International Journal of Renewable Energy Resources 12 (2022) 31-41
https://doi.org/10.22452/ijrer.vol12no1.3

IRON-BASED ADDITIVES AND BIOGAS PRODUCTION FROM ORGANIC WASTES USING ANAEROBIC DIGESTION PROCESS

Muhammad Muddasar [a,b]
[a] U.S.-Pakistan Centre for Advanced Studies in Energy (USPCAS-E), National University of Sciences & Technology (NUST), Sector H-12, Islamabad, Pakistan
[b] Stokes Laboratories, School of Engineering, Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland
e-mail: muhammad.muddasar@ul.ie

Abstract
The world is facing a serious energy crisis and environmental pollution problems due to a sharp increase in the world population. Bioenergy is an eminent solution to these problems. Anaerobic digestion is a green energy technology used worldwide for the conversion of organic waste to biogas. It is reported that organic wastes are hard to digest and need some technical improvement in the anaerobic digestion process to improve biogas yield. Iron-based additives, due to their electron acceptance and donation capabilities, have been emphasized as being exceptional in improving anaerobic digestion process efficiency amongst all other enhancement options. This study reviews the major available types of iron-based additives, their characteristics, and their preparation methods. The preferred iron-based additive that has a significant effect on the enhancement of biogas yield is also discussed. The use of iron-based additives in the anaerobic digestion process with varying dosages and their impact on the biogas generation rate is also being studied. Substrates, operating parameters, and types of anaerobic digesters used in recent studies while researching the effects of iron-based additives are also part of this review. Lastly, this study also confirms that iron-based additives have a significant effect on the reduction rate of the volatile suspended solids, methane content, biogas yield, and volatile fatty acids.

Keywords: Anaerobic digestion, iron additives, biogas, catalyst, bioenergy

1. INTRODUCTION

Due to a significant increase in the world population during the last decade, lots of problems have arisen, including deforestation, increased energy requirements, environmental pollution, and global warming. Around 82 percent of the world's energy requirements are fulfilled by burning conventional fossil fuels like natural gas, oil, and coal, which are the main causes of environmental pollution and increased GHG emissions in the atmosphere, resulting in global warming (BP, 2019; WBA, 2019). Bioenergy is a prominent option to mitigate these environmental concerns and reduce dependency on fossil fuels. It is obtained by the biological conversion of biomass (organic matter) into biofuels (Basu, 2018).

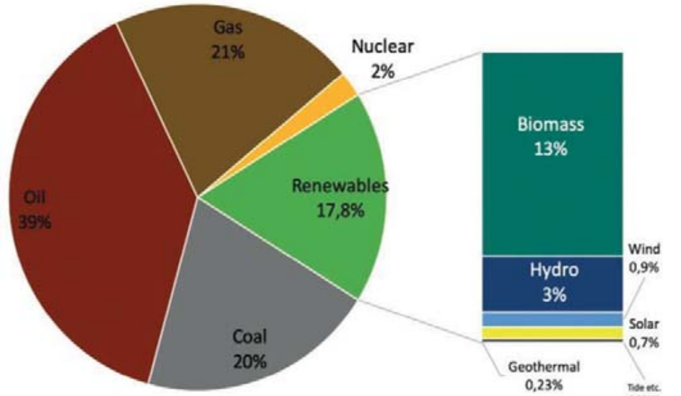

Fig. 1. World Energy Mix –(WBA, 2019)

Biomass is considered a renewable energy resource as green plants receive power from sunlight to initiate chemical reactions that store energy. The consequence of these chemical reactions results in the generation of numerous types of energy-rich resources, including plants and trees, forestry residues, fruits and vegetable residues, and animal wastes (Maletta & Díaz-Ambrona, 2020). Technologies used for biological conversion of organic matter are combustion, gasification, pyrolysis, anaerobic digestion, and microbial fermentation, and the biofuels obtained as a result are syngas, bio-diesel, charcoal, biogas, methanol, and ethanol bio-oil, (Gao et al., 2018). Biogas is one of the cleanest sources to generate electricity and for cooking and heating applications. The preferable technology used for biogas generation is anaerobic digestion (Omer, 2012).

The anaerobic digestion (A-D) process is an innovative technology for waste management that involves the conversion of organic wastes to biogas in the absence of oxygen. Organic content present in organic waste contains a large amount of lignocellulosic matter, which is hard to digest due to its complex structure. This leads to low substrate biodegradability and, ultimately, the longer time required for digestion (Li et al., 2018). Pretreatment of organic wastes has proven to be a feasible option to improve process performance by facilitating lignocellulosic breakdown, enhancing biogas yield, and reducing hydraulic retention time (HRT) (Carlsson, 2015). Pretreatment has several drawbacks, including a high energy cost and suppression of the methanogenic process owing to excessive salt production and an extreme pH value (Zhang et al., 2016).

Anaerobic decomposition driven by microbiology is a sophisticated, multi-stage set of biochemical events. Bacteria and Archaea are two species of microorganisms that primarily digest organic material, resulting in biogas production. Because these microorganisms are oxygen-intolerant, the process takes place in an anoxic environment. The final product contains approximately 60% methane, 30%–40% carbon dioxide, and trace quantities of gaseous water, hydrogen sulfide, and ammonia (Liu et al., 2011). Hydrolysis, acidogenesis, acetogenesis, and methanogenesis are the four steps of the A-D process, as shown in Fig. 2.

Hydrolysis is the hydro-driven lysis of bulk molecules into soluble monomers. Carbohydrates, polysaccharides, proteins, nucleic acids, lipids, and other insoluble high-molecular-mass components are broken down by enzymes. Acidogenesis includes acid-forming essential and heterotrophic anaerobes that convert the soluble end-products of hydrolysis. Acetic acid, butyric acid, propionic acid, ethanol, carbon dioxide, and hydrogen are some of the end products. Acetogenesis is the third phase, which consists of anaerobic oxidation processes. Acetate is created from the alcohol and acids released during acidogenesis. Methanogens mediate the creation of methane from acetate (acetoclastic methanogenesis), carbon dioxide, and hydrogen gas during this stage (hydrogenotrophic methanogenesis). Methane-forming bacteria do not use any of the chemicals from previous phases that have not been converted to acetate, thus they accumulate in the digester (Ganzoury & Allam, 2015).

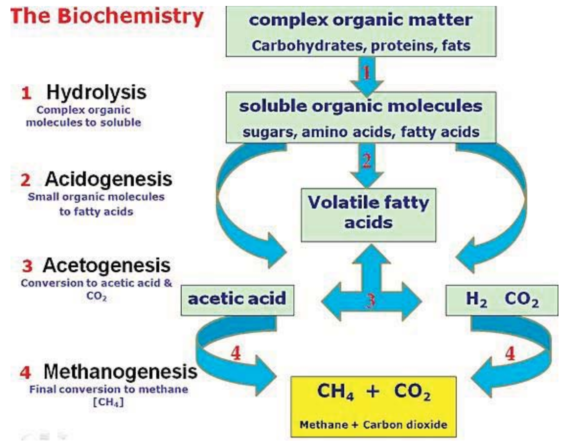

Fig. 2. Biochemical process flow diagram of Anaerobic digestion process – Adapted from Waste to Energy (Ogejo, 2013).

According to previous studies, adding additives to the A-D process speeds up starting, decreases contaminants, enhances biogas rate of production, lowers HRT, replenishes lacking nutrients, raises methane content, and improves reactor stability (Kim et al., 2017; Ward et al., 2008). Additives used for the A-D process cover a wide variety of materials and can be chemical, biological, organic, or inorganic, and can also have variability in their size (Abdelwahab et al., 2020). Nickel, Cobalt, Iron, Selenium, Sulfur, Carbon, etc. can be used as an additive for improvement of the A-D process (Ugwu & Enweremadu, 2020).

Iron is one of the cheapest ways to boost methane production from anaerobic digestion since industrial businesses create around 18,895 thousand tons of iron waste each year, with only 8000 thousand tons recycled. The remaining leftover iron scrap is disposed of in landfills (BP, 2019). If iron proves to be a critical answer for enhancing biogas yield, then biogas from the anaerobic digestion process will be a cost-effective solution, as we have approximately 10,000 tonnes of waste iron ready to be used as an additive in the A-D process.

Iron is a vital element for the methanogenesis process as it replicates the Deoxyribonucleic acid (DNA) structure and provides an environment for the survival of cells. Iron has exclusive ionization ability for Fe^{2+} and Fe^{3+} and it acts as both a donor and an acceptor of electrons. Iron-based additives have been reported to have unique advantages amongst all, like supplementation of nutrients, improvement of methane yield, improvement of substrate digestibility, control of hydrogen sulfide (H_2S) toxicity, etc. (Chen et al., 2018). Iron-based additives can also improve the hydrolysis enzyme activity by reducing oxidative-reductive potential and supporting the biological growth of enzymes (Feng et al., 2014). This article highlights all of the key advancements in biogas production that have been made by employing iron as an addition to the A-D process. The study also goes into different types of iron that may be used as an additive, substrates that can handle iron additives, optimum operating conditions with iron additives, digester types that can be employed, and the merits and demerits of employing iron as an additive.

2. BENEFITS OF ADDITIVE MATERIALS

Fig. 3 summarizes the effects of additives in the anaerobic digestion process. In commercial full-scale A-D plants, process stability is a critical concern, as inadequate process stability typically leads to uneven methane output. In addition, prolonged periods of instability might lead to process failure. As a result, several research projects have been undertaken to address the causes of A-D instability. Different forms of the inorganic component and packing materials (clay materials and zeolites) are often used to immobilize and retain microbial communities to manage and diminish A-D inhibition. Depending on particle size, porosity, surface area, absorbent capacity, and electric conductivity, different materials may influence the abundance and retention of diverse microbial communities at their surface. The A-D process's reaction kinetics are considerably improved by the support materials, allowing for higher chemical oxygen demand (COD) conversion rates even at a high organic loading rate (OLR) and low hydraulic retention time (HRT). By preserving the microbial flora, removing inhibitory elements, and serving as catalysts in metabolism, support materials play a critical role in manipulating the reaction kinetics of even resistant substrates and methane production (Arif et al., 2018).

This research is categorized into five areas, each of which covers a unique prospect of iron-based additions in anaerobic digestion. Before digging into the details of iron-based additions and their effects on the A-D process, an overview of the world population and its consequences, the demand for renewable energy, the importance of biofuels, and their environmental effects were investigated. The A-D process and its enhancement methods were also investigated. Finally, the significance of iron as an addition, as well as its influence on A-D process performance, are discussed.

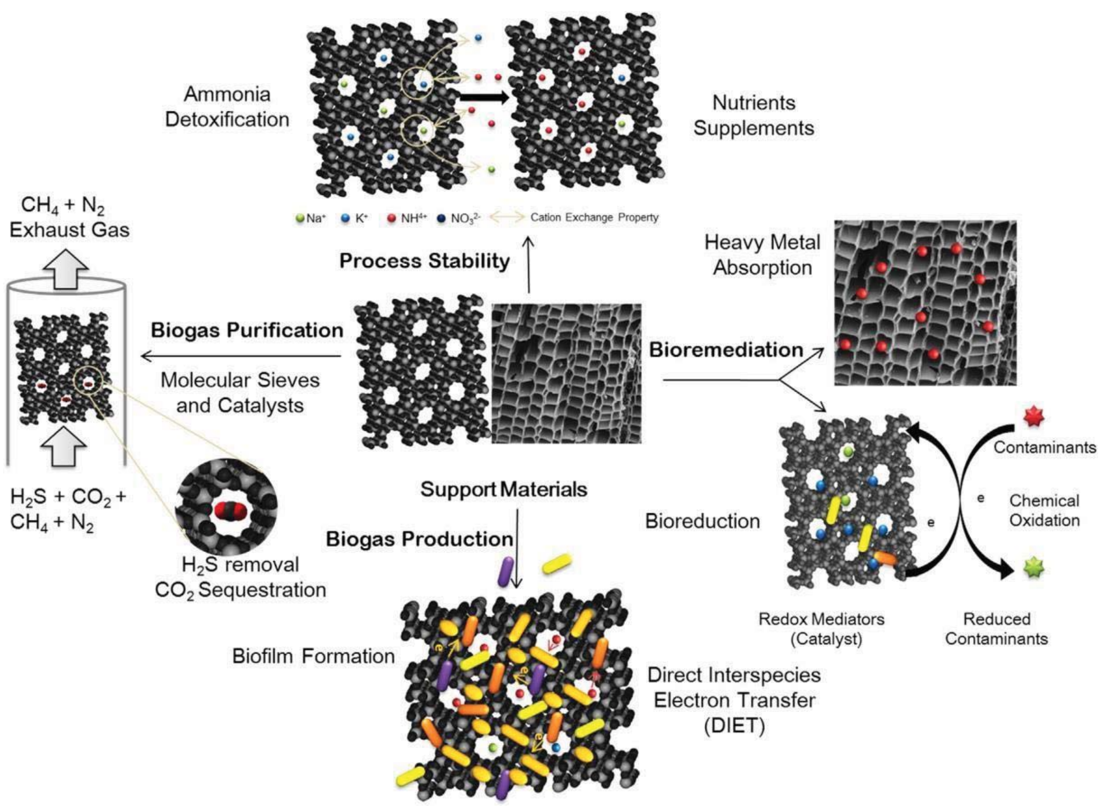

Fig. 3. Benefits of Additive materials in Anaerobic Digestion Process (Arif et al., 2018)

Fig. 4 depicts the approach and methods used in conducting this review. The global energy dilemma was initially discussed, followed by biomass energy prospects as a substitute for fossil fuels, biodegradation of biomasses challenges, and prospective intensification approaches for biogas production. On one hand, as shown in Table 1, reviews of the most often used iron-based additives for anaerobic digestion improvement were identified and classified into iron scraps and wastes, iron powders, iron nanoparticles, and the Fenton process. The impact of iron supplementation on biogas generation and methane content, solid reduction, pathogen reduction, and other topics were discussed. Finally, the development of iron precipitates and their fate following digestate disposal were discussed. It was suggested that future research into suitable additives for preventing iron complexes be conducted.

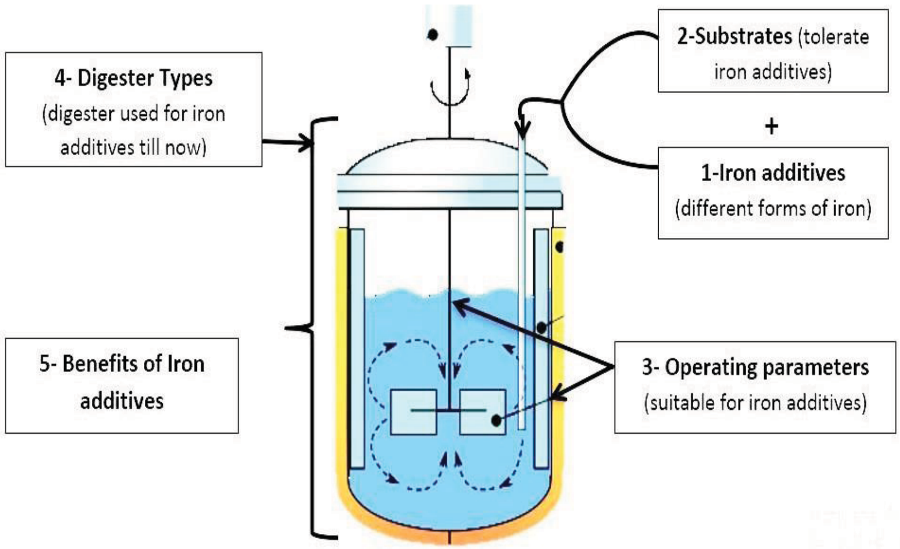

Fig. 4. Major Focus Areas of this Study

3. IRON AND IRON-BASED ADDITIVES

Because of its conductive qualities and inexpensive cost, iron has become one of the most popular additions for improving anaerobic digestion efficacy. The ability of iron to lower the oxidative–reductive potential (ORP) of anaerobic digestion media and thus provides a more favorable environment for anaerobic digestion; and (ii) its role as a cofactor of several key enzymatic activities, such as pyruvate–ferredoxin oxidoreductase, which contains Fe–S clusters and plays a key role in fermentation Anaerobic digestion has been reported to be stimulated by various iron types. On the one hand, Fe (III) reduction is a good way to oxidize organics directly into simple molecules. Nonetheless, because Fe (III) reduction is more thermodynamically advantageous than methanogenesis, it can limit the conversion of organics to methane. Due to its ability to operate as an electron donor, Fe0 (also known as zero-valent iron (ZVI)) has been discovered to speed up the hydrolysis and fermentation processes.

Previous studies show that different types of iron additives can be used in the A-D process for efficiency enhancement, nutrients supplement, and improved substrate digestibility. Iron-based additives can be prepared by adopting different methods before using them in the A-D process. Most commonly used iron-based additives are Waste iron scraps (Wiss), Iron Nanoparticles (Fe NPs), Iron chlorides ($FeCl_2$, $FeCl_3$), Zero Valent Scrap Iron (ZVSI), Iron oxides (Fe_2O_3, Fe_3O_4), Iron powder (Fe powder), Zero Valent Iron (ZVI), Iron sulfate ($FeSO_4$) and Nano Zero Valent Iron (NZVI). Table 1 depicts various types of iron-based additives reported until now and their preparation method

Fe_3O_4 additive to the A-D process reported having a significant effect on biogas yield followed by its nanoparticles (Fe_3O_4 NPs), Iron powder, and Iron nanoparticles. These additives also help to improve substrate digestibility by decomposition of lignocellulosic biomass into a simple structure (Zhao et al., 2017). It is also reported that Fe_3O_4 NPs produce higher biogas yield as compared to NZVI (Abdelsalam et al., 2017). The highest biogas yield ever reported from the A-D process is also achieved using Fe_3O_4 NPs additives (Casals et al., 2014). Studies show that $FeSO_4$, Fe(OH), Fe_2O_3, and $Fe(NO)_3$ additives have no significant effect to increase biogas yield and substrate digestibility (Ugwu et al., 2020).

4. SUBSTRATES

Various substrates can be used in the A-D process for biogas production. Lots of studies have been done that show that iron additives can increase the biogas yield and improve the process stability by utilizing different substrates. Ali et al. (2017) reported the use of Municipal Solid Waste (MSW) as a substrate for the A-D process with Fe_3O_4 nanoparticles additive. He suggested that a 75mg/L concentration of iron-based additive had a

72.09% improvement in methane generation. Abdelsalam et al. (2017) investigated the effect of iron nanoparticles and iron oxide nanoparticles on biogas and methane production using cattle dung slurry and found that Fe_3O_4 NPs having a 20mg/L concentration result in a 65.6% increase in biogas production.

Table 1. iron-based additives and their preparation method

Type	Color	Source	Size	Method of Preparation	Ref
WIS (Rusted)	Brown	The byproduct of manufacturing industries	0.5-8 mm	WIS has soaked in 0.1mol/L of NaOH solution for 1 day before use	(Hao et al., 2017)
ZVSI	Grey powder	Scrap from ironwork	2 mm width, 0.35 mm thickness	WIS is soaked in a 4% solution of $CuCl_2$ prepared in ethanol for 24 hours and wash with distilled water	(Wang et al., 2018)
Fe powder	Ash Grey	Commercially available	0.2 mm in diameter	commercially prepared by industries	(Suanon et al., 2017)
Fe_2O_3	Red powder	the by-product of bauxite ore from refining	50 to 300 mm in diameter	Method not defined	(Ye et al., 2018)
Fe_3O_4	Black powder	Commercially available	0.2 mm in diameter	commercially prepared by industries	(Chen et al., 2018)
NZVI	Black powder	Synthesized using Iron and $NaHB_4$	0.1 to 25 nm	$NaHB_4$ and $FeSO_4$ via liquid-phase reduction method in anaerobic conditions	(Suanon et al., 2017)
Fe_2O_3 NPs	Dark Red	Granular $FeCl_3.6H_2O$ and 25% ammonia solution	0.1 to 100 nm	Co-precipitation method	(Noonari et al., 2019)
Fe_3O_4 NPs	Black powder	$FeCl_2.4H_2O$ and $FeCl_3.6H_2O$	10-35nm	Hydrothermal Method	(Ali et al., 2017)

Wei et al. (2018) reported the use of ZVI to enhance the methane generation using wastewater sludge as a substrate for the A-D process. He found that there was a 26.9% relative increase in methane yield using ZVI as an additive because it improved the hydrolysis rate of reaction. Noonari et al. (2019) tested the use of canola straws and banana plant waste as Co-Digestion with buffalo dung as inoculum with Fe_3O_4 nanoparticles additive and found that methane generation from canola straw and buffalo dung was increased by 39.1% with 0.81 mg dosage of iron-based additive.

Farghali et al. (2020) reported the use of waste iron powder and iron oxide nanoparticles with cattle manure substrate (F/I ratio 2:1) and found that methane yield from cattle manure increased by 57% and the H_2S production rate also reduced by 77.2% using waste iron powder additive with a concentration of 1000 mg/L. Cheng et al. (2020) investigated the effect of rusted iron shavings on a mixture of food wastes and municipal sludge and noted that rusted iron shavings increase the removal rate of volatile suspended solids by 18% and methane yield by 64.4% compared with the case in which no iron shavings added. It also produces a reductive environment which leads to an increase in methane yield.

Previous studies have proved that Fe_3O_4 and its nanoparticles additives have a significant effect on the enhancement of methane and biogas generation using various substrates like cattle dung, municipal solid waste, wastewater sludge, canola straws, and banana plant waste with buffalo dung inoculum, food waste and municipal sludge waste are used in different anaerobic digesters and varying operating parameters.

5. OPERATING PARAMETERS & DIGESTER TYPE

Previous studies have proven to be very effective in improving methane generation, process stability, and digestion rate. All these improvements are subjected to the optimum selection of the anaerobic digester and operating parameters of the A-D Process. The batch reactor is the preferable mode for the anaerobic digestion process. Table 2 presents suitable operating parameters for the A-D process and their effects on biogas and methane yield for all the previous studies mentioned above.

6. BENEFITS OF IRON BASE ADDITIVES

Iron can act as an electron acceptor as well as an electron donor in the redox reaction of the A-D process that's why iron-based additives can be used for the improvement of methane generation. Iron-based additives have lots of advantages like improvement of methane yield, control of H2S inhibition, supplementation of nutrients, and much more. This section highlights the impact of iron-based additives on Volatile Fatty Acids (VFAs), reduction of Volatile Suspended Solids (VSS), and biogas content.

Table 2. Iron-based additives, operating parameters, digester type, and impact on biogas and methane production

Additive	Substrate	Size	Digester type and Temp.	HRT (Days)	RPM	pH	Dosage	Effects	Ref
Fe_3O_4 NPs	MSW	10-35 nm	Batch Anaerobic Digester 37±0.5°C	60	--	6.74	50mg/L	65.4% increase in methane generation	(Ali et al., 2017)
						6.99	75mg/L	72.1% increase in methane generation	
						7.01	100mg/L	44.2% increase in methane generation	
						7.11	125mg/L	42.5% increase in methane generation	
Fe NPs	Cattle Dung Slurry	9±0.3 nm	2-L wide neck culture vessel flask (batch mode) 37±0.3°C	50	20 for 1min per hour	6.13 (manure) and 5.85 (slurry)	5mg/L	43.7% increase in biogas generation	(Abdelsalam et al., 2017)
							10mg/L	45.1% increase in biogas generation	
							20mg/L	45.4% increase in biogas generation	
Fe_3O_4 NPs		7±0.3 nm					5mg/L	63.1% increase in biogas generation	
							10mg/L	64.5% increase in biogas generation	
							20mg/L	65.6% increase in biogas generation	
ZVI	Wastewater Sludge	0.2 mm	Batch Anaerobic Digester 35±1 °C	50	--	5.9 (substrate) 7.4 (inoculum)	1g/L	12.4% increase in methane production	(Wei et al., 2018)
							4g/L	26.9% increase in methane production	
							20g/L	21.7 % increase in methane production	
Fe_3O_4 NPs	Banana Plant Waste with Buffalo Dung	1μm	Continuous stirred tank reactor 37±1 °C	40	70 for 1min after every 30 min	6.9	0.4mg/L	26.1% increase in methane production	(Noonari et al., 2019)
						7.1	0.5mg/L	49.3% increase in methane production	

Additive	Substrate	Size	Digester type and Temp.	HRT (Days)	RPM	pH	Dosage	Effects	Ref
						7.2	0.82mg/L	33.9% increase in methane production	
						7.5	1.22mg/L	20.1% increase in methane production	
						7.6	1.63mg/L	17.7% increase in methane production	
Waste iron Powder	Dairy Manure	20 µm	Batch Anaerobic Bio-Digester with Thermo-cooled bath 38 °C	30	--	7.2-7.4	100mg/L	37% increase in methane yield	(Farghali et al., 2020)
						7.2-7.5	500mg/L	39.4% increase in methane yield	
						7.2-7.5	1000mg/L	56.9% increase in methane yield	
Iron oxide NPs		20–40 nm				7.2-7.4	100mg/L	19.7% increase in methane yield	
						7.3-7.5	500mg/L	18.1% increase in methane yield	
						7.3-7.5	1000mg/L	21.1% increase in methane yield	
Rusted Iron Shavings	Mixed Food Wastes & Municipal Sludge	10mm× 2mm× 0.5 mm	2.5 L lab-scale Anaerobic Digester 35±1 °C	36	A sample mixed by 6500 rpm for 15 min	5.6-7	25g/L	64.4% increase in methane production	(Cheng et al., 2020)
ZVI	Dewatered sludge	50 nm	3-L Continuous stirred tank reactor 35 °C	100	Sample agitated by 5000 rpm for 10 min	6.8-7.6	0.5g/L	18.7% increase in biogas yield	(Xiang et al., 2019))
							1g/L	21.7% increase in biogas yield	
							2g/L	16.8% increase in biogas yield	
							4g/L	14.3% increase in biogas yield	

6.1 Methane Content and Biogas Output

Iron additives can promote the total methane generation because they enhance the production of acetate which is an essential input to producing methane through the methanogenesis process. Iron-based additives can also act as a donor of electrons directly, which causes the reduction of carbon dioxide into methane through hydrogenotrophic methanogenesis triggering the enhancement of methane generation (Abdelsalam et al., 2017). Amen and Eljamal (2017) examined the effects of a pure nZVI, nZVI coated (ICZ), and nZVI mixed with zeolite (IMZ) augmented anaerobic response to a control bioreaction. The addition of 1000 mg/L iron-based nanoparticles to ICZ helped achieve the largest cumulative methane volume. The inclusion of nZVI and IMZ, on the other hand, resulted in upward stimulation of the greatest methane level of 88% and 74%, respectively. Similarly, the excess hydrogen released by nZVI (30 mol/L) oxidation enhanced hydrogenotrophic methanogenesis, resulting in a 30% increase in biogas output (He et al., 2017). The addition of a larger dose of nZVI/CuO (>1500 mg/L) on the other hand, decreased biogas generation (Amen et al., 2018).

Previous studies show that iron-based additives have a very significant impact on enhanced biogas production and the improvement of methane content. Ali et al. (2017) reported a 72.1%

escalation in methane content, Abdelsalam et al. (2017) reported a 65.6% increase in biogas production, Farghali et al. (2020) reported a 56.9% rise in methane generation and (Cheng et al., 2020) reported 64.4% increase in methane generation using various iron base additives.

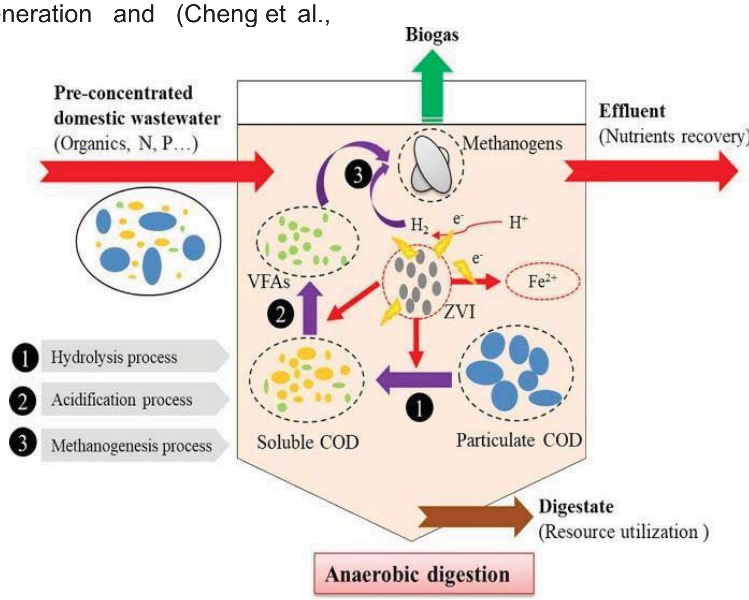

Fig. 5. ZVI effects on three anaerobic digestion processes- Adapted from Feng et al. (2014)

6.2 Avoiding VFAs

Excess VFAs are produced when substrates are hydrolyzed; this may lead to a lowering of pH and finally inhibition of the methanogens process. This problem can be solved using iron-based additives in the A-D process (Zhang et al., 2016). Feng et al. (2014) stated the reduction in the quantity of VFAs from 530 mg-COD/L to 19.8 mg-COD/L by using ZVI in the A-D process. Similarly, Hao et al. (2017) noted a sharp drop in the quantity of VFAs by using waste iron scrap additives. He reported a decline of 700 mg-COD/L. Intermediate products such as volatile fatty acids (VFAs) are critical in the biogas production process during anaerobic digestion. They are carboxylic short-chain fatty acids (C_2-C_6) generated by syntrophic bacteria following biomass hydrolysis. In an anaerobic digestion process, several parameters like pH and the inclusion of iron-based supplements might impact VFAs. At a pH below 2, propionic acid and butyric acid, the two primary VFA products in the acidification step, decompose exclusively into acetate. Propionate accumulation and disruption of pH balance between acidogenesis and methanogenesis are caused by the high rate of propionate production and low decomposition rate (much lower than other VFAs), but according to Zhang et al. (2016), the addition of trace iron could stabilize anaerobic digestion processes. Fig. 5 depicts the effects of ZVI on major parameters of the A-D process

6.3 VSS Reduction

Substrate degradation by microorganisms results in a decrease in the amount of total VSS. This is also known as Chemical Oxygen Demand (COD) (Ugwu & Enweremadu, 2020). In the studies of Hao et al. (2017) it was examined that the addition of iron scrap (waste) can improve the VSS reduction rate by 14%. Zhang et al. (2016) stated the use of clean iron scrap in the A-D process resulted in a maximum VSS rate of reduction of 49%. However, in the Fenton peroxidation process, the usage of H_2O_2 catalyzed by iron salts dissolved sludges and broke down cellular elements, resulting in higher soluble COD (sCOD) concentrations (Salihu and Alam 2016). Throughout the digestion phase, Uman et al. (2018) showed a rather low sCOD content of around 250 mg/L. Maamir et al. (2017) found that when the concentration of H2O2 grew from 125 to 1000 millimolar, the COD of Fenton-treated substrate increased from 1133 to 5594 mg/O_2 (56%) when compared to the control COD value of 1123 mgO_2/L until optimal working conditions were reached. The ideal Fenton procedure processed olive mill solid waste obtained an 82 percent sCOD rise under these working conditions (pH 3, 120 minutes, H_2O_2/[Fe^{2+}] = 1000 and [Fe^{2+}] = 1.5 mM) (Rezaei & Vione, 2018).

7. CONCLUSIONS

The addition of iron-based additives to an anaerobic digester can have significant effects like enhancement of biogas generation, increased VSS rate of reduction, improvement of process stability, and reduction of VFAs. A detailed literature analysis has been conducted for a better understanding of recent advancements in this field. Previous studies related to iron-based additives in the A-D process have been studied and are presented in this study. This study has discussed the following topics in detail:

- types of iron-based additives, their source, preparation method, color, and size.
- Substrates reported in previous studies to check the effect of iron-based additives
- Optimal operating parameters using iron-based additives
- preferred type and mode of anaerobic digester.
- Benefits of using iron-based additives include methane content, VFA limitation, and VSS reduction rate.

This study examined all these issues and concluded that Fe_3O_4 and Fe_3O_4 NPs additives had a considerable effect on biogas yield augmentation when compared to other iron-based additives. Most studies choose a mesophilic temperature range for the A-D process, mixing of the substrate at varying rpm to homogenize the substrate and inoculum, batch-mode anaerobic digesters for research reasons, and HRT ranging from 40 to 100 days depending on the nature of the study. Finally, it has been established that iron-based additions considerably improve the rate of biogas generation and increase the rate of VSS reduction. Since no essential research work has been done in these areas, it is recommended that future researchers investigate the effects of variations in organic load rating (OLR) and thermophilic operating temperature on the anaerobic digestion process utilizing iron-based additions.

STATEMENT AND DECLARATION

Acknowledgment: The author thanks the U.S. Pakistan Center for Advanced Studies in Energy (USPCAS-E), National University of Science and Technology (NUST) Islamabad to carry out this research work.

Funding: No funding source Availability of data and materials: The required supplementary data is available as per requirement.

Ethics: The author declares that he has no competing financial and personal interests

REFERENCES

Abdelsalam, E., Samer, M., Attia, Y. A., Abdel-Hadi, M. A., Hassan, H. E., & Badr, Y. (2017). Influence of zero valent iron nanoparticles and magnetic iron oxide nanoparticles on biogas and methane production from anaerobic digestion of manure. Energy, 120, 842-853. https://doi.org/https://doi.org/10.1016/j.energy.2016.11.137

Abdelwahab, T. A. M., Mohanty, M. K., Sahoo, P. K., & Behera, D. (2020). Application of nanoparticles for biogas production: Current status and perspectives. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 1-13. https://doi.org/10.1080/15567036.2020.1767730

Ali, A., Mahar, R. B., Soomro, R. A., & Sherazi, S. T. H. (2017). Fe3O4 nanoparticles facilitated anaerobic digestion of organic fraction of municipal solid waste for enhancement of methane production. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 39(16), 1815-1822. https://doi.org/10.1080/15567036.2017.1384866

Amen, T. W. M., & Eljamal, O. (2017). Biochemical methane potential enhancement of domestic sludge digestion by adding pristine iron nanoparticles and iron nanoparticles coated zeolite compositions. Journal of Environmental Chemical Engineering, 5(5), 5002-5013.

Amen, T. W. M., Eljamal, O., Khalil, A. M. E., Sugihara, Y., & Matsunaga, N. (2018). Methane yield enhancement by the addition of new novel of iron and copper-iron bimetallic nanoparticles. Chemical Engineering and Processing - Process Intensification, 130(8), 253-261.

Arif, S., Liaquat, R., & Adil, M. (2018). Applications of materials as additives in anaerobic digestion technology. Renewable and Sustainable Energy Reviews, 97, 354-366. https://doi.org/https://doi.org/10.1016/j.rser.2018.08.039

Basu, P. (2018). Chapter 11 - Biomass Combustion and Cofiring. In P. Basu & P. B. T. B. G. Torrefaction (Eds.), (pp. 393-413). Academic Press. https://doi.org/https://doi.org/10.1016/B978-0-12-812992-0.00011-X

BP. (2019). BP Statistical Review of World Energy.

Carlsson, M. (2015). When and why is pre-treatment of substrates for anaerobic digestion useful?

Casals, E., Barrena, R., Garcia, A., González, E., Delgado, L., Busquets-Fité, M., Font Segura, X., Arbiol, J., Glatzel, P., Kvashnina, K., Sánchez, A., & Puntes, V. (2014). Programmed Iron Oxide Nanoparticles Disintegration in Anaerobic Digesters Boosts Biogas Production. Small (Weinheim an der Bergstrasse, Germany), 10. https://doi.org/10.1002/smll.201303703

Chen, R., Konishi, Y., & Nomura, T. (2018). Enhancement of methane production by Methanosarcina barkeri using Fe3O4 nanoparticles as iron sustained release agent. Advanced Powder Technology, 29(10), 2429-2433. https://doi.org/https://doi.org/10.1016/j.apt.2018.06.022

Cheng, J., Zhu, C., Zhu, J., Jing, X., Kong, F., & Zhang, C. (2020). Effects of waste rusted iron shavings on enhancing anaerobic digestion of food wastes and municipal sludge. Journal of Cleaner Production, 242, 118195-118195. https://doi.org/https://doi.org/10.1016/j.jclepro.2019.118195

Farghali, M., Andriamanohiarisoamanana, F. J., Ahmed, M. M., Kotb, S., Yamamoto, Y., Iwasaki, M., Yamashiro, T., & Umetsu, K. (2020).

Prospects for biogas production and H2S control from the anaerobic digestion of cattle manure: The influence of microscale waste iron powder and iron oxide nanoparticles. Waste Management, 101, 141-149. https://doi.org/https://doi.org/10.1016/j.wasman.2019.10.003

Feng, Y., Zhang, Y., Quan, X., & Chen, S. (2014). Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron. Water Research, 52, 242-250. https://doi.org/https://doi.org/10.1016/j.watres.2013.10.072

Ganzoury, M. A., & Allam, N. K. (2015). Impact of nanotechnology on biogas production: A mini-review. Renewable and Sustainable Energy Reviews, 50, 1392-1404. https://doi.org/https://doi.org/10.1016/j.rser.2015.05.073

Gao, N., Zhang, L., & Wu, C. (2018). Biomass and Wastes for Bioenergy: Thermochemical Conversion and Biotechnologies. BioMed Research International, 2018, 9638380-9638380. https://doi.org/10.1155/2018/9638380

Hao, X., Wei, J., van Loosdrecht, M. C. M., & Cao, D. (2017). Analysing the mechanisms of sludge digestion enhanced by iron. Water Research, 117, 58-67. https://doi.org/https://doi.org/10.1016/j.watres.2017.03.048

He, C., S, P. P., He, H. Y., Yang, L. L., Li, Y., Lin, Y. M., & H.-Q, Y. (2017). Impact of zero-valent iron nanoparticles on the activity of anaerobic granular sludge: From macroscopic to microcosmic investigation. Water Research3, 127, 32-40.

Kim, M., Li, D., Choi, O., Sang, B.-I., Chiang, P. C., & Kim, H. (2017). Effects of supplement additives on anaerobic biogas production. Korean Journal of Chemical Engineering, 34(10), 2678-2685. https://doi.org/10.1007/s11814-017-0175-1

Li, W., Khalid, H., Zhu, Z., Zhang, R., Liu, G., Chen, C., & Thorin, E. (2018). Methane production through anaerobic digestion: Participation and digestion characteristics of cellulose, hemicellulose and lignin. Applied Energy, 226, 1219-1228. https://doi.org/https://doi.org/10.1016/j.apenergy.2018.05.055

Liu, X., Yan, Z., & Yue, Z. B. (2011). 3.10 - Biogas. In M. B. T. C. B. Moo-Young (Ed.), (pp. 99-114). Academic Press. https://doi.org/https://doi.org/10.1016/B978-0-08-088504-9.00165-3

Maletta, E., & Díaz-Ambrona, C. H. (2020). Lignocellulosic Crops as Sustainable Raw Materials for Bioenergy. In (pp. 489-514).

Noonari, A. A., Mahar, R. B., Sahito, A. R., & Brohi, K. M. (2019). Anaerobic co-digestion of canola straw and banana plant wastes with buffalo dung: Effect of Fe3O4 nanoparticles on methane yield. Renewable Energy, 133, 1046-1054. https://doi.org/https://doi.org/10.1016/j.renene.2018.10.113

Ogejo, J. A. (2013). Waste to Energy: Biogas and Anaerobic Digestion. In (pp. 1-1).

Omer, A. (2012). An overview of Biomass and Biogas for energy generation: Recent development and perspectives. Cellulose Chemistry and Technology, 46, 477-492. https://doi.org/10.31248/JBBD2016.010

Rezaei, F., & Vione, D. (2018). Effect of pH on Zero Valent Iron Performance in Heterogeneous Fenton and Fenton-Like Processes: A Review. In (Vol. 23).

Suanon, F., Sun, Q., Li, M., Cai, X., Zhang, Y., Yan, Y., & Yu, C.-P. (2017). Application of nanoscale zero valent iron and iron powder during sludge anaerobic digestion: Impact on methane yield and pharmaceutical and personal care products degradation. Journal of Hazardous Materials, 321, 47-53. https://doi.org/https://doi.org/10.1016/j.jhazmat.2016.08.076

Ugwu, S. N., Biscoff, R. K., & Enweremadu, C. C. (2020). A meta-analysis of iron-based additives on enhancements of biogas yields during anaerobic digestion of organic wastes. Journal of Cleaner Production, 269, 122449-122449. https://doi.org/https://doi.org/10.1016/j.jclepro.2020.122449

Ugwu, S. N., & Enweremadu, C. C. (2020). Enhancement of biogas production process from biomass wastes using iron-based additives: types, impacts, and implications. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 1-23. https://doi.org/10.1080/15567036.2020.1788675

Wang, Y., Wang, D., & Fang, H. (2018). Comparison of enhancement of anaerobic digestion of waste activated sludge through adding nano-zero valent iron and zero valent iron. RSC Advances, 8(48), 27181-27190. https://doi.org/10.1039/C8RA05369C

Ward, A. J., Hobbs, P. J., Holliman, P. J., & Jones, D. L. (2008). Optimisation of the anaerobic digestion of agricultural resources. Bioresource Technology, 99(17), 7928-7940. https://doi.org/https://doi.org/10.1016/j.biortech.2008.02.044

WBA. (2019). Global bioenergy statistics 2019 summary report.

Wei, W., Cai, Z., Fu, J., Xie, G.-J., Li, A., Zhou, X., Ni, B.-J., Wang, D., & Wang, Q. (2018). Zero valent iron enhances methane production from primary sludge in anaerobic digestion. Chemical Engineering Journal, 351, 1159-1165. https://doi.org/https://doi.org/10.1016/j.cej.2018.06.160

Xiang, Y., Yang, Z., Zhang, Y., Xu, R., Zheng, Y., Hu, J., Li, X., Jia, M., Xiong, W., & Cao, J. (2019). Influence of nanoscale zero-valent iron and magnetite nanoparticles on anaerobic digestion performance and macrolide, aminoglycoside, β-lactam resistance genes reduction. Bioresource Technology, 294, 122139-122139. https://doi.org/https://doi.org/10.1016/j.biortech.2019.122139

Ye, J., Hu, A., Ren, G., Chen, M., Tang, J., Zhang, P., Zhou, S., & He, Z. (2018). Enhancing sludge methanogenesis with improved redox activity of extracellular polymeric substances by hematite in red mud. Water Research, 134, 54-62. https://doi.org/https://doi.org/10.1016/j.watres.2018.01.062

Zhang, Q., Hu, J., & Lee, D.-J. (2016). Biogas from anaerobic digestion processes: Research updates. Renewable Energy, 98, 108-119. https://doi.org/https://doi.org/10.1016/j.renene.2016.02.029

Zhao, Z., Li, Y., Quan, X., & Zhang, Y. (2017). Towards engineering application: Potential mechanism for enhancing anaerobic digestion of complex organic waste with different types of conductive materials. Water Research, 115, 266-277. https://doi.org/https://doi.org/10.1016/j.watres.2017.02.067