Water Research 119 (2017) 234–241

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Enhancing denitrification using a novel *in situ* membrane biofilm reactor (isMBfR)

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ARTICLE INFO

Article history:
Received 4 January 2017
Received in revised form
18 April 2017
Accepted 23 April 2017
Available online 25 April 2017

Keywords:
Membrane biofilm reactor
Chemical oxygen demand
Nitrate reduction
Hydrogen

ABSTRACT

The insufficient supply of electron donor in surface water contaminated with nitrate leads to its incomplete reduction in natural or constructed wetlands. Although the addition of organic matter (represented as chemical oxygen demand, COD) can stimulate N removal by denitrification, direct supplementation of COD creates unacceptable risks to effluent quality. An alternative for stimulating denitrification is supplying hydrogen gas (H_2) as an inorganic electron donor. We evaluate an innovative means to do H_2-based denitrification of surface waters in a wetland setting: the *in-situ* membrane biofilm reactor (isMBfR), in which H_2 is delivered to a biofilm of denitrifying bacteria on demand based on the presence of nitrate. We carried out a proof-of-concept study in which an upper "photo zone" and a lower "MBfR root zone" were combined to remove nitrate and COD from simulated surface water. Employing mass-balances for H_2, COD, nitrate, and oxygen, we documented nearly complete removals of nitrate and COD, except when the H_2 supply was intentionally shut off. All nitrate removal was accomplished in the "MBfR root zone," where H_2 delivery supplemented the COD supply (as needed) and provided the large majority of electron equivalents to reduce nitrate to N_2.

1. Introduction

Wetlands contribute to surface-water quality and are natural habitats for fauna and flora (Drayer and Richter, 2016; Yang et al., 2016). Whether the wetland is natural or constructed, it can remove organic carbon (OC) and nitrogen (N) (Al-Isawi et al., 2017; Wu et al., 2010). The degrees to which OC and N coming to the wetlands can be removed depend on how the supply of electron donors (chemical oxygen demand (COD) and NH_4^+) is balanced by the input of electron acceptors (O_2 and NO_3^-) (Ifabiyi, 2008; Vagnetti et al., 2003). When a wetland is used for wastewater treatment, the influent generally contains considerable COD and NH_4^+, but relatively less O_2 and NO_3^- (Allen et al., 2010; Badhe et al., 2014). However, O_2 enters the water by surface aeration and photosynthesis (Allen et al., 2010; Badhe et al., 2014). With dissolved O_2 (DO) available, NH_4^+ can be nitrified to form NO_2^-, and NO_3^-, and COD is aerobically oxidized. As a result, the common situation in a wetland is that N accumulates in the form of NO_3^-, but little COD remains to drive microbial denitrification.

For this typical scenario, complete N removal requires that an electron donor be supplemented. While supplementing an organic electron donor is an option (Moussavi et al., 2015; Scherson et al., 2013), its addition to a wetland ecosystem may cause negative impacts, such as excessive formation of microbial biomass, increased turbidity, sediment build up, severe DO depletion, and residual COD in the effluent (Rittmann et al., 2005).

Hydrogen gas (H_2) is inorganic electron donor, and it has been extensively studied for end-of-pipe denitrification using the membrane biofilm reactor (MBfR) (Hasar et al., 2008; Lee and Rittmann, 2002; Tang et al., 2011; Xia et al., 2010). Compared to adding an organic donor, using H_2 offers numerous advantages: relatively low cost per electron delivered; not toxic to humans; low productions of biomass, turbidity, and sediment; no donor residual; less expensive than most organic donors; and can be delivered "on demand" with essentially 100% efficiency (Lee and Rittmann, 2002; Rittmann et al. 2004, 2005; Xia et al., 2011; Zhou et al., 2016).

For end-of-pipe treatment, the H_2-based MBfR has been applied

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http://dx.doi.org/10.1016/j.watres.2017.04.054
0043-1354/

to reduce one or several oxidized contaminants, including nitrate, perchlorate, selenate, chromate, vanadium (V), and uranium from waters having minimal or no COD (Chung et al., 2006; Ontiveros-Valencia et al., 2012; Rittmann, 2006, 2007; Rittmann et al., 2005; Xu et al., 2015; Zhao et al., 2011; Zhou et al., 2014, 2016). A biofilm dominated by H_2-oxidizing autotrophs accumulates on the exterior surface of non-porous hollow-fiber membranes. H_2 diffuses through the membrane wall and is consumed within the biofilm; the H_2 concentration in the bulk water is negligible (Lee and Rittmann, 2002; Ziv-El and Rittmann, 2009).

In a wetland setting, particularly when used for wastewater treatment, organic matter (i.e., COD) co-exists with NH_4^+ and NO_3^- (Wu et al., 2011a, 2011b; Zhao et al., 2016). Thus, the H_2-based MBfR has to function well when COD oxidation must be achieved in parallel. Hybrid aerobic/anoxic MBfR systems based on H_2 and O_2 delivery in integrated MBfR units successfully removed total N (Cowman et al., 2005; Hasar et al., 2008). However, in the wetland setting, O_2 delivery takes place by the usual means of advection in the influent, surface aeration, and photosynthesis. Thus, the role of the MBfR is to enhance denitrification that occurs in parallel with aerobic COD oxidation and nitrification.

The main objective of this study was to demonstrate that a H_2-based *in situ* MBfR (isMBfR) could augment denitrification in parallel with COD oxidation in synthetic wastewater with low COD/TN ratio. To achieve this goal, we examined the removal efficiencies of TN and COD in a bench-scale simulation of how an isMBfR can be integrated into a wetland.

2. Materials and methods

2.1. The isMBfR design

To test the isMBfR in a simple wetland scenario, a bench-scale system was divided into a top "photo zone" and a bottom "MBfR root zone." As illustrated in Fig. 1, a phototrophic top zone was simulated by using 150 cm^3 of low-density (18 kg/m^3) sponges; it had a volume of 210 cm^3 and was illuminated. The MBfR root zone held 7 bundles (with a total surface area of 0.07 m^2) of polypropylene fibers (products of Teijin Fibers Ltd., Osaka, Japan) sealed into H_2 ports to deliver H_2. The other ends of the fibers were shut with glue. Each bundle consisted of 12 fibers of 14-cm length. During experimentation, H_2 was supplied from the top through tubing and distributed to the 7 H_2 ports. The H_2 was supplied using a H_2 cylinder, and the H_2 pressure to the fibers using a pressure regulator. The volume of the bottom compartment (below the floating support and holding the isMBfR) was ~450 mL. Separating the top and bottom zones was a floating spacer of 2-cm thick polyethylene. A stir bar (325 rpm) mixed the contents of the bottom section, but mixing with the top photo zone was negligible. Tubing connected the outlet of the "photo-zone" removed effluent from the system.

2.2. Start-up and operating conditions

Initially, the isMBfR was inoculated with 30 ml of activated sludge from the Mesa Northwest Wastewater Reclamation Plant (Mesa, AZ, USA). The inoculation liquid was held in the system for 4 days to establish a biofilm, at which time the inoculum was flushed from the system before continuous feeding began.

The isMBfR was fed with synthetic wastewater with the following inorganic composition (per liter) for the standard condition: 0.087 g $NaNO_3$, 0.252 g $NaHCO_3$, 0.0053 g KH_2PO_4, 0.050 g $MgSO_4 \cdot 7H_2O$, and 1 ml trace mineral solution. The trace mineral solution contained (per liter): 100 mg $ZnSO_4 \cdot 7H_2O$, 30 mg $MnCl_2 \cdot 4H_2O$, 300 mg H_3BO_3, 200 mg $CoCl_2 \cdot 6H_2O$, 10 mg $CuCl_2 \cdot 2H_2O$, 10 mg $NiCl_2 \cdot 6H_2O$, and 30 mg Na_2SeO_3. The total

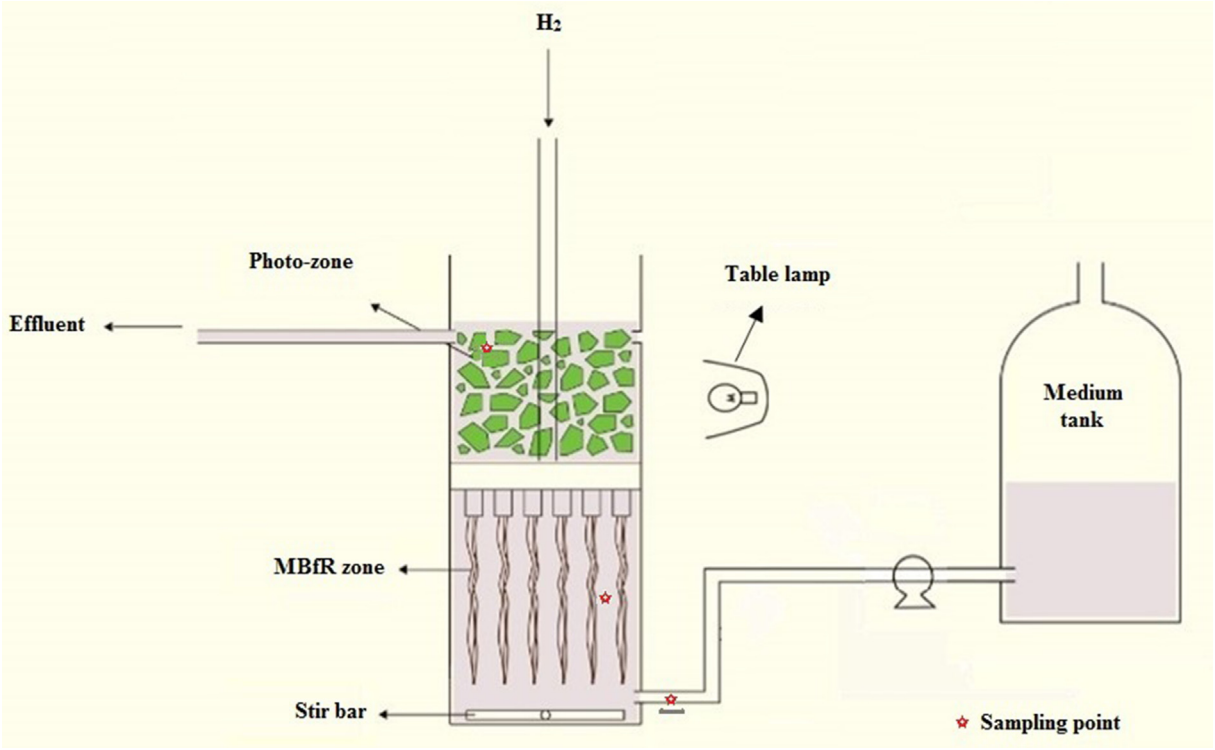

Fig. 1. Schematic of the isMBfR (height x diameter = 23.0 x 4.0 cm) used in this study. The flow was once-through. The influent (including nutrients and contaminants (i.e. organic materials and nitrate)) was delivered from a single medium tank during stages 1–4 (without COD supply). To minimize denitrification in the influent medium, the nutrients and the contaminants were input individually from two medium tanks (not shown here) from stage 5–7 (with COD supply). The light source was a table lamp delivering 875 lumens light intensity, and it stimulated the accumulation of photosynthetic microorganisms on the sponges in the photo zone.