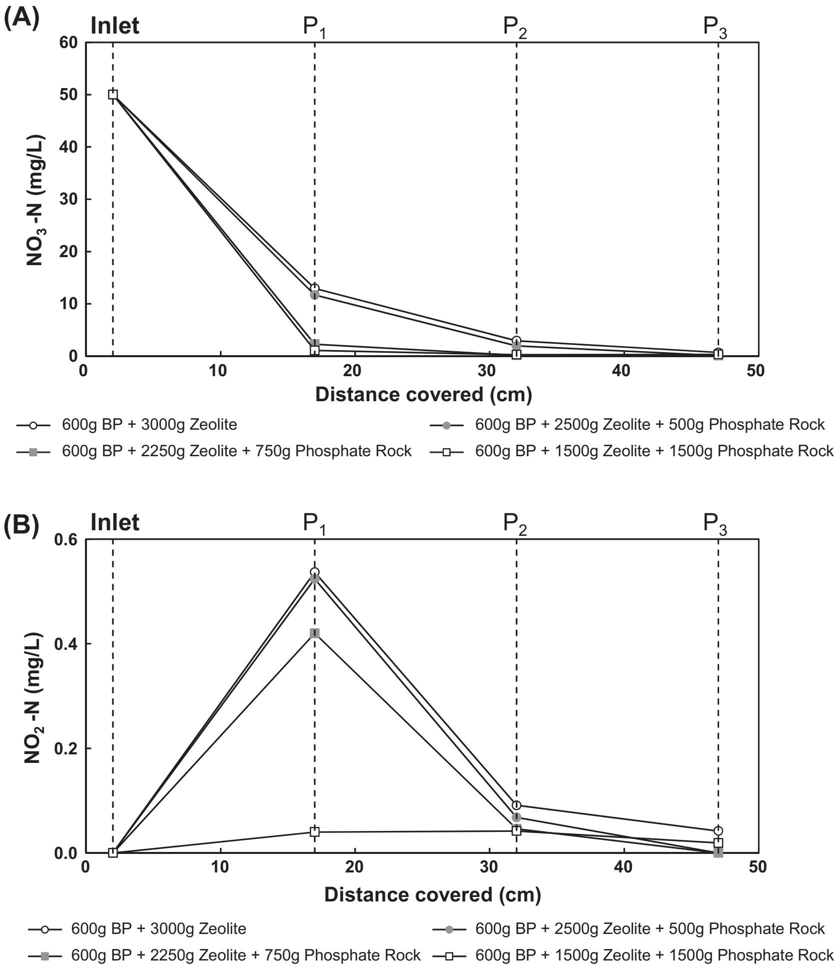

Fig. 5. Profile of nitrate and nitrite at different depth along the columns at 66 d. The concentration of the feed water for the column was 50 mg NO_3-N/L. Each column operated at a flow rate of 2 mL/min and at the temperature of 25 ± 2 ℃.

P_3, nitrite was found to decrease slightly with the passage of the groundwater through columns.

4. Conclusions

This study demonstrated that phosphate rock has the potential to enhance biological denitrification. In the leaching experiment, the release of TP indicated that phosphate rock could provide phosphorus for denitrifying bacteria growth. In column experiments, the nitrate removal efficiency of columns containing 1,500 and 750 g of phosphate rock was over 97%, and the nitrite concentrations were lower than 0.5 mg NO_2-N/L, which showed better nitrate removal performance than columns containing 500 and 0 g of phosphate rock when the temperature was 20 ± 2 ℃. When the influent flow rate was 3.6 mL/min, nitrate removal efficiency of columns containing 1,500 and 750 g of phosphate rock was higher than that of columns containing 500 and 0 g of phosphate rock. Moreover, nitrate in columns containing 1,500 and 750 g of phosphate rock was depleted at a shorter distance than in columns containing 500 and 0 g of phosphate rock. As a result, phosphate rock had the capacity for the promotion of denitrification and was applicable for use as a phosphorus source for nitrate-polluted groundwater remediation.

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