Bioresource Technology xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Aerobic methane oxidation coupled to denitrification in a membrane biofilm reactor: Treatment performance and the effect of oxygen ventilation

Fei-yun Sun *, Wen-yi Dong *, Ming-fei Shao, Xiao-mei Lv, Ji Li, Liang-yu Peng, Hong-jie Wang

ShenZhen Key Laboratory of Water Resource Application and Environmental Pollution Control, Harbin Institute of Technology Shenzhen Graduate School, Shenzhen 518055, China

HIGHLIGHTS

- Novel MBfR for denitrification combined with aerobic methane oxidation.
- PVDF membrane employed for membrane aeration and biofilm growth.
- Effective nitrate removal by MBfR stably achieved.
- Oxygen ventilation modes affect the performance of MBfRs.

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Aerobic methane-oxidation
AME-D
Biological nitrogen removal
Denitrification

ABSTRACT

Aerobic methane-oxidation coupled to denitrification (AME-D) process was successfully achieved in a membrane biofilm reactor (MBfR). PVDF membrane was employed to supply the methane and oxygen for biofilm, which was coexistence of methanotrophs and denitrifier. With a feeding NO_3^-—N of 30 mg/L, up to 97% nitrate could be removed stably. The oxygen ventilation modes impacted the denitrification performance remarkably, resulting in different nitrate removal efficiencies and biofilm microorganism distribution. The biofilm sludge showed a high resistance to the DO inhibition, mainly due to the co-existing methanotroph being capable of utilizing oxygen perferentially within biofilm, and create an anoxic micro-environment. The denitrification of both nitrate and nitrite by biofilm sludge conformed to the Monod equation, and the maximum specific nitrate utilization rate (k) ranged from 1.55 to 1.78 NO_3^-—N/g VSS-d. The research findings should be significant to understand the considerable potential of MBfR as a bioprocess for denitrification.

1. Introduction

Biological nitrogen removal (BNR) is the most common process that is used in wastewater treatment plant (Metcalf et al., 2002; Zhu et al., 2013). As for the post-denitrification, in which N-elimination occurs according to the natural nitrification/denitrification order, it is recognized that N can be theoretically completely removed from wastewater while sufficient carbon source provided (Rittmann and McCarty, 2001). However, extra addition of carbon source, a key factor affecting the TN removal effectiveness, inevitably increases the cost of the wastewater treatment process. Recently, a number of reports demonstrated that methane (CH_4) is one potentially inexpensive and widely available electron donor for denitrification (Mason, 1977; Raghoebarsing et al., 2006; Modin et al., 2007). According to stoichiometric equation Eq. (1) that is thermodynamically favorable under standard conditions, nitrate is reduced to dinitrogen gas and methane is oxidized to carbon dioxide. Thus, methane would be used for the N-removal from drinking water (in situ or at a treatment plant), wastewater or landfill leachate (Kjeldsen et al., 2002; Modin et al., 2007). In the latter two cases (wastewater and landfill leachate), methane will be especially suitable since that it can be generated onsite by the anaerobic digestion of sludge in wastewater treatment plants and biodegradation of organic waste in landfills.

$$5CH_4 + 8NO_3^- = 5CO_2 + 6H_2O + 4N_2 + 8OH^- \qquad \Delta G_f^0 = -767\ \mathrm{KJmol^{-1}}CH_4 \tag{1}$$

There are two microbial processes capable of carrying out denitrification with methane: one is anaerobic methane oxidation coupled to denitrification that is as of yet poorly understood and seems to be completed by some kinds of slow-growing microorganisms (Ettwig et al., 2008), and the other is aerobic methane oxidation coupled to denitrification (AME-D), which has been revealed in several laboratory studies (Mason, 1977; Costa et al., 2000;

* Corresponding author. Tel.: +86 755 2662 4592; fax: +86 755 2603 2718 (F.-y. Sun), tel./fax: +86 755 26033482 (W.-y. Dong).
E-mail address: sunfeiyun1982@gmail.com (F.-y. Sun).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.03.115

Eisentraeger et al., 2001; Modin et al., 2010). During the AME-D process, some previous studies believe that denitrification with methane under aerobic conditions is performed through two steps: firstly, methane is oxidized by aerobic methanotrophs in the presence of oxygen and release soluble organics, afterwards, the coexisting denitrifiers can utilize these organic matters to carry out denitrification (Eisentraeger et al., 2001; Knowles, 2005). However, some results of previous reports are often inconsistent, with research showing that aerobic methanotrophs can only provide carbon source, or that not only oxidize methane to organics, but also take some responsibility for denitrification (Eisentraeger et al., 2001; Knowles, 2005; Waki et al., 2005; Modin et al., 2010; Yao et al., 2013). Some investigators have suggested that AME-D process is rather sensitive to the environmental factors, i.e. temperature, water compositions, etc. (Waki et al., 2002; Modin et al., 2007), and sometimes is constrained by gaseous and substrates transport in bioreactors. As a result, nitrogen removal from complicated solution, such as wastewater and landfill leachate, with an acceptable effectiveness and efficiency, is rather difficult (Modin et al., 2007). Therefore, to develop an innovative system for AME-D process removing nitrogen from wastewater that may make the best use of methane as carbon source still needs to be investigated.

Membrane biofilm reactor (MBfR) is a new developed bio-system for the pollutants removal of domestic and industrial wastewater (Brindle et al., 1998; Martin and Nerenberg, 2012; Wei et al., 2012). Due mainly to that a gaseous substrate (oxygen, or methane) is supplied from the interior of a membrane to biofilm growing on the membrane surface, MBfR allows high transfer rates of sparingly soluble substrates directly to the microorganisms and prevents losses to the atmosphere or effluent liquid. Since the last two decades, increasing interest in the MBfR has been evident as a result of its effectiveness in chemical oxygen demand (COD) and total inorganic nitrogen (TIN) removal from wastewater (Semmens et al., 2003; Martin and Nerenberg, 2012), and also in oxidization of some emerging environmental contaminants (EEC) from water (Nerenberg and Rittmann, 2004; Martin and Nerenberg, 2012) and trichloroethylene from contaminated water (Clapp et al., 1999). In recent, the feasibility of MBfR for AME-D process to remove total inorganic nitrogen of water was evaluated, whilst the characteristics of the methanotrophic bacteria on the biofilm formed was also examined (Rishell et al. 2004; Modin et al., 2007, 2010). It was found that MBfR had considerable potential as a bioprocess that exploited methanotrophic to help denitrification. Modin et al. (2007) observed that denitrification and methane oxidation could occur simultaneously, and they achieved a higher nitrate removal efficiencies in terms of methane utilization (values ranging from 0.25 to 0.36 mol-N/mol-CH_4) than those observed previously in a suspended culture (Thalasso et al., 1997; Eisentraeger et al., 2001; Rishell et al. 2004; Keluskar et al., 2013). However, the membranes employed by these researchers were silicon-based with a rather low specific area, which to a larger degree inhibited the volumetric loading rate of MBfRs that have significantly negative impact onto its application. Therefore, it is likely highly expected that the employment of polymeric membrane in MBfR may improve the TN removal capability and effectiveness.

In this laboratory study, in the MBfR system, a polyvinylidene fluoride (PVDF) membrane for gaseous ventilation was developed, and the carbon source for TIN removal, i.e. denitrification, from wastewater was supplied by aerobic methane oxidation. Two oxygen ventilation modes, one is both methane and oxygen aerated by membrane, while the other is only methane provided from membrane, were applied in two MBfRs operated side by side. The objectives of this experimental works were: (i) to evaluate the feasibility of polymeric membrane for gaseous aeration in MBfRs, (ii) to correlate the oxygen ventilation modes and the denitrification behavior, and (iii) to investigate the respective effect of oxygen ventilation modes on the TIN removal paths and related microorganisms properties. The results herein would be significant to understand the considerable potential of MBfR as a bioprocess for the denitrification from domestic wastewater, and somewhat more specifically, some affecting factors.

2. Methods

2.1. Experimental set-up and operation

Two equal laboratory-scale MBfRs were operated for more than 200 d. The MBfR set-up consisted of an cubic tank ($L \times W \times H = 24 \times 6 \times 34$ cm) functioning as a bioreactor of 4.5 L in working volume and an immersed polyvinylidene fluoride (PVDF) hollow-fiber membrane module (0.1 m^2 in surface area, Mitsubishi Rayon) (Fig. 1). The membrane, with an outside diameter of 4 mm, a wall thickness of 0.4 mm, and a pore size of 0.4 μm was used to supply gaseous substrates for the microorganisms on its surface and also to those in MBfRs. The membrane was connected to a 600 mL gas reservoir where methane, oxygen helium were mixed at a certain elevated pressure (approximately 150 kPa). The flow-rate of the gaseous substrate was controlled using a flow-rate sensor (PTX Ex-0129, Druck), by which the amount of methane and oxygen penetrating into the biofilm was

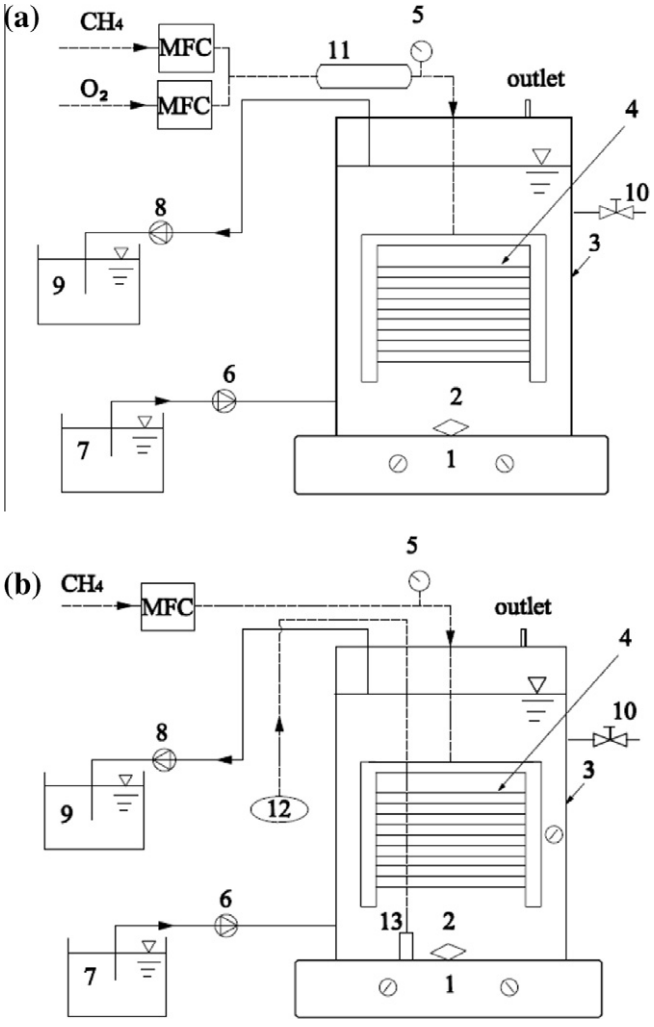

Fig. 1. Schematic diagram of MBfRs. (a) R_1 that both of oxygen and methane are supplied from membrane interior; (b) R_2 that only methane is supplied by membrane aeration.

Please cite this article in press as: Sun, F.-y., et al. Aerobic methane oxidation coupled to denitrification in a membrane biofilm reactor: Treatment performance and the effect of oxygen ventilation. Bioresour. Technol. (2013), http://dx.doi.org/10.1016/j.biortech.2013.03.115