



Effect of phenolic compounds on hydrogen production from municipal solid waste



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ABSTRACT

The present study evaluates the effect of phenolic inhibitors viz. m-cresol, pentachlorophenol, bisphenol-A, and catechol on hydrogen production from anaerobic digestion of organic fraction of the municipal solid waste. Various concentration range of phenolic compounds (0.5, 2.5, 5.0, 10 and 25 mg/L) was applied. The results revealed that the inhibition coefficient of pentachlorophenol was highest among all the inhibitors resulting in lowest hydrogen production and yield. In control, the cumulative hydrogen production was 227.9 ± 10.5 mL which declined to a minimum of 93.4 ± 10.1 mL, 36.4 ± 10.1 mL, 58.9 ± 10.4 mL and 85.8 ± 10.3 mL for experimental batches supplemented with m-cresol, pentachlorophenol, bisphenol-A and catechol respectively. The corresponding decline in the hydrogen yield was 28.0%, 43.8%, 37.1% and 31.8% respectively. Further analysis revealed that inhibitors were completely removed up to a concentration not exceeding 0.25 mg/L. However, at higher concentrations, inhibitors removal efficiency was declined. COD removal efficiency was also negatively affected by inhibitors.

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1. Introduction

The rapid consumption of non-renewable fossil fuels has resulted in environmental pollution and severe energy crisis, which emphasize the importance of renewable biofuel production. Biological hydrogen is a carbon-free renewable energy carrier, with the high energy density (Turner, 2004). Biological hydrogen production via anaerobic digestion is a less energy-intensive, environmental-friendly and sustainable method compared to the current energy production methods (Gomez-Flores et al., 2015). Several types of substrate have been utilized for biological hydrogen production through anaerobic digestion such as food waste (Nguyen et al., 2017), sugarcane straw (Janke et al., 2017), kitchen waste (Gao et al., 2015), fruits and vegetables waste (Scano et al., 2014), brown algae (Fasahati et al., 2017), organic waste (Lastella et al., 2002) and organic fraction of municipal solid waste (Barati et al., 2017). Anaerobic digestion for hydrogen production offers numerous significant advantages such as low sludge production and low energy requirement (Chen et al., 2008). Currently, organic fraction of municipal solid waste (OFMSW) has been given attention to be utilized for hydrogen production (Rao et al., 2000). The generation of MSW amounts to 0.11 kg/capita/day according to central pollution control board (GIZ, 2015). Approx, 60% of municipal solid waste is

organic fraction such as waste paper, urban greening waste and kitchen waste (Dong et al., 2009). Utilization of OFMSW for hydrogen production alleviates conflict between demand and energy supply as well as improves economic feasibility for treatment of municipal solid waste (Ionescu et al., 2013).

In the dark fermentation process, the theoretical hydrogen yield depends on the type of microorganisms used. Based on the results of our previous investigations, in the present study, co-culture of *E. coli* and *Enterobacter aerogenes* was used (Sharma and Melkania, 2017). Both the bacteria are facultative anaerobic and have the capability to grow under strict anaerobic as well as aerobic conditions. *Enterobacter aerogenes* and *E. coli* have been isolated from sewage sludge and applied for production of hydrogen in the previous studies (Rachman et al., 1997; Jame et al., 2011; Das and Veziroglu, 2001). Both the bacterial species can utilize a wide range of substrate with fast growth rate and high tolerance to hydrogen partial pressure and dissolved oxygen (Zhang et al., 2011). Both the bacteria produce hydrogen via formate and NADH metabolic pathway (Rosales-Colunga and Rodriguez, 2015). Under formate pathway, formate hydrogen lyase complex is involved, which transforms formate generated from glucose into hydrogen while in NADH pathway, the NADH is the precursor for hydrogen production (Morimoto et al., 2005). *E. coli* and *Enterobacter aerogenes* have been applied in mono-culture and co-culture systems in the previous studies (Maru et al., 2016). Sivagurunathan et al. (2014) applied *E. coli* for hydrogen production from fructose and achieved

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1.17 mol-hydrogen/mol-fructose of hydrogen yield. Kumar et al. (2015) applied co-culture of *E. coli* XL1-Blue and *Enterobacter cloacae* for hydrogen production from industrial wastewater and achieved a significant increase in the hydrogen yield. Co-culture of *E. coli* and *Enterobacter aerogenes* was applied by Maru et al. (2016) for hydrogen production from glycerol who reported a 3.1 fold higher hydrogen productivity by using co-culture as compared to control. Application of co-culture system offers the advantage of improved hydrogen production and yield as compared to mono-culture systems (Pachapur et al., 2015). In co-culture system, different microbial strains are mixed which improves the individual characteristic that other strain lacks. Thus, the co-culture system eliminates the need for pretreatment steps and use of expensive reducing agents (Pachapur et al., 2015). Therefore, the co-culture system is cost-effective as compared to mono-cultures. It offers various advantageous such as resistance to environmental fluctuation, reduction in lag phase and provides eight times more stability in hydrogen production rate as compared to mono-culture systems (Pachapur et al., 2015).

Anaerobic digestion has the main drawback that it is highly sensitive to toxicants (Chen et al., 2014). Phenolic compounds are environmental pollutants that are widely distributed due to their resistance to biotic and abiotic degradation (Yaoyu et al., 2014). Phenolic compounds are present in a significant amount of the household waste (Veeresh et al., 2005; Kougias et al., 2014) which is an important fraction of OFMSW. They are derived mostly from industrial and agricultural activities including waste discharge from coking, textiles, preservatives, dyes, herbicides, plastics and paper industries (Yaoyu et al., 2014). Presence of phenolic compounds indicates the co-disposal of hazardous waste in municipal solid waste (Kjeldsen et al., 1998; Slack et al., 2005). Apart from the aforementioned sources, the lignocellulosic material is present in the municipal solid waste, which consists of polymerized sugars such as celluloses and hemicelluloses which generates phenolic compounds as by-products of lignocellulosic hydrolysis (Gupta et al., 2014; Kongjan et al., 2010). Kurata et al. (2008) carried out an extensive study to find out the occurrence of phenols in municipal solid waste landfill leachates and reported that the phenols present there were- cresols, butylphenol, bisphenol A, and some chlorophenols. Tang et al. (2008) evaluated the concentration of catechol in municipal solid waste using artificial neural networks and laccase sensor and reported that catechol was present in the concentration range of 7.5×10^{-7} M to 4.4×10^{-4} M. Phenolic compounds are toxic in nature and difficult to degrade biologically (Kumar et al., 2011). These phenolic compounds have been found to be inhibitory for anaerobic digestion (Mussatto and Roberto, 2004). Kayembe et al. (2013) investigated the effect of phenol on biogas production by anaerobic digestion and found a 50% inhibition at phenol concentration of 1249 mg/L. The inhibition was caused due to integrity loss of biological membrane by phenol which resulted in reduced cell growth and assimilation of sugars (Mussatto and Roberto, 2004). Similarly, Hernandez and Edyvean (2008) evaluated the effect of seven phenolic compounds on anaerobic digestion and reported that 50% inhibition was caused by the addition of 328 mg catechol, 120 mg phenol or 271 mg 4hydroxybenzoic acid per gram-VSS biomass. Cao et al. (2010) has demonstrated the inhibitory effect of phenolic compounds using acid-pretreated corn stalk applying *Thermoanaerobacterium thermosaccharolyticum* W16. At higher concentrations, these inhibitors have a negative influence on lag phase and hydrogen yield (Kongjan et al., 2010). The phenolic compounds toxicity is very high even at smaller concentrations (Parajo et al., 1998). However, microbes can convert phenolic compounds to less inhibitory compounds to minimize their inhibitory effects if the concentration of the phenolic compound is within the limit of microbial tolerance (Liu et al., 2005). These investigations show

that the presence of phenolic compounds inhibits anaerobic digestion severely. Therefore, it is essential to understand the impact of these inhibitors on anaerobic fermentation so that loss of hydrogen yield due to the presence of these inhibitors can be prevented.

In the present study, the impact of phenolic compounds (viz. m-cresol, pentachlorophenol, bisphenol-A, and catechol) was evaluated on hydrogen production from anaerobic digestion of organic fraction of municipal solid waste using co-culture of *Enterobacter aerogenes* and *E. coli*.

2. Materials and methods

2.1. Microorganisms and media

In the present study, the facultative anaerobes *E. coli* and *Enterobacter aerogenes* were used. The bacteria were isolated from sewage sludge using EMB (Eosin Methylene Blue) agar. EMB agar is a differential and selective media for these bacteria. Luria Bertani medium (5 g yeast extract, 10 g peptone and 10 g NaCl per liter) was used for further growth of the isolated strains. The isolated bacteria were incubated at 37 °C. The isolated bacteria grown for five generations were used in the experiments.

2.2. Feedstock preparation

The OFMSW was collected from a locally situated municipal waste landfill site in Uttarakhand, India. The OFMSW comprised of mainly household wastes such as bread, beans, rice, fruits, vegetables, paper, and meat. An electrical grinder was used to grind the OFMSW resulting in the particle size of less than 2 mm. The feedstock (OFMSW) was stored at low temperature (4 °C) to avoid its degradation. The characteristics of the feedstock are given in Table 1.

Density = (kg/m³); volatile solids = % (w/w); Total solids = % (w/w); sCOD(soluble chemical oxygen demand) = (g/L) ; pCOD(particulate chemical oxygen demand) = (g/L); tCOD (total chemical oxygen demand) = (g/L); ammonia = (g/L); total Kjeldahl nitrogen = (g/L); proteins = (g/L); lipids = (g/L); C/N ratio =; butyrate = (g/L); acetate = (g/L); lactate = (g/L); propionate = (g/L); Total volatile fatty acids = (g/L).

2.3. Inhibitors

Phenolic compounds viz. m-cresol, pentachlorophenol (PCP), bisphenol-A (BPA) and catechol were purchased from Sigma-Aldrich, India. Their characteristics are given in Table 2.

Table 1
Characteristics and composition of OFMSW.

Parameters	Unit	OFMSW
Density	(kg/m ³)	1132.5 ± 20.1
Total solids	(TS)% (w/w)	19.3 ± 1.09
Volatile solids (VS)	% (w/w)	22.0 ± 2.45
Particulate chemical oxygen demand (pCOD)	(g/L)	46.0 ± 3.22
Soluble chemical oxygen demand (sCOD)	(g/L)	12.2 ± 1.67
Total chemical oxygen demand (tCOD)	(g/L)	60.2 ± 4.89
Total kjeldahl nitrogen (TKN)	(g/L)	3.89 ± 0.15
Ammonia	(g/L)	0.523 ± 4.02
Lipids	(g/L)	2.9 ± 0.7
Proteins	(g/L)	23.8 ± 2.72
C/N		45.55 ± 3.67
Acetate (HAc)	(g/L)	0.589 ± 0.12
Butyrate (HBu)	(g/L)	0.496 ± 0.11
Propionate (HPr)	(g/L)	0.083 ± 0.04
Lactate (HLA)	(g/L)	0.127 ± 0.15
Total volatile fatty acids (TVFAs)	(g/L)	1.295 ± 0.42

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