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Kinetics of combined thermal pretreatment and anaerobic digestion of waste activated sludge from sugar and pulp industry

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HIGHLIGHTS

- Thermal pretreatment of waste activated sludge from sugar and pulp mills.
- Growth rate of methane yield revealed the kinetic variation after pretreatment.
- Share of the rapidly biodegradable matter is estimated by methane yield percentage.
- Simplified Reaction Curve model provides a quick assessment of methane yield.

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ABSTRACT

The purpose of this work was to evaluate the effects of thermal pretreatment temperature (from 100 °C to 200 °C) and time (15–60 min) on the characteristics and the anaerobic biodegradability of wasted activated sludge from sugar and pulp mills. Reaction Curve model and First-order kinetics were used to obtain a better understanding of the data from the anaerobic biodegradability tests. Sludge characteristics and methane production prior and after thermal pretreatment confirmed that temperature exerted the major influence on sludge solubilization and biodegradability. The optimal methane yield (182 ml CH_4/g VS_{Feed}) and ultimate methane production rate (72.1 ml CH_4/g VS_{Feed} d) was obtained at 165 °C for 30 min. However, the negative effects of melanoidins and Amadori compounds appeared and the rising trend of biodegradability reversed at 200 °C. The growth rate of methane yield topped out at 476% at 100 °C, and the maximum methane yield (range from 28.9 to 72.1 ml CH_4/g VS_{Feed} d) were also observed at the first day, showing the radical kinetics improvement after pretreatment. This remarkable initial methane yield was attributed to the raising share of the rapidly biodegradable organics generated in thermal pretreatment, which were estimated with methane yield percentage of day 3. Both Reaction Curve model and First-order kinetics fitted with the experimental data well, and a Simplified Reaction Curve model without lag time provides a feasible tool to estimate methane yield of the rapidly biodegradable substrates.

1. Introduction

The Clean Production Act (China) enacted since 1999 aims to redirect the conventional industrialization towards a sustainable route, with less energy consumption and pollutant emission. The ambitious goals regarding the reduction of chemical oxygen demand (COD) emission in sugar and pulp industry, led to the wide application of activated sludge process. Guangxi province, the major sucrose supplier of China, provided 4.9 million tons of sugar in 2014. Despite the anaerobic processes (e.g. upflow anaerobic sludge bed) were used, wasted activated sludge has still merged as an important issue of the industrial waste management [1]. Landfilling, the current option for sludge disposal accepted by sugar and pulp industry, has been constrained by the raising concerns on landfill maintenance, site shortage and greenhouse gas emission [2,3]. However, for the advantages of economics and operability, landfilling of waste activated sludge would not phase out in the near future for sugar and pulp industry.

Anaerobic digestion of complex organic matter, a proven solution to minimize the drawback of sludge landfill is limited by particle hydrolysis [4]. Thermal pretreatment has been applied to

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improve sludge dewaterability in early 1970 s [5,6]. Li and Noike suggested that the optimum pretreatment temperature and duration to maximize methane yield of waste activated sludge were 170 °C and 60 min [7]. During 1980 s, thermal treatment had been used by sugar and pulp industry to improve sludge dewatering and reduce disposal cost [8]. But those processes were obsoleted due to the energy consumption, secondary contamination and operation failures. In the past decades, several full-scale thermal pretreatment processes came into operation mainly in Europe [9,10]. Thermal pretreatment prior to anaerobic digestion was a potential solution for S&P biosolid management. Therefore, a feasible methodology to estimate and evaluate the effectiveness of thermal pretreatment becomes necessary.

Most previous studies had evaluated the effectiveness of thermal pretreatment with organic solubilization, biodegradability and kinetic models using municipal waste activated sludge [11–14]. However, few studies dealing with waste activated sludge from S&P mills, had evaluated the effects of thermal pretreatment on anaerobic digestion with mathematical models [15]. The solubilization of volatile solids (VS) and/or soluble chemical oxygen demand (SCOD) were used to quantify the transfer of particle organics to soluble organic matter [11,14]. However, anaerobic biodegradability test was conducted to obtain the methane from soluble and particle organic matter, collectively. As thus, the correlations between the solubilization degree and biodegradability were rarely specified and quantified. Therefore, methane yield and methane production rate were used to evaluate the variation of biodegradability prior and after sludge pretreatment.

Therefore, the objective of this study on waste activated sludge from S&P industry was to assess the effect of thermal pretreatment on sludge characteristics and anaerobic biodegradability. Pretreatment temperatures and time o considered in this study ranged from 100 °C, 135 °C, 165 °C to 200 °C at 15 min, 30 min and 60 min, respectively. Methane yields, methane production rate and the growth rate of methane yield were obtained in anaerobic biodegradability test to investigate the mechanism of thermal pretreatment. A comparison between Reaction Curve model and First-order model was conducted to obtain a suitable model to represent methane yield from anaerobic biodegradability test.

2. Materials and methods

2.1. Substrates and inoculum

Dewatered wasted activated sludge (total solids, TS = 136.5 g/L; VS = 93.3 g/L) was obtained from Guigang Sugar Group, located at Guigang, (Guangxi, China). Dewatered wasted activated sludge was diluted to TS = 100 g/L with distill water and homogenized with a grinder (WBL25B26, Midea Limited, China).

Mesophilic anaerobic sludge (TS = 63.6 g/L, VS = 53.6 g/L) was collected from an UASB reactor treating bagasse pulp wastewater (GSG, Guangxi), and used as inoculum for all batches in this study. The inoculum was pre-incubated in the water bath (37 ± 0.5 °C) for at least 10 days to deplete any residual biodegradable organics.

2.2. Thermal pretreatment

Thermal pretreatment was conducted in a 15 L electric-heating reactor, model number HK-ZZ01 (Hengke Instruments, China), equipped with four identical hydrothermal synthesis vessels (1000 ml) inside the chamber. Once the reactor reached the objective temperatures, temperature remained constant for the setting times. Thereafter, the reactor was cooled down with cold water batch to room temperature. Thermal pretreated sludge were stored at 4 °C for at most 3 day before further analysis and tests.

2.3. Anaerobic biodegradability test

Anaerobic biodegradability test were conducted to determine the methane yield and the methane production rate, using raw sludge and thermal pretreated sludge as substrates. Batch experiments were conducted in a series of serum bottles (liquid volume of 300 ml and headspace volume of 200 ml, sealed with butyl rubber stoppers). Anaerobic batch reactors were operated under mesophilic condition (37 ± 0.5 °C), and feeding/inoculum ratio (0.5 g VS_{Feed}/g VS_{Ino}) suggested by I. Angelidaki [16] was used. Anaerobic biodegradability tests were conducted for 20 days, a typical hydraulic retention time of mesophilic anaerobic digestion [10]. Methane yield was measured on daily basis by liquid displacement, using 2% NaOH to scrub the acidic gases (e.g. carbon dioxide and hydrogen sulfide). All tests, including the controls and blanks, were conducted in triplicate to guarantee the reproducibility.

The batch anaerobic biodegradability test evaluated the effects of thermal pretreatment by the amount and rate of methane production, referring to methane yield and methane production rate. Methane yield and methane production rate were normalized per substrate mass VS added (ml CH_4/g VS_{Feed} and ml CH_4/g VS_{Feed} d).

2.4. Analysis methods

All analyses were conducted in triplicate and the results were given as mean values ± standard deviation. The soluble fraction of sludge was separated by centrifugation at 8000 rpm for 20 min. and the supernatant was then filtered to obtain the soluble fraction, to analyze SCOD, ammonia, alkalinity, pH, and volatile fatty acids (VFA). VFA concentration was conducted according to the five-point titration method [17]. SCOD, TS, VS, pH and alkalinity were determined according to the standard methods [18].

2.5. Calculation

2.5.1. Growth rate of methane production

Growth rate of methane production was calculated to estimate the average growth of methane yield in a temperature interval.

$$G_{T-T'}(\%) = (M_T - M_{T'})/M_{T'} * 100\% \quad (1)$$

where $G_{T-T'}$ is the average growth rate of methane production (%) in a certain temperature interval ($T > T'$), M_T and $M_{T'}$ (ml CH_4/g VS_{Feed}) are the average methane yield of pretreated sludge at T and T'.

2.5.2. Methane yield percentage

Methane production percentage (Y_t%) was calculated to describe the progress of methane yield in the biodegradability test.

$$Y_t(\%) = (M_t/M) * 100 \quad (2)$$

where M is the maximum methane yield (ml CH_4/g VS_{Feed}), M_t is the methane yield (ml CH_4/g VS_{Feed}), and Y_t (%) is the share of the total methane yield obtained at day t.

2.5.3. Modeling

Experimental data, i.e., the methane yield was fitted to Reaction Curve model and First-order model for an evaluation of the kinetics parameters.

Reaction Curve model (Eq. (3)) used to describe methane yield with three parameters: the maximum specific growth rate, R_m, is defined as the tangent in the inflection point; the lag time, λ is defined as the x-axis intercept of this tangent; and the asymptote is the maximal value reached [7,19].