Remediation of nitrate–nitrogen contaminated groundwater using a pilot-scale two-layer heterotrophic–autotrophic denitrification permeable reactive barrier with spongy iron/pine bark

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HIGHLIGHTS

- We proposed a heterotrophic–autotrophic denitrification permeable reactive barrier.
- The barrier achieved a high NO_3^-–N removal efficiency (>91%) before 38 PVs.
- The packing structure over previous ones generated more H_2 and CO_2.
- Aerobic heterotrophic bacteria played a dominant role in oxygen depletion.
- Spongy iron ensured a robust oxygen removal in addition to form H_2.

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ABSTRACT

A novel two-layer heterotrophic–autotrophic denitrification (HAD) permeable reactive barrier (PRB) was proposed for remediating nitrate–nitrogen contaminated groundwater in an oxygen rich environment, which has a packing structure of an upstream pine bark layer and a downstream spongy iron and river sand mixture layer. The HAD PRB involves biological deoxygenation, heterotrophic denitrification, hydrogenotrophic denitrification, and anaerobic Fe corrosion. Column and batch experiments were performed to: (1) investigate the NO_3^-–N removal and inorganic geochemistry; (2) explore the nitrogen transformation and removal mechanisms; (3) identify the hydrogenotrophic denitrification capacity; and (4) evaluate the HAD performance by comparison with other approaches. The results showed that the HAD PRB could maintain constant high NO_3^-–N removal efficiency (>91%) before 38 pore volumes (PVs) of operation (corresponding to 504 d), form little or even negative NO_2^-–N during the 45 PVs, and produce low NH_4^+–N after 10 PVs. Aerobic heterotrophic bacteria played a dominant role in oxygen depletion via aerobic respiration, providing more CO_2 for hydrogenotrophic denitrification. The HAD PRB significantly relied on heterotrophic denitrification. Hydrogenotrophic denitrification removed 10–20% of the initial NO_3^-–N. Effluent total organic carbon decreased from 403.44 mg L^{-1} at PV 1 to 9.34 mg L^{-1} at PV 45. Packing structure had a noticeable effect on its denitrification.

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1. Introduction

Nitrate–nitrogen contamination of groundwater has become an environmental and public health problem worldwide (Della Rocca et al., 2007). High NO_3^-–N concentration (>10 mg L^{-1}) has been recorded in numerous aquifers in China (Zhang et al., 2013), Italy (Sacchi et al., 2013), Mexico (Pastén-Zapata et al., 2014), Spain (Boy-Roura et al., 2013), America (Su and Puls, 2007), Canada (Levallois et al., 1998), Portugal (Mendes and Ribeiro, 2010), Germany (Shomar et al., 2008), and Australia (Salvestrin and Hagare, 2009). It is worth mentioning that most NO_3^-–N laden groundwater also contains dissolved oxygen (DO) (Huang et al., 2012). Public health concerns arise from the potential reduction of NO_3^-–N to NO_2^-–N and the endogenous formation of N-nitroso compounds,

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which can cause methemoglobinemia, hypertension, cancers, malformation, mutation, and even death (Huang et al., 2012).

Remediating NO_3^-–N contaminated groundwater has been and continues to be an area of active research. Among the available remediation approaches (Westerhoff and James, 2003; Wang et al., 2009; Demiral and Gündüzoğlu, 2010), biological denitrification, falling into heterotrophic denitrification and autotrophic denitrification, is receiving increasing attention. Heterotrophic denitrification is widely studied and applied in the field due to high denitrifying rate and high treatment capacity (Liu et al., 2009). Even so, it has shown some shortcomings such as remnant organic carbon (requiring an intensive post-treatment process) and high cell yield (0.6–0.9 g cells g^{-1} NO_3^-–N) (Ergas and Reuss, 2001; Shrimali and Singh, 2001). Autotrophic denitrification supported with hydrogen, which is known as hydrogenotrophic denitrification, is particularly promising due to clean nature of hydrogen, low biomass yield, relatively low cost, no external carbon source, and avoidance of secondary organic carbon contamination (Lee and Rittmann, 2002; van Rijn et al., 2006; Moon et al., 2008). Nevertheless, hydrogenotrophic denitrification is limited by inadequate carbon dioxide, low solubility (1.6 mg L^{-1} at 20 °C), high flammability, and high cost of hydrogen gas (Haugen et al., 2002; Jha and Bose, 2005; Della Rocca et al., 2006; Ghafari et al., 2008; Shin and Cha, 2008).

To take the advantages and overcome the disadvantages of single heterotrophic denitrification and autotrophic denitrification, a combined heterotrophic–autotrophic denitrification (HAD) approach was proposed by Della Rocca et al. (2006) and further developed by Liu et al. (2014) and Huang et al. (2012). In the HAD processes, zero-valent iron (ZVI) via chemical reduction removes most oxygen to rapidly create an anaerobic environment, supporting biological denitrification. Heterotrophic denitrifiers via heterotrophic denitrification utilize organic carbons (cotton, methanol, and pine bark) as electron donors to biologically reduce most NO_3^-–N and meanwhile generate CO_2, favoring hydrogenotrophic denitrification. ZVI via anaerobic Fe corrosion forms cathodic hydrogen with the aid of hydrogenase enzymes, supporting hydrogenotrophic denitrification as well. Hydrogenotrophic denitrifiers employ the carbon dioxide and cathodic hydrogen to biologically reduce the remaining NO_3^-–N. Additionally, the solid materials serve as biofilm carriers. Although the symbiotic, synergistic, and promotive effects of the mechanisms mentioned above in the HAD processes were encouraging, questions arise regarding capacity of hydrogenotrophic denitrification and performance evaluation by comparison with other denitrification approaches.

Passive permeable reactive barrier (PRB) is considered one of the innovative technologies widely accepted as an alternative to the conventional pump-and-treat for sustainable in situ groundwater remediation (Obiri-Nyarko et al., 2014) due to more cost effectiveness and lower maintenance in the long-term (Phillips, 2009). PRBs have been successful in removing a variety of groundwater contaminants such as NO_3^-–N, petroleum hydrocarbon, and heavy metals (Guerin et al., 2002; Schipper et al., 2005; Zhang et al., 2012). Over the past decades, much research work has been done on refining site characterization techniques, developing reactive media (or sorbents), and improving installation and design (Phillips, 2009). However, only a few attempts have been made to combine multiple remediation mechanisms and optimize packing structures.

More recently, for target NO_3^-–N, several column studies have paid particular attention to HAD PRBs. For instance, Della Rocca et al. (2006) investigated the effect factors (e.g., flow rate, influent NO_3^-–N, and retention time) using four parallel columns packed with steel wool and cotton (R1–R4). Liu et al. (2014) determined the spatial and temporal variations of water quality indices using two parallel columns (Columns 1 and 2) packed with spongy iron and pine bark. In the two studies, both single- and double-layer packing structures were designed. For the single-layer structure, the mixed reactive materials (spongy iron and pine bark) were packed in a reactive zone; whereas for the double-layer structure, the ZVI (steel wool or spongy iron) was placed in the upstream layer and the solid carbon (cotton or pine bark) was filled in the downstream layer. Unfortunately, the packing structure of an upstream solid carbon layer followed by a downstream ZVI layer has been neglected, and furthermore data on the feasibility and effectiveness of this packing structure are rather scarce.

Here, we report the performance of a novel two-layer HAD PRB to remediate NO_3^-–N contaminated groundwater in an aerobic environment and further develop HAD processes and PRB systems. Our HAD PRB concept, mainly involving a combination of biological deoxygenation, heterotrophic denitrification, hydrogenotrophic denitrification, and anaerobic Fe corrosion, was composed of an upstream pine bark layer and a downstream spongy iron and river sand mixture layer. The packing structure over the previous packing ones is expected to allow the generation of more cathodic hydrogen and carbon dioxide to support hydrogenotrophic denitrification. Heterotrophic denitrification contributed to the removal of most NO_3^-–N. Aerobic heterotrophic bacteria played a dominant role in oxygen depletion. Spongy iron potentially ensures a robust oxygen removal in case of temporary insufficient biological deoxygenation. The objectives of this study were to: (1) investigate the NO_3^-–N removal and inorganic geochemistry caused by the proposed HAD PRB; (2) explore the nitrogen transformation and clean up mechanisms; (3) identify the hydrogenotrophic denitrification capacity in the HAD PRB; and (4) evaluate the HAD performance by comparison with other approaches.

2. Materials and methods

2.1. Materials and chemicals

Spongy iron (0.15–2.00 mm, Brunauer–Emmett–Teller area 0.49 $m^2 g^{-1}$, micropore volume 0.0012 $cm^3 g^{-1}$, micropore diameter 101.87 Å) was obtained from Kaibiyuan Co., Beijing, China, which consisted of Fe^0 (60.60 wt%), C (0.78 wt%), S (0.06 wt%), P (0.04 wt%), Mn (0.29 wt%), Ni (0.02 wt%), Cr (0.02 wt%), Cu (0.02 wt%), and Al (0.26 wt%). Pine bark (2–11 mm, Brunauer–Emmett–Teller area 0.46 $m^2 g^{-1}$, micropore volume 0.0018 $cm^3 g^{-1}$, micropore diameter 159.42 Å) was purchased from a local nursery store in Beijing, China. Gravel (2–5 mm) and river sand (0.45–2 mm) were donated by a quarry in Beijing, China. Hydrogen gas (industrial grade, purity 99.9%) was purchased from Beijing Hua Yuan Gas Chemical Industry Co., Ltd., Beijing, China. Deionized water was used to prepare reagent solutions. Beijing tap water was spiked with $NaNO_3$, $NaHCO_3$, and K_2HPO_4 acting as synthetic groundwater. In addition to NO_3^-–N (20–105 mg L^{-1}), the synthetic groundwater contained the following (final concentration in mg L^{-1} except pH): NO_2^-–N (<0.1), NH_4^+–N (<0.8), F^- (0.3), Cl^- (20.8), HCO_3^- (254.2), SO_4^{2-} (46.4), Na^+ (142.3–281.9), K^+ (11.7), Ca^{2+} (48.5), Mg^{2+} (28.1), DO (5–9), P (3.0), and pH (7.5–8.5). Unless otherwise indicated, all chemicals used were analytical reagent grade as received.

2.2. Column experiment setup and operation

A pilot-scale flow through HAD PRB experiment was conducted employing a plexiglas column (20.6 cm i.d., 150 cm in length) (Fig. 1a and b). A lower support layer of 5 cm of gravel was packed at the bottom of the column, and a 5 cm gravel cap was placed at the top. The reactive zone was composed of an upstream layer