Bioresource Technology 190 (2015) 431–437

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Phosphate enhancing fermentative hydrogen production from substrate with municipal solid waste composting leachate as a nutrient

Qiang Liu [a,b], Wen Chen [a], Xiaolei Zhang [c], Lijia Yu [d], Jizhi Zhou [a], Yunfeng Xu [a,*], Guangren Qian [a]

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China
[b] Shanghai Key Laboratory of Bio-energy Crops, Shanghai University, Shanghai 200444, China
[c] School of Civil, Environmental and Chemical Engineering, RMIT University, GPO Box 2476, Melbourne, VIC 3001, Australia
[d] Shanghai Pudong Environmental Protection Development Co. Ltd., No. 1229, Dongxiu Road, Shanghai 201207, China

HIGHLIGHTS

- Phosphate was supplemented into co-substrate of glucose and MSW fresh leachate.
- Orthophosphate show better H_2 producing performance than pyrophosphate.
- The optimal COD/P ratio for H_2 production being 27.64 mg/mg for orthophosphate.
- Orthophosphate has duel effects: supplying nutrient and relieving Ca^{2+} inhibition.

ARTICLE INFO

Article history:
Received 8 December 2014
Received in revised form 28 January 2015
Accepted 30 January 2015
Available online 11 February 2015

Keywords:
Fresh leachate
Biohydrogen production
Orthophosphate
Pyrophosphate
Precipitation

ABSTRACT

To overcome phosphorus deficiency in municipal solid waste composting leachate, orthophosphate (OP) and pyrophosphate (PP) were separately added into leachate to evaluate the possibility of fermentative H_2 production with leachate and phosphorus-rich streams as a full nutrient source. Results indicate H_2 production is significantly promoted by OP addition but slightly facilitated by PP in some cases, depending on initial pH and P dosage. The highest hydrogen yield (1.95 ± 0.07 mol H_2/mol glucose) was achieved at a COD/P ratio of 27.64 (mg/mg) with OP as phosphorus source at initial pH 5. For PP, a maximum yield of 1.58 ± 0.09 mol H_2/mol glucose can be attained at the optimal COD/P ratio of 221.12 (mg/mg) and initial pH 5. OP promotes H_2 production *via* dual approaches: supplying nutrient and relieving inhibition from excessive Ca^{2+} on granule sludge. However, both the roles in nutrient supply and Ca^{2+} removal by PP addition are limited.

1. Introduction

Hydrogen is a clean, recyclable, and efficient energy carrier and has been considered to play a potentially key role in sustainable energy usage in future (De Gioannis et al., 2013). Among a variety of hydrogen production approaches, dark fermentation attracts extensive attention due to its environmental friendliness and high efficiency (Chaubey et al., 2013). In recent years, considerable researchers (Ismail et al., 2010; Kim et al., 2013; Sydney et al., 2014) have employed carbohydrate-rich waste or wastewater for H_2 production by dark fermentation since this process can simultaneously achieve dual benefits, i.e., waste/wastewater treatment as well as bio-energy recovery. Microbial conversion of organic matters to H_2 by anaerobic fermentation can be influenced by a lot of factors, among which nutrient is a common one that highly affects the activity of hydrogen production bacteria (HPB). To overcome the deficiency of nutrient in waste-based feedstock, some experiments (Mohanakrishna et al., 2010; Liu et al., 2011, 2013) utilized co-substrate with balanced nutrient/substrate ratio to facilitate H_2 production.

Fresh leachate from municipal solid waste (MSW) composting is characterized with high content of organic matters, nitrogen pollutants, and a certain amount of metal ions. Abundances in readily biodegradable organic matters and multiple nutrients endorse fresh leachate with an applicable feedstock for anaerobic fermentative (Sarah et al., 2013). However, our previous study demonstrated H_2 production from fresh leachate is hampered by some toxic species contained in this waste stream and the co-fermentation of carbohydrate-rich waste/wastewater with

* Corresponding author at: School of Environmental and Chemical Engineering, Shanghai University, No. 99 Shangda Road, Shanghai 200444, China. Tel.: +86 21 6613 7745; fax: +86 21 66137761.
E-mail address: yfxu@shu.edu.cn (Y. Xu).

http://dx.doi.org/10.1016/j.biortech.2015.01.139
0960-8524/

fresh leachate (as a nutrient source) seems to be a more practical strategy for H_2 production purpose (Liu et al., 2011). Despite of this, the deficiency of bio-available phosphorus in leachate usually leads to low hydrogen productivity.

Phosphorus is an essential nutrient required by microbial growth. Moreover, phosphate species, such as HPO_4^{2-} and $H_2PO_4^-$, have strong buffering ability to mitigate pH fluctuation caused by volatile fatty acids (VFAs) accumulation (Wang and Wan, 2009). Therefore, a lot of researchers employed high phosphorus content in culture medium to improve microbial activities and enhance H_2 production (Davila-Vazquez et al., 2009; Thong et al., 2011; Sittijunda and Reungsang, 2012). However, this strategy inevitably increases the costs of fermentative H_2 production. Actually, phosphate is abundant in effluents from many industries, such as fertilizer industry (4.5–45 g/L) (Al-Harahshe et al., 2014) and metal surface treatment (up to 1.8 g/L) (Sun et al., 2014), and the disposal of these waste streams are expensive. If phosphate-rich wastewater is available as a minor nutrient for the co-digestion of fresh leachate and carbohydrate-rich waste/wastewater, this synergistic treatment will provide a promising alternative for wastewater synergistic disposal.

To this end, two phosphate species, orthophosphate (PO_4^{3-}, abbreviated as OP) and pyrophosphate ($P_2O_7^{4-}$, abbreviated as OP) were added into a co-substrate of glucose and fresh leachate (the former was used as carbon source and the later acted as major nutrient source) to investigate their effects on fermentative hydrogen production. OP and PP were employed because they are the most common phosphorus species in industrial effluents. The effects of phosphate species and concentration on H_2 production as well as liquid metabolites generation were explored. On the basis of experimental results, the optimal C/P ratio was proposed for the co-fermentation of fresh leachate and phosphate-rich wastewater.

2. Methods

2.1. Materials

Fresh MSW leachate used in this experiment was collected from a MSW compost plant in Shanghai, China. This plant has a MSW disposal capacity of 1300 t/d and generates about 100 tons of composting leachate per day. The fresh leachate is characterized with significantly high concentrations of organic matter and calcium ion. Detailed information about the composition of leachate is presented in Table 1.

Anaerobic granular sludge was obtained from an internal circulation bioreactor of a citric acid production plant in Shanghai, China. The seed sludge contained well-settled black granules with diameter in 0.28–2 mm and had a mixed liquor volatile suspended solid (MLVSS) and mixed liquor volatile suspended solid (MLSS) contents of 30.5 and 41.4 g/L, respectively. The inoculums were settled to remove coarse particles and washed by tap water for five times to remove impurities. Afterwards, the sludge was heated in a thermostat water bath at 99 °C for 90 min to enrich H_2-producing bacteria.

Table 1
Characteristics and composition of fresh leachate used in this experiment.

Parameter	Value (mg/L)	Parameter	Value (mg/L)
CODcr	55,689	Ca	2677
TN[a]	10,056	Fe	969.9
TS[b]	967.8	Mg	364.8
Protein	14,400	Zn	15.8
TVFA[c]	3077.6	Cu	0.32
TP[d]	71	Ni	0.43
		Cr	ND[e]

[a] Total nitrogen concentration.
[b] Total sugar concentration.
[c] Total volatile fatty acid content.
[d] Total phosphorus concentration.
[e] Not detected.

2.2. Batch experiments

Batch fermentative test was conducted in a 500 mL conical flask connected with a 500 mL biogas collector. Each conical flask was filled with 50 mL granular sludge and 400 mL liquid and sealed with a butyl rubber stopper.

Fermentative substrate contained an optimal proportion of glucose (6200 mg/L) and composting leachate (3380 mg COD/L) that was found to be favorable for H_2 production in a previous study (Liu et al., 2011). To facilitate H_2 production, different amounts of OP or PP (AR, purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai) were added into substrate to increase total phosphorus (TP) content from 4.3 mg/L to about 45, 90, 180, 360 and 720 mg/L, respectively. Apart from phosphorus, no further nutrient was supplemented in all tests.

Initial pH of fermentative substrate was adjusted to 5, 7 or 9 by 0.1 M HCl or NaOH. After flushed with a mixed gas of N_2 (80%) and CO_2 (20%) in void space, the sealed flask was incubated in a rotary shaker (150 r/min) at 35 ± 1 °C to start anaerobic digestion. Batch test in each flask continued until total biogas volume kept constant for a consecutive 4 h. All tests were carried out in triplicate and blank tests (TP concentration is 4.3 mg/L) at three pH levels without phosphate addition were also included.

2.3. Analytical methods

Standard methods (American Public Health Association, 2005) were used to determine COD, TN and TP concentrations in fermentation liquid. pH value was measured with a Delta 320 pH-meter (Mettler-toledo). Metal ion contents in fresh leachate and fermentation liquid were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu, ICPS-7510). The concentrations of total sugar (carbohydrate) and protein were measured by phenol-sulfuric acid method (Han et al., 2012) and colorimetric method (Reddy et al., 2011), respectively.

The volume of biogas was measured by water displacement method. Biogas composition was analyzed by a GC9800 gas chromatography (Kechuang Chromatograph Instruments Co., Ltd., shanghai, China) equipped with a thermal conductivity detection (TCD) and a stainless steel column (1 m × 3 mm) packed with TDX-01. Nitrogen was used as carrier gas at a flow rate of 15.5 mL/min. Operational temperatures of column, oven and detector were 30, 50 and 55 °C, respectively. Cumulative hydrogen volume was calculated from the measurement of flask headspace and adjusted to standard condition (0 °C and 760 mmHg). Total volume of biogas produced in each time interval was determined by mass balance according to Bao et al. (2012). Molar hydrogen yield was calculated from cumulative hydrogen volume (mol) and glucose consumption (mol) in each test. Hydrogen production profiles were fitted with modified Gompertz equation as following:

$$P = P_s \exp\left[-\exp\left(\frac{R_m \cdot e}{P_s}(\lambda - t) + 1\right)\right] \quad (1)$$

where P is cumulative hydrogen volume at t moment (mL), P_s is H_2 production potential (mL), R_m represents the maximum H_2 production rate (mL/h), e is 2.71828, λ denotes the lag time (h), and t is incubation time (h). The kinetic parameters (P_s, R_m and λ) were estimated *via* Origin 8.0.