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Reappraisal of chemical interference in anaerobic digestion processes

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ABSTRACT

Anaerobic digestion is a process, which leads to energy generation as well as pollution minimization. Both industrial and agricultural wastes can be digested anaerobically due to the presence of biodegradable materials. However, the presence of potential chemical inhibitors has been identified as one of the primary factors contributing to process instability and reactor failure. Over the last decades, research has highlighted various inhibitory substances and their elucidated role and underlying inhibitory mechanism interfering with anaerobic processes. The present review summarizes the potential impact of different organic and inorganic toxicants on anaerobic digestion based on a survey of the literature. A better understanding of potential toxicants and their effects will lead to improvements in anaerobic digestion efficiency and process stability.

1. Introduction

Anaerobic digestion comprises of the breaking down and stabilization of organic materials under anoxic conditions by microbes leading to biogas and microbial biomass formation [1]. It offers a technique of reducing pollution from agricultural and industrial sectors while compensating the usage of fossil fuels. In addition, it provides other substantial benefits such as lowering of energy requirements and less sludge production compared with traditional aerobic treatments [2]. This microbiological process has been widely used for the treatment of municipal sludge and organic industrial wastes including those from fruit and vegetable processing and agriculture [3,4].

1.1. Biogas generation process

Anaerobic digestion, a multistep process, involves a variety of microorganisms such as the hydrolyzing and acid forming community, syntrophic oxidizers and the methane generating archaeal community, which differ widely in terms of physiology, nutritional needs, growth kinetics and sensitivity to environmental conditions [5] while performing their specific roles. Anaerobic digestion is a complex process, divided into four principal stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolytic bacteria or fungi break down insoluble complex molecules such as carbohydrates, proteins and fats into their monomeric building blocks such as sugars, fatty acids and amino acids. During acidogenesis, the fermentative bacteria transform sugars and other monomeric organic products obtained from hydrolysis into organic acids, alcohols, carbon dioxide, hydrogen and ammonia. In the next phase, the hydrogen producing acetogenic bacteria growing in syntrophic association with hydrogen scavengers convert the volatile fatty acids (VFA) and dicarboxylic acids to acetate in the leading to the ultimate step in which the methanogens utilize the products of acetogenesis [6]. The increased attention towards anaerobic digestion of organic waste is due to methanogenesis, which results in decomposition of organic wastes with concomitant generation of energy.

1.2. Inhibitors

A material can be considered inhibitory for microbes when it causes an unfavourable alteration in the microbial population or inhibits the growth and metabolic activity of microbes. One of the potential shortcomings of anaerobic digestion is its apparently higher sensitivity towards toxicants than an aerobic treatment [7]. The leading causes of an anaerobic reactor failure are the presence of inhibitory compounds at substantial concentrations in wastewaters and various substrates feeding the digester and their release from the substrate by or formation in the process. The *Bacteria* and methanogenic

Abbreviations: ATP, Adenosine triphosphate; BCM, Bromochloromethane; BES, 2-Bromoethanesulfonate; BSC_{LAS}, Critical biomass specific LAS; CCl_4, Carbontetrachloride; CH_3F, Methylfluoride; DFS, Diluted fermenter sludge; DMI, Dry matter intake; FISH, Fluorescent in situ hybridization; FM, Fresh matter; GA, Gallotannic acid; GTO, Glycerol trioleate; LAS, Linear alkylbenzene sulfonates; LCFA, Long chain fatty acid; MRA, Martian regolith analogs; ODM, Organic dry matter; PAD, Psychrophilic anaerobic digestion; PFOS, Perfluorooctane sulfonate; SBR, Sequencing batch reactors; SDS, Sodium dodecylsulfate; SMA, Specific methanogenic activity; SMP, Specific methane production; SRT, Solid retention time; TAN, Total ammonia nitrogen; TES, Trace element solution; T-RFLP, Terminal restriction fragment-length polymorphism; VFA, Volatile fatty acid; VS, Volatile solid; VSS, Volatile suspended solid; 3-NOP, 3-Nitrooxypropanol

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Euryarchaeota involved in the anaerobic food chain differ in terms of physiology and susceptibility to environmental stressors [8]. Failure in maintaining the balance within these microbial communities becomes the preliminary cause of reactor instability [9]. The methanogens are considered more sensitive to inhibitors than the other microbial groups involved in the anaerobic food chain [10]. Their slow growth rate coupled with biomass washout often leads to process failure in a mixed system [8].

1.3. Chemicals affecting anaerobic digestion

Sensitivity of the anaerobic digestion to potential toxicants is one of the considerable drawbacks. The fact that various inorganic and organic chemicals interfere with methane formation from organic matter under anaerobic conditions was already reported more than 100 years ago [11]. When incubating river sediment receiving sewage rich in organic matter under anoxic conditions, Popoff observed a markedly decreased methane production in the presence of chemicals such as chloroform, KCN and oxygen [11]. Similarly, Tappeiner demonstrated that the presence of chloroform and thymol inhibited the gas yielding anoxic fermentation of cellulose [12]. Subsequent research confirmed that numerous organic or inorganic chemicals can affect anaerobic digestion processes (Fig. 1). A variety of compounds (Table 1) are known to hinder anaerobic digestion such as heavy metals [13], ammonia [14], nitrate [15], sulfide [16], oxygen [17] and salt [18].

Similarly, many organic chemicals including long chain fatty acids (LCFAs) [26], volatile acids [27], aromatic compounds [28], halogenated aliphatics [29], antibiotics [30], cyanide [31], surfactants [32] and tannins [33] are known to be inhibitory, the underlying inhibitory mechanisms being gradually better understood. This review presents a comprehensive summary on the inhibition of anaerobic digestion and methane generation by chemical compounds.

2. Inorganic toxicants

2.1. Influences of metal toxicity on anaerobic digestion

Heavy metals can be present in substantial concentrations in municipal sewage and sludge. In addition, heavy metals can be released from the fermentation substrate by the anaerobic digestion process as was demonstrated recently for poultry manure [34]. Unlike other toxic substances, one of the distinctive features of heavy metals is that they are not biodegradable and accumulate to potentially toxic concentrations [35]. However, at the same time several essential metals are required for the activation or functioning of enzymes and coenzymes involved in anaerobic digestion. The heavy metals in industrial wastewaters and municipal sludge recognized to be of specific concern and present in inhibitory concentrations are chromium, iron, cobalt, copper, zinc, cadmium, and nickel [36]. Some heavy metals, such as nickel, cobalt and molybdenum are requisite at small concentrations, while the order of heavy metal composition in archaeal cells was observed to be Fe > > Zn≥Ni > Co=Mo > Cu when analyzing methanogenic strains [37]. However, an excessive quantity of these heavy metals may lead to inhibition of anaerobic digestion [38].

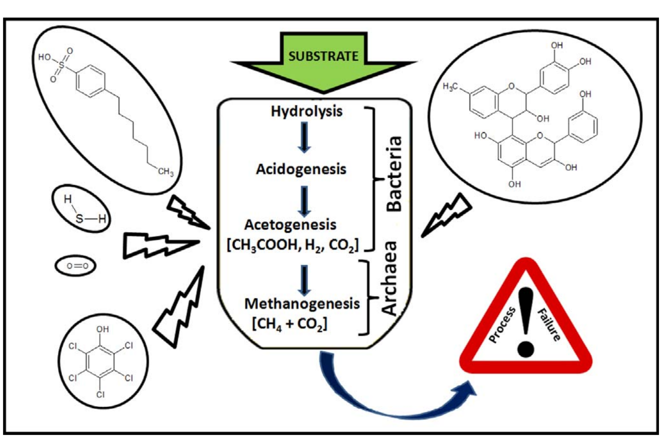

Fig. 1. Potential effect of various inhibitors on anaerobic digestion. The illustration shows the impact of organic and inorganic inhibitors on anaerobic processes hence, potentially leading to process failure.

Whether the nature of heavy metals would be stimulatory or inhibitory to anaerobic microbes is determined by the total metal concentration [39]. Accumulation of cadmium up to 5.2 µmol per 10–15 mg protein resulted in methane production increased up to 4.5 fold on acetate [40]. In a study conducted by Swanwick et al. [41], heavy metal toxicity was identified as the primary cause of reactor failure. The toxic effects of heavy metals are attributed to enzyme structure and function disruption as metals bind to thiol groups of protein molecules or replace naturally available metals in prosthetic groups [42]. The following section summarizes studies on the influence of heavy metal concentrations on anaerobic digestion.

Metals from the iron family such as Fe, Co, and Ni are considered essential for anaerobic digestion processes. Unal et al. [13] studied the effect of trace metals in coal bed methane producing water of Wyoming, USA. Enrichment cultures without defined trace element solution (TES), comprising of 1.5 g/L $FeCl_2\times4H_2O$, 70 mg/L $ZnCl_2$, 100 mg/L $MnCl_2\times4H_2O$, 6 mg/L H_3BO_3, 190 mg/L $CoCl_2\times6H_2O$, 2 mg/L $CuCl_2\times2H_2O$, 24 mg/L $NiCl_2\times6H_2O$, 36 mg/L $Na_2MoO_4\times2H_2O$, 15 mg/L Na_2WO_4, 15 mg/L $Na_2SeO_3\times5H_2O$ and 25% HCl (10 mL), amendment generated a maximum methane production of ≈8.4 µmol/mL after 6 weeks of incubation. A maximum methane production of ≈8.5 µmol/mL amendment was observed for 5× TES whereas for 1× TES and 2.5× TES addition up to ≈11.5 and 9.8 µmol/mL of methane was detected after 6 weeks. While increasing concentration of TES up to 2.5× concomitantly increased the methane production rate, 5× TES amendment decreased the methane production rate, thereby indicating a negative impact on fermentation. The study revealed that addition of 1× TES to enrichment cultures was required for optimum methanogenic growth and activities [13].

Pobeheim et al. [43] investigated the influence of nickel and cobalt on biogas production using a defined model substrate for maize. Nickel and cobalt limitation in semi-continuous fermentations, using a defined substrate for maize, showed a negative influence on biogas production and process stability. Nickel concentrations below 0.1 mg/kg fresh matter (FM) at organic loading rates >2.6 g-organic dry matter (ODM)/L×d, with general cobalt concentrations below 0.02 mg/kg FM, resulted in organic acid accumulation followed by decreased pH which in turn reduced biogas production from 4.9 NL/d to 4.5 NL/d. Stable fermentation and biogas production between 4.8 and 5.8 NL/d was detected with OLR up to 4.3 g-ODM/L-d and nickel and cobalt concentrations at 0.6 and 0.05 mg/kg FM respectively [43]. A study on the influence of heavy metals on methanogenesis of starch degrading granules [44] showed that heavy metals in electroplating effluent negatively affected methane formation. Cadmium toxicity for the anaerobic degradation of starch was evident with only 50% of specific methanogenic activity (SMA) at a heavy metal: biomass ratio > 400 mg-Cd/g-Volatile suspended solid (VSS). For chromium, a 50% reduction of SMA was detected at 310 mg-Cr/g-VSS, whereas for cobalt, nickel and zinc this was obtained at180 mg-Co/g-VSS, 120 mg-Ni/g-VSS and 105 mg-Zn/g-VSS, respectively [44].

The impact of different concentrations of various martian regolith analogs (MRA) such as JSC Mars 1-A, P-MRA, S-MRA on the activity of methanogens was analyzed by Schirmack et al. [45]. At lower concentrations (1% wt.), the methane production for *Methanosarcina soligelidi* increased from 2.6 $nmolCH_4$/h×mL (control) to 5.8, 6.0 and 4.1 $nmolCH_4$/h×mL when amended with JSC Mars 1-A, P-MRA, S-MRA respectively [45]. Similarly, the methane production increased in