



Applications of materials as additives in anaerobic digestion technology

Sania Arif^a, Rabia Liaquat^{a,*}, Manal Adil^b

^a US-Pakistan Center for Advanced Studies in Energy, National University of Science and Technology (NUST), Islamabad, Pakistan

^b Department of Industrial Biotechnology, Atta-ur-Rahman School of Applied Biosciences, National University of Science and Technology (NUST), Islamabad, Pakistan



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ABSTRACT

Production of renewable energy is one of the prime focuses of modern research and industry. Anaerobic digestion (AD), as a mean for biogas production, is hence the fastest growing segment within the waste management industry. AD is a naturally occurring series of microbial processes, encompassing the breakdown of organic materials, ensuring energy recovery with the reduction of greenhouse emissions and facilitating a sustainable development of energy supply from waste. Nevertheless, the efficacy of AD may drastically reduce due to problems such as substrate diversity, ammonia inhibition, microbial flora washout, low methane yield, feedstock purity, etc. In this review, we cater to these problems that lead towards process instability and inefficiency through the applications of various synthetic, biological and nanomaterials. Different support materials tend to enhance biogas production by facilitating the microbial growth, via electron transfer, avoiding toxic concentrations of ammonia, biofilm/anaerobic granular sludge formation, nutrient supplements, H₂S removal, CO₂ sequestration and bio-augmentation. This review focuses on the unique features of support materials and their role in microbial and substrate dynamics as the reinforcement strategies in AD biogas production.

1. Introduction

Global challenges of clean energy supply and climate preservation has led researchers to develop alternate energy sources. Emission of greenhouse gases from energy generation is heating up the environment, resulting in climate changes, an emerging challenge that is severely affecting the environment, human, and wildlife. In contrast to 13% renewable energy consumption, about 81% of energy demand is fulfilled by fossil fuels [1]. Biomass and organic wastes are preferable sources of renewable energy over fossil fuels in terms of managing the waste and reducing the environmental impacts. As direct burning of biomass and landfilling leads to uncontrolled CO₂ and methane emissions in environment which ultimately brings climate change. Moreover, the total generated solid waste and organic waste increases at an even higher rate, posing deadly environmental impacts upon improper treatment. Organic solid waste has vegetable and food waste 52%, straw and wood 14%, clothes 3.1%, paper 3.5% and garbage, further impressing the need for efficient waste reduction and energy recovery [2]. One of the most cost-effective and advanced organic waste to energy conversion technologies is Anaerobic Digestion (AD) because of simultaneous energy and nutrient recovery. AD is a globally emerging

waste management strategy as it can also be integrated with other renewable technologies and synthesis of value-added compounds through mixed culture biotechnological approaches is promising [3].

With the caloric value of 21–25 MJ/m³, biogas is an excellent replacement for natural gas and fossil fuels and can lower more than 80% green gas emissions to the environment. In addition to this renewable energy source, the other advantages of AD that make it a preferred organic waste management technology are comparatively reduced sludge formation, pathogens, odours, energy input and nutrient demands. Historically, the process of anaerobic digestion is amongst the oldest utilized techniques of humans. The process occurs naturally within anthropogenic and natural sources. The natural sources composed of animal intestines, aquatic sediments and wetlands account for 70% release of methane in the atmosphere. Whereas the anthropogenic sources namely rice fields and landfills account for 30%. AD through biological activity, also known as bio-methanogenesis, results in 80% of the flux of atmospheric methane and drives the carbon cycle in the ecosystems [4].

Microbiologically driven anaerobic decomposition is a complex, multi-stage series of biochemical processes. Majorly, two groups of microorganisms; Bacteria and Archaea metabolize organic material,

Abbreviations: A_{AO}, Anaerobic ammonium oxidation; AD, Anaerobic digestion; B_{OD}, Biological oxygen demand; C_{FT}, Carbon fiber textiles; C_{OD}, Chemical oxygen demand; D_{IET}, Direct interspecies electron transfer; H_{RT}, Hydraulic retention time; O_{LR}, Organic loading rate; T_{AN}, total ammonia nitrogen; T_{KN}, Total Kjeldahl nitrogen; T_S, Total solids; U_{SAB}, Up flow anaerobic sludge blanket; V_{FAS}, Volatile fatty acids; V_S, Volatile solids

* Corresponding author.

E-mail addresses: rabia@uspcase.nust.edu.pk, rabialiaquat_mib@yahoo.com (R. Liaquat).

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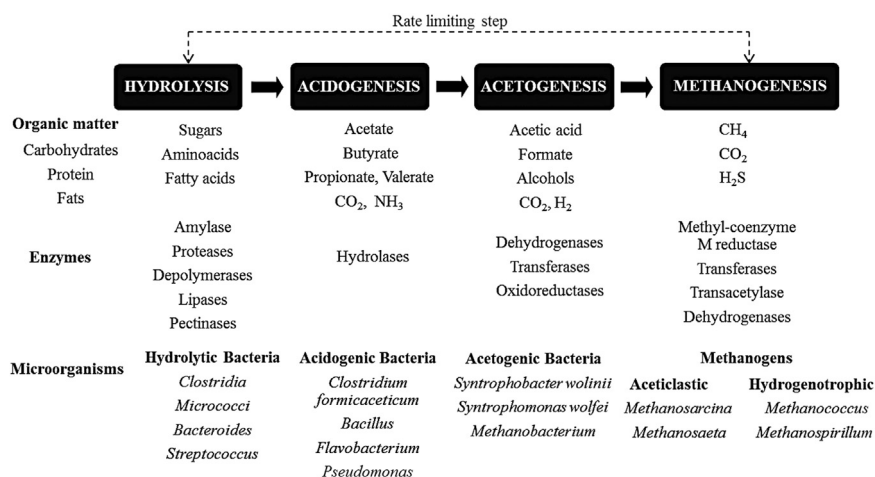


Fig. 1. Biochemical series of AD. The bioconversion of organic waste to biogas takes place via the action of enzymes produced by anaerobic microbes in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis.

resulting in biogas production. The process occurs in an anoxic environment as these microbes are intolerant to oxygen. The end product comprises about 60% methane and 30–40% carbon dioxide and trace elements of gaseous water, hydrogen sulfide, and ammonia [5]. The AD process consists of four phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis, as summarized in Fig. 1.

Phase 1- Hydrolysis: The process can be simply described as hydro-driven lysis of large compounds into soluble monomers. It involves an enzyme-mediated breakdown of insoluble components of high molecular mass like carbohydrates, polysaccharides, proteins, nucleic acids, fats etc. Transformation results in small soluble organic components like monosaccharides, sugars soluble in amino acids, glycerol and carboxylic acids (long chain). The enzymes (cellulases, proteases and lipases) released by the hydrolytic or facultative anaerobes (*Clostridia*, *Bacteroides* and *Streptococci*) carry out the process.

Phase 2- Acidogenesis: The soluble end-products from the hydrolysis are transformed by acid-forming obligatory and facultative anaerobes. The end products include acetic acid, butyric acid, propionic acid, ethanol, carbon dioxide and hydrogen.

Phase 3- Acetogenesis: The stage comprises of anaerobic oxidation reactions. The alcohol and acids produced during acidogenesis are transformed into acetate. The pre-requisite for this step is a symbiotic relationship between microorganisms carrying out anaerobic oxidation and methane forming species. A hydrogen transfer between these two species facilitates the process. Methanogenic organisms discovered till now belong to Archaea, while acidogens, and acetogens are mainly bacteria.

Phase 4- Methanogenesis: In this stage, the methanogens mediate production of methane from acetate (Aceticlastic methanogenesis), carbon dioxide and hydrogen gas (hydrogenotrophic methanogenesis). Aceticlastic methanogens belong to the two specific genera: *Methanosaeta* or *Methanosarcina* and contribute to 70% of the methane production in AD while rest of methane, 30% is produced by the hydrogenotrophic methanogens. This is a critical stage as it requires stringent anaerobic conditions and is the slowest biochemical reaction of the AD process. All the compounds from preceding stages that have not been transformed into acetate are not utilized by methane-forming bacteria and accumulate in the digester [6].

Rate limiting step depends on the accessibility and kinetics of biochemical conversions by microbial consortium. Hydrolysis is rate limiting step for slowly degrading and particulate materials, for instance in solid digesters when there are no inhibitory factors. Under the conditions of stress, the presence of inhibitors or rapidly degradable primary substrate, the rate limiting step is usually aceticlastic methanogenesis. Aceticlastic methanogenesis controls treatment systems where the

reactors are operated at high organic loading rates (O_{LRs}). The first condition leads to decreased performance as the non-degraded substrate washes out while the outcome of the second context is increased effluent organic-acid concentrations [7].

AD is a delicate balance of complex microbial communities and the physiological parameters of the bioreactor, and it can be easily failed by fluctuation in the pH, temperature, concentration, and composition of the sludge, modes of operation, liquid dynamics, ionic strength and tank configurations [8]. Moreover, different organic wastes may need special treatments because of toxic and recalcitrant components that may have detrimental effects at the performance of AD. Thanh et al. [9] reported that AD of raw natural rubber processing wastewater is difficult to achieve because of high residual organic matter, ammonia (for natural latex preservation), and latex suspended solids. Jiménez et al. [10] reported that phenolic compounds, present in the molasses, hinders with the activity of methanogens, removal of organic contents and thus increasing the hydraulic retention time (H_{RT}). The high salinity of distillery slops or vinasses may cause osmotic pressure problems for the microbes. Substrates with high C_{OD} , B_{OD} , T_{KN} and salt contents may often result in process failure [11], especially in the reactors with high H_{RTs} where the washout of biomass is inevitable (Table 1). To solve the problem, active retention of the delicate methanogenic community using granular sludge or biofilm formation on membrane separation systems has been practiced often [12]. However, membranes are very costly and vulnerable to fouling [13] while granular sludge (in an up-flow anaerobic sludge blanket U_{SAB} system) takes time to build up and is prone to frequent washouts [11]. Consequently, an alternate solution is required to fix the biomass and achieve high loading densities with low H_{RTs} , irrespective of the reactor and substrates types.

Support materials provide the low-cost alternative approach to ensure stable methanogenesis in many bioreactors such as fixed bed reactors [20], through selective enrichment of the methanogens as biofilm, during AD of complex waste streams [21], even with increased C_{OD} and V_{FAS} contents [22]. They actively retain the microbial flora and protect it from drastic changes in pH and chemical loads. In addition to the microbial retention [23], the materials are major additives in the biodigester due to their ion exchange property for ammonia removal [24], CO_2 sequestration [25], effects on microbial dynamics [26], biogas purification [27], heavy metal adsorption [28] and nutrient supplements [29] (Fig. 2). Nevertheless, synthetic, biological and nanomaterials have found most suitable applications in the AD process as their presence significantly influence the process stability, microbial growth and productivity of the reactors, making it possible to significantly enhance the efficacy of waste to bioenergy conversion.

Although materials have been used in the biogas digesters as

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