



Effect of thermal pretreatment on the physical and chemical properties of municipal biomass waste

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ABSTRACT

The effects of thermal pretreatment on the physical and chemical properties of three typical municipal biomass wastes (MBWs), kitchen waste (KW), vegetable/fruit residue (VFR), and waste activated sludge (WAS) were investigated. The results show that thermal pretreatment at 175 °C/60 min significantly decreases viscosity, improves the MBW dewatering performance, as well as increases soluble chemical oxygen demand, soluble sugar, soluble protein, and especially organic compounds with molecular weights >10 kDa. For KW, VFR and WAS, 59.7%, 58.5% and 25.2% of the organic compounds can be separated in the liquid phase after thermal treatment. WAS achieves a 34.8% methane potential increase and a doubled methane production rate after thermal pretreatment. In contrast, KW and VFR show 7.9% and 11.7% methane decrease because of melanoidin production.

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1. Introduction

In 2009, 157.3 million tons of municipal solid waste was produced in China (China Statistical Yearbook, 2010). More than 60% of this amount is organic matter classified as municipal biomass waste (MBW). MBW comprises kitchen waste (KW), vegetable/fruit residue (VFR), and waste activated sludge (WAS). Both the biodegradable organic content and water content of MBW are high. As a result, severe environmental problems concerning the traditional waste management system have arisen. Such problems include greenhouse gas emissions, high-concentration leachate from landfills, unstable burning conditions, dioxin releases from incineration, odor pollution, and low-quality fertilizers from composting.

Anaerobic degradation, an effective technology that can convert biomass waste to green energy, has been widely used for the treatment of MBW in recent years. However, the high particulate organic content of MBW has resulted in a low hydrolysis rate, which has become the limiting step of the anaerobic digestion (Li and Noike, 1992). Several methods (i.e., thermal, microwave, and ultrawave pretreatments) have been developed to enhance the solubilization of a complex particulate organic substrate to accelerate the hydrolysis rate and efficiency of the anaerobic digestion process (Qiao

et al., 2010; Liu et al., 2008; Mata-Alvarez et al., 2000; Rughoonundun et al., 2010).

Thermal pretreatment is considered as a promising method to improve MBW properties because of the solubilization of particulate organics and promotion of biogas production (Wang et al., 2010). Most of the studies reported that optimal temperatures for thermal pretreatment of WAS range from 160 to 180 °C, and that treatment times range from 30 to 60 min. These optimal conditions can lead to a volatile solid (VS) hydrolysis ratio of 40–60% and a 40–100% biogas production increase for WAS (Bougrier et al., 2008; Christopher and John, 2009; Li and Noike, 1992). Thermal pretreatment is also reported as a well proven method to remarkably increase the dewaterability of WAS by 50–100% which resulting in significant solid–liquid separation and mass reduction of digestate dewatered cake (Neyens and Baeyens, 2003). Bougrier et al. (2008) reported that thermal pretreatment could reduce the viscosity of sewage sludge. Viscosity is a useful parameter for operation and monitoring of biological processes, and the reduction of viscosity means that the sludge is more fluid so that a higher solid concentration of 8–12% can be fed to the digester. In addition, thermal pretreatment has the benefit of sterilization and sanitation by killing most of the pathogens and bacteria in the feedstock, but on the other side thermal pretreatment is responsible to the inactivation of methanogenic archae in the feedstock (Hu and Chen, 2007). In the process of anaerobic digestion, the inoculums addition can mask the contribution of microorganisms already in the waste. In spite of the enhancement of MBW properties, thermal pretreat-

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ment has been found to be responsible for the formation of refractory dissolved organic compounds, while most of them have been revealed as melanoidins (Eskicioglu et al., 2006). Penaud et al. (2000) have founded that by removing the compounds responsible for brown color from the thermally treated sludge, the biodegradability increased. This highlighted that melanoidins may be undegradable to biological treatment. There is not a quantificational measurement for melanoidins, and the most often used method to characterize melanoidins is the ultraviolet absorbance at 254 nm (Dwyer et al., 2008).

Previous studies mostly focused on the thermal hydrolysis of WAS, and very few reports have addressed on other MBWs such as KW and VFR. In addition, most studies just concerned the changes of volatile suspended solid (VSS) and soluble chemical oxygen demand (SCOD), and few reports have discussed the internal relations between physical and chemical properties and anaerobic digestion. Therefore, the impacts of physical and chemical properties due to thermal pretreatment, and how the impacts affect the choice of subsequent anaerobic digestion technology, then whether all the MBWs should be treated by thermal pretreatment, these questions are gaining interesting. Finally, although a number of studies have indicated that melanoidins are formed during the thermal hydrolysis process, the study of biodegradability and melanoidins still needs to be further proved.

In the present paper, the physical and chemical characteristics of three kinds of MBW (KW, VFR, and WAS) before and after thermal pretreatment were analyzed. The object of this study was to obtain a better understanding of the influences of thermal pretreatment on physical and chemical properties of MBWs. The physical properties include viscosity and the dewatering performance, and the chemical properties include the VSS solubilization rate, the existing form of various organic components, the molecular weight (MW) distribution of soluble organics, and anaerobic biodegradability. The impacts of physical and chemical properties changes on further anaerobic digestion of MBWs were focused and the possible relationship between biodegradability and melanoidin production was also discussed.

2. Materials and methods

2.1. MBWs

Three types of MBW (KW, VFR, and WAS), were used in the present study. KW was from a student canteen at the Tsinghua University, VFR from a local trade market in Beijing, and WAS from the thickener centrifuge of the Beixiaohe wastewater treatment plant (Northern Beijing; capacity = 100,000 m³/d). Before thermal pretreatment, KW and VFR were shredded into particles with an average size of 1.0 mm. WAS from the treatment plant was diluted by deionized water to a 1:1 volume ratio to ensure liquidity and to improve the heat transfer of the sample.

2.2. Thermal pretreatment

Thermal pretreatment were performed in a 2 L stainless steel hydrolysis vessel (height, 40 cm; and diameter, 8 cm). During thermal pretreatment, about 1.5 kg sample was transferred into the vessel and the vessel was immersed into an oil bath which had been preheated to 175 °C. The samples were hydrolyzed at 175 °C for 60 min, and were then chilled in 10 °C water until the vessel cooled to room temperature. After thermal pretreatment, the samples were stored at 4 °C to minimize the volatilization of organic compounds.

After pretreatment, both raw and pretreated MBW samples were centrifuged at 5000 rpm for 10 min. The centrifuged superna-

tants were filtered through a 0.45 µm pore-size filter membrane. The filtered supernatant was used to analyze the soluble organic compound contents.

Hydrolysis ratio was used to represent the solubilization of particulate organic fractions during thermal pretreatment. The hydrolysis ratio of VSS, protein, polysaccharide, and crude fiber was calculated by Eq. (1). *A* refers to VSS, protein, polysaccharide or crude fiber content in solid phase.

$$\text{Hydrolysis ratio of } A = (A_{\text{Before TH}} - A_{\text{After TH}}) / A_{\text{Before TH}} \times 100\% \quad (1)$$

2.3. Apparent molecular weight distribution

The apparent molecular weight distribution of the organic components in the supernatants was determined via ultrafiltration using low-organic-adsorption hydrophilic Millipore membranes in a 400 mL Amicon model 8400 stirred cell. Membranes with MWs of 1 (YM1), 5 (YM5), 10 (YM10), 30 (YM30), 100 (YM100), and 300 (PES300) kDa were prepared in a cascading series to decrease the risk of membrane clogging. Then, 300 mL of primary-filtered (0.45 µm) and diluted (100:1) supernatant were loaded for ultrafiltration. After 270 mL of effluent had passed through the membrane, the cell was depressurized and a retentate volume of 30 mL was collected. The procedure was repeated with all the membranes until sufficient retentate and permeate volumes were separated.

2.4. Biological methane potential (BMP) tests

To determine the biodegradability of the raw and thermally treated materials, BMP tests were conducted in 250 mL glass bottles at 35 °C. The inoculum sludge was obtained from a steady operation experimental reactor with a VS concentration of 35.5 g/L. Each bottle was fed with 150 mL of inocula, and the sub-inoculation ratio was 1:5. Distilled water was added to the bottle to obtain 180 mL of inocula. Each sample was tested triplicate. After inoculation, the pH was adjusted to 7.5 using 1 M sodium hydroxide or 1 M hydrochloric acid. The headspace of each bottle was flushed with nitrogen for 30 s, capped with butyl rubber plugs, and sealed with aluminum ring seals. The absolute methane composition was analyzed by gas chromatography (Shimadzu GC-2010) with a thermal conductivity detector and a Porapak N column.

2.5. Analytical methods

Total solid (TS), volatile solid (VS), suspended solid (SS), and volatile suspended solid (VSS) analyses were based on the Standard Analytical Methods promulgated by the National Environmental Protection Agency of China (1989). SCOD was measured using the Hach closed reflux method (APHA, 2005). The measurement of crude fiber and crude protein were according to ISO 6865:2000 and ISO1871:2009, respectively. Crude fat content was determined using soxhlet extraction method according to ISO 6492:1999. Carbohydrates were obtained based on the assumption that organic compounds was composed by carbohydrates, crude protein and crude fat. Polysaccharide was calculated by subtracting crude fiber from carbohydrates. Viscosity was measured by a rotational viscometer (NDJ-1). Dewaterability of MBWs and thermally hydrolyzed MBW (THMBW) samples were analyzed by a frame filter pressing system (pore size of filter, 20 µm) under 1 MPa of pressure for 40 min. Soluble sugar was measured via the anthrone method using D-glucose as a standard, and soluble protein was measured via the folin-phenol method using bovine serum albumin as a standard (Dreywood, 1946; Lowry et al., 1951). C, H, and N were analyzed by an elemental analyzer (EAI CE-

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