Energy xxx (2016) 1–12

Contents lists available at ScienceDirect

Energy

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

Influence of zero valent iron nanoparticles and magnetic iron oxide nanoparticles on biogas and methane production from anaerobic digestion of manure

E. Abdelsalam [a], M. Samer [b, *], Y.A. Attia [a, d], M.A. Abdel-Hadi [c], H.E. Hassan [a], Y. Badr [a]

[a] National Institute of Laser Enhanced Sciences (NILES), Cairo University, 12613 Giza, Egypt
[b] Department of Agricultural Engineering, Faculty of Agriculture, Cairo University, 12613 Giza, Egypt
[c] Department of Agricultural Engineering, Faculty of Agriculture, Suez-Canal University, Egypt
[d] Physical Chemistry Department, Faculty of Chemistry, and NANOMAG Laboratory, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain

ARTICLE INFO

Article history:
Received 8 February 2016
Received in revised form
7 November 2016
Accepted 27 November 2016
Available online xxx

Keywords:
Nanotechnology
Nanoparticles
Anaerobic digestion
Biogas
Methane production
Trace metals
Chemical additives
Manure management
Slurry treatment

ABSTRACT

In this study, nanoparticles (NPs) were hypothesized to enhance the anaerobic process and to accelerate the slurry digestion, which increases the biogas and methane production. The effects of NPs on biogas and methane production were investigated using a specially designed batch anaerobic system. For this purpose, a series of 2 L biodigesters were manufactured and implemented to study the effects of the nanoparticles of Iron (Fe) and Iron Oxide (Fe_3O_4) with different concentrations on biogas and methane production. The best results of NPs additives were selected based on the statistical analysis (Least Significant Difference using M-Stat) of biogas and methane production, which were 20 mg/L Fe NPs and 20 mg/L Fe_3O_4 magnetic NPs ($p < 0.05$). The aforementioned NPs additives delivered the highest biogas and methane yields in comparison with their other concentrations (5, 10 and 20 mg/L), their salt ($FeCl_3$) and the control. Furthermore, the addition of 20 mg/L Fe NPs and 20 mg/L Fe_3O_4 magnetic NPs significantly increased the biogas volume ($p < 0.05$) by 1.45 and 1.66 times the biogas volume produced by the control, respectively. Moreover, the aforementioned additives significantly increased the methane volume ($p < 0.05$) by 1.59 and 1.96 times the methane volume produced by the control, respectively. The highest specific biogas and methane production were attained with 20 mg/L Fe_3O_4 magnetic NPs, and were 584 ml Biogas g^{-1} VS and 351.8 ml CH_4 g^{-1} VS, respectively compared with the control which yielded only 352.6 ml Biogas g^{-1} VS and 179.6 ml CH_4 g^{-1} VS.

1. Introduction

Trace metals have been found to significantly influence reactor performance. Anaerobic digestion (AD) can be considered as one of the most important techniques to convert organic waste into renewable energy in the form of methane byproduct as a form of fuel may reduce treatment cost [1–3]. AD with high biological transformation is a well-established technology to deal with livestock manure, and it can be used for electricity generation, residential heating, and cooking, etc. to save energy expenditure and produce renewable energy [4,5]. The overall result of anaerobic digestion is a nearly complete conversion of the biodegradable organic material into methane, carbon dioxide, hydrogen sulphide, ammonia and new bacterial biomass [6,7]. The AD carried out by a consortium of microorganisms and depends on various factors like pH, temperature, C/N ratio, etc.; it is a relatively slow process. Lack of process stability, low loading rates, slow recovery after failure and specific requirements for waste composition are some of the other limitations associated with AD [4,5]. The temperature inside the digester has a major effect on the biogas production process [8]. Anaerobic digestion consists of a series of microbial processes that convert organics to methane and carbon dioxide, and can take place under psychrophilic (<20 °C), mesophilic (25–40 °C) or thermophilic (50–65 °C) conditions, although biodegradation under mesophilic conditions is most common. It also enables higher loading rates than aerobic treatment, and a greater destruction of pathogens [9]. Some attempts have been carried out to increase biogas production by stimulating the microbial activity using

* Corresponding author.
E-mail address: samer@cu.edu.eg (M. Samer).

http://dx.doi.org/10.1016/j.energy.2016.11.137
0360-5442/

various biological and chemical additives under different operating conditions. The use of additives in biogas plant could improve its performance significantly. The suitability of an additive is expected to be strongly dependent on the type of substrate [10].

Qiang et al. [11] mentioned that the growth of methanogenic bacteria is dependent on Fe, Co, and Ni during enzyme synthesis. Some studies have been done to determine the requirements and optimal concentration for trace metals in pure culture of methane fermentation. Trace metals are essential constituents of cofactors and enzymes and their addition to anaerobic digesters has been shown to stimulate and stabilize the biogas process performance [12,13]. Luna-delRisco et al. [14] reported that the presence of heavy metal ions (i.e., Cu, Zn, Fe, Ni, Co, Mo) during anaerobic biodegradation of organic matter is known to be fundamental for numerous reactions. However, high concentrations of these elements can inhibit the biological degradation process in anaerobic reactors. One of the problems with heavy metal compounds is that these elements are not biodegradable. Due to this, these compounds are known to accumulate, reaching potentially toxic concentrations for anaerobic bacteria [15]. Karlsson et al. [16] concluded that addition of trace elements improves the anaerobic digestion. In a batch study, Demirel and Scherer [12] reviewed that the improvement of biogas production through addition of Fe was investigated using cow dung and poultry litter. For both substrates, addition of $FeSO_4$ improved biogas production and CH_4 content of biogas. Addition of $FeCl_3$ during anaerobic digestion of water hyacinth-cattle dung was also reported to result in an increase of more than 60% in biogas production. Furthermore, addition of $FeCl_2$ during batch experiments with swine excreta was reported to counteract the sulphide inhibition. Zhang et al. (2010) [17] mentioned that when Zerovalent Iron (ZVI) is added into an anaerobic reactor, it not only serves as an electron donor, but is also expected to help create an enhanced anaerobic environment that may improve the performance of reactors used for wastewater treatment. Zhang et al. [17] provided direct evidence that ZVI promoted the growth of methanogens, which enabled the reactor to achieve greater COD removal under low temperatures and a short hydraulic retention time. Nanotechnology has been evolved to be an attractive option in engineering and environmental science [18].

Nanotechnology is recognized by the European Commission as one of its six "Key Enabling Technologies" that contribute to sustainable competitiveness and growth in several industrial sectors. The current challenges of sustainability, food security and climate change are engaging researchers in exploring the field of nanotechnology as new source of key improvements for the agricultural sector [19]. Nanotechnology is the engineering and art of manipulating matter at the nanoscale (1–100 nm); that considered as one of the most important advancements in science and technology of the last decades. It is also expected to revolutionize our ability to improve the environment [20]. Moreover, it offers the potential of new functional materials, processes and devices with unique activity toward obstinate contaminants, enhanced mobility in environmental media. Particles in nanometric size range are termed nanoparticles (NPs). The size greatly depends on the process used for their synthesis. They can be obtained by bottom-up assembly of atoms through chemical process or, on the contrary, from top-down fragmentation of bulk material. The latter allows the synthesis of smaller particles [21,22]. Nano-size is the cardinal property for interaction with biological systems since it determines the ability to penetrate cell membranes, thus facilitating the passage across biological barriers, interaction with immune system, uptake, absorption, distribution and metabolism [21,23].

NPs have unique properties such as large surface area, high reactivity due to high surface area to volume ratio, high specificity, self-assembly and dispersibility [24–27]. Iron NPs have been suggested to be a major portion of the bioavailable fraction of the metal [28]. Kadar et al. [29] showed that synthetic nano-iron was preferred over EDTA–Fe used in laboratory cultures in generic growth media suggesting that the nanoparticulate form of the metal may be more bioavailable to microalgae. Compared to atomic or bulky counterparts, nano-sized materials owe superior physical and chemical properties due to their mesoscopic effect, small object effect, quantum size effect and surface effect. Recently, Fe_3O_4 magnetic nanoparticles (MNPs) have been intensively investigated because of their super paramagnetic, high coercivity and low Curie temperature. In addition to these characteristics, Fe_3O_4 MNPs are also non-toxic and biocompatible [30]. Therefore, Casals et al. [31] hypothesized that maintaining optimal iron concentrations in an anaerobic digester is a critical step to improve bacterial activity. Mu et al. [32] investigated four metal oxides nanoparticles (nano-TiO_2, nano-Al_2O_3, nano-SiO_2 and nano-ZnO) and concluded that only nano-ZnO has inhibitory effects on methane generation, and the influence of nano-ZnO is dosage dependent. Lower nano-ZnO (6 mg/g-TSS) gave no impact on methane generation. Vintiloiu et al. [33] showed that the addition of EDTA to heavily undersupplied substrates with high fatty acids content increases the methane yield by improving the bioavailability of metals. Vintiloiu et al. [34] concluded that several trace elements and macronutrients have a strong significant effect on the stability of the biogas process.

The objectives of this study were to investigate the effects of the nanoparticles of Fe and Fe_3O_4 on the methanogenic bacteria which are the main player in the anaerobic digestion of the livestock manure for biogas production. For this purpose, we have designed and manufactured biodigesters and biogas production system for carrying out the experiments in the biogas laboratory of the National Institute of Laser Enhanced Sciences at Cairo University. Such applications were selected to increase the biogas yield, methane percentage and decrease the digestion time. The objectives of this study can be further elaborated as follows: (1) preparing and characterizing different trace metals nanoparticles such as Fe and Fe_3O_4, and (2) studying the effects of these nanoparticles with different concentrations on biogas production (biogas yield and methane percent) from livestock manure compared with their bulk material ($FeCl_3$) and control.

2. Materials and methods

2.1. Samples analysis

The fresh raw manure (feces and urine) was collected randomly from a livestock holding pen unit located in the Western Farm of the faculty of Agriculture, Cairo University, Giza City, Egypt. The collected raw manure was homogenized by a mixer for 30 min. The pH and temperature of substrate were measured using a pH meter (QIS, proline B210, Oosterhout, Netherlands) equipped with long pH-electrode (QP174X, Epoxy, 300 mm). Total solids (TS), volatile solid (VS) and ash were determined every 10 days during the experiments, by the standard methods using muffle furnace (Vulcan D-550, Ney Tech, York, USA) as shown in Table 1. The total and volatile solids can be calculated using the standard method (EPA METHOD 1684, 2001) and the organic carbon was calculated using the following equation [35]:

$$\text{Organic carbon } (\%) = \text{VS } (\% \text{ from TS}) / 1.724 \quad (1)$$

2.2. Experimental set up

A batch anaerobic system was designed and manufactured