Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Conversion of sulfur compounds and microbial community in anaerobic treatment of fish and pork waste

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ARTICLE INFO

Article history:
Received 17 January 2018
Revised 1 March 2018
Accepted 4 April 2018
Available online xxxx

Keywords:
Volatile sulfur compounds
Fish and pork waste
Odor
Anaerobic treatment
Microbial diversity

ABSTRACT

Volatile sulfur compounds (VSCs) are not only the main source of malodor in anaerobic treatment of organic waste, but also pose a threat to human health. In this study, VSCs production and microbial community was investigated during the anaerobic degradation of fish and pork waste. The results showed that after the operation of 245 days, 94.5% and 76.2% of sulfur compounds in the fish and pork waste was converted into VSCs. Among the detected VSCs including H_2S, carbon disulfide, methanethiol, ethanethiol, dimethyl sulfide, dimethyl disulfide and dimethyl trisulfide, methanethiol was the major component with the maximum concentration of 4.54% and 3.28% in the fish and pork waste, respectively. The conversion of sulfur compounds including total sulfur, SO_4^{2-}-S, S^{2-}, methionine and cysteine followed the first-order kinetics. Miseq sequencing analysis showed that *Acinetobacter*, *Clostridium*, *Proteus*, *Thiobacillus*, *Hyphomicrobium* and *Pseudomonas* were the main known sulfur-metabolizing microorganisms in the fish and pork waste. The C/N value had most significant influence on the microbial community in the fish and pork waste. A main conversion of sulfur compounds with CH_3SH as the key intermediate was firstly hypothesized during the anaerobic degradation of fish and pork waste. These findings are helpful to understand the conversion of sulfur compounds and to develop techniques to control ordor pollution in the anaerobic treatment of organic waste.

1. Introduction

With the development of society and the increase of human being's living level, municipal solid waste (MSW) generation has been increasing quickly in China (Nie, 2010). In 2015, the collection and transportation amount of MSW was about 1.91×10^9 ton in China and more than 40% was kitchen waste (Qu et al., 2009; NBSC, 2016; Wang et al., 2016). Kitchen waste contains a high proportion of biodegradable organic compounds, and can therefore be treated by microorganisms. Anaerobic treatment including anaerobic digestion and anaerobic compost is a sustainable way to handle kitchen waste to produce energy (not only CH_4, but also H_2) and compost. Novel combined bioprocess and techno-economic feasibility have also been conducted to study biofuels production from kitchen waste (Han et al., 2015, 2016, 2017). Besides of the main components of CH_4 and CO_2, biogas from the degradation of kitchen waste includes some trace gases, such as NH_3, H_2S and volatile organic compounds (Staley et al., 2006; Font et al., 2011; Maulini-Duran et al., 2013). Some of the biogas components are toxic and pose a threat to ecological environment and human health (Durmusoglu et al., 2010; Font et al., 2011; Mustafa et al., 2017).

Volatile sulfur compounds (VSCs), including H_2S, methanethiol (CH_3SH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), carbon disulfide (CS_2) and ethanethiol (CH_3CH_2SH), are typical trace gases in the anaerobic degradation of organic waste. Although the concentrations of VSCs are low in biogas, VSCs constitute the main group of odorants emitted from the degradation of MSW, due to their low odor threshold (Scaglia et al., 2011; Fang et al., 2012). Of the odorous compounds identified from the trace component database as potentially present in biogas from landfills (landfill gas), H_2S, CH_3SH and CS_2 are the greatest potential compounds to cause Odor (Parker et al., 2002; Kim et al., 2005). VSCs can also cause diverse indirect health effects such as nausea and vomit, reaction of hypersensitivity, and even alteration in the respiratory model (Finkelstein and Benevenga, 1986; Yaegaki and Sanada, 1992; He et al., 2011). H_2S and CS_2 are listed the 25 most significant trace components in landfill gas assessed by toxicity (Parker et al., 2002).

During the anaerobic degradation of kitchen waste, VSCs are mainly produced from the degradation of organosulfur compounds such as methionine, cysteine as well as their derivatives methyl methionine and cysteine methyl ester (Kiene and Visscher, 1987;

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https://doi.org/10.1016/j.wasman.2018.04.006
0956-053X/

Smet et al., 1998; Lomans et al., 2002). The intermediate and end products of MSW in anaerobic treatment (mainly protein degradation) generate many types of VSCs. Methionine can be degraded by microorganisms such as *Pseudomonas putida* and *Brevibacterium linens* to produce VSCs such as CH_3SH, DMS, DMDS, dimethyl trisulfide (DMTS) and dimethyl tetrasulfide (DMTeS) (Ito et al., 1976; Amarita et al., 2004). H_2S, CH_3SH, DMS, DMDS and CS_2 are generated from the decay of food waste (snipe egg, mackerel, and squid) (Kim et al., 2009). These VSCs are continuously converted into each other by a combination of biological, chemical and geochemical processes (Lomans et al., 2002; Schäfer et al., 2010). For example, methanogens can reduce DMS to methane and CH_3SH, and the latter is subsequently disproportionated to methane, CO_2 and H_2S (de Bok et al., 2006; Higgins et al., 2006). *Methylophaga sulfidovorans*, an obligate methlotroph, can convert DMS to CS_2 and thiosulfate (de Zwart et al., 1996). DMS and CH_3SH can also be degraded by aerobic microorganisms (e.g. *Thiobacillus*, *Hyphomicrobium*) to sulfide and formaldehyde, which were further oxidized to SO_4^{2-} and CO_2 (Cho et al., 1991; Pol et al., 1994). In anaerobic treatment of kitchen waste, VSCs production and interconversion are dominated by biological processes. Microbial community and environmental factors play an important role in balancing VSCs formation, degradation and ventilation. However, little is known about the bioconversion of sulfur compounds and microbial diversity in the anaerobic degradation of kitchen waste. The information is important for cost-effective operation and optimization of anaerobic degradation of kitchen waste and to take technologies to control VSCs odor pollution.

Fish and pork waste is abundant in organosulfur compounds and is considered as the major source of VSCs in the anaerobic degradation of kitchen waste (Chen et al., 2017). Although there is no data about the production of fish and pork waste, the average purchase quantity of fish and pork is high and accounts for 16% in China (NBSC, 2016). Thus, in this study, fish and pork waste was chosen as the research object. The concentrations and production rates of VSCs were detected during the anaerobic degradation of fish and pork waste. The conversion of sulfur compounds (i.e. total sulfur (TS), SO_4^{2-}-S and S^{2-}) and its kinetics were evaluated, as well as the degradation of total amino acids and sulfur-containing amino acids including methionine and cysteine. Additionally, quantitative PCR (Q-PCR) and Miseq sequencing were applied to analyze microbial community and sulfur-metabolizing microorganisms in the anaerobic treatment of fish and pork waste.

2. Materials and methods

2.1. Experimental materials

The fish (silver carp hypophthalmichthys molitrix) and pork waste were collected from the student dining room of Zhejiang University. The fish and pork waste was both cut into about 1 cm and used for the experimental material. The total organic carbon (TOC) and total nitrogen (TN) contents of the original fish waste were detected as described by Bao (2005) and were 542.8 ± 1.7 and 140.1 ± 2.9 g $kg^{-1}_{dry\ weight}$ (g kg^{-1}_{dw}), respectively. The water content of the original fish waste was 79.1%. The TOC and TN contents of the original pork waste were 676.2 ± 3.09 and 120.1 ± 2.04 g kg^{-1}_{dw}, respectively. The water content of the original pork waste was 53.1%.

2.2. Experimental operation

The experimental microcosm of anaerobic treatment of fish and pork waste was constructed using 1 L glass bottle (Fig. 1). Each type of waste was filled into the glass bottle to about 80% volume. The loading amount of the fish and pork waste were 598.3 ± 2.3 and 738.5 ± 3.1 $g_{wet\ weight}$, respectively, due to the different densities of the fish and pork waste. Since the fish and pork waste was abundant in microbes, we did not add any inoculum. The bottles were blew with high purity N_2 (99.99%) at the flow rate of about 200 mL min^{-1} for ~10 min to remove the air and then sealed with butyl rubber stoppers. Two ports (about 0.8 cm) were installed in the butyl rubber stopper. One was for gas collection and the other was for gas sampling. Each of the experimental wastes was performed in twelve replicates. All the bottles were incubated at 30 °C. After balancing the gas pressure in the glass bottle with the atmospheric pressure at 30 °C for ~4 h, the gas production rate from the wastes was measured with the modified draining water gathering of gas law (i.e. saturated $NaHCO_3$ solution instead of water in this method) every day.

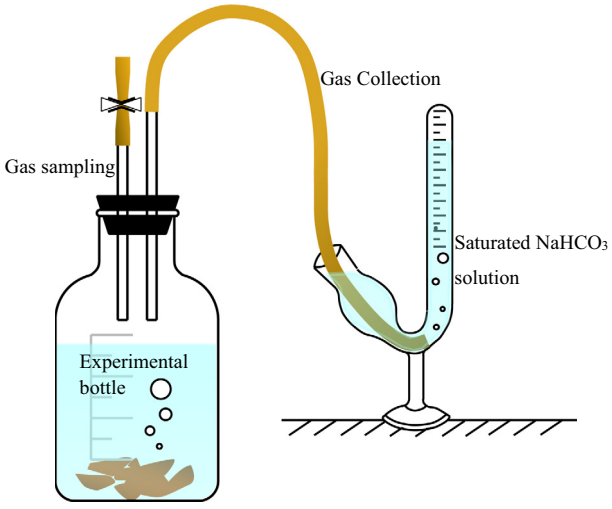

Fig. 1. The experimental diagram used in this study.

2.3. Analytical methods

Gas samples were collected from the headspace of the bottle for the analysis of VSCs on days 5, 20, 50, 110, 190 and 245, respectively. The main VSCs in the gas samples were detected by full-scan using a triple quadrupole-type mass spectrometry (MS) apparatus (Agilent 7890A GC and 5975C MS). The GC/MS was equipped with a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). He was used as carrier gas at a rate of 1.4 mL min^{-1}. The temperatures of the injector and detector were 200 and 280 °C, respectively. The oven temperature was increased from 38 to 280 °C at the rate of 10 °C min^{-1}. The concentrations of VSCs were detected using HC-3 trace sulfur analyzer and gas chromatograph (GC) equipped with a flame ionization detector (FID) as described by Chen et al. (2017).

Solid and liquid samples were collected destructively on days 5, 20, 50, 110 and 245, respectively. Each sampling point was collected in two replicates. The solid waste sample used for molecular analysis was kept at −70 °C. The other was kept at 4 °C for determining the moisture content as well as the contents of TOC, TN, TS, SO_4^{2-}-S, S^{2-} and amino acids. The water content was detected by drying to a constant weight at 105 °C. The TS content of the solid and liquid samples was detected by the turbidimetric method of sulfate after $HNO_3 + Mg(NO_3)_2$ oxidation (Bao, 2005). The contents of S^{2-} and SO_4^{2-}-S were detected according to the methods described by Qiu et al. (1992), respectively. The TOC and TN contents of the solid sample were determined by the methods described by Bao (2005). The content of amino acid was determined by Hitachi L-8900 amino acid analyzer. The sample for amino acids analysis was preheated with hydrochloric acid

Please cite this article in press as: He, R., et al. Conversion of sulfur compounds and microbial community in anaerobic treatment of fish and pork waste. Waste Management (2018), https://doi.org/10.1016/j.wasman.2018.04.006