



Removal of ammonium-nitrogen from groundwater using a fully passive permeable reactive barrier with oxygen-releasing compound and clinoptilolite



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ABSTRACT

A novel fully passive permeable reactive barrier (PRB) with oxygen-releasing compound (ORC) and clinoptilolite was proposed for the removal of ammonium-nitrogen from groundwater. The PRB involves a combination of oxygen release, biological nitrification, ion exchange, and bioregeneration. A pilot-scale performance comparison experiment was carried out employing three parallel columns to assess the proposed PRB. The results showed that the PRB achieved nearly complete $\text{NH}_4^+ - \text{N}$ depletion (>99%). $\text{NH}_4^+ - \text{N}$ of 5.23–10.88 mg/L was removed, and $\text{NO}_2^- - \text{N}$ of <1.93 mg/L and $\text{NO}_3^- - \text{N}$ of 2.03–19.67 mg/L were generated. Ion exchange and biological nitrification both contributed to $\text{NH}_4^+ - \text{N}$ removal, and the latter played a dominant role under the condition of sufficient oxygen. Biological nitrification favored a delay in sorption saturation and a release of exchange sites. The ORC could sufficiently, efficiently supply oxygen for approximately 120 pore volumes. The clinoptilolite ensured a robust $\text{NH}_4^+ - \text{N}$ removal in case of temporary insufficient biological activities. No external alkalinity sources had to be supplied and no inhibition of aerobic metabolism occurred. The ceramicite had a negligible effect on the biomass growth. Based on the research findings, a full-scale continuous wall PRB was installed in Shenyang, China in 2012.

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1. Introduction

Ammonium-nitrogen contamination of groundwater has become an environmental and public health issue in developing and developed countries. In Shenyang, China, $\text{NH}_4^+ - \text{N}$ of up to 10 mg/L in an approximately 40 m deep aquifer beside Hun River has been observed by our research group. Further, in America, Australia, England, and Korea, high $\text{NH}_4^+ - \text{N}$ has been recorded in numerous groundwater contamination plumes (Park et al., 2002; Manning and Hutcheon, 2004; Patterson et al., 2004; Miller and Smith, 2009). It is most likely that $\text{NH}_4^+ - \text{N}$ forms harmful disinfection by-products, chlorine-related tastes and odors during

drinking water treatment, and causes nitrifying bacterial regrowth in drinking water distribution systems (Zhang et al., 2014).

In situ permeable reactive barrier (PRB) is regarded as one of the most promising alternatives to conventional ex situ technologies (e.g., pump-and-treat) for groundwater remediation, and is receiving increased attention in the literature (Della Rocca et al., 2007; Thiruvengkatachari et al., 2008; Moraci and Calabrò, 2010; Hashim et al., 2011; Perego et al., 2013; Erto et al., 2014). Recently, several lab- and full-scale PRBs have been reported for remediating groundwater contaminated with $\text{NH}_4^+ - \text{N}$, involving aerobic biological nitrification and/or physicochemical sorption (Park et al., 2002; Patterson et al., 2004; van Nooten et al., 2010, 2011). For single biological nitrification (Lahav and Green, 2000; Yusof et al., 2010; Mousavi et al., 2012), two semipassive PRBs were packed with polymer mats for delivering oxygen gas to induce

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oxidation of $\text{NH}_4^+ - \text{N}$ into $\text{NO}_3^- - \text{N}/\text{NO}_2^- - \text{N}$ (Patterson et al., 2002). Another semipassive PRB was equipped with diffusive oxygen emitters to provide a nonlimiting molecular oxygen supply (van Nooten et al., 2008). Even though these PRBs achieved good nitrification performances, they produced high residual dissolved oxygen (DO) of 24.0 ± 9.7 mg/L (van Nooten et al., 2008), and caused higher operation and maintenance costs as well as operational complexity arising from the use of oxygen injection systems (reservoirs + pumps + plumbing) and electric power. To overcome these shortcomings, oxygen-releasing compound (ORC) including calcium peroxide and magnesium peroxide presents a potential choice because it can combine with water to form oxygen gas (Cassidy and Irvine, 1999; Liu et al., 2006; Dong et al., 2009). ORC mixed well with cement, sand, and other materials has been successfully applied to aerobic biodegradation of some organic contaminants such as BTEX (benzene, toluene, ethylbenzene, and p-xylene), MTBE (methyl tert-butyl ether), and COD (chemical oxygen demand) (Liu et al., 2006; Dong et al., 2009; Yeh et al., 2010). However, very little is known about ORC for supporting biological nitrification in PRBs. The corresponding ORC oxygen-releasing capacity, N removal and transformation mechanisms, and inorganic geochemical characteristics are worthy of further study. For single ion exchange (Cooney et al., 1999; Dong et al., 2009), zeolite, including clinoptilolite, mordenite, heulandite, etc. is the most common ammonium ion exchanger. Zeolite has been well demonstrated to be effective for treatment of $\text{NH}_4^+ - \text{N}$ and suitable for in situ applications as a PRB material (Booker et al., 1996; Park et al., 2002; Du et al., 2005; Wen et al., 2006). Even so, questions arise regarding sorption saturation and regeneration. As is well known, either a periodical material replacement or chemical regeneration after saturation renders the PRB technology less passive and less economically favorable (van Nooten et al., 2010). Chemical regenerants account for more than 50–60% of the total costs even with regenerant reuse (Njoroge and Mwamachi, 2004). Until now, a few research studies have focused on in situ biological regeneration of zeolite by means of injecting external molecular oxygen into PRBs (van Nooten et al., 2008, 2010, 2011). However, using ORC to accomplish bioregeneration or delay $\text{NH}_4^+ - \text{N}$ breakthrough is still lacking.

Here, we report a novel fully passive ORC and clinoptilolite PRB for removing $\text{NH}_4^+ - \text{N}$ from groundwater. The concept is based on a combination of oxygen release-biological nitrification-ion exchange-bioregeneration for the efficient depletion of $\text{NH}_4^+ - \text{N}$ and the delayed saturation of clinoptilolite. The main function of ORC in an upgradient zone is to release oxygen. Clinoptilolite in a downgradient zone is to remove residual $\text{NH}_4^+ - \text{N}$, ensuring a robust $\text{NH}_4^+ - \text{N}$ removal. Shifts in exchange equilibria allow the occurrence of $\text{NH}_4^+ - \text{N}$ desorption when ammonium-poor groundwater is flowing through the saturated clinoptilolite. The nitrifying bacteria on the reactive media utilize the released oxygen to oxidize soluble $\text{NH}_4^+ - \text{N}$ in water, increasing the N products and delaying the $\text{NH}_4^+ - \text{N}$ breakthrough. The objectives of this study were to: (1) evaluate the $\text{NH}_4^+ - \text{N}$ removal performance of the proposed PRB; (2) characterize the ORC oxygen-releasing capacity; (3) explore the clean up mechanisms; (4) investigate the inorganic geochemistry; (5) determine the feasibility of bioregeneration or delayed sorption saturation; and (6) identify the effect of ceramicite on biomass growth.

2. Materials and methods

2.1. Materials and chemicals

River sand (~1 mm) was donated by a quarry in Shenyang, China. Natural clinoptilolite (1–2 mm, purity 97%, cation exchange

capacity 130–150 mg/100 g, Brunauer–Emmett–Teller area $670 \text{ m}^2/\text{g}$) was obtained from Faku, China and found to contain SiO_2 (67.09 wt%), Al_2O_3 (12.44 wt%), CaO (8.81 wt%), MgO (1.22 wt%), K_2O (1.20 wt%), and Fe_2O_3 (0.78 wt%). ORC beads (2–3 cm) were obtained from China University of Geosciences (Beijing), China, which consisted of CaO_2 (20 wt%, purity 50%, main impurity $\text{Ca}(\text{OH})_2$), Ca-bentonite (10 wt%), portland cement (25 wt%), river sand (15 wt%), and tap water (30 wt%) (trial production). Ceramicite (1–2 mm) was purchased from Ma'anshan Huaqi Environmental Protection Sci-Tech Development Co., Ltd., China. Shenyang tap water spiked with ammonium chloride was used as synthetic groundwater with initial $\text{NH}_4^+ - \text{N}$ of 5.0–11.0 mg/L. Unless otherwise indicated, all chemicals used were analytical reagent grade as received.

2.2. Column experiment setup and operation

A pilot-scale performance comparison experiment was carried out employing three parallel Plexiglas columns (PRBs 1–3, 20 cm i.d., 180 cm high) (Fig. 1 and Table 1). PRB 1 was packed with clinoptilolite (150 cm high) to control for the effects of oxygen release, ion exchange, and biological nitrification. PRB 2 was packed with ORC (30 cm high) and clinoptilolite (120 cm high) to simulate the proposed PRB. PRB 3 was packed with ORC (30 cm high), ceramicite (30 cm high), and clinoptilolite (90 cm high) to identify the effect of ceramicite as supporting material on the biological growth. 8 intermediate sampling ports were positioned along the height of each PRB, at 20 (port 1), 40 (port 2), 60 (port 3), 80 (port 4), 100 (port 5), 120 (port 6), 140 (port 7), and 160 cm (port 8) from the inlet end. River sand (30 cm high) in the sand zones near the inlets was to simulate a natural aquifer and ensure flow distribution. River sand was mixed well with ORC beads in the ORC zones in an effort to buffer the rise in pH. U-bend polyvinyl chloride tubing was utilized to control water table and carry effluent away for disposal.

It is important to note that the PRBs were not inoculated and their packing media were not replaced during operation. Each PRB was continuously fed with synthetic groundwater in a downflow mode using a multiport peristaltic pump set (BT 100-1F drive, DG-4 pump head, Baoding Longer Precision Pump Co., Ltd., China) at a flow rate of 15 mL/min (Darcy velocity = 0.7 m/d). PRBs 1, 2, and 3 were operated for 183, 282, and 234 pore volumes (PVs) (corresponding to 147, 188, and 188 days) in the dark at 13–28 °C, respectively. Water samples were collected from the inlets, outlets, and intermediate sampling ports, and stored at 4 °C until analysis.

2.3. Analytical methods, instruments and data processing

$\text{NH}_4^+ - \text{N}$ was determined using a flow injection analyzer (Lachat, Model QC 8000, USA), employing spectrophotometry with salicylic acid. $\text{NO}_3^- - \text{N}$ and $\text{NO}_2^- - \text{N}$ were measured using an ion chromatograph (Dionex, Model ICS-2100, USA). The lower detection limits for $\text{NH}_4^+ - \text{N}$, $\text{NO}_3^- - \text{N}$, and $\text{NO}_2^- - \text{N}$ were 0.01, 0.10, and 0.03 mg/L, respectively. DO and water temperature were measured using a portable DO meter (Hach, Model HQ30d, USA). pH was monitored using a digital pH meter (Hach, Model MP-6, USA). Total hardness (TH) was determined using EDTA (ethylenediaminetetraacetic acid) titration method (APHA, 2005). Total alkalinity (TA) was measured using an alkalinity test kit (Hach, Model AL-DT, USA), employing 0.16 N H_2SO_4 with a digital titrator (Model 16900). In each analysis, at least one in five samples was duplicated and the deviation between the two samples was always less than 5%. Total nitrogen (TN) (mg/L) was defined as the sum of $\text{NH}_4^+ - \text{N}$ (mg/L), $\text{NO}_2^- - \text{N}$ (mg/L), and $\text{NO}_3^- - \text{N}$ (mg/L). The number of PVs was expressed as the ratio of accumulated water volume (L) over time to pore volume of reactive media (L). Data are

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