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Effects of Different Materials on Biogas Production during Anaerobic Digestion of Food Waste

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Abstract: One of the best methods for turning different types of biomass into clean energy is anaerobic digestion (AD). Organic and inorganic additives may be employed in the AD process to increase biogas output. It has been demonstrated that inorganic additives, such as micronutrients, can improve the efficiency of biogas producing reactors. These trace items can be introduced to the AD process as powders. The use of metal oxides in engineering and environmental research has become more popular. This study focuses on the role of TiO_2 and ZnO/Ag powders on anaerobic digestion. Food waste studies on biochemical methane potential were performed with and without TiO_2 and ZnO/Ag powders to examine their impact on AD. All powders are grown through the hydrothermal procedure, which has proved to be environmentally friendly and low in cost, presenting the capability to simply control the materials' characteristics at mild temperatures. The addition of ZnO/Ag and TiO_2 improved the biogas cumulative yield by 12 and 44%, respectively, compared to the control reactor. In addition, volatile solids (VS) removal efficiency increased by 5.7% in the food wastes (FW) and TiO_2 reactor, while total chemical oxygen demand (TCOD) removal efficiency increased by 22% after the addition of ZnO/Ag.

Keywords: anaerobic digestion; metal oxide; biogas production; powders; hydrothermal procedure; food waste treatment

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Citation: Dompara, I.; Maragkaki, A.; Papastefanakis, N.; Floraki, C.; Vernardou, D.; Manios, T. Effects of Different Materials on Biogas Production during Anaerobic Digestion of Food Waste. *Sustainability* **2023**, *15*, 5698. https://doi.org/10.3390/su15075698

Academic Editors: Paolo S. Calabrò and Alessio Siciliano

Received: 6 January 2023
Revised: 17 March 2023
Accepted: 23 March 2023
Published: 24 March 2023

1. Introduction

Since fossil fuel prices have been steadily rising and their negative effects on the environment have increased, the use of sustainable and clean fuels, mainly biofuels, has been deemed necessary [1]. One of the energy source categories that may produce heat, light and electricity without harming the environment is known as renewable energy. The obvious benefit of renewable energy is that it does not require fuel, which prevents carbon dioxide emissions [2].

Agricultural, municipal, animal, and other raw materials are used to make biogas, another renewable energy source. This is a mixture of several gases, mainly methane and carbon dioxide [3]. Organic waste emissions from the biological process known as anaerobic digestion (AD), which generates biogas, can be effectively reduced [4–6]. Anaerobic digestion has gained more attention lately. Under oxygen-limited circumstances, a variety of microorganisms break down organic waste as part of the process of anaerobic digestion. The organic component of municipal solid waste includes a considerable amount of food waste. Food waste is currently underutilized and frequently dumped or burned, contributing to about 20% of the total global output of greenhouse gases such as CO_2, CH_4, and N_2O [7]. Food waste can decompose in one of four major stages, hydrolysis, acidogenesis, acetogenesis, and methanogenesis [8]. Complex organic compounds (such as proteins, polysaccharides, and lipids) are hydrolyzed into soluble monomers in the first phase of AD. These monomers are subsequently transformed via acid fermentation and ethanol fermentation processes into volatile fatty acids (VFAs) and ethanol, respectively. The VFAs and ethanol are then converted to acetates by H_2-producing acetogens, which also produce H_2 and carbon dioxide. Anaerobic methanogens then further transform the oxidation products into CH_4. It has been found that an effective and stable AD process often depends on syntrophic connections between various microbe species, and that the electron transfer between these microorganisms is important in AD [9].

Summers et al. (2010) [10] first observed direct interspecies electron transfer (DIET), an alternative to indirect interspecies electron transfer (IIET), in co-cultures of *Geobacter sulfurreducens* and *G. metallireducens*. Since DIET does not require H_2 as an electron carrier, it has been recommended as a possible strategy for enhancing the present AD process [11]. During DIET, cytochromes, electrically conductive pili (e-pili), and conductive materials enable extracellular electron exchanges between several bacteria [12]. It has been suggested that the AD processes of acetogenesis, acetate oxidation, and methanogenesis occur when bacteria and archaea join electrically to create CH_4 [13]. Additionally, it has been asserted that mechanisms mediated by DIET result in faster electron transport and more effective cellular conversion [14]. For instance, it has been found that promoting DIET with the addition of magnetite and other conductive materials increases the rates of organic decomposition and CH_4 generation [15].

It has been demonstrated that the conductive material enrichment of functional syntrophic microorganisms is effective for forming electrical connections via DIET. The conductive materials provide long-range electron transport channels that allow for direct electron exchange between syntrophic partners. Therefore, adding conductive materials could be a long-term strategy for improving DIET. The types of feedstocks and microorganisms used in the AD phases have a major impact on the efficiency of the process [16]. Organic and inorganic additives can be added in the AD process to increase biogas production. It has been demonstrated that inorganic additives such as micronutrients can improve the efficiency of biogas-producing reactors [17]. These trace elements can be added to the AD [9].

Enhancing sludge AD performance with the addition of additives is becoming a common practice. Nanomaterials are currently the most widely utilized additives to enhance AD performance [18]. The extracellular electron transfer between exoelectrogenic bacteria and methanogenic archaea could be increased with the use of several nanomaterials (nano-Al_2O_3, nano-ZnO, nano-carbon powder, and nano-CuO), which have greater specific surface area and improved conductivity for electrons [19].

With at least one dimension less than 100 nm, nanoparticles (NPs) are frequently used in engineering and environmental processes [20]. NPs can be applied to a variety of environmental applications due to their superior mechanical, structural, thermal, and morphological properties [2]. Since nanoscale materials exhibit amazing features that bulk materials do not, the concerns of sustainability, energy, and climate change are forcing researchers to investigate the science of the nanoscale as a new source of advances in the sphere of the energy and the environment. The small size of NPs allows them to slip through biological barriers and affect drug uptake, absorption, distribution, and metabolism. A large surface area, large surface-to-volume ratio, high reactivity within microorganisms even at minimum concentrations, self-assembly, and dispersibility should all work to their advantage [21]. It has been demonstrated that adding trace element supplements in the form of NPs enhanced AD performance. The nanomaterials utilized in AD can be classified in four groups: zero valent metallic NPs (Fe, Cu, Ag, etc.), metal oxide NPs (ZnO, TiO_2, Fe_2O_3, etc.), carbonaceous materials (graphene, nanotube and nanofibers), and multi-component NPs [22]. The zero valent metallic nanoparticles have been extensively studied, presenting an enhanced methane production from sewage sludge of up to 25.2% during the application of 100 mg/L in batch reactors [23]. Similar behaviour was shown with the addition of 0.1 wt. % of 10 mg/L zero valent metallic nanoparticles during 17 days of batch experiments producing biogas and methane of up to 30.4% and 40.4%, respectively [24]. Regarding the metal oxide NPs, iron oxide is a promising candidate because it is an environmentally friendly n-type semiconductor, and the magnetic properties of iron can be used to recover the oxide for recycling [25]. The biogas volume dramatically increased when 20 mg/L Fe NPs and 20 mg/L Fe_3O_4 of magnetic NPs were added, respectively reaching 1.45 and 1.66 times the levels produced by the control [26]. Generally, the TiO_2 NPs had no significant impact on hydrolysis, acidification and methane production during the AD of sludge even at high concentrations (150 mg/g total suspended solids—TSS) in short- and long-term exposure [27]. Concerning the carbon-based nanomaterials, it has been indicated that the addition of 1.0 g/L of graphene resulted in an enhancement of 25% in methane yield and 19.5% in the biogas production rate [28]. Other studies have also found that short-term exposure of graphene with concentrations of 30 and 120 mg/L had a beneficial impact on the methane production rate, which increased by 17% and 51.4%, respectively [29]. Finally, the distribution of metal/metal oxide NPs over the support materials (TiO_2, Al_2O_3, SiO_2, etc.) can increase the surface-exposed atoms of NPs, and consequently, enhance their reactivity [30]. In particular, it has been concluded that the ratio 2:1 zero valent nanoparticles to activated carbon as a support is the optimum ratio for maximum nitrate and phosphate removal [31].

One of the benefits of NPs is the delayed rate of trace element dissolution, which makes metal ions more bioavailable in the AD medium and boosts enzyme activity. When energy crops, animal waste, crop leftovers, the organic portion of municipal solid wastes, or any other type of organic waste are used in agricultural biogas digesters, trace metals as micronutrients have a substantial impact on their stability and performance [21]. Since it may pass through cell membranes and interact with the immune system, uptake, absorption, distribution, and metabolism, nano-size is the key characteristic for interactions with biological systems. Because of the mesoscopic effect, micro object effect, quantum size effect, and surface effect, nanoscale materials exhibit superior physical and chemical properties over their atomic or significant equivalents [32]. Owing to the conductivity of metal NPs, NP addition might be employed to enhance DIET, which would facilitate the growth of biofilms in the AD system [33]. According to recent research, the DIET between electroactive microorganisms can be increased by including electrically conductive materials [34].

Among the four groups of nanomaterials utilized for AD, metal oxides are regarded as promising since they are environmentally friendly with minimal toxicity in humans, abundant, and facilitate the growth of nanomaterials with tailored sizes and shapes [35,36]. In particular, TiO_2 has strong thermal and chemical stability. It also indicates an enhanced lifetime that prevents degradation when exposed to bacteria or chemical molecules [37]. In addition, zinc oxide (ZnO) is the earliest and most widely utilized material [37]. Due to their distinctive features, ZnO nanoparticles have been used in a variety of applications, including optoelectronics, cosmetics, catalysts, ceramics, and pigments [38]. Furthermore, due to its features, such as photocatalytic degradation and ultraviolet (UV) absorption, titanium dioxide (TiO_2) has been extensively researched and employed in a variety of sectors during the past several years [39].

Numerous researchers have used nanoparticles or nanostructures, including the reforming of methane using CO_2 [40], materials and composites with a unique composition [41–43] in hydrogen production [44], electrocatalysis [45,46], the food industry [47], heat transfer enhancement [48,49], sensors [50,51], fuel cells [52,53] and water purification and treatment [54,55]. Recent research indicates that the use of nanotechnology in the biofuel industry has a promising future. Analyses and developments in the application of nanotechnology to enhance biofuels have thus far been presented [56,57]. The effect of these oxides on acetoclastic and hydrogenotrophic methanogenic activities was investigated and found to be highest for TiO_2 and lowest for ZnO. The lowest performance of ZnO was due to the release of toxic divalent Zn^{2+}, which influences the microorganisms [58].

According to the above analysis, there is space for research to assess the role of TiO_2 and ZnO/Ag powders on anaerobic digestion. To the best of our knowledge, this is the first time ZnO/Ag was chosen for investigation of its performance as a multi-component material for the first time to the best of our knowledge. Consequently, food wastes (FW) are tested for their biological methane potential, either with or without powders, to examine the impact of these materials on the AD process. Anaerobic tests are performed in mesophilic (37 °C) conditions. The purpose of this work is to study the effect of TiO_2 and ZnO/Ag on anaerobic digestion and whether these different materials help to enhance the production of biogas and increase the efficiency of chemical oxygen demand (COD) removal. All powders are grown through the hydrothermal procedure, which is environmentally friendly (i.e., mainly aqueous solution) and simple (i.e., one step process without further heating of the material).

2. Materials and Methods

2.1. Raw Materials, Substrates and Inoculum

Food waste (FW) was obtained from the student restaurant at the Hellenic Mediterranean University in Heraklion and used in the current investigation. The FW composition included 26% vegetables and salads, 12% bread and bakery and 62% cooked meals (on a wet-weight basis). A mechanical mixer was used to homogenize the FW (approximately 4.0 mm). The sewage treatment facility (STP) of the city of Heraklion, Greece provided inoculum, which was taken from the anaerobic digester (population about 200,000). The average flow for the STP of Heraklion is 150 m^3/day, with a hydraulic retention time (HRT) of 22 days and an organic loading rate (OLR) of 1.0 $kgVSm^{-3}d^{-1}$. Table 1 summarizes the average composition of raw inoculum and FW.

Table 1. Composition of food waste (FW) and inoculum.

Parameters	Inoculum	FW
pH	7.6 ± 0.0	4.9 ± 0.1
TS—total solids (g/kg)	28.99 ± 1.09	226.21 ± 2.31
VS—volatile solids (g/kg)	16.68 ± 0.80	216.89 ± 1.95
TCOD—total chemical oxygen demand (g/L)	-	151.3 ± 10.0
N—nitrogen (g/L)	-	2.32 ± 0.04

2.2. Synthesis of Powders

The growth of TiO_2 powder was performed by the hydrothermal route using 1.5 mL titanium (IV) bis(ammoniumlactato)dihydroxide solution, 50 mL deionized H_2O, and an appropriate amount of NH_3 to adjust the pH solution to 11. The concentration of the titanium (IV) bis(ammonium lactato)dihydroxide 50 wt. % solution in H_2O was adjusted to 1.7 M. This was necessary to control the precipitation of the TiO_2 powder. The solution preparation involved the addition and stirring of all precursors. Finally, the solution was heated at 95 °C under atmospheric pressure for 24 and 48 h in a Pyrex glass bottle with a propylene autoclavable screw cover. After the end of the 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 $ZnSO_4$, and 20 mL, 0.1 M NaOH. Following this, 1.5 mL, 0.1 M $AgNO_3$ was added in order to evaluate the effect of Ag on anaerobic digestion. In this case, two solutions were prepared, one for the pure ZnO and another for ZnO/Ag powders. The solutions were then transferred to Pyrex glass bottles (as above) and heated at 95 °C for 24 h. After the end of this period, the solutions were treated as above. In both cases, the powders were transferred to vials for further analysis.

2.3. Biogas—Methane Potential Experiments

At mesophilic temperatures (37 °C), batch studies were conducted in triplicate to ascertain the impact of TiO_2 and ZnO/Ag particles on the methane potential of fresh food wastes. Different substrates (FW, ZnO/Ag, TiO_2, FW & TiO_2 and FW & ZnO/Ag) were assessed to identify which were the most successful in achieving the highest methane yield. The powders were added to batch reactors as 20 mg NPs/gr volatile solids (VS). The experiments were carried out using a method based on Angelidaki and Sanders (2004) [59]. One inoculum (64 mL) to substrate (FW, 2.46 g) ratio (ISR) was examined, 2:1 (VS). Reactors made out of 120 mL serum bottles were used for the research. Immediately after adding the inoculum and substrates, the reactors were flushed with a gas combination of 70%

nitrogen and 30% carbon dioxide to create anaerobic conditions. After that, rubber septa and aluminum crimp closures were used to seal serum vials. For a period of more than two months, the output and content of biogas were monitored in each bottle at regular intervals (about 60 days).

2.4. Analytical Methods

Using a pH meter, the pH was measured in accordance with APHA (2005) [60] (model GLP21, Crison, Barcelona, Spain). The COD was measured using spectrophotometry (DR 2800, Hach-Lange, Berlin, Germany) and standard test kits (Hach-Lange). According to APHA (2005) guidelines and appropriate laboratory ovens (Memmert UF 30, Schwabach, Germany and Protherm PC442, Ankara, Turkey), total solids (TS) and VS were measured gravimetrically. The total chemical oxygen demand decrease (%) was computed as (TCODin − TCODout/TCODin) × 100, where TCODin and TCODout are the concentrations of feed and digested substrate, respectively. A gas chromatograph was used to evaluate the composition of the biogas (Agilent 6890N GC System, HP Agilent, Santa Clara, CA, USA). Gas-tight syringes were used to collect gas samples, and the needles were then sealed with butyl rubber stoppers before being transferred to the gas chromatograph. A gas chromatograph received 20 microliters to analyze methane and carbon dioxide. A capillary column (GS Carbonplot, 30 m × 0.32 mm, 3 lm) and a thermal conductivity detector (TCD) were used. The detector port operated at 150 °C, while the column operated isothermally at 80 °C. The carrier gas was helium, flowing at a rate of 15 mL/min. All individual sample analyses were performed in triplicate.

2.5. Statistical Analysis

Origin 9 (OriginLab, Northampton, MA, USA) was used in this study's data and findings for statistical analysis (analysis of average values, variance, and standard deviation). Using one-way analysis of variance (ANOVA), differences in the biogas output, TCOD removal, and VS removal among the outcomes of the co-digestion of FW and various NPs were assessed. Tukey analysis was utilized to find differences in the average values of the normally distributed variables that were statistically significant ($p < 0.05$).

3. Results and Discussion

The cumulative biogas production is presented in Figure 1. Specifically, the maximum biogas production was 435 mL/gr VS, 486 mL/gr VS,628 mL/gr VS, 28 mL/gr VS, and 29 mL/gr VS for FW, FW & ZnO/Ag, FW & TiO_2, ZnO/Ag, and TiO_2, respectively. The literature reports that biogas production from FW ranged between 467 and 529 mL/g VS_{added} due to its high protein and lipid content [61]. According to Kazimierowicz et al. (2021) [62], the biogas yield from FW can range between 307.1 mL/g ODM and 740.4 mL/g ODM under mesophilic conditions depending on the composition of food waste products. In every situation, adding powders increased the amount of biogas produced. Although the addition of powders to the feed had no detrimental effects on the reactor's performance, it appeared that biogas output was increased. Additionally, co-digestion with powders increased biogas output by a factor of 1.1–1.4. Methane in the biogas varied in content between 71.2% and 71.4%. Following the addition of FW and TiO_2, the biogas methane content reached its highest level, at 71.4%. The best improvement of biogas production of approximately 44% was achieved for the FW & TiO_2 substrate, with an improvement of approximately 12% with the FW & ZnO/Ag substrate. As a result, samples using NPs as a substrate in addition to food residues produced more biogas than samples using only food residues. This outcome demonstrates that the powders have no negative effects on the process. Moreover, Figure 2 shows the total biomethane production of each substrate. With a p-value of 0.05, different letters represent significant differences. As indicated, the best biomethane production (448 mL/grVS) was achieved for the FW & TiO_2 substrate. A related investigation [63] looked at the impact of Fe_2O_3 and TiO_2 NPs on the generation of biogas from cow manure. As a consequence, the generation of specific biogas and CH_4 increased by 336.25 and 192.31 mL/g VS, respectively, when 500 mg/L TiO_2 was added, while the corresponding values in the control were 286.38 and 158.55 mL/g VS (approximately 17% increase). Our situation turned out to be more effective than this study after the addition of TiO_2. Additionally, Cervantes—Aviles et al. (2018) [64] investigated how anaerobic digestion performed when TiO_2 NPs were present, as well as what happened to them in anaerobic reactors, indicating an average of 14.9% methane generation.

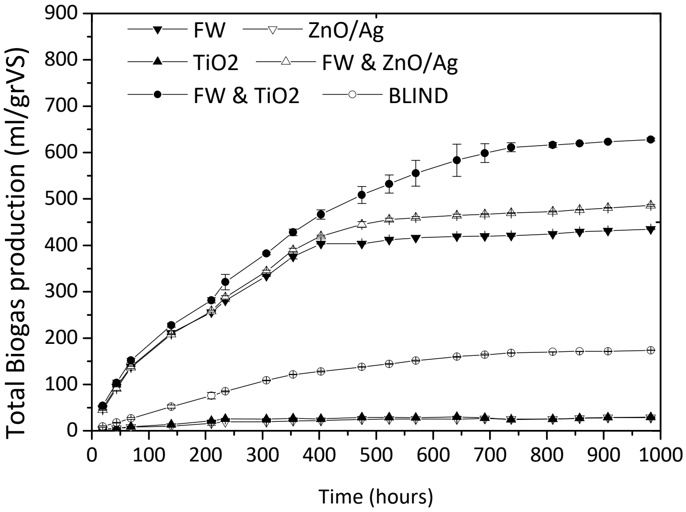

Figure 1. Cumulative biogas production for different substrates.

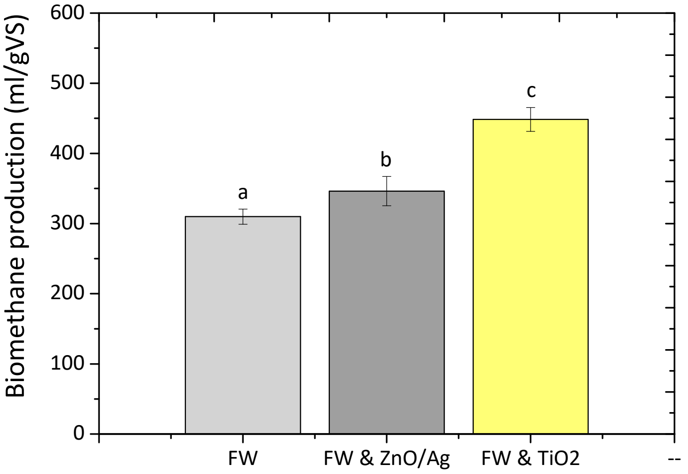

Figure 2. Biomethane production (ml/grVS) for different substrates. With a p-value of 0.05, different letters represent significant differences. The error bars show the biogas production standard deviation.

The literature reports an increase in methane production during anaerobic digestion when TiO_2 NPs are present, although the cause is not entirely evident. TiO_2 NPs may help with the electron transfer during anaerobic digestion, according to Zhao et al. (2016) [65]. Anaerobic bacteria have the ability to export electrons from within the cell to the extracellular solids or ions in the place of oxygen, a process known as extracellular electron transfer (EET), according to Wang et al. (2016) [66]. As a result, TiO_2 NP-induced EET may increase the production of methane during anaerobic digestion. On the other hand, there are studies [27,58,67] that claim that even at high concentrations, (1500 mg/L) TiO_2 NPs had no obvious effects on the hydrolysis, acidification, and methane production during the AD of sludge, and that anaerobic treatment procedures could tolerate large concentrations of these NPs. According to Garcia et al., 2012, in the thermophilic anaerobic test, TiO_2-NPs had a slightly positive impact on biogas generation (10% increase). At mesophilic temperature (35 °C), TiO_2 NP addition has an effect on the anaerobic digestion of waste-activated sludge, according to Chen et al. (2022) [15]. For a long time (105 days), TiO_2 NPs with an average particle size of 185 nm were added to the sludge, but they had no effect on the overall amount of methane production compared to the control sample.

As mentioned above, the addition of ZnO/Ag improved the biogas production by approximately 12%. Similar results for the addition of ZnO NPs have also been found by other researchers. Hassaan et al. (2019) [68] used chemical agents and green ZnO nanoparticles made from durum wheat extract to treat five types of biomass (abyssinian cabbage, barley, rapeseed, durum wheat, and triticale) anaerobically. The results showed that the maximum specific biogas generation was achieved when 10 mg/L of chemical and green ZnO nanoparticles were applied to the durum wheat. This produced 422 mL/gVS and 457 mL/gVS compared to the control, which only produced 353 mL/gVS. ZnO NPs, which, however, caused damage to the bacterial cell membrane, as discovered by earlier research [69]. Metal ions emitted ZnO during the sewage sludge treatment process and reduced microorganism populations, especially at greater concentrations of ZnO NPs [20]. According to Wang et al. (2021) [70], ZnO NPs have negative impacts on the Euryarchaeota community, which play a significant role as methanogens in the anaerobic digestion. Faisal et al. (2019) [71] showed that the exposure concentration of ZnO at 1000 mg/L resulted in inhibition of 65.3% of the biogas volume and 47.7% of the methane composition, while when ZnO nanoparticle doses of 120 and 240 mg/L were added to the feed, they reported an inhibition of 43% and 74% of the biogas generation at Day 14. Moreover, Olaya et al. (2021) [72] found that ZnO at high concentrations (150 mg NPs/g TS of mixed sludge) had a negative impact on the production of biogas under both mesophilic and thermophilic conditions. This can be attributed to the sensitivity of microorganisms to ZnO under thermophilic and mesophilic conditions. Therefore, the results of the present study are in contrast to corresponding ones regarding the effect of ZnO, which together with FW and the addition of Ag increased biogas production. Specifically, in most studies [71], the effect of this specific nanomaterial was either suppressive or negligible. Notably, Ag alone had no effect on biogas production in other studies [73]. In contrast to the interventions studied, Ag prevented the suppressive effect of ZnO, presenting a 12% increase in biogas production and making the intervention more effective compared to the FW intervention.

Examining the effectiveness of the reduction in the volatile solids is another method of evaluating a substrate's performance. Volatile solids are partially decomposed and converted to biogas throughout the digestion process. The amounts of VS in the feed and the substrate after digestion are denoted by VSin and VSout, respectively. VS reduction is equal to (VSin-VSout/VSin) multiplied by 100. As shown in Figure 3, high total VS removal efficiencies (between 39.6% and 46.5%) were obtained after the addition of ZnO/Ag and TiO_2 nanoparticles. Among the different powders, the TiO_2 addition exhibited the greatest reduction in VS (46.5%), which is consistent with one of the greatest methane yields. Compared with the FW reactor, VS removal efficiency increased by 5.7% in the FW & TiO_2 reactor, while there was a small reduction in the FW & ZnO/Ag reactor. The results suggest that the addition of TiO_2 enhanced VS removal efficiencies. However, according to Chen et al. (2020) [19], the VS removal efficiency of nano-ZnO was 30.08%, which was lower than the control reactor (52.39%). Therefore, our results are in contrast to Chen et al. (2020) [19], since there was no reduction in VS removal efficiency due to the prevention of the suppressive effect of ZnO after the presence of Ag. Lower VS reduction was found by Nguyen et al. (2015) [74] when they examined different concentrations of nanoparticles (CeO_2 and ZnO) on the biogas production of sludge. The results of their experiments showed that VS reduction ranged between 16.2–24.9% after the addition of 1000 mg/L ZnO and 100 mg/L ZnO, respectively. Slightly higher VS reduction was found by Farghali et al. (2019) [63]. According to them, VS reduction was estimated at 59.16% after the addition of 500 mg/L TiO_2 to biogas production from cattle manure. Using this concentration of 500 mg/L TiO_2, they achieved the highest specific production of biogas and CH_4.

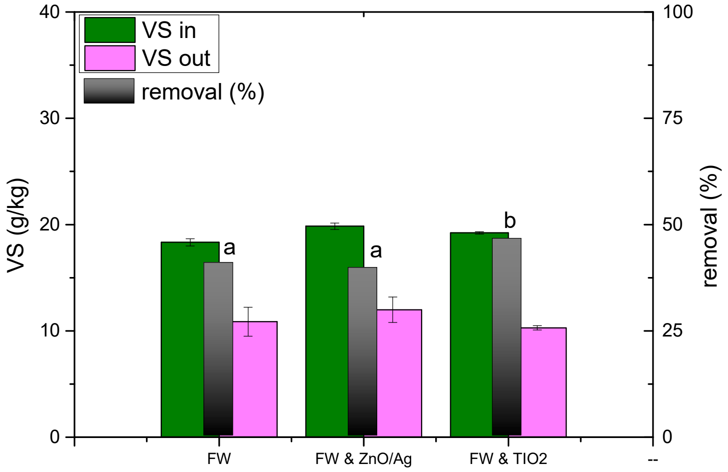

Figure 3. VS concentrations and removal in the influent (in) and effluent (out) stages. With a *p*-value of 0.05, different letters represent significant differences. Standard deviation is indicated by error bars.

The total COD was measured in both the digestate and the feeding substrate. As shown in Figure 4, high TCOD removal efficiencies (between 37.8% and 49.3%) were obtained after the addition of ZnO/Ag and TiO_2 nanoparticles. The best TCOD removal efficiency was achieved after the addition of ZnO/Ag, approximately 50%. However, adding ZnO/Ag had a positive impact on organic matter removal efficiency. Similar results were found by Olaya et al. (2021) [72] when they examined the effect of type (coated and non-coated) and dose (6, 75 and 150 mg/g feed total solids (TS)) of ZnO NPs on anaerobic sludge digestion under mesophilic and thermophilic conditions. The results of their experiments showed that the TCOD removal was 53–54% for the mesophilic digesters and 57–58% for the thermophilic digester. Our results are in contrast to Chen et al. (2020) [19], where the nano-ZnOs COD removal ratio was decreased by 92.25% compared to the control reactor. The cell membrane of anaerobic bacteria was reportedly damaged by harmful Zn^{2+} ions generated from nano-ZnO in Chen et al. (2020) [19]. Even some anaerobic microorganisms died as a result of the decreased anaerobic bacterial activity. Obviously, the addition of Ag prevented the suppressive effect of ZnO. Moreover, Nguyen et al. (2015) [74] showed that the COD reduction ranged between 30.5 and 97.4% after the addition of 1000 mg/L ZnO and 10 mg/L ZnO, respectively.

Table 2 displays the biogas output and increment results in relation to t**he** FW substrate. The outcomes of the biogas chemical makeup (CH_4), VS and TCOD removal are also indicated. The biogas production after the addition of hydrothermally grown TiO_2 powders (i.e., 44%) is higher compared to the Fe_3O_4 nanoparticles in TiO_2 (15.09%) and comparable with modified biochar in combination with α-Fe_2O_3 (i.e., 40%) [75,76]. There is, however, limited research on the hydrothermally grown TiO_2 powders for the biogas production. Hence, further research is needed to explore the effect of the hydrothermal processing parameters of the TiO_2 catalyst on the biogas production and understand the relation of materials properties with performance. Regarding the ZnO/Ag powders, the data indicated 12% biogas production, which comes in contrast with what has been reported for ZnO powders (i.e., showing negative impact on anaerobic digestion [58]. In this study, the Ag has been chosen since it was expected to serve as an active site for the adsorption of organic molecules reducing the inhibition effects in the biogas production process [77]. Nevertheless, it is required to further evaluate the Ag % needed for the optimum biogas production to have a clear picture of the particular material's performance.

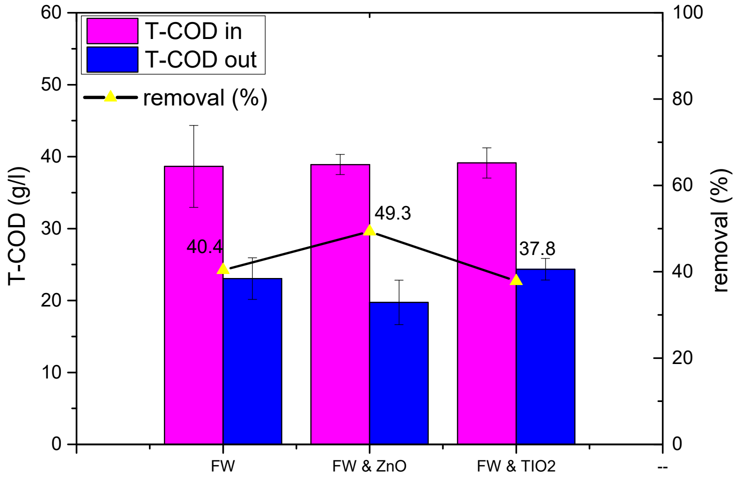

Figure 4. Concentrations of TCOD removal in the influent (in) and effluent (out) stages. Standard deviation is indicated by error bars.

Table 2. Production of biogas and biomethane, biogas composition and TCOD and VS removal for various substrates.

Parameter		FW	FW & ZnO/Ag	FW & TiO_2
Total biogas production (mL/grVS)		435 ± 11	486 ± 21	628 ± 17
Biogas increment (mL/grVS) & (%)		-	51 (12%)	193 (44%)
Biogas composition (%)	CH_4	71.2 ± 2.1	71.2 ± 4	71.4 ± 2.1
Total biomethane production (mL/grVS)		310	346	448
TCOD removal (%)		40.4	49.3	37.8
VS removal (%)		40.8	39.6	46.5

We strongly believe that the data obtained in this work are a good basis for further development on hydrorthermally grown metal oxide powders for the enhancement of biogas production based on a simple, one-step processing route.

Clearly, the expense of NPs will be the biggest obstacle to their widespread usage in large-scale anaerobic digesters in the future. In this study, all powders are grown through the hydrothermal procedure, which has proved to be environmentally friendly and low in cost. Based on the findings of this study, it is not advised to employ NPs in powder form on an industrial scale due to issues with economic viability and the fate of NPs in the effluent, which could have a negative influence on the environment. Alternative approaches, such as coating NPs on the outside of pellets in reactors to stop NP release to the environment, can be employed to commercialize their use in anaerobic digestion plants. Another important point for decreasing the cost of nanomaterials is the reuse of NPs in several cycles of anaerobic digestion. The characterization and potential applications of digestate are also future problems that have not not adequately addressed in the existing studies. Our solution is coating NPs on the outside of pellets, as mentioned above.

To ensure that employing additives such as Ti, ZnO, and Ag NPs in large-scale AD systems will not have a harmful impact on the environment, a lot more research is required. This includes investigating the potential environmental effects of NPs, the field where digester effluent is applied, and the crops raised for both humans and animals. In order to examine the possibilities of their reuse and reduce their influence on the environment, Hassainein et al. (2021) [78] studied the impact of employing effluent that contains nanoparticles on the plant, as well as several techniques for tracking nanoparticles inside the digester. In addition, Hassanein et al. (2019) [79] developed a new technique for nanoparticles extraction from the digestion. However, their research cannot be easily applied to large-size digesters, so more research is needed to solve this issue.

Cost is undoubtedly the biggest obstacle to the widespread use of NPs in large-scale anaerobic digesters in the future. It does not help with their implementation that the majority of studies are conducted in laboratories or, at most, at a pilot scale. They are considerably more constrained in the case of batch investigations because the circumstances are not comparable to those of continuous or semicontinuous full-scale digesters.

4. Conclusions

The growth of TiO_2 and ZnO/Ag powders was performed for their evaluation in the anaerobic digestion of food waste. Despite appearing to increase biogas generation, the addition of powders in the feed did not appear to have an adverse impact on reactor performance. Co-digestion with NPs additionally increased biogas generation by a factor of 1.1–1.4. The addition of ZnO/Ag and TiO_2 improved the biogas cumulative yield by 12–44%, respectively, compared to the control. The addition of TiO_2 improved biogas production by 44%, which can be an effective way of enhancing biomethane in large-scale systems. However, it is not advised to employ powder form on an industrial scale due to issues with economic viability and the fate of powders in the effluent, which could have a negative influence on the environment. Alternative approaches, such as coating metal oxides on the outside of pellets in reactors to stop their release in the environment can be used to commercialize their use in anaerobic digestion plants. In order to ensure that this method has no unfavorable effects on the environment, it is important to precisely evaluate the possibility of metal oxides in both the liquid and solid effluent stages. Finally, taking the important data into consideration, we will continue the hydrothermal growth of powders in order to fine-tune their characteristics (size, shape and composition) and investigate their effect on biogas generation.

Author Contributions: Methodology, A.M., N.P. and D.V.; Formal analysis, I.D., A.M., C.F. and D.V.; Writing—original draft, A.M., N.P. and D.V.; Writing—review & editing, A.M., N.P. and D.V.; Supervision, D.V. and T.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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