Insights into the formation of inhibitory byproducts during the pretreatment of biomass and their effects on anaerobic digestion

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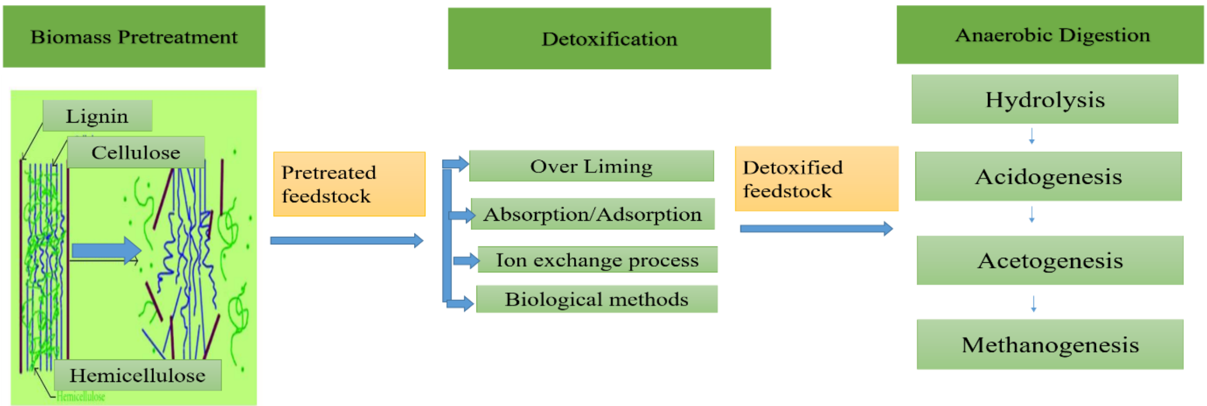
Graphical abstract



Introduction:

A rise in the demand for fossil fuels and increased energy usage has forced mankind to look for alternative energy sources. Problems associated with the management of solid wastes (agricultural residues, organic fraction of municipal solid waste (OFMSW), sewage sludge, etc) can be overcome by the production of biogas using anaerobic digestion technique. Hydrolysis is the rate-limiting step in AD that generally reduces the efficiency of the process resulting in reduced methane yield. To increase solubilization and to enhance methane production, methods such as Physical, chemical, and biological pretreatment have been employed (Tyagi & Lo, 2011). However, these pretreatments sometimes can have counter effects on the process such as the production of inhibitory byproducts such as phenols, furans, and weak acids. The presence of these Inhibitory byproducts beyond a certain limit can cause digester upset or reactor failure (Yuan & Zhu, 2016). Hence there is a necessity to understand the mechanisms of inhibitory byproduct formation and techniques to alleviate the problems caused by inhibitory products. The main objective of this extended abstract is to provide an understanding of the mechanisms behind the formation of inhibitory byproducts during different pretreatments, their effects on anaerobic digestion, and techniques to mitigate the problem caused by inhibitory byproducts to enhance methane production.

Mechanism behind the formation of Inhibitory byproducts :

Inhibitory byproducts that are formed during pretreatment can be broadly divided into Furans, Phenolic derivatives, and weak acids (Palmqvist & Hahn-Hägerdal, 2000). Furan derivatives are formed by the degradation of pentose and hexose sugars. Further hexose degrades to form HMF and furfural. HMF and furfural further break down to form formic acid. During thermal pretreatments above 165^{o}C, Maillard and caramelization reaction occurs leading to the formation of inhibitory byproducts such as furfural, HMFs, caramelans, and melanoidins. At higher temperatures, the reaction occurring between reducing sugars and amino acid groups results in the formation of dark brown colored and hardly biodegradable polymers. Caramelization is a nonenzymatic browning reaction that occurs in low water activity (Bolado-Rodríguez et al., 2016). When acid-based pretreatments are used, hydrolysis of hemicellulose occurs which results in the formation of pentose and uranic acids that degrades to furfural. Partial decomposition of biomass at higher temperatures has been reported however partial conversion of lignin and polysaccharides to phenolic compounds may occur in temperatures above 160^{o}C. Oxidation of lignin could also result in the formation of phenolic compounds and aliphatic carboxylic acids (Jönsson et al., 2013). Depolymerization that is caused by hydrolysis and repolymerisation between carbonium ions and nucleophiles results in the formation of inhibitory byproducts such as phenols. During alkaline pretreatment, carbohydrate degradation occurs results in the formation of carboxylic acids. Acetic acid is formed by the saponification of acetyl groups (Jönsson & Martín, 2016).

Effects of inhibitory byproducts on Anaerobic digestion:

Furfural damages the cell membranes by causing the accumulation of Reactive oxygen species (ROS). Also, it affects the enzymatic activity during glycolysis and the tricarboxylic acid cycle. Reduced cell growth and extended lag phase have been observed because of the presence of HMF (Kim, 2018). Complete inhibition of methanogenesis at an HMF concentration of 2mg/L has been observed (Ghasimi et al., 2016). Phenolic derivatives can cause inhibition of volumetric productivity and biogas yield. DNA breakdown can be caused by the presence of phenolics. Phenolics such as syringic acid, syringaldehyde, coniferyl aldehyde, hydroxybenzaldehyde, and vanillin have been proven to show strong inhibition effects on anaerobic digestion (Ko et al., 2015). Weak acids such as Acetic acid, lactic acid, formic acid, levulinic acid, gallic acid, vanillic acid, furoic acid, caproic acid, and benzoic acid are present in pretreated biomass slurry can cause detrimental effects on anaerobic digestion. After entering inside the cell, these weak acids dissociate into protons and anions because of the neutral cytosolic pH. With the increase in the concentration of weak organic acids, more ATP has to be hydrolyzed, which demands more energy. When the influx of protons exceeds the capacity of the ATPase, acidification of the cytosol will occur, followed by cell death (Pampulha & Loureiro-Dias, 1989).

Detoxification techniques for removal of inhibitory byproducts :

Techniques such as Alkali pretreatment, sulfide addition for toxicity reduction, biological detoxification, adsorption using activated carbon, ion exchange, calcium-oxide-based pH adjustment are generally used techniques for the removal of inhibitory byproducts from pretreated hydrolysates(Gurram et al., 2011; Persson et al., 2002; Ranatunga et al., 2000). Also, the use of conductive materials such as granular activated carbon (GAC), magnetite, hematite, Carbon cloth has been reported.The addition of carbon-based conductive materials results in Direct interspecies electron transfer (DIET), which is the main reason behind the increased removal of inhibitors and enhanced biogas production (Wu et al., 2020; Zhuang et al., 2018).

Conclusions:

The presence of inhibitory compounds results in reduced biogas yield with a longer lag phase in the anaerobic digestion process. Hence it is necessary to optimize the process conditions during pretreatment and also a detoxification step before anaerobic digestion can minimize the effect of inhibitors on anaerobic digestion. In the future there is a need for much research on the novel pretreatment methods or combination of pretreatments to reduce the formation of inhibitors and to enhance biogas production.

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