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A continuous stirred hydrogen-based polyvinyl chloride membrane biofilm reactor for the treatment of nitrate contaminated drinking water

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ABSTRACT

A continuous stirred hydrogen-based polyvinyl chloride (PVC) membrane biofilm reactor (MBfR) was investigated to remove nitrate from the drinking water. The reactor was operated over 100 days, and the result showed that the average nitrate denitrification rate of 1.2 g NO_3^-–N/m^2d and the total nitrogen (TN) removal of 95.1% were achieved with the influent nitrate concentration of 50 mg NO_3^-–N/L and the hydrogen pressure of 0.05 MPa. Under the same conditions, the average rate of hydrogen utilization by biofilm was 0.031 mg H_2/cm^2d, which was sufficient to remove 50 mg NO_3^-–N/L from the contaminated water with the effluent nitrate and nitrite concentrations below drinking water limit values. The average hydrogen utilization efficiency was achieved as high as 99.5%. Flux analysis demonstrated that, compared to sulfate reduction, nitrate reduction competed more strongly for hydrogen electron, and obtained more electrons in high influent nitrate loading.

1. Introduction

Removing nitrates and nitrites from drinking water has gained significant attention in recent years due to the risk posed to human health from their contaminated groundwater and surface water. In general, nitrate was mainly from the usage of nitrogen fertilizers (Su and Puls, 2004) and the irrigation with domestic wastewater (Shrimali and Singh, 2001; Soares, 2000). The nitrate concentration in many abstracted waters worldwide now exceeded regulatory standards (WHO and EU, 10 and 11.3 mg NO_3^-–N/L, respectively) (WHO, 2003). These phenomena instigated people to safeguard the risk of methemoglobinemia and cancer induced by nitrosamines, metabolites of nitrate (Bouchard et al., 1992).

The greatest past experience is with abiotic, or physical–chemical treatment methods to remove nitrate and nitrite from drinking water. Abiotic processes include ion exchange (Bae et al., 2002; Boumediene and Achour, 2004), reverse osmosis (Schoeman and Steyn, 2003), and electro-dialysis (Elmidaoui et al., 2002). However, these processes were limited in applications due to high capital and energy costs and subsequent disposal problem of large volumes of waste brine (Shrimali and Singh, 2001).

The biological process that removes nitrate and nitrite is denitrification, which reduces nitrate and nitrite to nitrogen (N_2). Generally, with the low concentration of biodegradable carbon sources in the drinking water, the reduction of nitrate requires addition of electron donor substrates, which include organic carbon sources, such as methanol, ethanol or acetate (belonging to heterotrophic denitrification) (Mohseni-Bandpi and Elliott, 1998; Wang et al., 2009) and a few inorganic electron donors, such as hydrogen and sulfur (belonging to autotrophic denitrification) (Ergas and Reuss, 2001; Koenig and Liu, 1996). While, there are some problems with the heterotrophic denitrification processes, such as bringing carry-over of added organic carbon and microbial biomass to the final effluent.

Autotrophic denitrification using hydrogen as the supplemental donor has been extensively investigated to remove nitrate from polluted drinking water or waste water (Dries et al., 1988; Hasar et al., 2008; Kapoor and Viraraghavan, 1997; Kurt et al., 1987; Lee and Rittmann, 2000). The autohydrogenotrophic denitrifiers are able to respire on NO_3^-–N in the absence of molecular oxygen. Otherwise, hydrogen is cheaper, nontoxic, lower biomass yield, and without a residual.

Generally, there are two ways to transfer hydrogen to the bulk fluid, i.e., sparging the gas or transferring hydrogen to the biofilm through bubbleless gas-permeable membrane (Dries et al., 1988; Kurt et al., 1987; Lee and Rittmann, 2000). With the danger of explosion and low hydrogen utilization rate for the sparging methods, the bubbleless gas-permeable membrane technology has been developed to be a promising way to reduce nitrate, and there are more highlighted advantages for the membranes, such as effective gas transferring and utilization, safe environment for denitrification. To date, a few of bubbleless gas-permeable membranes have been used for hydrogen delivery, such as a double-skinned

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polyethylene fiber with a dense internal polyurethane layer (1 μm) (Lee and Rittmann, 2000), polypropylene (Terada et al., 2006), silicone-coated reinforced fiberglass fibers (Haugen et al., 2002), silicone-coated ferro-nickel slag (Terada et al., 2006). Although such technology is conceptually promising, there are some challenges to be overcome for the robust reactor development, such as the limit of gas diffusion by the mineral sedimentation and biofilm layer (Visvanathan et al., 2008), deterioration of denitrification performance caused by biofilm sloughing from the membrane (Sawyer and Hermanowicz, 1998). PVC, as a synthetic premise plumbing materials, was extensively used in homes and distribution systems (Cerrato et al., 2006; Heim and Dietrich, 2007), and was safe to drinking water. While PVC fibers were normally used as ultrafiltration membranes in water treatment (Guo et al., 2009; Qiao et al., 2008), they were seldom used as attaching membranes for the biofilm. With the excellent performance of gas diffusing and the cost-effective of membrane fabrication, PVC membrane would be a powerful alternative for hydrogenotrophic denitrification.

This research, which focuses on H_2 as a clean and economical source of electronic donor substrate, investigates the performance of a new PVC hollow fiber membrane biofilm reactor for drinking water denitrification with varied nitrate loading and influent concentrations.

2. Methods

2.1. Membrane biofilm reactor

The experimental set-up of the continuous stirred MBfR used in this study is shown in Fig. 1. A transparent plastic cylinder was used as a hollow fiber membrane reactor, in which two membrane modules were directly submerged in the bulk fluid and gas sealed with the plastic ring and the cap of the reactor (Fig. 1). At the same time, the modules were easily disassembled from the reactor for rinsing or repairing the membranes when the membranes were polluted or damaged. The reactor was 22 cm in height and 6 cm in inner diameter. The system made the feed-media to be mixed well in the biofilm reactor because the stirring power was generated by a magnetic stirrer set in the bottom of the reactor. The hollow fibers were made of PVC with pore size of 0.01 μm, manufactured by Litree Company (Suzhou, China). The outside and inner diameters of the fiber are 0.15 and 0.085 cm, respectively, which provides 633.3 cm^2 of surface area with total 96 hollow fibers (each module consisted of 48 hollow fibers). The total available volume of the reactor system was 560 ml. The void ratio of the working reactor volume (volume of fiber was 23.7 ml) was 95.8%. A single peristaltic pump (Longer BT50-1J, Baoding, PRC) was used to keep a nitrate-medium-feed rate of 1.1 ml/min. Pure H_2 was supplied to the inside hollow fibers through a H_2 gas tank via a metering value.

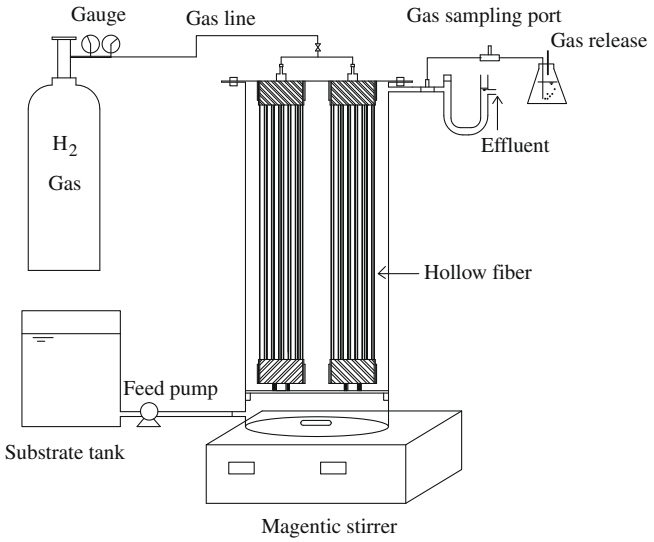

Fig. 1. Schematic of the MBfR.

2.2. Synthetic influent

In present study, the components of synthetic influent for simulating drinking water were KH_2PO_4 (0.128 g/L), Na_2HPO_4 (0.434 g/L), $MgSO_4{\cdot}7H_2O$ (0.2 g/L), $CaCl_2{\cdot}2H_2O$ (0.001 g/L), $FeSO_4{\cdot}7H_2O$ (0.001 g/L), and $NaHCO_3$ (0.252 g/L), and 1 ml trace mineral solution, respectively. Nitrate concentrations ranged from 10 to 50 mg NO_3^-–N/L. The trace mineral solution consisted of: $ZnSO_4{\cdot}7H_2O$ (100 mg/L), $MnCl_2{\cdot}4H_2O$ (30 mg/L), H_3BO_3 (300 mg/L), $CoCl_2{\cdot}6H_2O$ (200 mg/L), $CuCl_2{\cdot}2H_2O$ (10 mg/L), $NiCl_2{\cdot}2H_2O$ (10 mg/L), $Na_2MoO_4{\cdot}2H_2O$ (30 mg/L), and Na_2SeO_3 (30 mg/L), respectively. The feed-media was prepared in a 20 L (available volume) glass bottle, and was purged with N_2 gas to eliminate dissolved O_2 in the influent. $NaNO_3$ and $NaHCO_3$ were used as inorganic nitrogen and carbon sources for the growth of autotrophic microorganisms, respectively. Phosphate buffer (KH_2PO_4 + - Na_2HPO_4) was used to keep initial pH value of the influent around 7.2 and prevent pH from sharp rise during denitrification process.

2.3. Cultivation of microorganisms, start-up and experimental conditions

Start-up of the continuous stirred MBfR began when hydrogen was supplied to the membrane under the hydrogen pressure of 0.02 MPa, and the MBfR was inoculated with mixed-culture biofilm collected from another bioreactor, in which the autohydrogenotrophic denitrifying bacteria had been acclimated for several months. At the beginning of start-up, the reactor had intermittently run for 2 days to establish a biofilm on the membrane surface. Then, under the flow rate of 1.1 ml/min, the performance of continuous stirred MBfR was evaluated over 102 days with varied nitrate loading and influent concentration or hydrogen pressure. The other operation conditions of the reactor were listed in Table 1.

2.4. Analytical method

All the fluid samples collected from the reactor were kept in the refrigerator at 4 °C and analyzed within 2 days. The concentrations of NO_3^-–N, NO_2^-–N, SO_4^{2-} and pH value were analyzed according to Chinese NEPA standard methods (2002). The gas sample in the headspace of the reactor was taken by inserting a gas-tight syringe through the rubber stopper on the gas-sampling port. The gas concentrations were measured by a GC 14-B quipped with a TCD detector (Shimadazu Co.). The liquid phase concentrations of H_2 in the reactor were calculated by H_2 headspace concentrations using Henry's law.

Table 1
Operation conditions of the membrane biofilm reactor.

	Run 1	Run 2	Run 3	Run 4	Run 5
Operation period (day)	1–14	15–28	29–46	47–66	67–102
H_2 pressure (MPa)	0.02	0.02	0.04	0.05	0.05
Influent NO_3^-–N (mg/L)	10	10	20	40	50
Hydraulic retention time (h)			8.5		