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Nitrogen removal performance of anammox process with PVA–SA gel bead crosslinked with sodium sulfate as a biomass carrier

N.V. Tuyen[a], J.H. Ryu[a], J.B. Yae[b], H.G. Kim[b], S.W. Hong[a,b], D.H. Ahn[a,b,*]

[a] Department of Environmental Engineering and Energy, Myongji University, Yongin, Gyeonggi-do 17058, Republic of Korea
[b] Bluebank Co., Ltd., Myongji University, #18109-1, Business Incubator Center 116, Myongji-ro, Cheoin-gu, Yongin-si, Gyeonggi-do 17058, Republic of Korea

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ABSTRACT

In this study, the result shows that polyvinyl alcohol–sodium alginate (PVA–SA) gel bead crosslinked with sodium sulfate are better among the different methods by comparing the relative mechanical strength, mechanical strength swelling and expansion coefficient of beads in water. Subsequently, anammox biomass entrapment by PVA–SA gel was introduced into continuous stirred tank reactor (CSTR). After 24 operation days, the nitrogen removal efficiency achieved 60%, while the nitrogen loading rate (NLR) was 0.14 kg N/m^3/d and the experiment data indicated that PVA–SA gel bead crosslinked with sodium sulfate can be used to initiate anammox process. Furthermore, it is an alternative for culturing anammox in a long-term operation.

Introduction

Since the anammox process was identified in a denitrifying fluidized bed reactor in deft, evidence for anammox activity has been obtained in a variety of laboratory and engineered systems, pilot plants for ammonium removal, surface and subsurface sediments of deep ocean, temperate estuarine, coastal and offshore sediments, lakes, freshwaters, polar region sediments and multi-year sea ice, oil reservoirs, deep sea hydrothermal vent and the sub-oxic zone of the Black Sea [1–4]. The anammox process is considered having enormous potential in the treatment of high nitrogen content wastewater such as landfill leachate, wastewater from seafood processing industries, etc. In this process, ammonium is oxidized with nitrite serving as the electron acceptor under anaerobic condition, producing nitrogen gas [1] with CO_2/bicarbonate as the sole carbon source like the following formula:

$$1NH_4^+ + 1{,}32NO_2^- + 0{,}066HCO_3^- + 0{,}13H^+ \rightarrow 1{,}02N_2 + 0{,}26NO_3^- + 0{,}066CH_2O_{0,5}N_{0,15} + 2{,}03H_2O \quad (1)$$

However, there are still some important challenges in practical application of anammox because of its slow growth rate and unstable start-up period. Therefore, the maintenance of a sufficient amount of anammox bacteria during the start-up is one of the most essential step with an anammox reactor.

Immobilization of microorganism in spherical polymeric matrices is promising for improvement of the efficiency of bioprocess, especially in the production of metabolites and biological treatment of wastewater. Advantages of the immobilized cells compared with free cells include: protection from harsh environment conditions such as pH, temperature, organic solvent and toxic compound, relative ease of product separation, reusability, increased cell density, and reduced susceptibility to contamination by foreign microorganism. Recently polyvinyl alcohol (PVA) has been used widely in the field of wastewater treatment, these advantages include lower cost, high durability and chemical stability, non-toxicity to viable cells [5–7], non-biodegradable, high mechanical strength and long-life span of gel. Moreover, with porosity, PVA gel has a large amount of water and allows for effective transition of oxygen and nutritional values inside the gel beads.

With a porous microstructure, PVA gels bead can be an efficiency way to anammox reactor, it allows the microorganism to live inside the polymeric matrix, protects the anammox bacteria from inhibition factor in surrounding environment like oxygen and substrates still can diffuse to the bacteria, prevents anammox biomass from being washout through the effluent. Furthermore, PVA has several advantages including low cost, high durability and chemical stability, and especially non-toxic to microorganism [8,9]. However, the boric acid technique is often used to produce PVA gel bead and it also has drawbacks

* Corresponding author at: Department of Environmental Engineering and Energy, Myongji University, Yongin, Gyeonggi-do, 17058, Republic of Korea.
E-mail address: dhahn@mju.ac.kr (D.H. Ahn).

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that the bacteria in the PVA matrix can be damaged by boric acid during the process and has a tendency to agglomerate [10]. To eliminate these problems, this study focused on the enrichment and performance of anammox bacteria in a continuous stirred tank reactor (CSTR) with the gel beads which are made by boric acid method with sodium sulfate. The combination of PVA and sodium alginate (SA) was used to improve the surface properties of the beads, reducing the tendency to agglomerate, while the PVA–SA gel bead crosslinked with sodium sulfate has lower toxicity to bacteria than boric acid, higher stability in water and greater biological activity than conventional PVA–boric acid hydrogels bead [11]. After that, the characteristic of nitrogen removal with anammox biomass entrapped in PVA–SA gel bead and anammox performance in the CSTR are evaluated to develop the anammox process in conventional CSTR for further application in wastewater treatment.

Material and methods

Seed sludge

For experiment, the active sludge from a wastewater treatment plant operated under anoxic/anaerobic and aerobic conditions is used. (MLSS = 20–25 g/L, MLVSS = 15–20 g/L). The sludge is washed with distilled water and PBS solution to remove the residual substrate before using.

Anammox sludge used in this study was obtained from a lab scale reactor. Sludge was washed three time with phosphate buffered saline (PBS, pH = 7.4, 0.1 M) solution to remove any residual substrate on the sludge surface. Afterwards, the sludge was centrifuged for 5 min at 2000 rpm.

Immobilization methods

The seed sludge prepared from the previous step was encapsulated in polymer gel by different methods. 200 mL of solution containing 12% PVA (w/v) and 2% sodium alginate (SA) (w/v) was autoclaved at 121 °C for 20 min. After cooling to 37 °C, this solution is mixed with 200 mL of seed sludge completely. The mixture is dropped into a solution of saturated $B(OH)_3$ and $CaCl_2$ 2% (w/v) to form spherical beads. Then, with the method A, the beads are cursed in $B(OH)_3/CaCl_2$ solution for 1 h, transferred to 0.5 M Na_2SO_4 solution and cursed for 1 h [12]. With method B, the beads are cursed in $B(OH)_3/CaCl_2$ solution for 3.5 h, transferred to 0.5 M KH_2PO_4 solution and cursed for 5.6 h. In method C, the mixture is dropped into $CaCl_2$ 4% (w/v) solution and cursed in the same solution for 12 h [11]. Finally, all of beads are removed, washed and stored at 4 °C with distilled water before using.

Characterization of the PVA–SA gel beads

Different methods were applied to make PVA–SA gel beads. In order to determine the better method, relative mechanical strength, mechanical strength swelling of beads in water and expansion coefficient were used following the most suitable gel beads is chosen to culture anammox bacteria in CSTR.

Mechanical strength

20 immobilized granules of similar size of each material type were selected and placed in a 100 mL beaker. Then, 80 mL of deionized water (DI water) was added to the beaker. The mixture was magnetically stirred at 500 r/m for 24 h by using Thermo Scientific™ Cimarec™ Digital Stirring Hotplates, after which the ratio of intact gel bead to the original number of immobilized gel beads was determined [13].

Relative strength

20 immobilized granules of similar size of each material type were selected and placed in a 100 mL beaker with 80 mL of DI water. The beads were stirred by Thermo Scientific™ Cimarec™ Digital Stirring Hotplates while the speed is controlled from 500 to 2500 rpm and the intact gel beads is counted daily [10].

Swelling of bead in water

20 immobilized granules of similar size of each material type were selected and placed in a 100-mL beaker with 80 mL of DI water. The beaker was mixed for 7 days by magnetic stirrer machine and the size of gel beads were checked daily.

Expansion coefficient

20 immobilized granules of similar size of each material type were selected and placed in a 100-mL beaker with 80 mL of DI water. The beaker was slowly shaken at 35 °C for 72 h (exactly same with reactor operation in the next step) then the diameter of the gel beads before and after were measured. The ratio of the mean diameter of the gel beads after 72 h of treatment to the mean diameter of the original gel bead was the expansion coefficient [13].

Reactor and experiment method

A continuous stirred tank reactor with total working volume of 3 L and 30% packing ratio of gel beads is used with synthetic wastewater. The temperature is maintained at36 °C by using water jacket and pH is controlled around 7.5–8 by HCL 1 M. Stirring speed is set to 100 rpm. Stirring was essentially required to mix the influent and remove nitrogen gas bubble which formed on the surface of the gel beads [14]. The influent was supplied by an inflow peristaltic pump from the synthetic wastewater tank through a feed line tubing (Figs. 1 and 2).

The CSTR reactor was operated with a hydraulic retention time ranged between 12–24 h, with the nitrogen loading rate from 0,09 to 0,134 kg N/m^3/d. The synthetic wastewater used through the experiments contained (per lit): NH_4^+-N 50–60 mg, NO_2^--N 40–50 mg, $KHCO_3$ 500 mg, KH_2PO_4 27,2 mg, 0.3 g of $CaCl_2{\cdot}2H_2O$, 0.2 g of $MgSO_4{\cdot}7H_2O$, 0.00625 g of $FeSO_4$, 0.00625 g of EDTA and 1 mL/L of trace element solution. Trace element solution was composed of $ZnSO_4{\cdot}7H_2O$, 0.43 g; $CoCl_2{\cdot}6H_2O$, 0.24 g; $MnC1_2{\cdot}4H_2O$, 0.99 g; $CuSO_4{\cdot}5H_2O$, 0.25 g; $NaMoO_4{\cdot}2H_2O$, 0.22 g; $NiCl_2{\cdot}6H_2O$, 0.19 g; $NaSeO_4{\cdot}10H_2O$, 0.21 g; H_3BO_4·0,014 g (1 mL/L).

The effluent sample was collected daily to evaluate the treatment performance. According to the standard method, NO_2^--N, NH_4^+-N, NO_3^--N were measured by kit HACH and standard method. The pH was measured using a pH-meter and DO was measured by a portable meter (Figs. 1 and 2)

Results and discussion

Characterization of the PVA–SA gel bead

The Table 1 lists the data of the mechanical strength and expansion coefficient of 4 types of gel bead in this study. Following this table, the mechanical strength of method C was lowest, after 24 h of experiment and only 47% of gel beads were intact. With method A, PVA–SA gel beads crosslinked with sodium sulfate, the mechanical strength of these beads were 0.87, many times higher than that of method C, and close to that of method B, 0.73. Gel bead of method A has highest mechanical strength, however it's expansion coefficient is lowest, only 1.17. The expansion coefficient of method C was 2, and the size of gel bead increases from 3 mm to 6 mm in day under specific condition of water, resulting in gel beads becoming very soft and easy to dissolve in the water following the raising of the rate of stirring machine. Takei et al. also