

Ammonium removal from groundwater using a zeolite permeable reactive barrier: a pilot-scale demonstration

Shengpin Li, Guoxin Huang, Xiangke Kong, Yingzhao Yang, Fei Liu, Guohua Hou and Honghan Chen

ABSTRACT

In situ remediation of ammonium-contaminated groundwater is possible through a zeolite permeable reactive barrier (PRB); however, zeolite's finite sorption capacity limits the long-term field application of PRBs. In this paper, a pilot-scale PRB was designed to achieve sustainable use of zeolite in removing ammonium ($\text{NH}_4^+\text{-N}$) through sequential nitrification, adsorption, and denitrification. An oxygen-releasing compound was added to ensure aerobic conditions in the upper layers of the PRB where $\text{NH}_4^+\text{-N}$ was microbially oxidized to nitrate. Any remaining $\text{NH}_4^+\text{-N}$ was removed abiotically in the zeolite layer. Under lower redox conditions, nitrate formed during nitrification was removed by denitrifying bacteria colonizing the zeolite. During the long-term operation (328 days), more than 90% of $\text{NH}_4^+\text{-N}$ was consistently removed, and approximately 40% of the influent $\text{NH}_4^+\text{-N}$ was oxidized to nitrate. As much as 60% of the nitrate formed in the PRB was reduced in the zeolite layer after 300 days of operation. Removal of $\text{NH}_4^+\text{-N}$ from groundwater using a zeolite PRB through bacterial nitrification and abiotic adsorption is a promising approach. The zeolite PRB has the advantage of achieving sustainable use of zeolite and immediate $\text{NH}_4^+\text{-N}$ removal.

Key words | adsorption, ammonium, denitrification, nitrification, PRB

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INTRODUCTION

Nitrogen contamination of the subsurface originates from various industries, wastewater, and agricultural fertilizer use (Malekian *et al.* 2011). Generally speaking, the main nitrogen contamination species is nitrate ($\text{NO}_3^-\text{-N}$); however, $\text{NH}_4^+\text{-N}$ can become the main form of nitrogen contamination in some special conditions. Compared with conventional techniques for the remediation of contaminated groundwater, *in situ* remediation technologies cost less and have fewer deleterious effects (Van Nooten *et al.* 2008). *In situ* remediation of nitrogen compounds in the subsurface is possible through the use of a permeable reactive barrier (PRB) (Park *et al.* 2002; Bastiaens *et al.* 2005). PRBs offer the potential for low-cost remediation because they take advantage of natural groundwater flow to bring the contaminants in contact with the reactive materials in the barrier (Patterson *et al.* 2004; Carniato *et al.* 2012).

The reactive medium used in a barrier varies depending on the contaminants of concern. Zeolites obtained from abundant natural deposits were investigated by many researchers for the purpose of cleaning up wastewaters

(Lin *et al.* 2013; Belviso *et al.* 2014). Natural zeolite is of special interest for $\text{NH}_4^+\text{-N}$ removal due to its low cost, ease of handling, and suitability for use in PRBs (Wang *et al.* 2007; Zhang & Bi 2012; Lv *et al.* 2013).

Despite zeolite's promise for removing $\text{NH}_4^+\text{-N}$ from groundwater, the one obvious disadvantage of zeolite used in a PRB is that it has a finite sorption capacity. Regeneration is possible, but would be a complicated process *in situ* (Van Nooten *et al.* 2010). This limitation necessarily requires that zeolite performs dual roles in the PRB by removing $\text{NH}_4^+\text{-N}$ through cation exchange and serving as a surface for the growth of denitrifying bacteria (Green *et al.* 1996; Lahav & Green 1998; Van Nooten *et al.* 2010). The concept of zeolite adsorption combined with biological nitrification–denitrification relies on the use of a zeolite-filled buffer compartment to ensure robust $\text{NH}_4^+\text{-N}$ removal that is independent of the level of microbial activity (Green *et al.* 1996; Lahav & Green 1998; Jung *et al.* 2004; Van Nooten *et al.* 2010). Compared to the large number of the laboratory-scale evaluations of bio-zeolite PRBs, very few data on long-term

and large-scale PRBs, which provide detail on the contamination reactive performance of PRBs, are available in the literature (Phillips *et al.* 2010; Wilkin *et al.* 2014).

In this paper, a pilot-scale PRB was designed to achieve sustainable use of zeolite in removing ammonium ($\text{NH}_4^+\text{-N}$) through sequential nitrification, adsorption, and denitrification. An oxygen-releasing compound (ORC) was synthesized and added to ensure aerobic conditions in the upper sand layer of the PRB, where the $\text{NH}_4^+\text{-N}$ would be microbially oxidized to $\text{NO}_3^-\text{-N}$; during passage through this layer, the dissolved oxygen in the groundwater would be consumed by the nitrifiers. Any remaining $\text{NH}_4^+\text{-N}$ would then be removed abiotically in the zeolite layer. Under these lower redox conditions, nitrite ($\text{NO}_2^-\text{-N}$) and $\text{NO}_3^-\text{-N}$ formed during nitrification would be removed by denitrifying bacteria that would colonize the zeolite.

MATERIALS AND METHODS

Materials

The natural clinoptilolite zeolite (1–2 mm) used was obtained from Faku, Liaoning Province, PRC. The chemical composition of the zeolite was: 67.09% SiO_2 , 12.44% Al_2O_3 , 0.78% Fe_2O_3 , 0.26% Na_2O , 1.22% MgO , 8.81% CaO , 1.20% K_2O , and 13.32% other. The zeolite adsorption capacity for ammonium was about 4.74 mg/g.

ORC was made from cement (25%), calcium peroxide (20%), bentonite (10%), sand (15%), and water (30%). The size of ORC was 3 cm in diameter and the oxygen releasing mechanism was: $2\text{CaO}_2 + 2\text{H}_2\text{O} = 2\text{Ca}(\text{OH})_2 + \text{O}_2 \uparrow$

The particle size of the sand used in the experiment was between 0.5 and 3.5 mm.

Design of pilot-scale PRB

The PRB (6.0 m long, 4.0 m wide, 3.0 m high) was composed of three layers (from the top): the sand layer (0.5–1.0 m) was aimed at retaining suspended solids; the ORC + sand layer (1.0–1.3 m) was used to enhance bacterial nitrification by releasing oxygen to the groundwater; the zeolite layer (1.3–2.5 m) was used to ensure robust $\text{NH}_4^+\text{-N}$ removal via physical adsorption and to induce anaerobic conditions to allow for bacterial denitrification by providing a place for microorganisms to reproduce (Figure 1).

The PRB was equipped with nine monitoring wells which were able to obtain samples from each of the three layers of the PRB: at the based of the ORC + sand layer (1.3 m), in the middle of the zeolite layer (1.9 m), and at the bottom of the zeolite layer (2.5 m) (Figure 1).

The goal of the PRB was to achieve the following effluent concentrations: ≤ 0.5 mg/L $\text{NH}_4^+\text{-N}$, ≤ 20 mg/L $\text{NO}_3^-\text{-N}$ and ≤ 0.3 mg/L nitrite ($\text{NO}_2^-\text{-N}$).

Operation of pilot-scale PRB

Infiltrating groundwater from the River Hun served as the source water for the pilot-scale PRB. The initial influent concentration of $\text{NH}_4^+\text{-N}$ was between 0.3 and 36.6 mg/L without adjusting. The flow rate was about 1 m/d, which was similar to the groundwater velocities in the riparian

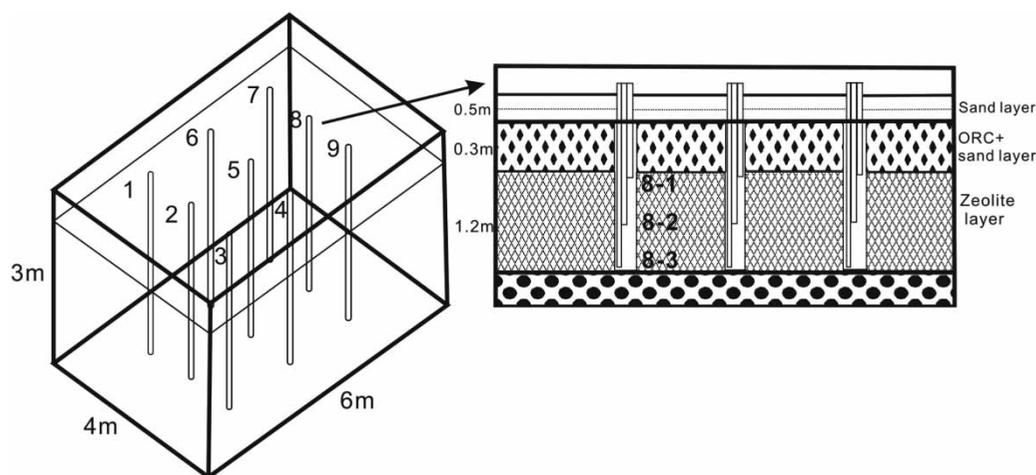


Figure 1 | Schematic diagram of the pilot-scale PRB.

aquifer of the Hun River in Shenyang, PRC. The operation of the PRB was started in August 2011 and lasted as long as 328 days. The temperature in the PRB was in the range of $\sim 5\text{--}20^\circ\text{C}$ during the whole operation.

During 0–69 days and 292–328 days, the measurements were done twice a week on average; during 69–292 days the measurements were done once a month, because the temperature was too low to cultivate microorganisms in this period.

Analytical methods

Total elemental analysis was performed by X-ray diffractometry using JADE software (Version 5.0). The concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were determined by a UV-Vis spectrophotometer (HP-8353) at 420 nm and 540 nm, respectively. The concentration of $\text{NO}_3^-\text{-N}$ was determined at 220 and 275 nm also with the UV-Vis spectrophotometer. Dissolved oxygen was measured by a Hach HQ 30d portable dissolved oxygen meter. The pH was determined by a pH meter (Sartorius PB-10).

RESULTS AND DISCUSSION

The assessment of $\text{NH}_4^+\text{-N}$ removal process

Based on the patterns of observed $\text{NH}_4^+\text{-N}$ removal in the PRB, two distinct phases can be described, which are due to nitrifiers needing time to grow and reproduce before contributing to $\text{NH}_4^+\text{-N}$ removal (Kim *et al.* 2013). During Phase I (days 0 to 292), influent and effluent concentrations of $\text{NH}_4^+\text{-N}$ ranged from 0.3 to 11.1 mg/L and 0.02 to 0.49 mg/L, respectively (Figure 2(a)), while influent and effluent concentrations of $\text{NO}_3^-\text{-N}$ varied from 0.2 to ~ 2.3 mg/L and 0.5 to 5.0 mg/L, respectively (Figure 2(b)). $\text{NH}_4^+\text{-N}$ concentrations decreased without any obvious increases in $\text{NO}_3^-\text{-N}$, suggesting that $\text{NH}_4^+\text{-N}$ removal was due to zeolite adsorption only.

During Phase II (days 292–328), corresponding with regional runoff of agricultural fertilizers, the influent concentrations of $\text{NH}_4^+\text{-N}$ increased obviously (Abalos *et al.* 2014; Montalvo *et al.* 2014), but with only two values higher than the effluent standards (0.5 mg/L) on days 316 (0.74 mg/L) and 319 (1.43 mg/L) (Figure 2(a)). Compared

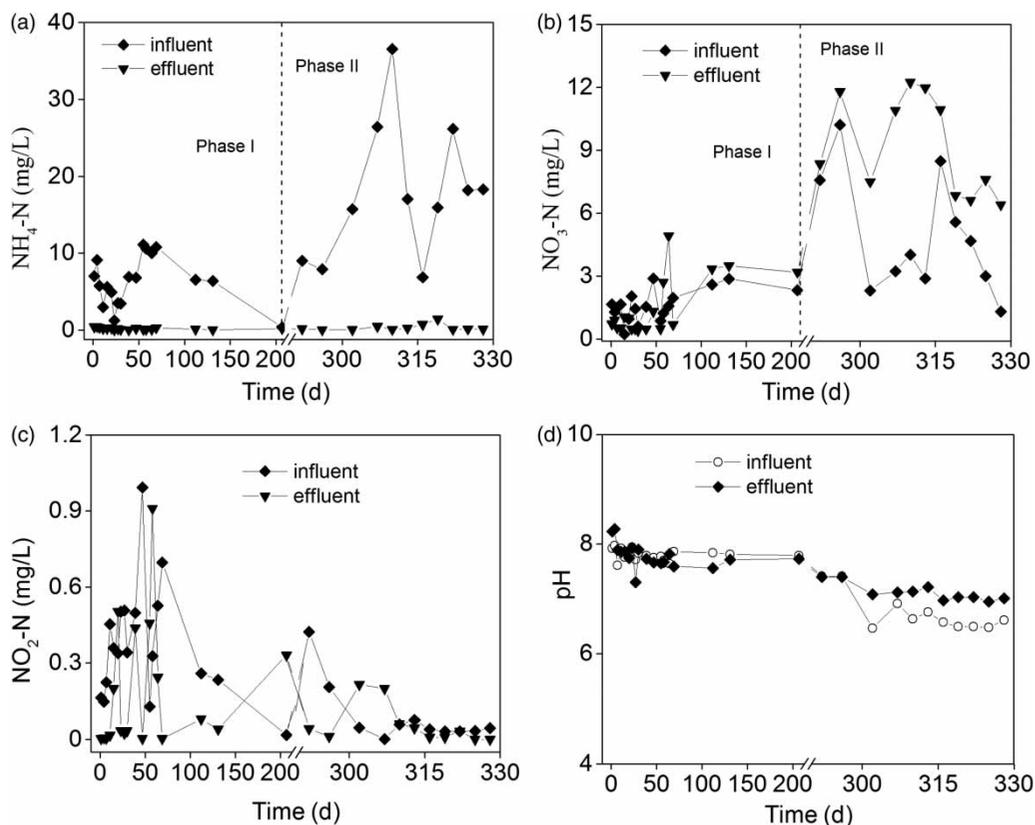


Figure 2 | The concentrations of (a) ammonium, (b) nitrate and (c) nitrite in the influent and effluent of the pilot-scale PRB; (d) pH in the influent and effluent of the pilot-scale PRB.

with the influent, effluent concentrations of NO_3^- -N increased significantly after day 292, varying from 6.4 to 12.2 mg/L (Figure 2(b)), since NO_3^- -N is not a product of either zeolite adsorption or cation exchange. These values suggested that bacterial nitrification occurred in the pilot-scale PRB during this period.

pH is one of the most important parameters controlling the ion exchange process and microbial activity. The pH ranged from 6.4 to 7.9 in the pilot-scale PRB (Figure 2(d)), which is suitable for zeolite to adsorb NH_4^+ -N (Karadag *et al.* 2007), and has little effect on the nitrification and denitrification process (Semmens *et al.* 1977; Vidal *et al.* 2002).

NO_2^- -N was a minor constituent in the influent at concentrations of 0–1 mg/L over the course of the experiment. Effluent concentrations of NO_2^- -N varied from 0.004 to 0.91 mg/L (Figure 2(c)).

The adsorption process in ammonium removal (Phase I)

The concentrations of nitrogen species measured on days 1, 39, 69, 131, and 292 (from monitoring well No. 5, located in

the middle of the PRB) are plotted in Figure 3. As Figure 3 illustrates, the concentrations of both total nitrogen (TN) and NH_4^+ -N decreased sharply in the upper half of the zeolite layer. In contrast, NO_3^- -N concentrations exhibited no significant change, because both nitrifiers and nitrate-reducing bacteria were absent or in small numbers in the initial phase of operation of the PRB (Qiu *et al.* 2012). NO_2^- -N concentrations decreased slightly.

These results indicated that the removal of NH_4^+ -N during the first 292 days in the PRB was solely due to zeolite adsorption with no significant evidence of either microbial ammonia oxidation or bacterial nitrate occurring.

Microbial process in ammonium removal (Phase II)

The concentrations of nitrogen species quantified during Phase II (on days 307, 313, 322, 325 and 328) are plotted in Figure 4. In contrast to Phase I, most of the NH_4^+ -N removal appears to have occurred in the ORC + sand layer, not in the zeolite layer. The concentrations of

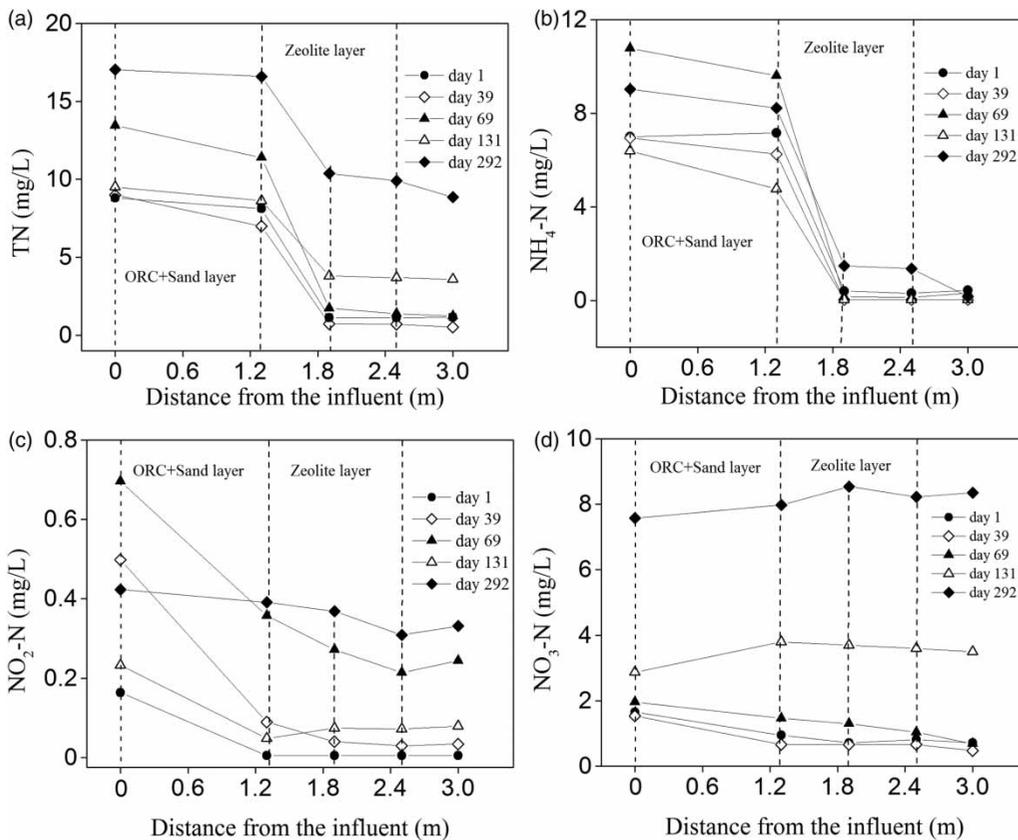


Figure 3 | The concentrations of (a) TN, (b) ammonium, (c) nitrite and (d) nitrate in the three layers of the pilot-scale PRB during Phase I (0–292 days).

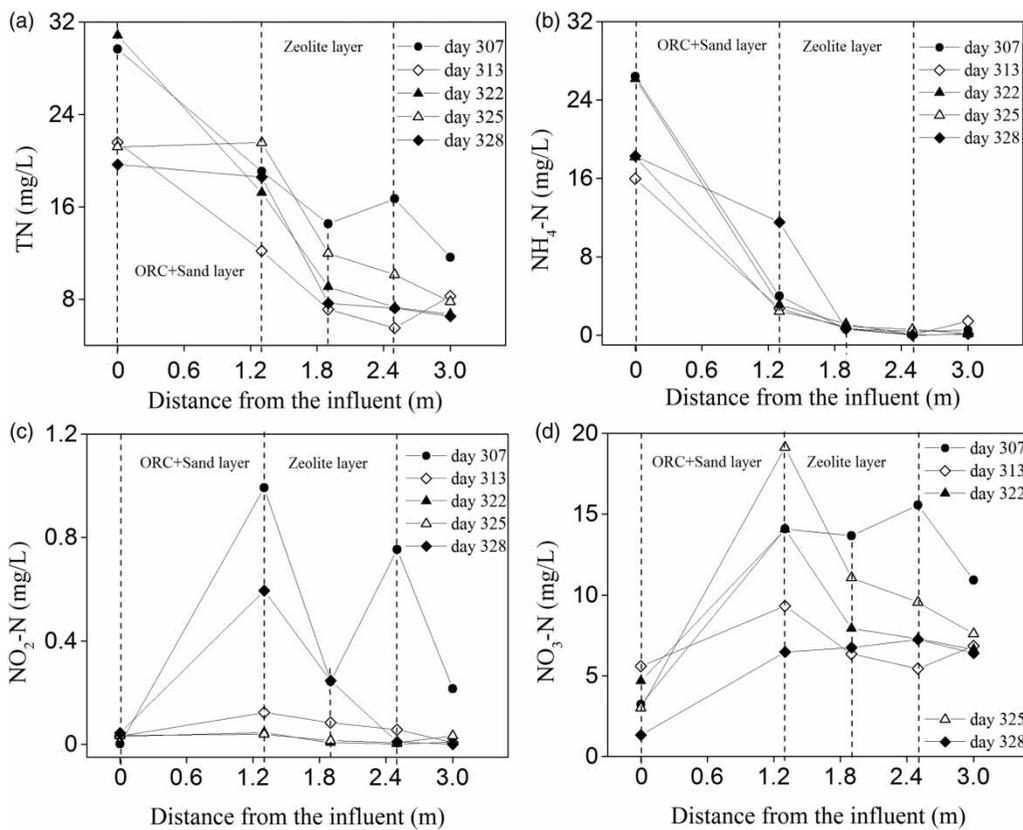


Figure 4 | Changes in concentrations of (a) TN, (b) ammonium, (c) nitrite and (d) nitrate in the three layers of the pilot-scale PRB during Phase II (292–328 days).

NO_2^- -N and NO_3^- -N were increased dramatically near the interface of the ORC + sand and zeolite layers. Since NO_3^- -N and NO_2^- -N are products of neither zeolite adsorption nor cation exchange, some significant fraction of the observed NH_4^+ -N removal was due to microbial nitrification (Li *et al.* 2013).

To simulate the natural groundwater conditions, no additional electron donors were added. However, NO_3^- -N was subsequently removed in the zeolite layer. NO_3^- -N can be degraded to N_2 through denitrification, resulting in the removal of NO_3^- -N; the zeolite surface is negatively charged, so NO_3^- -N has little possibility to be absorbed (Zhang & Bi 2011). NO_3^- -N decreased in the zeolite layer without any increase in TN, NH_4^+ -N, and NO_2^- -N, which suggests that bacterial denitrifiers successfully colonized it and reduced the NO_3^- -N to N_2 (Figures 4(c) and 4(d)).

According to patterns observed in the data and illustrated in Figure 4, nitrogen removal in the PRB may be graphically separated into the three vertical sections as follows. Section 1 is the ORC + sand layer (0–1.3 m) where TN is removed and the concentrations of NO_3^- -N increased.

Section 2 is the upper section of the zeolite layer (1.3–1.9 m) where additional ammonium removal may occur and the concentrations of NO_3^- -N decreased sharply. Section 3 is the bottom-most layer of zeolite (1.9–2.9 m) where additional ammonium adsorption may occur.

There was sufficient oxygen in Section 1 to support bacterial nitrification (≥ 2 mg/L; (Guo *et al.* 2013) as evidenced by the consistent formation of both NO_2^- -N and NO_3^- -N (Figures 4(c) and (d)). Since not all of the NH_4^+ -N was oxidized to nitrite or nitrate in Section 1, some of the NH_4^+ -N removal may be attributed to adsorption. Examining the data from day 322, the removal of NH_4^+ -N and TN was 23.06 and 13.66 mg/L, respectively. The increased concentrations of NO_3^- -N and NO_2^- -N were 9.39 mg/L and 0.01 mg/L, respectively. A nitrogen mass balance shows that the amount of NH_4^+ -N (23.05 mg/L) removed is nearly equal to the sum of the TN removed (13.66 mg/L) and the NO_3^- -N and NO_2^- -N formed (9.38 + 0.02 mg/L). This means that about 40% of the influent NH_4^+ -N being converted to nitrite and nitrate in Section 1, and about 60% of the NH_4^+ -N removal was due to sorption. Overall, these results indicated that NH_4^+ -N removal

in Section 1 was due to a combination of adsorption and bacterial nitrification.

The oxygen released in Section 1 was largely consumed by the nitrifying bacteria, resulting in lower redox conditions in the subsequent layers of the PRB which, in turn, favors denitrifying bacteria that reduce nitrate to nitrogen gas (Guerrero *et al.* 2013; Paulo *et al.* 2013). In Section 2, not all of the observed TN removal may be accounted for as nitrite and nitrate: some TN removal may be attributed to adsorption. Again, examining data obtained on day 322, nitrogen mass balance calculations indicate that the amount of TN removed (8.13 mg/L) is equal to the amount of $\text{NH}_4^+\text{-N}$ removed (1.96 mg/L) plus the amount of $\text{NO}_2^-\text{-N}$ (0.03 mg/L) and $\text{NO}_3^-\text{-N}$ (6.16 mg/L) reduced. These results suggest that both adsorption and microbial denitrification occur in Section 2, although most of the nitrogen removal is due to bacterial nitrate reduction.

Section 3 exhibits additional removal of both $\text{NH}_4^+\text{-N}$ (1.06 mg/L) and $\text{NO}_3^-\text{-N}$ (Figures 4(b) and 4(d)). The nitrogen mass balance conducted on day 322 indicates that the TN removed (2.37 mg/L) is equal to the amount of $\text{NH}_4^+\text{-N}$ removed (1.06 mg/L) plus the amount of nitrate that is reduced (1.31 mg/L). These data suggest that adsorption and denitrification processes occur in Section 3 to achieve nearly complete removal of nitrogen species in the groundwater.

During the 328 days' operation of the PRB, ~40–98% of the incoming $\text{NH}_4^+\text{-N}$ was removed over the seasonally variable range of influent concentrations (0.3–36.6 mg/L) (Figure 5(a)); however, that means the removal rate was much greater (>90%) and more consistent at all concentrations greater than 0.3 mg/L. A nitrogen mass balance suggests that about 60% of the observed $\text{NH}_4^+\text{-N}$ removal

may be attributed to adsorption in the ORC + sand layer (Section 1). About 40% of the influent $\text{NH}_4^+\text{-N}$ was microbially oxidized to nitrate, but only after colonization by nitrifying bacteria (after ~300 days of operation; Figure 5(b)). Because of the microbial activities, the life of zeolite was extended and achieved a sustainable role in $\text{NH}_4^+\text{-N}$ removal. Nitrate removal by denitrifying bacteria was evident in both the upper (Section 2) and lower (Section 3) layers of the zeolite, but again only after nitrate-reducing bacteria had successfully colonized the media.

CONCLUSIONS

In this study, a pilot-scale PRB was designed to remove $\text{NH}_4^+\text{-N}$ from groundwater. More than 90% of $\text{NH}_4^+\text{-N}$ was removed over a wide range of influent concentrations, with adsorption, nitrification and denitrification all contributing to the *in situ* remediation of nitrogen species.

After some 300 days of operation, about 40% of the influent $\text{NH}_4^+\text{-N}$ was converted to nitrite and nitrate through nitrification; zeolite contributed to ~60% of the observed removal of $\text{NH}_4^+\text{-N}$ through adsorption; zeolite also supported the growth and activity of the denitrifying bacteria resulting in as much as 60% of the nitrate removal which formed in the PRB through bacterial ammonia oxidation.

Based on these results, it is concluded that $\text{NH}_4^+\text{-N}$ removal from groundwater through bacterial nitrification and adsorption to zeolite in a PRB is a valuable approach for groundwater management. It requires refinement, but has the advantages of immediate ammonium removal followed by more sustainable processes that employ naturally occurring microbial communities.

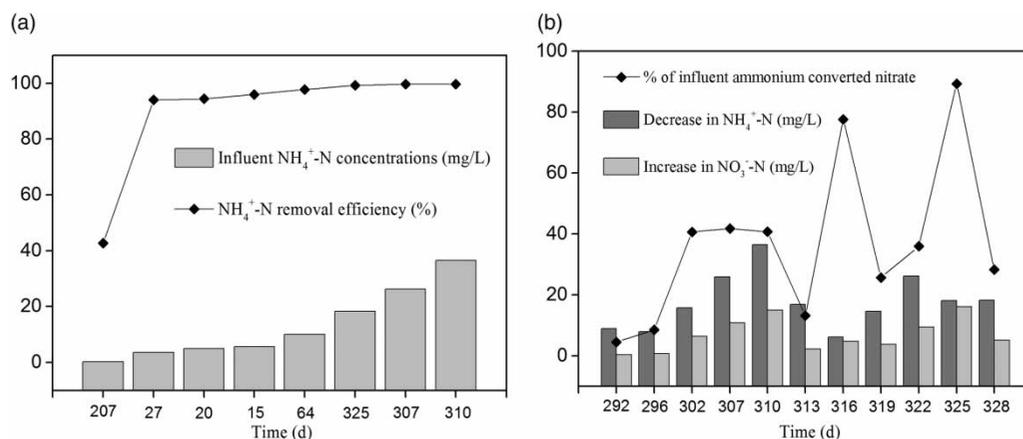


Figure 5 | (a) Removal efficiency of $\text{NH}_4^+\text{-N}$ versus influent concentrations; (b) conversion of ammonium to nitrate during 328 days of operation.

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