# Effects of different nanoparticles on biogas production during anaerobic digestion of food waste

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## 1. Introduction

Anaerobic digestion (AD) is one of the most efficient processes to treat various kinds of raw biomasses into clean energy. The main goal of this process is to efficiently convert a waste in renewable biofuel, biogas. Efficiency of the AD is mainly dependent on microorganisms involved in AD steps and types of feedstocks (Kim et al., 2017). In order to enhance biogas production in AD process can be used organic and inorganic additives. Inorganic additives such as micronutrients have been proven to stimulate the performance of biogas production reactors (Gustavsson et al., 2013). These trace elements can be added to AD process in the form of nano-structure materials.

Many types of nanomaterials have been used in many fields. Nanoparticles (NPs) are released into the environment as waste after their application and treatment. Since the nanotechnology has been emerged as an attractive choice in engineering and environmental science, researchers investigate the effects of trace elements in the form of nano-structured materials on AD performance of many substrates.

The toxicity of zinc oxide nanoparticles (ZnO NPs) on the environment has received more attention than that of other nanomaterials owing to their widespread applications. ZnO nanomaterials have been employed in many applications, such as optoelectronics, cosmetics, catalysts, ceramics and pigments due to their unique properties and finally led to their ubiquitous occurrence in the environment (Jin & Jin, 2019). Furthermore, during the past years, titanium dioxide (TiO<sub>2</sub>) has been widely explored and applied in different fields attributed to its properties, e.g., photocatalytic degradation and ultraviolet (UV) absorption (Noman et al., 2019).

According to the above, it is important to assess the role of the existence of  $TiO_2$  and ZnO/Ag NPs on anaerobic digestion. Consequently biochemical methane potential tests were carried out on food wastes (FW), with or without NPs to examine the impact of those materials in AD process. Anaerobic tests were carried out in mesophilic (37°C) conditions. The aim of this work is to study the effect of NPs, such as titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO) and silver (Ag) in anaerobic digestion.

# 2. Materials and methods

## 2.1. Raw materials, substrates, inoculum and NPs

Food waste (FW) used in the present study was collected from the students' restaurant at the Hellenic Mediterranean University, Heraklion. The FW composition was 62% cooked meals, 12% bread and bakery and 26% vegetables and salads (on a wet-weight basis). FW was homogenized using a mechanical mixer (approximately 4.0 mm). Inoculum was obtained from the anaerobic digester of the sewage treatment plant (STP) of the city of Heraklion, Greece (population about 200,000).

The growth of  $TiO_2$  powder was performed by hydrothermal route using 1.5 ml titanium (IV) bis(ammoniumlactato)dihydroxide solution, 50 ml deionized H<sub>2</sub>O and an appropriate amount of NH<sub>3</sub> to adjust the pH solution at 11. The latest was necessary for the control on the precipitation of TiO<sub>2</sub> powder. The solution preparation involved the addition and stirring of all precursors. Finally, the solution was placed in a Pyrex glass bottle with propylene autoclavable screw cap and heated at 95 °C under atmospheric pressure for 24 h and 48 h. After the end of growth period, the solutions were centrifuged and the powders were dried in air at 95 °C.

The solution preparation for the growth of ZnO involved the stirring of 30 ml, 0.1 M ZnSO<sub>4</sub> and 20 ml, 0.1 M NaOH. Following this, 1.5 ml, 0.1 M AgNO<sub>3</sub> was added in order to evaluate the effect of Ag on the anaerobic digestion. In this case, two solutions were prepared, one for the bare ZnO and another for ZnO/Ag powders. Afterwards, the solutions were transferred in Pyrex glass bottles (similar as above) and heated at 95 °C for 24 h, after the end of the particular period, the solutions were centrifuged and the powders were dried as above. In both cases, the powders were transferred in vials for further analysis.

#### 2.2. Methane potential experiment

Batch experiments were carried out in triplicate at mesophilic conditions (37  $^{\circ}$ C) to determine the methane potential of fresh food wastes (FW) and a mixture of food waste and Nanoparticles (NPs), such as titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO) and silver (Ag). NPs were added in order to examine the impacts in anaerobic digestion of those materials. The NPs, were added to batch reactors in one concertation 20 mgNPs/grVS. They were carried out using a method based on Angelidaki & Sanders, 2004. One inoculum to substrate ratio (ISR) was examined 2:1 (VS). The experiments were conducted in 120 ml serum bottle reactors. The reactors were flushed with a gas mixture of nitrogen and carbon dioxide (70% and 30% respectively) immediately after the addition of inoculum and substrates to remove air and achieve anaerobic conditions. Serum bottles were then sealed with rubber septa and aluminum crimp caps. Biogas production and content was measured in each bottle at regular time intervals for a period of more than 2 months (about 60 days).

#### 2.3. Analytical Methods

The pH was analyzed according to APHA (2005) using a pH-meter (model GLP21, Crison). COD were determined spectrophotometrically by use of standard test kits (Hach). TS and VS were measured gravimetrically according to APHA (2005).

## 3. **Results and Discussion**

Cumulative biogas production is presented in Figure 1. Specifically, the maximum biogas production was 435 ml, 486 ml and 628 ml for FW, FW & ZnO/Ag and FW & TiO<sub>2</sub>, respectively. In all cases the addition of NPs resulted in higher biogas production. The NPs added to the feed did not have a negative effect on reactor performance, but seemed to have higher biogas production. Moreover, co-digestion with NPs improved biogas production by 1.1-1.4 times. The best improvement of biogas production of approximately 44% was achieved for FW & TiO<sub>2</sub> substrate while an improvement of approximately 12% with FW & ZnO/Ag substrate was achieved. Therefore, when NPs were used as a combination of substrate with food residues it produced larger amounts of biogas than samples containing only food residues. This result highlights the fact that the NPs do not adversely affect the process.



Figure 1. Cumulative biogas production for different substrate.

## 4. Conclusions

The NPs added to the feed did not have a negative effect on reactor performance, but seemed to have higher biogas production. Moreover, co-digestion with NPs improved biogas production by 1.1-1.4 times. The addition of ZnO/Ag and TiO<sub>2</sub> improved the biogas cumulative yield by 12-44%, respectively as compared to the control reactor. The addition of TiO<sub>2</sub> improved biogas production by 44%, which could be a promising method to improve biomethane in large scale units.

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