



Perspective: Catalytic Increase of Biogas Production in an Anaerobic Co-Digestion System

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Abstract

The use of iron nanoparticles (NPs) has proven attractive due to the NPs' abundance, non-toxicity, and cost effectiveness. However, there is a significant literature gap in biogas-production kinetics based on the addition of iron in the presence and in the absence of organic wastes in an anaerobic co-digestion system, despite the potential advantages of using iron to enhance the decomposition of organic substrates, thereby increasing biogas production. Addition of iron additives to a co-digestion system could considerably increase biogas production with greater chemical oxygen demand removal compared to a co-digestion system without iron additives (the control), thus increasing the co-digestion system's microbial activity compared to that of the control. Similarly, more production of biogas from a co-digestion system containing pretreated waste sludge (e.g. biosolids) and cow manure can occur because of the addition of iron additives. Iron-containing wastes can be utilized to increase biogas production as a catalyst in co-digestion of organic wastes. This perspective is used to address possible application of novel waste materials and environmentally sustainable nanomaterials such as green tea-extracted iron, which both contain iron, to organic wastes in an anaerobic co-digestion system for the efficacy of biogas production, along with a discussion of further research directions.

Keywords

Shotblast dust, Green tea-extracted iron, Co-digestion, Organic wastes, Biogas

Introduction

Recovering renewable energy through waste treatment processes can improve operation efficacy. Anaerobic digestion (AD), one of the most cost-effective processes of biomass to biogas conversion, has been widely applied for its multiple advantages in areas such as renewable energy production, the conservation of landfill space [1-4], and lower the resultant costs while contributing to the minimization of greenhouse gas emissions. Due to the growing generation of municipal solid waste (MSW) and biosolids, attention to alternative strategies to treat and manage MSW and biosolids has intensified. However, there are a number of issues associated with AD and its operation [5-

7]. First, sudden changes in temperature during the process are the major issue, as they influence the overall performance of the AD process. Although the literature indicated that the AD process needs to maintain a consistent mesophilic condition between 32 °C and 35 °C (90 °F and 95 °F) [8], AD can be operated at 20-55 °C and different temperatures can influence microbial groups and formation of byproducts. A high temperature range could result in more rapid sludge reduction and methane generation, but it does not necessarily bring better outcomes. As an example, with nitrogenous residues, there is inhibition of the process in the thermophilic range due to the formation of ammonia.

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Recent review studies have indicated that trace metals offer a critical role in AD performance, particularly in the stability of biogas digesters [6,7,9]. The study [9] indicated that the absence of trace metals in biogas digesters can be detrimental, leading to poor process efficiency regardless of suitable maintenance, such as controlling operational and environmental parameters. Thus, it is critical to investigate the role of trace elements in the AD process in order to overcome issues associated with AD and develop a sustainable way to generate renewable energy sources. Recent studies [10-12] showed that iron and Fe₃O₄ NPs were effective in generating more biogas, and the optimum concentration of both Fe and Fe₃O₄ NPs was 20 mg/L. There seems to be a significant benefit in adding iron (either Fe or iron oxide forms) to the anaerobic digester, but there is a significant literature gap regarding reaction mechanisms and kinetics as well as a lack of any further detailed studies on the effect of different types of iron nanoparticles (NPs), including waste iron. Iron synthesized with various types of tea extract (e.g., polyphenols acting as reducing and stabilizing agents) has been used in the removal of contaminants [13-15]. Polyphenols from various sources (e.g., tea, proteins, and vitamins), which have chemical structures of aromatic rings and hydroxyl groups and contribute to the synthesis of iron NPs, have been used due to their cost effectiveness and eco-friendly nature [16-18].

Among various sources, recent studies found green-tea polyphenol extract to be the most promising reducing and capping agent with a superior degradation of contaminants [19-23]. Such effective iron NPs can accelerate digestion of organic biomass, thereby producing more biogas. Thus, green tea-extracted iron NPs (GT-Fe) is one of iron additives that can be used to understand iron additives' influence on biogas production. As another iron additive, steel industry byproducts containing iron and iron oxides can be applicable as a catalyst to increase biogas production. In this study, perspective of the efficacy of iron additives (e.g., as a form of a waste byproduct produced from the US Foundry or a green-tea extract) in accelerating degradation of organic wastes and increasing biogas production in an anaerobic digestion system is discussed.

This perspective study aims to discuss the efficacy of iron additives as a catalyst to enhance biogas production in co-digestion of organic wastes and to identify applicability of the waste byproduct (shotblast dust: SB), which is otherwise landfilled, as a resource for a rapid breakdown of organic wastes.

The Role of Iron NPs on Biogas and Methane Production of the Anaerobic Co-Digestion System

The co-digestion of multiple substrates, including

co-digestion of biosolids and organic fraction of municipal solid waste, have proven to be effective in the performance of AD due to synergisms in the digestion medium, greater stability, a more voluminous supply of nutrients, reductions of ammonia inhibition, and economic advantages [24-29]. While co-digestion has also shown improved nutrient balance and digestion, as well as additional biogas production, co-digestion also has limitations, such as high effluent COD concentrations and additional pretreatment requirements [25]. An alternative method incorporated in the biodigester system could be the application of modified iron nanoparticles (NPs) to the co-digestion of wastes. However, current literature provides limited information.

While only three recent studies have begun to look at the influence of metal nanoparticles in either AD of manure [10] or in waste activated sludge [11,30], no studies have systematically investigated the influence of modified iron NPs on anaerobic co-digestion of organic wastes into biogas and methane production. Research is required to better understand how iron NPs interact not only with methanogens but also with all other microbial groups and how iron NPs influence biogas production of the co-digestion process, since organic wastes are commonly utilized as biomass in the AD process. It is hypothesized that the accumulation of volatile fatty acids (VFAs) is increased by the addition of iron additives, thereby reducing pH; this may inhibit the methanogenesis, since the addition of organic wastes may offer more substrates for methanogenesis. Additionally, in the AD of complex residues, it is often observed that hydrolysis is the limiting step. Factors that affect hydrolysis on addition of iron additives warrant further investigation. Future research is also suggested regarding the potential influence of different types of iron additives on the initial hydrolysis step. The nature of iron additives in terms of their physicochemical properties such as size, surface area, shape, polymorphs, and the types of metallic nanoparticles could also affect the overall performance of the AD process.

The addition of iron NPs could eliminate pH reduction and alleviate high COD concentration in the effluent. The extent and kinetics of biogas production of modified iron NPs are a function of the surface reactivity, which depends on the physicochemical properties of different types of iron NPs. The relative importance of enhancing biogas may depend on not only the properties of the NP surface but also compositions of biomass. For instance, biosolids as one of the types of biomass may yield different amounts of biogas under the same operation conditions compared to co-digestion of organic waste compositions. Even different types of biosolids (Class A versus Class B) may influence the efficacy of AD performance in terms of the production of biogas, since Class B biosolids

that contain a higher level of detectable pathogens may inhibit digestion of biomass in the AD biodigester.

In an anaerobic digestion system, iron additives may stimulate interactions of organic substrates with methanogens to produce biogas through the methanogens' biostimulating mechanisms on the co-digestion of organic wastes [10,11,30-34]. The availability of surfaces may also enhance microbial activity. Studies are strongly encouraging for increasing biogas production by the addition of modified iron NPs to a co-digestion system. The addition of iron additives may serve as a catalyst to enhance the AD process for substrates with varied compositional characteristics.

Interactions and Roles of Iron NPs on Acetotrophic and Hydrogenotrophic Methanogens during AD Conversion of Biomass to Methane

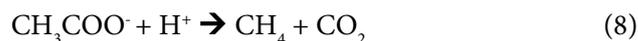
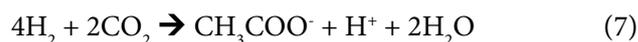
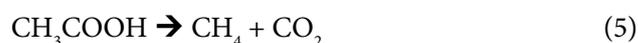
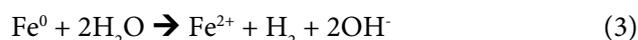
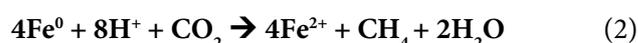
Research on the interactions of modified iron NPs with acetotrophic and hydrogenotrophic methanogens and how they play a critical role in the last step of methanogenesis could provide insight into the reaction mechanisms that occur between iron additives and organic substrates in a biodigester system. Studies dispute the effects of trace elements on biogas and methane production. For instance, Demirel and Scherer [9] indicated that trace metals are imperative for the performance and stability of biogas production in digesters operated with biomass composed of organic fractions of solid wastes or other types of organic waste. Another study indicated that the AD of food waste using trace metal solutions including Fe, Zn, Cu, and Mo showed increased production of CH₄ up to 8% and 15% increases in biogas production [35]. Such enhancement through the addition of trace nutrients was also found in other studies [36,37].

On the other hand, several studies showed inhibitory effects by NPs composed of ZnO, CuO, Mn₂O₃, Cr₂O₃ etc. due mainly to oxidative stress responses and membrane damage [6,31-33,38-44]. Nonetheless, there is little data or information on reaction mechanisms responsible for the effect of trace element requirements in the AD process fed with organic fractions of municipal solid waste [9]. Moreover, neither information nor scientific

knowledge on the reaction pathways of iron NPs with methanogens is available.

Studies that cover the role of iron NPs on both acetotrophic and hydrogenotrophic methanogens of particulate solid biomass for biogas and methane production are scarce. It is hypothesized that the different types of iron NPs influence methane formation in AD. Such effects may depend on electron release and hydrogen generation, which can lead to accelerated methanogenic reactions under anaerobic condition as follows, in addition to other possible effects due to physicochemical properties such as surface morphologies and size.

Proposed reactions involving iron NPs in the AD system are as follows:



Zero-valent iron releases two electrons upon oxidation to ferrous iron (reaction 1). Electron release from metallic particles (iron particles as one of the examples) offers anaerobic conditions that favor hydrogenation pathways to consumer CO₂ and thus production of methane. The electrons released by iron NPs can be consumed by inorganic CO₂, thereby promoting CH₄ (reaction 4) or by acids (e.g., acetic acid) (reaction 5). Dehydrogenation through the decomposition of formic acid (one of the major byproducts from biomass) can result in the formation of CO₂ and H₂ (reaction 6) [34]. Hydrogenation pathways can be accelerated by iron under the anaerobic condition (reaction 3) and thus produce more methane (reaction 4). In addition, iron NPs can serve as a catalyst to remove toxic compounds that may hinder microbial activities (e.g. $\text{Fe}^0 + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2$) [45]. Figure 1 is a schematic diagram that illustrates the addition of iron additives to AD of biomass to produce biogas.

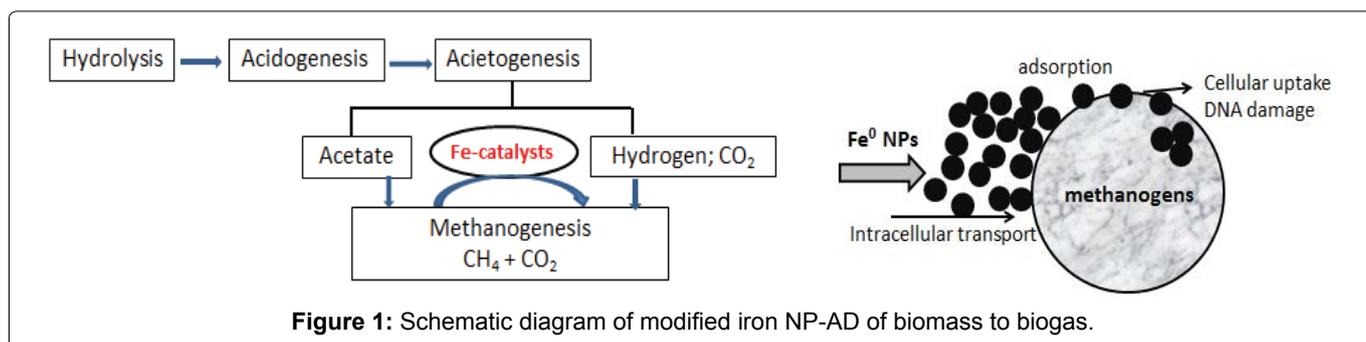


Figure 1: Schematic diagram of modified iron NP-AD of biomass to biogas.

Future Research Needs and Directions

Given the aforementioned discussion and perspective of catalytic enhancement of biogas by iron additives in the AD co-digestion system, future research needs, and directions are drawn as follows.

First, the role of modified iron NPs mixed with organic substrates in AD needs to be examined in depth, particularly how different types of iron additives influence the performance of AD co-digestion with the fundamental reaction mechanism. Second, characterization of iron NP modification before and after exposure to co-digestion of biomass would be valuable, since the extent of catalytic increase of biogas in an AD co-digestion system may depend on different types of iron NPs (e.g., green tea-extracted iron NPs, shotblast dust, and waste iron). Such a characterization study is also essential to elucidating the effect of modified iron NPs on bioenergy and their role in methanogenesis of AD.

A study on the effect of different dosages of modified iron NPs on biogas production over fermentation times is essential. Particularly, research is encouraged to involve the biogas and methane production kinetics by modified iron NPs on cow manure of AD as a function of different dosages and types of iron NPs over fermentation times. Assessing the methanogenic activity is another future study direction, which could be performed by analyzing the composition of biomass to identify any influence of iron additives on the production of methane. Iron NPs, as other types of NPs, should have electrostatic interactions. High specific areas of the iron NPs may be attributed to the cellular uptake of NPs inside the methanogens. Transmission electron microscope (TEM) analyses will provide such insight prior to beginning more in-depth studies. Several studies [31,46-48] have investigated the stimulating effects of NPs on the cellular uptake inside the methanogens by NPs in sludge digestion. These studies indicated that NP sizes have a strong effect on the binding and activation of membrane receptors and their resultant protein appearance. A recent study [10] also indicated consistent results with increasing biogas and methane improvement through the spherical shape of magnetic NP additives. As briefly discussed previously, different types of iron NPs that have different surface morphologies and sizes may alter the breakdown of biomass by interacting with methanogens in the AD system to produce biogas and methane.

Investigating a microorganism community of inoculum after exposure to modified iron NPs would aid in exploring any changes in methanogens using advanced biology tools by employing fluorescent *in situ* hybridization (FISH) and fluorescent quantitative polymerase chain reaction (FQ-PCR). NPs should be adsorbed onto manure surfaces after long-term the surfaces' exposure to the NPs, possibly due to electrostatic interactions

and the high specific area of the NPs. FISH and confocal laser-scanning microscopy (CLSM) can identify the primary cow manure components in the absence of iron NPs and any changes/shifts of the microorganism components after exposure to various types of iron NPs at various concentrations (0, 5, 10, and 20 mg/L). Real-time FQ-PCR assays can be used to further examine how different dosages at different types of iron NPs affect the abundance of methanogens in an AD process.

Lastly, investigating the role of iron NPs as a catalyst for an interspecies electron transfer (IET) mechanism of acetotropic and hydrogenotrophic methanogens is another research direction to be taken in the future. Such a study would be valuable in exploring whether different types of iron NPs can serve as a catalyst for the IET pathway among the two important acetotropic and hydrogenotrophic methanogens. Scanning electron microscopy (SEM)/TEM images of methanogens (each methanogen and mixed methanogens) formed in the absence and presence of different types of iron NPs (e.g., cell surfaces vs. cell-attaching iron NPs), along with EDS and Malvern Zetasizer, could assist in the identification of any changes in morphology, aggregation, size distribution, and chemical compositions. As discussed earlier, iron plays a critical role as an electron donor and is assumed to be one of the critical factors in the reaction pathways that enhance biogas and methane production. The extent to which iron-released electrons are transferred among methanogens and whether there are any inhibiting effects due to the presence of biomass byproducts (acetate, formate, and ammonia nitrogen) during AD fermentation are unclear. Moreover, there is a literature gap in terms of quantitative information regarding cumulative electrons transferred from iron NPs to methanogens.

In conclusion, all the suggested research directions are significant, given that such crucial information can affect the ability of waste-disposal and wastewater-treatment industries as well as the research society and community's ability to identify an environmentally sound approach to the conventional AD system, which involves utilizing waste as either a resource or a non-toxic chemical addition (i.e. green tea-extracted iron) to the AD system. A potential pitfall may need to be addressed concerning the aggregation effect from some of the iron NPs (e.g., steel-industry byproducts and waste iron), because aggregation might affect the overall performance of modified iron NPs. To address such a potential issue, research is suggested on coating iron NPs with stabilizers to examine the effect of coating materials on the overall efficiency of the AD process in production of biogas and the decomposition of organic substrates.

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