



Short Communication

Long term effect of MnO₂ powder addition on nitrogen removal by anammox processSen Qiao^{a,*}, Zhen Bi^a, Jiti Zhou^a, Yingjun Cheng^b, Jie Zhang^{c,*}, Zafar Bhatti^d^a Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, PR China^b Division of Resource Conservation and Environmental Protection, Dalian Municipal Development and Reform Commission, Dalian 116001, PR China^c State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China^d Safe Drinking Water Branch, Ontario Ministry of the Environment, 2-St. Clair Ave. W, 19 Fl., Toronto, Canada ON M4V 1L5

HIGHLIGHTS

- ▶ Nitrogen removal performance of anammox process increased with MnO₂ powder addition.
- ▶ The crude enzyme activity of anammox biomass with MnO₂ powder addition increased 78.2%.
- ▶ The T-Mn content of anammox biomass with MnO₂ powder increased 50-fold.
- ▶ The filament-like structure and larger particles in anammox cell of the reactor with MnO₂ powder were observed.

ARTICLE INFO

Article history:

Received 12 June 2012

Received in revised form 21 July 2012

Accepted 23 July 2012

Available online 7 August 2012

Keywords:

Anammox

MnO₂

Enzyme activity

Long-term effect

ABSTRACT

This study examined long-term effect of MnO₂ powder (average diameter of 4–7 μm) on nitrogen removal in anammox process. Two lab-scale up-flow anammox reactors were operated for 380 days, one with and one without MnO₂ powder addition. During the period when only substrate concentrations varied, the maximum nitrogen removal rate in the reactor with MnO₂ addition reached 920.9 g-N/m³/d. This value was 2-folds higher than that (464.6 g-N/m³/d) of the reactor without MnO₂ addition. The crude enzyme activities of the anammox biomass from the two reactors was measured as 0.531 ± 0.019 and 0.298 ± 0.007 μmol cytochrome c reduced/mg protein/min, respectively. Transmission electron microscopy observation demonstrated more undefined particles existing inside anammox bacterial cell in the reactor with MnO₂ powder addition. Furthermore, filament-like structures inside anammoxosome were observed, which formed a net-like structure with particles as the connecting nodes. The experiment results demonstrated that MnO₂ improved nitrogen removal performance of anammox process.

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1. Introduction

Anaerobic ammonium oxidation (anammox) process is now recognized as a novel and important process in biological nitrogen removal, which can directly convert NO₂⁻-N to N₂ gas with NH₄⁺-N as the electron donor under anaerobic conditions (Strous et al., 1999). Compared with the conventional nitrification–denitrification processes, anammox process offers significant advantages such as no demand for oxygen and organic carbon, low sludge production and reduced CO₂ or N₂O emissions (Schmid et al., 2003). The first full-scale anammox reactor (75 m³) in the world was reported to treat anaerobic sludge digester liquor with average N re-

moval rate of 750 kg-N/d (Van der Star et al., 2007). Recently, Tang et al. (2010) reported a very high nitrogen removal rate of 74.3–76.7 kg-N/m³/d in a lab-scale anammox UASB reactor, in which the biomass concentration was as high as 42.0–57.7 g-VSS/L. These results suggested high potential of anammox process in biological nitrogen removal from wastewaters. However, extremely slowly growth rate of anammox bacteria with a doubling time of 11 days (Strous et al., 1999) causes the longer start-up period. Consequently, enhancing the bacterial activity of anammox bacteria or shortening the start-up period of anammox reactors is subject of great interest and challenge.

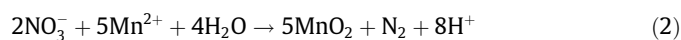
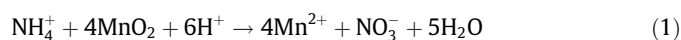
Recently, a number of exciting studies have also been published, which utilized external field energy such as magnetic field, electric field and low intensity ultrasound to increase the activity of anammox bacteria. For instance, Liu and Yang (2009) reported the maximum nitrogen removal rate of anammox biomass increased by

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30% at magnetic value of 60.0 mT and 20% at an electrode voltage of $-0.05V_{SCE}$. Similarly, Duan et al. (2011) demonstrated that total nitrogen removal rate of anammox bacteria increased by 25.5% by applying ultrasound intensity of 0.3 w/cm^2 with the optimal irradiation time of 4 min. The ultrasound effect could last for 6 days after ultrasound applied once. Zhang et al. packed with a Fe-electrode to enhance the activity of anammox biomass, who found that the N removal performance with the Fe-electrode was about 24% higher than that of the reactor without Fe-electrode. Zhang et al. speculated that the released Fe^{2+} from the Fe-electrode was in favor of the growth of retaining of anammox biomass (Zhang et al., 2012).

Luther et al. (1997) and Hulth et al. (1999) have suggested that the interaction between Mn-oxides and nitrogen compounds under anaerobic condition will catalyze the production of dinitrogen gas, as shown in Eqs. (1) and (2).



Luther et al. (1997) provided field and laboratory evidence that N_2 could be produced by the oxidation of NH_3 and organic-N with MnO_2 . While the reduced Mn^{2+} could be reoxidized to MnO_2 by O_2 in a catalytic cycle that affected nitrogen speciation and marine nitrogen cycle. However, Thamdrup and Dalsgaard (2000) demonstrated that the oxidation of NH_4^+ with MnO_2 was insignificant. Thamdrup and Dalsgaard (2002) measured the average rate of anaerobic ammonium oxidation of samples taken from three sediments, which were 30, 99, and $83 \mu\text{M/d}$, respectively. Thamdrup and Dalsgaard (2002) deduced that anaerobic ammonium oxidation might be particularly favored over denitrification as a sink of nitrate in manganese oxide-rich sediment. Engström et al. (2004) found that anammox process contributed to almost 80% N_2 production in the sediment with Mn-oxides concentration over $300 \mu\text{mol/g}$ dry sediment. Engström et al. (2004) speculated that the presence of Fe- or Mn-oxides possibly enhanced buffering capacity, acted as an oxidant potentially significant for the limited organic carbon in marine sediments. Fe- or Mn-oxides may stimulate and contribute to conditions more favorable for anammox than traditional denitrification. Hulth et al. (1999) and Engström et al. (2004) also suggested that availability of Mn and Fe-oxides seemed to occasionally accelerate total rates of N_2 formation from anammox process compared to traditional denitrification in surface marine sediments. Anammox, in the presence of Mn-oxides to produce nitrate, was also suggested to occur in natural marine sediments on the basis of co-occurrence of peak of Mn (II) and NO_3^- (Bartlett et al., 2008). Furthermore, *Candidatus Kuenenia stuttgartiensis* (one kind of anammox bacteria) was proved to have a versatile lifestyle (Kartal et al., 2007). It could also employ Fe^{3+} , Mn-oxides and nitrate as electron acceptor in their metabolism (Strous et al., 2006), which supported the role of Fe- and Mn-oxides in anammox process. The results of the above studies demonstrated that Mn-oxides favored N_2 production and anammox process in the natural ecosystem, especially in the marine sediments environments. The effects of Mn-oxides on nitrogen conversion and anammox process in man-made ecosystem, such as bioreactor system or municipal wastewater treatment plants, are still not well known or explored.

The objective of this study was to investigate long term effect of MnO_2 on nitrogen removal in anammox bioreactor system. Two lab-scale up-flow anammox reactors were operated in parallel, one with and one without MnO_2 powder addition. In addition to the nitrogen removal performances, we also examined the crude enzyme activity of anammox bacteria cells and cell morphotypes with transmission electron microscopy (TEM) technique in two parallel. The possible mechanism of effect of Mn-oxides on anammox biomass was also discussed.

2. Methods

2.1. Microorganisms and feed substrates

The anammox sludge used for inoculation originated from a laboratory-scale anammox upflow column reactor in our lab. Anammox bacteria, belonging to two groups: *Candidatus Kuenenia stuttgartiensis* and *Candidatus Jettenia asiatica*, accounted for 57% of the total biomass (Duan et al., 2011). The substrates used in the experiments mainly consisted of ammonium and nitrite in the form of $(NH_4)_2SO_4$ and $NaNO_2$. The composition of the trace mineral medium was as same as described by Third et al. (2001), only removing the compound of $MnCl_2 \cdot 4H_2O$ to avoid its interference. The detailed information is shown Table 1.

2.2. Batch experiments

In order to ascertain the initial effects of addition of MnO_2 on N_2 gas production in anammox process, three sets of batch experiments were conducted with the same biomass. The tests were carried out in three 120 ml serum vials containing 100 ml medium. Three serum vials contained only anammox biomass, only MnO_2 powder (5 g dry weight, 90%, activated at 200°C for 6 h, average diameter of $4\text{--}7 \mu\text{m}$), and both anammox biomass and MnO_2 powder, respectively. The anammox mixed liquor volatile suspended solid (MLVSS) concentration of each batch experiments was set as 2240 mg/L (wet weight 5 g). Biomass samples were taken from the reactors and washed three times with mineral medium to remove residual nitrogen. The pH was adjusted to 7.5 and the temperature was maintained at $35 \pm 1^\circ\text{C}$. The serum bottle contents were purged with argon gas to remove dissolved oxygen. Initial $NH_4\text{-N}$ and $NO_2\text{-N}$ concentrations were set at 50 mg-N/L . Samples were taken at the same interval to analyze the $NH_4\text{-N}$, $NO_2\text{-N}$, $NO_3\text{-N}$, total Mn concentrations and N_2 contents in spare space of the serum vials.

2.3. Continuous experiments

Two identical upflow fixed bed column reactors A and B had the working volumes of 0.5 L with the inner diameter of 5 cm and the height of 25.5 cm. Both reactors contained 50 g (wet weight) anammox biomass having a MLVSS concentration of 1320 mg/L . 50 g MnO_2 powder were added to the bottom of reactor A only to study the long-term effect of MnO_2 on the performance of anammox reactors. The two reactors were continuously fed with the substrates, which was purged with 99.5% N_2 to maintain dissolved oxygen below 0.5 mg/L . The pH of the influent was adjusted to 7.5 ± 0.2 by dosing with 2 M HCl and the two reactors' temperature was maintained at $35 \pm 1^\circ\text{C}$ using a water bath (please see Fig. S1).

2.4. Analytical methods

Concentrations of nitrite and nitrate were determined by using ion-exchange chromatography (ICS-1100, DIONEX, AR, USA) with an IonPac AS18 anion column after filtration with $0.22 \mu\text{m}$ pore size membranes. $NH_4\text{-N}$, mixed liquor suspended solid (MLSS) and MLVSS concentrations were measured according to the Standard Methods (APHA, 1995). pH measurement was done using a digital pH meter (PHS-25, Leici Company, China), while DO was measured using a digital DO meter (YSI, Model 55, USA). N_2 was determined by a gas chromatograph (GC-17A, Shimadzu, Japan). The anammox bacterial samples for TEM observations were taken from reactors A and B on day 240, which was carried out according to the methods described by Duan et al. (2011).

For determining the content of total Mn in the microbial cells, 0.3 g (wet weight) of biomass was taken from the both reactors

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