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Nitrogen removal during anaerobic digestion of wasted activated sludge under supplementing Fe(III) compounds

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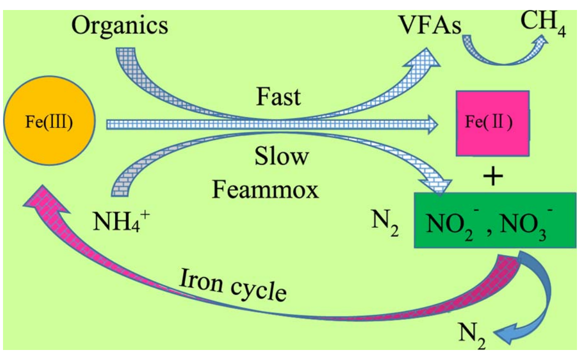
GRAPHICAL ABSTRACT



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ABSTRACT

Anaerobic ammonium oxidation coupled to Fe(III) reduction, i.e., Feammox, is playing an important part in nitrogen cycle of natural environments, which however has been rarely investigated in waste water/solid treatment processes. Ammonium as a byproduct of nitrogenous substance decomposition during anaerobic digestion of waste activated sludge usually presents a quite high content and poses a great risk to environment. This study focused on investigating the effects of supplementing Fe(III) compounds in anaerobic digestion of sludge and especially evaluating the roles in nitrogen removal. Supplementing magnetite, Fe_2O_3 and $Fe(OH)_3$ in anaerobic digesters all increased the methane production and sludge reduction. Importantly, these Fe(III) compounds induced Feammox to occur continuously. NO_2^- and NO_3^- were generated in the Fe(III)-added reactors, especially in $Fe(OH)_3$-added reactor. Afterwards, NO_x^- would be reduced with organics or Fe(II) as electron donors. Consequently, 20.1% of total nitrogen was removed in $Fe(OH)_3$-added reactor after 40 days. As a product of dissimilatory iron reduction (including Feammox), the Fe(II) content was far less than theoretical production through the stoichiometrical NH_4^+ removal in Feammox, implying that the Fe(II)/Fe(III) cycle likely occurred to trigger the successive nitrogen loss.

1. Introduction

Waste activated sludge (WAS) produced from municipal wastewater treatment plant has been getting more and more attention because of its high organic content, environmental risk and huge production [1–3]. Anaerobic digestion (AD) has been considered to be an efficient method to recover energy from wastes [4,5]. During AD, decomposition of nitrogen-rich substrates like protein could produce high content of

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ammonium, which poses a great risk to cause eutrophication of water bodies [6,7]. Traditional nitrification-denitrification that is operated in separate aerobic and anaerobic tanks is energy-intensive and difficult to treat such high concentration of ammonium. Besides, anaerobic ammonium oxidation (anammox) has been reported as an effective measure to remove ammonium with nitrite as electron acceptor under anaerobic condition ($NH_4^+ + NO_2^- = N_2 + 2H_2O$). But the proliferation of anammox bacteria is slow [8]. and the reactant NO_2^- requires to obtain ahead of the process, which makes this technology inaccessible to practical application.

It has recently been discovered that NH_4^+ could be anaerobically oxidized coupled to Fe(III) reduction. This so-called Feammox has been playing an important role in the nitrogen cycle in natural environments such as freshwater, marine, wetland, tropical forest and paddy soils [9,10]. Yang et al. used ^{15}N-labeled NH_4^+-based isotopic tracing to identify that N_2, NO_2^- or NO_3^- can be produced from Feammox in tropical upland soils (Eqs. (1)–(3)) [11]. It was estimated that Feammox metabolizes 7.8–61 (3.9–31% of N fertilizer loss) and 1–4 kg $NH_4^+ ha^{-1} year^{-1}$ in paddy soil and upland surface soil, respectively [11,12]. However, to date, there have been no reports on removal of ammonium produced from AD of sludge by Feammox.

$$3Fe(OH)_3 + 5H^+ + NH_4^+ = 3Fe^{2+} + 9H_2O + 0.5N_2 \quad \Delta_r G_m = -245\ KJ\ mol^{-1} \tag{1}$$

$$6Fe(OH)_3 + 10H^+ + NH_4^+ = 6Fe^{2+} + 16H_2O + NO_2^- \quad \Delta_r G_m = -164\ KJ\ mol^{-1} \tag{2}$$

$$8Fe(OH)_3 + 14H^+ + NH_4^+ = 8Fe^{2+} + 21H_2O + NO_3^- \quad \Delta_r G_m = -207\ KJ\ mol^{-1} \tag{3}$$

Anaerobic sludge digestion is commonly operated under a long hydraulic retention time (HRT) that is partly similar to natural Feammox system, which likely provides an ideal condition for Feammox to occur in anaerobic digestion system. However, to date, there have been no reports on Feammox in sludge digestion as well as in wastewater treatment systems. We speculated that Feammox may occur when supplementing Fe(III) during AD of WAS, resulting in nitrogen removal. On the other hand, Fe(III) have reportedly promoted AD because it could stimulate dissimilatory iron reduction to enhance the decomposition of complex substrates to simples [13]. Therefore, Fe(III) compounds not only probably promote the AD of sludge, but also are expected to reduce the nitrogen content via Feammox. In this study, $Fe(OH)_3$, Fe_2O_3 and magnetite were respectively supplemented into anaerobic sludge digesters to investigate their effects on sludge fermentation and evaluate nitrogen removal.

2. Material and methods

2.1. Experimental materials

Dewatered WAS (solid content of 20%) used as substrate in this study was collected from a municipal wastewater treatment plant (Dalian, China). The collected waste sludge was stored in a refrigerator at 4 °C for use. Prior to the experiments, the WAS was diluted to about 5% of the solid content using deionized water. Inoculant sludge (solid content of 9%) was taken from a sludge treatment plant in Dalian (China). $Fe(OH)_3$ (powder), Fe_2O_3 (powder) and magnetite (diameter of 10–15 mm) (Sigma-Aldrich, USA) were applied in this study.

2.2. Experimental procedures

250 mL conical flasks were used as anaerobic digestion reactors. In this study three Fe(III), i.e., $Fe(OH)_3$, Fe_2O_3 and magnetite, were applied, and each was supplemented at the dosage of 2 g Fe(III) per conical flask in $Fe(OH)_3$, Fe_2O_3 and magnetite groups respectively, while Fe(III) was not supplemented in control. Each bottle was fed with 150 mL mixture of diluted WAS and the cultured inoculant sludge at a volume ratio of 9:1. Before digestion, each bottle was aerated using nitrogen gas for 30 min to remove oxygen. Afterwards the bottles were sealed by a cap that was drilled two holes to connect with a biogas sampling bag and a sludge slurry sampling pipe, respectively. The bottles were placed in an shaker (120 rpm) at 37 °C for 40 days. Each batch of digestion was operated for 40 days that was longer than common AD to investigate the changes of nitrogen and iron. The experiments were repeated in triplicate.

2.3. Analysis methods

Volatile suspended solid (VSS) and total suspended solid (TSS) were analyzed according to the Ref. [14]. Protein was determined based on the method described by Frolund et al. [15]. Biogas production collected with the gas sampling bag was measured by a syringe, and CH_4 content of biogas was measured using a gas chromatograph (Shimadzu, GC-14C). Volatile fatty acids (VFAs, including acetate, propionate and butyrate) were analyzed with another gas chromatograph (Shimadzu, GC2010). The analytic methods of gas chromatograph were described in our previous paper [16]. NO_3^-–N, NO_2^-–N, NH_4^+–N and total nitrogen were measured according to Zhu et al. [17].

Fe(II) would be generated from dissimilatory Fe(III) reduction (including potential Feammox), while Fe(II) was probably oxidized into Fe (III) again with NO_x^-, leading Fe(II) and Fe(III) releasing from the original Fe compounds to enter into the sludge. To assess these processes, Fe(III) and Fe(II) in sludge were determined. After settling the digesters, the sludge was carefully sampled from the upper layer of sludge. Considering that $Fe(OH)_3$ powder and Fe_2O_3 powder were inevitably immersed into the sludge and difficult to be separated, determination of Fe(III) content in these two powder-Fe systems was meaningless. Differently, after the settlement the granule magnetite could be completely separate from the sample sludge because of its big size (diameter of 10–15 mm). Therefore, Fe(III) was only determined in the magnetite-supplemented and control digesters to assess the Fe(III) generation in the sludge. On the other hand, Fe(II) was determined in all three iron-supplement digesters since it was definitely a result of Fe (III) reduction, unlike part of Fe(III) determined might be resulted from the original Fe(III) powder. Considering that parts of Fe(II) and Fe(III) in the sludge might be bounded with the sludge, the sample was pretreated with a HCl solution to extract iron according to a method described by Ding et al. [12]. In brief, 1 mL sludge slurry was extracted immediately with 5 mL 0.5 M HCl for 2 h at room temperature, then centrifuged at 10000 rpm for 10 min. The Fe(II) and total Fe of the supernatant was measured according to the standard method [18] The amount of Fe(III) was calculated as the difference between total Fe and Fe(II). All extractions were conducted in the anaerobic glovebox.

3. Results and discussion

3.1. CH_4 production and organic substrate removal

To investigate the sludge digestion in a longer digesting time, each batch of digestion experiment was extended to 40 days. During this period, accumulated CH_4 production of the control (without adding Fe (III) compounds) was 386.2 mL, while it increased by 12.7%, 31.3% and 60.5% in $Fe(OH)_3$, Fe_2O_3 and magnetite groups, namely reaching to 435.3, 507.0, 620.1 mL, respectively (Fig. 1). The result was in accordance with Baek et al.[19] who observed ferric oxyhydroxide and magnetite significantly enhanced CH_4 production during AD of dairy wastewater. This was likely because Fe(III) could stimulate dissimilatory iron(III) reduction coupled to directly oxidize complicated matters of sludge, which facilitated sludge destruction and hydrolytic-acidification to then accelerate the CH_4 generation [20]. In this experiment, most of CH_4 was produced in the initial 10 days. From day