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Effect of nanoscale zero-valent iron on sludge anaerobic digestion

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A R T I C L E I N F O

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A B S T R A C T

Nanoscale zero-valent iron(NZVI) was prepared with a method of reduction in liquid phase by the reaction of $FeSO_4$ and $NaBH_4$, and characterized by SEM. This study investigated the effect of different concentration of NZVI on biogas production and methane content during the anaerobic digestion process at the medium temperature of 35 °C. The results indicated that the group with 1000 mg/L NZVI maintained ammonia at the level of 600–800 mg/L, pH between 6.5-8.0, and improved CODcr degradation rates at 2.91%; this concentration of NZVI produced maximum concentration of VFAs, which can reach 3846 mg/L, and strengthen the use of acetic acid. Relative to the control group, the system increased cumulative biogas production of 18.11%, decreased biogas production cycles of three days and increased the methane content by 6.93%.

1. Introduction

With the wastewater increasingly generated, there is accompanied by a large amount of sludge production. The treatment and disposal of sludge is facing great challenge. If these sludge is not handled properly, it can cause the flies breeding, produce the stench, take up a lot of land, harm the animals and plants and so on (Mohamed and Nageh, 2015). Using appropriate techniques for sludge treatment, not only can eliminate the environmental problems, but also can recycle energy and realize sustainable development (Suanon et al., 2016).

Anaerobic digestion(AD) is a complicated biochemical process that converts complex organics into biogas, a mixture of methane, carbon dioxide gas and other residuals in the absence of oxygen under the effect of anaerobic microorganisms (Al Seadi et al., 2008; Themelis and Kim, 2002; Madsen et al., 2011). On the one hand, it can reduce the sludge volume; on the other hand, it can also produce biogas. So the technology is becoming a hot spot of sludge treament (Speece, 1983; Albertson, 1961). However, AD has several shortcomings, such as lower efficiency, longer reaction time and more limited steps (Borowski, 2015; Khalid et al., 2011; Cho et al., 2013; Chen et al., 2008).

Nanoscale zero-valent iron(NZVI) has increasingly been used in environmental remediation and industrial wastewater treatment for the removal of chlorinated contaminants, nitroaromatic compounds, and heavy metals such as arsenic (APHA et al., 2005; Auffan et al., 2008; Bai et al., 2009). NZVI has a certain role in promoting anaerobic digestion process. It can be used as electron donor, increase the total consumption of hydrogen methanogens and activity, release Fe^{2+} into the anaerobic system and participate in the synthesis of the key enzymes (Ren et al., 2007; Karri et al., 2005). NZVI can also optimize the structure of microbial population, change the hydrolysis fermentation types and promote the acetic acid content (Zhang et al., 2011b; Liu et al., 2011; Zhang et al., 2011c; Zhang et al., 2011a). In addtion, trace elements is necessary for methanogens in anaerobic digestion process. The addition of NZVI can provide for iron element (Schmidt, 2011).

At present, the research of NZVI used in wastewater treatment is more, but less research are to explore the mechanism of anaerobic digestion. NZVI has a mixed effect on the biogas production according to its concention. Therefore, this study put forward to add a certain particle size of NZVI in the anaerobic digestion, probing into its influence on the anaerobic digestion process, finding out the best additive amount. The experiment determined the ammonia nitrogen, pH, CODcr, VFAs, biogas production and methane content, so as to explore the functional mechanism of NZVI effect on anaerobic digestion, and provide the basis of the application of nanometer materials in the sludge anaerobic digestion.

2. Material and methods

2.1. Experimental reactors

The experimental reactor with a working volume of 500 mL included 200 mL inoculum and 300 mL substrate. Different concentration of NZVI (500 mg, 1000 mg, 1500 mg, 2000 mg, 50–70 nm in diameter) were added into the reactors. The control reactor was the same as other reactors but without NZVI. The device was connected according to the required and then beginning after blowing the nitrogen for 5 min to kee

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Table 1
The indicators of the substrate.

pH	CODcr/(mg/L)	TS/%	VS/%	NH_3-N/(mg/L)
7.15	72453.1	4.28	2.10	1529.5

Table 2
The indicators of inoculum.

pH	CODcr/(mg/L)	TS/%	VS/%	NH_3-N/(mg/L)
7.23	58923	5.65	2.85	978.5

the reactors anaerobic. In the process of anaerobic digestion, the biogas production was measured by flowmeter and recorded regularly every day. In addition, the CODcr, pH, NH_3-N, VFAs and methane content were measured every three days. The experimental reactors were operated at 35 °C.

2.2. Inoculum and substrate

The raw sludge obtained from the sedimentation tank of a municipal sewage plant in Qingdao (China). The moisture content of the raw sludge was 81.05%. The substrate was made up of the raw sludge at solid-liquid ratio of 8%. The indicators of substrate were shown in Table 1.

The inoculum was cultivated by the substrate with a C: N: P ratio of 100:5:1. The indicators of inoculum were shown in Table 2.

2.3. Analysis methods

The physical and chemical parameters pH, VS, TS, ammonia nitrogen (NH_3-N), and COD were determined according to standard methods (Ministry of Environmental Protection, China(MEP), 2002). The pH was recorded using a pH analyzer (Sartorius PB-20, Germany). The filtrate was analyzed for NH_3-N parameters; the mixed liquor was analyzed for NH_3-N and total COD (TCOD) parameters. Volatile fatty acids (VFA) were analyzed using Peasee gas chromatograph equipped with a flame ionization detector (FID) and a KB-FFAP column (30 m*0.25 mm*0.50 um). Operating conditions were injector temperature 230 °C, FID temperature 230 °C, oven temperature program: 70–180 °C (20 °C/min), held for 5 min.

The methane content of the biogas was analyzed by a gas chromatography (GC-1100, Peasee Corporation, China). Gas samples were taken using a 1.0 mL syringe equipped with metal hub needles to measure the gas composition. A volume of 0.5 mL of biogas was injected into a gas chromatography (GC-1100, Peasee Corporation, China) to measure biogas composition. The temperature of injector, detector and column was set 100 °C, 150 °C, and 120 °C, respectively. The GC column used for the analysis detected relative proportions of methane, and carbon dioxide. The gas composition was measured once every other day. Digestion experiment was conducted until biogas production ceased.

2.4. NZVI synthesis and characterization

Nanoscale zero-valent iron(NZVI) was prepared with a method of reduction in liquid phase by the reaction of $FeSO_4$ and $NaBH_4$. NZVI stock suspensions were freshly prepared by reducing ferrous chloride with sodium borohydride as reported earlier (He et al., 2006). Briefly, deionized (DI) water and 0.2% (w/w) sodium carboxymethyl cellulose solution were purged with highly pu-rified nitrogen gas for at least twenty minutes before use. Then 50 mL of 0.625 M ferrous chloride was gradually added to 200 mL of 0.2% CMC solution under nitrogen gas purging. Finally, a total of 100 mL of 1.5% (w/w) sodium borohydride

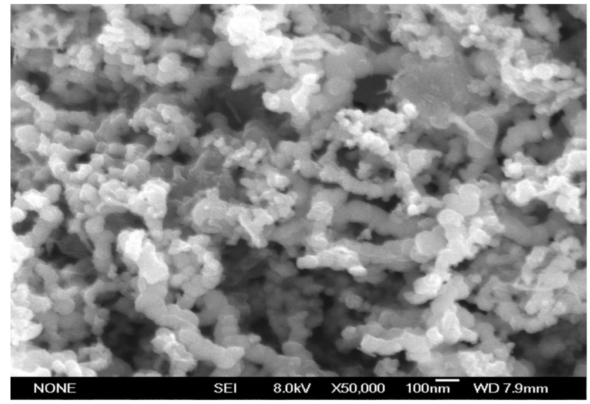

Fig. 1. SEM of NZVI.

($NaBH_4$, Sigma) was added drop wise to the 250 mL solution containing ferrous chloride and CMC while the solution was vigorously stirred at 1100 rpm at room temperature. The final concentrations of NZVI and CMC in the stock solution were 0.11 M and 0.14% (w/w), respectively. The NZVI stock solution was purged with nitrogen gas throughout the synthesis process following the protocols described elsewhere to ensure that only NZVI was formed (Yang et al., 2013).

3. Results and discussion

3.1. Analysis of NZVI apparent morphology

As shown from Fig. 1, the size of NZVI was 50–70 nm.

3.2. The connection of NZVI, ammonia nitrogen and biogas production

Concentration of ammonia nitrogen is an important index in anaerobic digestion process. In order to study the effect of NZVI on ammonia nitrogen in anaerobic digestion, this experiment determined the ammonia nitrogen every two days. Combined with the change of daily biogas production,we had a further research on the relationship between the concentration of NZVI, ammonia nitrogen production and the biogas production.

By the change of the concentration of ammonia nitrogen (Fig. 2), we can see that the addition of different concentration of NZVI had the different influences on the system of ammonia nitrogen. Before the two days, the five groups of concentration of ammonia nitrogen were basically the same, because of the lower microbia activity in the anaerobic digestion process. The group of 1000 mg/L NZVI, relative to the other

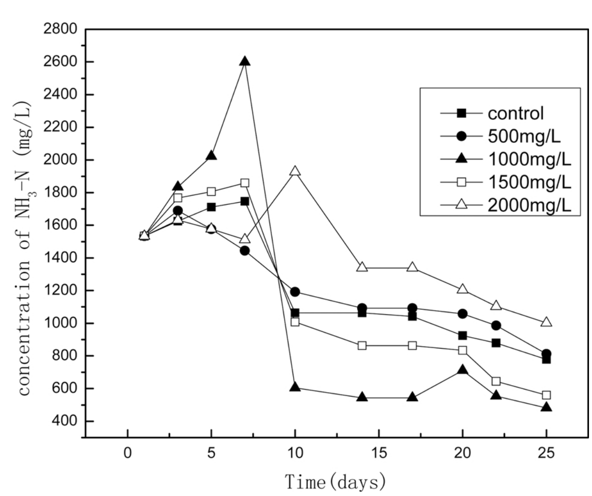

Fig. 2. NH_3-N Variation during AD.