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Comparison of nanoparticles effects on biogas and methane production from anaerobic digestion of cattle dung slurry

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A B S T R A C T

Nanoparticles (NPs) of trace metals such as Co, Ni, Fe and Fe_3O_4 were implemented in this study to compare their effects on biogas and methane production from anaerobic digestion of livestock manure. The most effective concentrations of NPs additives were determined based on our previous studies, and were 1 mg/L Co NPs, 2 mg/L Ni NPs, 20 mg/L Fe NPs and 20 mg/L Fe_3O_4 NPs. These concentrations of NPs additives were further investigated and compared to each other in this study and were found to significantly ($p < 0.05$) increase the biogas yield by 1.7, 1.8, 1.5 and 1.7 times in comparison with control, respectively. The methane yield significantly ($p < 0.05$) increased by 2, 2.17, 1.67 and 2.16 times the methane volume of the control, respectively. The results of this study showed that the Ni NPs yielded the highest biogas and methane production compared to Co, Fe and Fe_3O_4 NPs.

1. Introduction

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. The AD is carried out by a consortium of microorganisms and depends on various factors like pH, temperature, Hydraulic Retention Time (HRT), C/N ratio, etc.; it is a relatively slow process [1]. The temperature inside the digester has a major effect on the biogas production process. AD 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 [2]. 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 [3]. Trace metals as micronutrients plays a very significant role on the performance and stability of agricultural biogas digesters, which are operated with energy crops, animal excreta, crop residues, organic fraction of municipal solid wastes or any other type of organic waste [4].

Limiting the metals required by the enzymes may disturb the total process, as reported in literature [5]; Co and Ni are all involved in the biochemical process of methane production. The efficiency of the biogas production process, i.e., the methane production and the degree of degradation, has in several studies been shown possible to increase by the addition of trace elements [6]. Positive effects by trace elements addition have also been observed in specific methanogenic activity (SMA) assays with various substrates, including methanol (Co and Ni [7]), acetate and propionate (Ni, Co and Fe [8]). Bini [9], reported that nickel is an essential cofactor for Ni–Fe hydrogenases, carbon monoxide dehydrogenase, methyl *CoM* reductase, and urease. Cobalt is found mainly in coenzyme B12. At least six systems for Ni/Co uptake are known [10]. Such systems are required for the high-affinity uptake of nickel or cobalt because their environmental concentration is usually below the

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required levels.

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 [4,12]. Luna-del Risco et al. [13] 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. In a batch study, Demirel and Scherer [4] 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 AD 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. [14] 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. [14] provided direct evidence that ZVI promoted the growth of methanogens, which enabled the reactor to achieve greater chemical oxygen demand (COD) removal under low temperatures and a short HRT.

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. Moreover, it offers the potential of new functional materials, processes and devices with unique activity toward obstinate contaminants, and 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 [15]. 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 [16].

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 paramagnety, high coercivity, non-toxic and biocompatible [17]. Mu et al. [18] concluded that among four metal oxide nanoparticles (nano-TiO_2, nano-Al_2O_3, nano-SiO_2 and nano-ZnO) investigated it was found that only nano-ZnO showed inhibitory effect on methane generation, and the influence of nano-ZnO was dosage dependent. Lower nano-ZnO (6 mg/g-TSS) gave no impact on methane generation.

Abdelsalam E. [19]. compared the effects of Co and Ni NPs on biogas and methane production from slurry anaerobic digestion and concluded that Ni NPs yielded the highest biogas and methane compared to Co NPs. Furthermore, the effects of Fe and Fe_3O_4 NPs on biogas and methane production were also investigated and concluded that Fe_3O_4 NPs attained the highest biogas and methane yield compared with Fe NPs. Therefore, the main objective of this study was to compare the effects of Co, Ni, Fe and Fe_3O_4 NPs on biogas and methane production using livestock manure and to determine which of these NPs will yield the highest biogas and methane production. For this purpose, we have used the biodigesters and biogas production system designed by Abdelsalam et al. [20] for carrying out the experiments in the biogas laboratory of the National Institute of Laser Enhanced Sciences at Cairo University. Such applications were hypothesized to increase the biogas yield, methane percentage and decrease the hydraulic retention time (HRT). The main objective of this study can be further elaborated as follows: (1) preparing and characterizing different trace metals nanoparticles such as Co, Ni, Fe and Fe_3O_4; (2) comparing the effects of these nanoparticles to each other and investigating their effects on biogas production (biogas yield and methane concentration) from anaerobic digestion of livestock manure compared with the control.

2. Materials and methods

2.1. Fresh manure samples

The fresh raw manure (feces and urine) was collected randomly from a livestock waste holding pen unit located in the Western Farm of the faculty of Agriculture, Cairo University, Giza City, Egypt. The slurry was obtained by adding distilled water to fresh manure (1:1 by weight) and homogenized by a mixer for 30 min.

2.2. Samples analysis

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 (EPA METHOD 1684, 2001) using muffle furnace (Vulcan D-550, Ney Tech, York, USA) as shown in Table 1.

2.3. Experimental set up

A batch anaerobic system was designed and manufactured according to the design guidelines and parameters developed by Samer [21], and implemented in this study. The experimental setup of the batch anaerobic system consists of: (1) a biodigester; 2-liter wide neck culture vessel flask (Pyrex, FV2L, Scilabware, Staffordshire, UK) plugged with tightly Teflon cap (HOME MADE), equipped with step motor (ASMO, 24 V, 90 rpm, Japan) with maximum speed 90 rpm for mixing the slurry, and gas outlet connected to biogas holder with 1/4″ connectors through 8 mm plastic hose. (2) The temperature control; a thermostatic water bath (HOME MADE, 60 L, 0–100 °C), where the software of the control unit maintained the temperature at mesophilic conditions (37 ± 0.3 °C), and the speed of the step motor was controlled to be 20 rpm for mixing the slurry in an interval of 1 min every hour. (3) Biogas measurements; the volume of biogas produced was measured on a daily basis using

Table 1
Chemical composition of fresh manure and slurry.

Parameter	Fresh manure	Slurry
TS (%)	14.8	7.16
VS (%)	11.67	5.85
VS (% from TS)	82.24	81.28
Ash (%)	2.51	1.34
Organic carbon (% from VS)	47.7	47.15
Total Nitrogen (%)	1.83	1.96
C:N ratio	26:1	24:1
pH value	6.13	5.85