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Effects of operational parameters on dark fermentative hydrogen production from biodegradable complex waste biomass

Anish Ghimire [a,b,*], Fabio Sposito [b], Luigi Frunzo [c], Eric Trably [d], Renaud Escudié [d], Francesco Pirozzi [b], Piet N.L. Lens [e], Giovanni Esposito [a]

[a] Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, via Di Biasio 43, 03043 Cassino, FR, Italy
[b] Department of Civil, Architectural and Environmental Engineering, University of Naples Federico II, via Claudio 21, 80125 Naples, Italy
[c] Department of Mathematics and Applications Renato Caccioppoli, University of Naples Federico II, via Cintia, Monte S. Angelo, I-80126 Naples, Italy
[d] INRA, UR0050 Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, F-11100 Narbonne, France
[e] UNESCO-IHE Institute for Water Education, Westvest 7, 2611 AX Delft, The Netherlands

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ABSTRACT

This work aimed to investigate the effect of the initial pH, combination of food to microorganism ratio (F/M) and initial pH, substrate pre-treatment and different inoculum sources on the dark fermentative biohydrogen (H_2) yields. Three model complex waste biomasses (food waste, olive mill wastewater (OMWW) and rice straw) were used to assess the effect of the aforementioned parameters. The effect of the initial pH between 4.5 and 7.0 was investigated in batch tests carried out with food waste. The highest H_2 yields were shown at initial pH 4.5 (60.6 ± 9.0 mL H_2/g VS) and pH 5.0 (50.7 ± 0.8 mL H_2/g VS). Furthermore, tests carried out with F/M ratios of 0.5, 1.0 and 1.5 at initial pH 5.0 and 6.5 revealed that a lower F/M ratio (0.5 and 1.0) favored the H_2 production at an initial pH 5.0 compared to pH 6.5. Alkaline pre-treatment of raw rice straw using 4% and 8% NaOH at 55 °C for 24 h, increased the H_2 yield by 26 and 57-fold, respectively. In the dark fermentation of OMWW, the H_2 yield was doubled when heat-shock pre-treated activated sludge was used as inoculum in comparison to anaerobic sludge. Overall, this study shows that the application of different operating parameters to maximize the H_2 yields strongly depends on the biodegradability of the substrate.

1. Introduction

Dark fermentation (DF) of organic waste is one of the promising technologies for biohydrogen (H_2) production. The DF processes are usually preferred over other light dependent, photofermentation or biophotolysis processes because of the high bioreactor productivities and the potential to utilize a wide range of organic wastes as feedstock (Hallenbeck et al., 2009; Urbaniec and Bakker, 2015). In addition, the associated production of organic acids and alcohols, among others, can be either used in sidestream processes like anaerobic digestion for methane or photofermentative H_2 production for energy recovery, or can be used for the production of platform molecules (Bastidas-Oyanedel et al., 2015; Sarma et al., 2015).

Waste biomass is abundant and can sustain DF processes in scaled-up applications. Easily degradable food waste (the organic fraction of municipal solid waste (OFMSW)), more slowly degradable agricultural residues (i.e. rice straw) as well as agro-industrial waste such as olive mill wastewaters (OMWW) can serve as sustainable feedstock sources for dark fermentative H_2 production (Guo et al., 2010; Kapdan and Kargi, 2006; Ntaikou et al., 2010; Show et al., 2012). A major bottleneck in the utilization of these low cost waste biomasses is the rather low H_2 yields observed in the DF processes (Ghimire et al., 2015a; Urbaniec and Bakker, 2015). Nevertheless, H_2 yields and process kinetics can be enhanced by optimizing operating parameters, such as pre-treatment of inocula, food to microorganisms (F/M) ratio (also substrate to inoculum ratio), pre-treatment of substrates, culture temperature and pH (De Gioannis et al., 2013; Guo et al., 2010; Ntaikou et al., 2010; Wang and Wan, 2009a,b). During recent years, extensive experimental research has been devoted to the establish the optimal operational conditions for maximizing H_2 production, with a special focus on operational pH, temperature and substrate utilization (De Gioannis et al., 2013; Ghimire et al., 2015a; Wong et al., 2014).

* Corresponding author at: Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, via Di Biasio 43, 03043 Cassino, FR, Italy.
E-mail addresses: a.ghimire@unicas.it, anishghimire@gmail.com (A. Ghimire).

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A wide range of optimal pH values have been reported for different substrates to enhance H_2 yields: an initial pH of 6.5 for food waste (Cappai et al., 2014), initial pH of 8.0 for food waste (Kim et al., 2011a,b), a controlled pH of 7.0 for vegetable kitchen waste (Lee et al., 2008), an initial pH of 6.5 for rice straw (Chen et al., 2012), an initial pH of 6.0 for cheese whey (De Gioannis et al., 2014) and an initial pH of 4.5 for sucrose and starch (Khanal et al., 2004). This considerable variability in culture pH is mainly due to differences in temperature, substrate type and concentration (F/M ratio), inoculum types and their pre-treatment methods.

H_2 yields in DF of organic waste are strongly affected by the operational temperature as it can influence the rate of hydrolysis and the production of volatile fatty acids (VFAs) and thus the final pH of the fermentation (De Gioannis et al., 2013; Ghimire et al., 2015a). A thermophilic temperature has been reported to favor the dark fermentative H_2 production (Shin et al., 2004; Valdez-vazquez et al., 2005). Likewise, the physico-chemical characteristics of the substrates, and most importantly the biodegradability or bioavailability (can also be defined as the fraction of easily accessible carbohydrates for fermentative conversion) crucially affects the H_2 production (Monlau et al., 2013a). Therefore, several studies have established a strong correlation between H_2 yields and the initial carbohydrate fraction (soluble sugars in some cases) present in the substrates (Alibardi and Cossu, 2016; Guo et al., 2013; Monlau et al., 2012).

In this context, alkaline pre-treatment methods have been popularly adopted for the saccharification of lignocellulosic biomass (plant stalks, rice and wheat straw), which could enhance the production of H_2 in DF and CH_4 in DF coupled to anaerobic digestion, respectively and could thus give economic credentials (Monlau et al., 2015, 2013c; Sambusiti et al., 2013). Alkaline pre-treatment of lignocellulosic biomass has been reported to be carried out at different concentrations of alkaline agents (2–12% NaOH, weight basis), temperature (40–190 °C) and treatment period (30 min–24 h), with varying level of effectiveness in terms of increase in biogas yields (H_2 and CH_4) with consequent higher net energy recovery and economic return (Monlau et al., 2015, 2013b; Sambusiti et al., 2013). However, alkaline agents (i.e. Na^+ from NaOH) might exert inhibitory effects on dark fermentative microbial communities (Kim et al., 2009). Consequently, an investigation of selected alkaline pre-treatment conditions for a particular substrate type becomes vital to study the conditions that enhance the H_2 production.

H_2 production from organic waste is influenced by the presence of an effective hydrolyzing, H_2 producing microbial community, which depends on the inoculum source and inoculum pre-treatment method (Abreu et al., 2009; Bellucci et al., 2015; Chen et al., 2012; Pakarinen et al., 2008). Abreu et al. (2009) and Chen et al. (2012) showed that the H_2 yields mainly depend on the inoculum sources. However, the response of fermentative microorganisms toward the presence of inhibiting substances present in a substrate can influence the DF process. In a recent study, Bellucci et al. (2015) reported a varying response of fermentative microbial communities for H_2 production, when the inhibitor 5-hydroxymethylfurfural (HMF) was added. This was linked to the difference in inoculum pre-treatment methods applied. Likewise, the presence of polyphenolic compounds in substrates such as OMWW can exhibit inhibitory effects on fermentative microbial communities and H_2 yields (Hamdi, 1992; Ntaikou et al., 2009). Subsequently, investigating the effect of the inoculum source on H_2 production performance from substrates like OMWW is fundamental to reach an optimum in H_2 production.

Despite some studies attempted to establish the optimal operational conditions of initial pH, F/M ratio, alkaline pre-treatment of substrate and inoculum selection, dissimilarities in H_2 production exist due to the differences between substrate types and experimental conditions. Therefore, it becomes essential to investigate the optimum initial pH for food waste under thermophilic DF conditions. So far, only few studies have considered the combined effects of F/M ratio and initial pH on thermophilic DF of food waste (Ginkel et al., 2001; Pan et al., 2008). Ginkel et al. (2001) revealed a profound impact of the concentration of substrate and pH on the H_2 yields in sucrose DF of, with an optimum pH and substrate concentration at pH of 5.5 and 7.5 g COD/L, respectively. In other study, Pan et al. (2008) established a F/M ratio of 6.0 as optimum for thermophilic DF of food waste, without the consideration of initial pH. Similarly, past studies on pre-treatment of substrates seemed more focused on maximizing the methane yields in anaerobic digestion by adopting higher concentrations of alkaline agents and treatment temperature (Monlau et al., 2013a). Therefore, optimum conditions of alkaline pre-treatment for dark fermentative H_2 production need to be investigated for lignocellulosic agricultural residues such as rice straw. Finally, different inoculum sources can be explored to study the effect on H_2 production from a typical poorly biodegradable feedstock such as OMWW, which contains polyphenolic compounds (Ntaikou et al., 2009).

The present study aims to investigate the effects of (i) the initial pH and combined pH and F/M ratio on food waste, (ii) alkaline substrate pre-treatment on dark fermentative H_2 production from rice straw and (iii) the effect of inoculum source and pre-treatment on H_2 production from OMWW. Cumulative H_2 production, H_2 yields, H_2 production rates, lag phase and accumulation of DF metabolites (mainly organic acids and ethanol) were used to evaluate the efficiency of these various strategies to improve the H_2 production performance from these complex organic wastes.

2. Materials and methods

2.1. Inoculum

Two types of inoculum, i.e. anaerobic digested sludge (ADS) and waste activated sludge (WAS) were used in the experiments. ADS was collected from the effluent of an anaerobic digestion plant of a dairy farm located in Capaccio (Salerno, Italy). The plant features include a 100 m^3 CSTR operating at a hydraulic retention time of 24 days and operating within a pH and temperature range of 7.4–7.5 and 52–56 °C, respectively. The plant is continuously fed with buffalo manure, cheese whey of buffalo milk and sludge from an industrial wastewater treatment plant. WAS was collected from a secondary clarifier unit at the Nola Municipal Wastewater Treatment Plant located in Naples (Campania, Italy). The characteristics of the ADS and WAS before pre-treatment are presented in Table 1. The inocula were stored at 4 °C until used. The WAS and ADS underwent a heat shock treatment (HST) at 105 °C for 1.5 and 4 h, respectively, in order to enrich spore forming *Clostridium* sp. and inhibit methanogens (Ghimire et al., 2015b). WAS had a shorter time for HST than ADS because it was obtained from an aerobic activated sludge process.

2.2. Preparation of feedstock

Three types of waste as reference models of complex waste biomass with different characteristic biodegradability, were used in this study: (i) food waste, representative of moderately biodegradable organic waste was selected to study the effect of initial pH and substrate concentration on H_2 yields, (ii) rice straw as a representative of slowly degrading lignocellulosic agricultural residues was used to study the technical feasibility of substrate pre-treatment on biohydrogen production and (iii) OMWW was used to study the effect of the inoculum type and its adaptation to toxicants, as OMWW contains phenolic compounds and long chain fatty acid

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