Chemical Engineering & Processing: Process Intensification 130 (2018) 253–261

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

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

Methane yield enhancement by the addition of new novel of iron and copper-iron bimetallic nanoparticles

Tareq W.M. Amen[a], Osama Eljamal[a,*], Ahmed M.E. Khalil[a,b], Yuji Sugihara[a], Nobuhiro Matsunaga[a]

[a] Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen Kasuga, Fukuoka, Japan
[b] Department of Chemical Engineering, Faculty of Engineering, Cairo University, Giza, 12613, Egypt

ARTICLE INFO

Keywords:
Nanoscale zero valent iron
Iron copper bimetallic
Sludge digestion
Biogas production

ABSTRACT

The potential effect on methane content from anaerobic digestion of municipal sludge was systematically examined by implementing wide-range concentrations of copper iron-based bimetallic (nZVI/Cu°) nanoparticles and was compared by the results with zero-valent iron nanoparticles (nZVI) influences. The effective concentrations that yielded the highest methane content were determined by tracing the iron dissolution ions. Through the experimental work, bio-digester systems were assembled and used. The most effective concentration of nZVI/Cu° was 1500 mg/L while it increased the biogas production three times the control. The bimetallic concentration of 3000 mg/L showed inhabitation of methanogens due to its disruption of cell integrity. The relatively high nZVI additives also proved biogas stimulation and exposed the sludge to only 50 and 100 mg/L nZVI concentration conversely confirmed inhibitory effects and the biogas generation decreased from 229 mL that the control produced to 192 and 209 mL respectively. The methane content results showed that the methane was constantly accelerated due to the plenty of iron ions which demonstrated that both the nanoparticles could act as electron donors and the dissolved ions could be direct electron transfer, in which methanogens work as iron oxidizer, taking electron from the nanoparticles to reduce the carbon dioxide to methane.

1. Introduction

Anaerobic digestion (AD) is a complicated biochemical process that converts complex organic wastes into a mixture of methane (CH_4), carbon dioxide (CO_2) gas and other residuals, this mixture is called biogas [1]. The main compositions of biogas are CH_4 and CO_2, with other gases such as hydrogen (H_2) and hydrogen sulfide (H_2S) [2]. Biogas is considered as a renewable energy, which ensures more energy supply as clean, secure and continuous resource. It can be used instead of fossil fuel in various engineering applications and can decrease the running cost of wastewater treatment plants. Wastewater inside the treatment plants is treated via biological processes and sedimentation, the settled product is known as sludge. Sludge management remains a great challenge and digesters as one of crucial facilities inside municipal wastewater treatment plants are used for treating the sludge, which is capable of stabilizing the sludge and producing biogas as a clean renewable energy source [3]. Sludge is stabilized through hydrolysing the organic matter, fermented acetic acid and H_2, which can be converted to CH_4 gas that represents 30%–60% of the biogas production [4].

The AD process consists of four microbial sequential steps: the first one is hydrolysis in which carbohydrates and proteins are decomposed into amino and fatty acids, these components are converted into intermediates volatile fatty acids (VFAs), like propionic acid and butyric acid during the second step that called acidogenesis. Acetogenesis as third step converted the intermediates components into acetic acid and H_2. In the final step, the biogas is produced through acetoclastic and hydrogenotrophic methanogenesis [5,6].

However, the biogas production is limited because of the degree of acidification and solubilisation of waste sludge. To overcome this problem, various pretreatment technologies are used to improve the waste sludge solubilisation efficiency and short chain VFAs production, as thermal [7], chemical [8] and thermos chemical [9] methods. Moreover, there is great interest in developing methods to raise the microbial activity of the AD through both chemical biological and amendments [7].

Additionally, some researchers focus on employing the powder of genetic engineering to improve the biogas production by handling genes incorporating specific DNA fragments into target species of sludge [10].

* Corresponding author.
E-mail address: osama-eljamal@kyudai.jp (O. Eljamal).

https://doi.org/10.1016/j.cep.2018.06.020
Received 6 December 2017; Received in revised form 23 May 2018; Accepted 23 June 2018
Available online 27 June 2018

Recently, zero valent Iron (ZVI) particles have been used in water remediation and contaminants removal in different particle sizes e.g.: nanoparticles (nZVI), microparticles size (μZVI), powder and scrap. ZVI particles were used in environmental applications while it has catalytic effects for chemical conversion of a set of pollutants like phosphorus and nitrate [11,12]. ZVI can also work as chemical reductant and electrons donor to boost contaminants reduction by microorganisms resulting in an increase of biogas production rate [13,14]. Therefore, with the rapidly practical application of iron nanoparticles for remediating the wastewater and water purification, iron particles at the end will be settled and accumulated at wastewater treatment plants.

nZVI has considerable interest in the field of wastewater treatment and reuse due to its relatively high specific area that warrants its particles to play a great role in sludge stabilization and biogas production [15]. Several studies were carried out to study the catalytic effect of nZVI on biogas production rate but the core concept of most published studies in the area of AD was focused on comparing the same dosing concentration of iron particles with different particle size range [16]. For instance, Su L. et al. [17] studied the impact of adding 0.1 wt% nZVI on the AD of waste activated sludge under mesophilic temperature (37 °C) for 17 days. The results showed an increase in the generated biogas by 30.4%. Yang Y. et al. [16] also examined the impact of nZVI on the AD of anaerobic sludge from Columbia municipal waste water treatment plant for 14 days at 37 °C. The results showed that the addition of 30 mM μZVI resulted in a 10% increase in CH_4 production whereas, adding 1, 10 and 30 mM nZVI to the sludge resulted in 20%, 20% and 70% decrease in CH_4 production respectively. The authors referred the inhibitory behavior of nZVI to the rapid hydrogen ions production that resulted from the dissolution of nZVI but the μZVI dissolution showed a slow release of hydrogen ions which enabled methanogenesis processes and increased CH_4 production. As well as Estrella et al. [18] compared the nZVI effect with other inorganic nanoparticles on methanogenic activity in anaerobic granular sludge, the results showed that nZVI inhibit methanogenesis activities by 85%. In contrast, Xiu Z. et al. [19] attributed the increase of CH_4 production from 58 mmol to 275 mmol when adding 1 g/L nZVI to the high amount of H_2 produced upon the dissolution of nZVI.

Different field scale experiments assigned the low impact of nZVI due to the agglomeration and the poor mobility of nanoparticles which attributed to strong attractive internal forces between nanoparticles [20,21]. Various methods of modification were proposed to overcome the nZVI deficit [22]. One promised strategy involves depositing a noble metal onto the nZVI surface. Copper is placed onto the iron surface through iron salt reduction reaction in the presence of copper chloride. The nanoparticles which composed of iron and copper are basically in a two-dimensionally confined space, which would limit the efficiency of reaction between the contact interfaces for reactants [23,24].

Although the impact of nZVI on anaerobic sludge degradation and its function on AD were investigated, the effect of iron copper bimetallic nanoparticles (nZVI/Cu°) still remains unknown. Thus, the questions remain as to whether and how nZVI/Cu° will affect AD.

Consequently, overcoming the nanoparticles agglomeration through planting copper particles onto the surface of nZVI should have a positive effect on AD because added copper can accelerate corrosion rate of nZVI and raise its reactivity significantly [25,26]. Additionally, the nZVI/Cu° bimetallic particles have similar physiochemical characteristics [27]. Thus, it is necessary to compare the nZVI/Cu° bimetallic particles performance with pristine nZVI under different concentrations.

Thereafter, adding nanoparticles may sustain the CH_4 production which might not only decrease the operation cost of sludge treatment, but also promise a considerable digestion space to increase the sludge stabilization.

In this work, nZVI/Cu° was employed in laboratory scale anaerobic digestion system for improving the biogas production and CH_4 yield through dosing wide-range bimetallic concentrations. To the extent of our knowledge, this is the first time to examine the effects of nZVI/Cu° bimetallic dosage onto anaerobic sludge and comparison with the outcomes of nZVI influences. For more than 14 days, the impact of nZVI and nZVI/Cu° bimetallic particles on AD of municipal wastewater was evaluated by determining the changes in cumulatively produced gas volume, soluble chemical oxygen demand, pH and other chemical properties in the sludge.

The changes in microbial populations by quantitatively counting the number of colonies to describe the bacterial life through the digestion period with exposure to nanoparticles were also determined.

2. Material and methods

2.1. Preparation of nZVI and nZVI/Cu° nanomaterials

Firstly, nZVI stock suspension was freshly synthesized by adding equal masses of ferric chloride ($FeCl_3 \cdot 6H_2O$, Junsei chemical Co., Japan) and sodium borohydride ($NaBH_4$, Sigma-Aldrich, USA) as reducing agent. Briefly, one gram of nZVI was prepared by using peristaltic pump to drop 120 mL solution that contains five grams of $NaBH_4$ into another 120 mL of 5 g $FeCl_3 \cdot 6H_2O$ solution at 27 °C under a nitrogen atmosphere as schematized in Fig. 1. All aqueous solutions have been deoxidized using nitrogen purged into deionized water for 20 min.

The nZVI/Cu° bimetallic particles used in this research were prepared by adding copper II chloride ($CuCl_2$, Sigma-Aldrich, USA) to the $FeCl_3 \cdot 6H_2O$ solution before dropping the reducing reagent of $NaBH_4$.

The mixtures were continuously stirred at 250 rpm. Subsequently, the prepared nanoparticles were separated from the aqueous solution by vacuum filtration and rinsed two times with diluted and absolute ethanol (purity > 99.5%, Wako Co., Japan) respectively. Eventually, the nanoparticles slurries were anaerobically sorted prior to use. All above processes have been carried out in a nitrogen environment.

2.2. Activated sludge source

The activated sludge samples that were used in the experiments were sampled from two consecutive stage digestion tanks at Mikasagawa domestic wastewater purification center located in the city of Fukuoka, Japan. Mikasagawa treatment center purifies the municipal wastewater by applying anaerobic-anoxic-aerobic process and has a capacity to treat a daily volume of 300,000 cubic meters. The flow chart of sludge treatment process with the sampling spot place is presented in Fig. 2. Samples were kept at 4 °C to maintain its freshness and the main physicochemical properties of activated sludge were given in Table1.

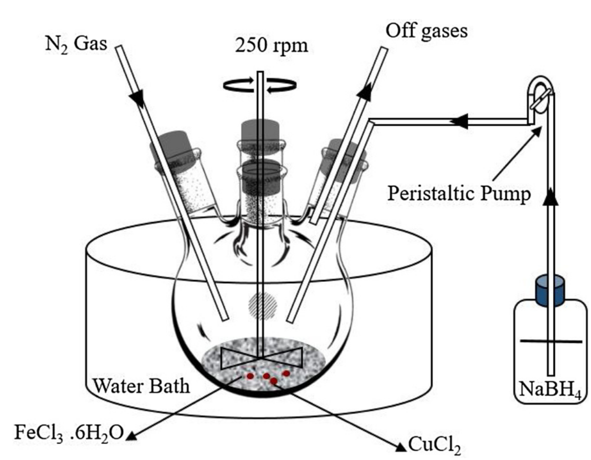

Fig. 1. Schematic diagram of nanoparticles synthesis process.