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Technical Note

Slowly released molasses barrier system for controlling nitrate plumes in groundwater: A pilot-scale tank study

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HIGHLIGHTS

- A well-type barrier system with solidified molasses was studied for NO_3 removal.
- Removal efficiency for 142 mg L^{-1} of NO_3 was 79–84% at the pilot-scale tank.
- Pore clogging and hydraulic disturbance were not evident in the barrier system.

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ABSTRACT

A well-type barrier system containing solidified molasses as a reactive medium was developed to promote the indigenous denitrifying activity and to treat nitrate plumes in groundwater. Three slowly released molasses (SRM) barrier systems harboring 60, 120, and 120 SRM rods, which were named System A, B, and C, respectively, were operated to examine nitrate removal efficiency in a pilot-scale sandy tank. These SRM systems induced a consistent removal of nitrate without pore clogging and hydraulic disturbance during the test period. The initial nitrate concentration was 142 mg L^{-1}, and the concentrations decreased by 80%, 84%, and 79% in System A, B, and C, respectively. In particular, System C was inoculated with heterotrophic denitrifiers, but the nitrate removal efficiency was not enhanced compared to System B, probably due to the prior existence of indigenous denitrifiers in the sandy tank. The presence of nitrite reductase-encoding gene (i.e. *nirK*) at the site was confirmed by denatured gradient gel electrophoresis analysis.

1. Introduction

Nitrate contamination in shallow groundwater has been found in many parts of rural area worldwide in the last few decades due to the excessive usage of animal manures and nitrogenous fertilizers to enhance crop yields and the land disposal of domestic wastewaters. Nitrate contamination of groundwater can cause methemoglobinemia in infants and other health-related problems in rural populations who use shallow groundwater as a water supply. In addition, the discharge of nitrate-contaminated groundwater into wetlands, rivers, estuaries, and the coastal environment can contribute to toxic algal blooms in these water bodies (Appleyard and Schmoll, 2006).

Conventional technologies such as ion exchange, reverse osmosis, electrodialysis, and distillation are available for treating nitrate in groundwater. However, these technologies are mechanically complex, require periodical maintenance, and are costly (Moon et al., 2008). As alternatives, available organic compounds such as acetic acid, glucose, ethanol, and methanol are widely utilized for denitrification due to their high solubility and lessened cause of coprecipitation or adsorption (Her and Huang, 1995; Mohseni-Bandpi et al., 1999; Chou et al., 2003; Louzeiro et al., 2003). Some studies have proposed molasses, a byproduct from the sugar production process, as a reliable carbon source for denitrification due to rapid nitrate destruction and highly denitrifying efficiencies (Hamlin et al., 2008; Quan et al., 2005; Roy et al., 2010). For *in situ* denitrification in groundwater, subsurface biofilm barriers with an injected mixture of liquid-phase molasses and nutrients were designed (Cunningham et al., 2003; Dutta et al., 2005). In their studies, nitrate concentrations of 443–1217 mg L^{-1} were decreased by 94–99% with 99% reduction of average hydraulic conductivity during 6–12-month test periods.

Recently, heterotrophic denitrification combined with a well-type reactive barrier system using solidified molasses named slowly released molasses (SRM system) has been developed as a

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long-term *in situ* remedial option for treating nitrate in groundwater (Lee et al., 2010; Lee et al., 2012). An SRM system was designed to operate with periodic additions of SRM rods into the well-type barriers. The long-term molasses release characteristics of the SRM system were confirmed with a pilot-scale sandy tank, and the longevity of the SRM system was determined using mathematical modeling (Lee et al., 2012). In this study, the nitrate removal efficiency of the SRM system in the presence or absence of indigenous denitrifiers was tested in a pilot-scale sandy tank as an *in situ* remedial approach.

2. Materials and methods

2.1. Experimental set-up

An SRM rod (od × L = 4 × 30 cm) was made by dispersing 177 g of molasses (Hydex, Korea) in 360 g of paraffin wax–cellulose–silica sand matrix (215 g of paraffin wax, 109 g of cellulose, and 36 g of silica sands) in a cylindrical mold at ambient temperature. The paraffin wax–cellulose–silica matrix could accomplish slow dissolution and diffusion-controlled transport of molasses from the rod. Apparent molasses solubility from the SRM rod was approximately 6000 mg L^{-1} as chemical oxygen demand (COD) value, which was measured in a batch-type release test conducted for 112 d (Lee et al., 2012).

The pilot-scale flow tank ($L \times W \times D$ = 8 × 4 × 2 m) was filled with 95 t of natural soil materials, which was packed to a density of 1.68 g cm^3, a porosity of 0.45, a total organic carbon content of 0.11%, and a depth of 2 m. The soil texture of the filling material was sand (sand 96%, silt 4%) based on the textural diagram of the United States Department of Agriculture. The sand used for this study was from a river mouth in Korea. The input and output chambers on the upstream and downstream ends of the tank were separated from the sand by rigid stainless steel screens to prevent sands from entering the chambers. Water levels of the input chambers at the upstream and the output chambers at the downstream were kept at a constant level, which lets the groundwater flow in the longitudinal direction with a constant rate. The flow velocity was controlled by the hydraulic head of each end, and it was maintained at 120 cm d^{-1}. A total of 120 polyvinylchloride (PVC) screened wells (od × L = 10 × 150 cm) consisted of three discrete barriers installed at 1-m intervals in natural sand in the flow tank as shown in Fig. 1. PVCs were manufactured to be fully screened wells (slit interval <1 mm). In each barrier, forty wells were arrayed in a zigzag shape vertical to the flow direction. A hydrologic conductivity in the sandy tank was estimated to be 8.01 × 10^{-2} cm s^{-1} based on a tracer test (Lee et al., 2009).

2.2. SRM system operation

Synthetic nitrate-contaminated groundwater (142 mg L^{-1}) was made by mixing tap water (600 L d^{-1}) and a diluted nitrate solution of 312 mg L^{-1} (500 L d^{-1}). The tap water from the water supply line and the nitrate solution from a large nitrate storage tank were introduced into the input chamber. Mixing was facilitated by two underwater circulators in the input chamber. This synthetic groundwater contained four basal salts in mg L^{-1}: 19NH_4Cl, 7KH_2PO_4, 19K_2HPO_4, and 19$MgSO_4$. The natural sand in the flow tank was pretreated with 142 mg L^{-1} nitrate-contaminated groundwater for 1 month. The SRM rods were placed in the wells to perform nitrate removal tests. The operating conditions of the three SRM systems were as follows: (i) System A: single straight line type with 60 SRM rods as shown in Fig. 1a, with a test period of 13 d, (ii) System B: double straight lines type with 120 SRM rods as shown in Fig. 1b, with a test period of 21 d, (iii) System C: double straight lines type with 120 SRM rods, an additional inoculation of an external denitrifier *Pseudomonas* sp. KY1 with *nirK* (Lee, 2010) into the sand to increase nitrate removal efficiency, with a test period of 55 d. The systems were operated at room temperature.

Pseudomonas sp. KY1 was enriched in a 1000 L volumetric water tank at room temperature for 15 d. The solution in the water tank

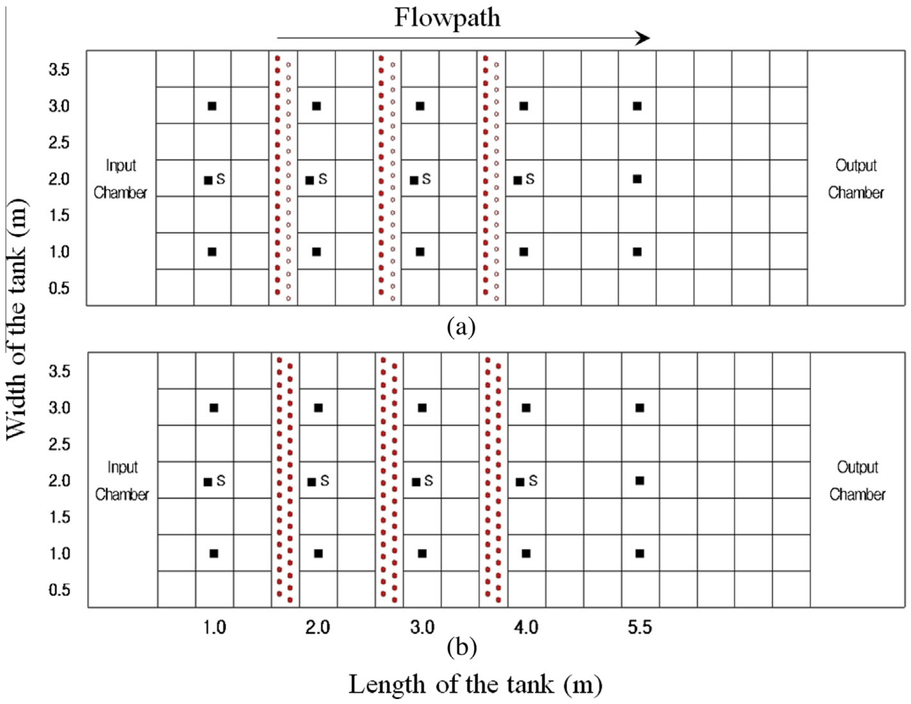

Fig. 1. Schematic diagram of the large test tank setup (A top view); (a) single straight line type SRM system (System A), (b) double straight lines type SRM system (System B and C). Closed circle (●), closed square (■), and letter (S) represent for SRM rod, groundwater-, and soil-sampling point, respectively.