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Degradation properties of protein and carbohydrate during sludge anaerobic digestion

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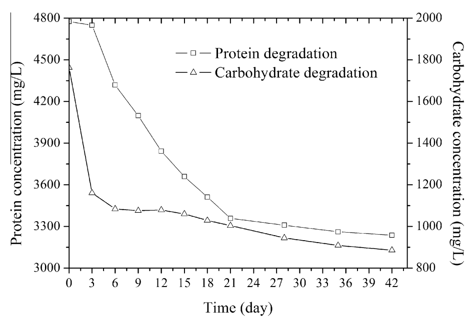
HIGHLIGHTS

- Carbohydrate and protein degradation properties were studied in detail.
- Carbohydrate was degraded prior to protein during sludge anaerobic digestion.
- The first 3 days were a lag phase for protein degradation.
- Protein degradation is a complex multi-stage process.
- Carbohydrate degradation is a stepwise process.

GRAPHICAL ABSTRACT



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ABSTRACT

Degradation of protein and carbohydrate is vital for sludge anaerobic digestion performance. However, few studies focused on degradation properties of protein and carbohydrate. This study investigated detailed degradation properties of sludge protein and carbohydrate in order to gain insight into organics removal during anaerobic digestion. Results showed that carbohydrate was more efficiently degraded than protein and was degraded prior to protein. The final removal efficiencies of carbohydrate and protein were 49.7% and 32.2%, respectively. The first 3 days were a lag phase for protein degradation since rapid carbohydrate degradation in this phase led to repression of protease formation. Kinetics results showed that, after initial lag phase, protein degradation followed the first-order kinetic with rate constants of 0.0197 and 0.0018 d^{-1} during later rapid degradation phase and slow degradation phase, respectively. Carbohydrate degradation also followed the first-order kinetics with a rate constant of 0.007 d^{-1} after initial quick degradation phase.

1. Introduction

Large amount of waste activated sludge has been generated in biological wastewater treatment processes (Wu et al., 2014; Zhang et al., 2008). Sludge has been a serious problem due to its great environmental risk and high cost for treatment and disposal (Wong et al., 2006). Anaerobic digestion is a widely used method to treat sludge with the purposes of mass reduction, organics stabilization, and energy (biogas) production (Carrère et al., 2010; Luostarinen et al., 2009). The essence of anaerobic digestion is degrading and converting the organic matters to biogas by microorganisms. The digestion process primarily occurs via macromolecular organic matter degradation. Protein and carbohydrate are the dominant macromolecular organic matters which account for more than 60% of the total organic matter of sludge (Neyens and Baeyens, 2003), so their degradation is vital for the digestion performance.

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Protein and carbohydrate degradation has been studied in sludge anaerobic digestion in literatures. Some researchers reported the degradation efficiency of these components after sludge anaerobic digestion. Pinnekamp (1989) observed that 39% of protein and 52% of carbohydrate was degraded after sludge anaerobic digestion. Bougrier et al. (2007) reported that the final degradation efficiency of protein and carbohydrate was 35% and 50%, respectively. Some studies investigated the impacts of various pretreatments on protein and carbohydrate degradation, e.g., acid pretreatment and thermal pretreatment. Devlin et al. (2011) reported that the degradation efficiency of protein and carbohydrate was improved 7% and 9% by acid pretreatment, respectively. Appels et al. (2010) observed that the final degradation efficiency of protein and carbohydrate was not enhanced by low temperature (60–90 °C) thermal pretreatment. The impacts of trace metals supplementation on protein and carbohydrate degradation were also investigated such as zero valent iron. Feng et al. (2014) reported that the final degradation efficiency of protein and carbohydrate increased from 59.1% to 67.8% and from 32.3% to 43.4% after sludge anaerobic digestion by addition of zero valent iron. In addition, Shao et al. (2013) compared the protein degradation between sludge anaerobic and aerobic digestion and found that sludge aerobic digestion was more efficient for protein degradation than anaerobic digestion. So far, most of previous studies centered on the degradation efficiency of protein and carbohydrate and achieving higher degradation efficiency by various methods. However, there are few studies focused on the detailed degradation properties of protein and carbohydrate during sludge anaerobic digestion process.

In order to gain insight into organics removal during sludge anaerobic digestion and provide some basis to improve sludge anaerobic digestion efficiency, protein and carbohydrate degradation properties and their degradation interactions were investigated in detail in this study. Protein and carbohydrate degradation kinetics were evaluated. In addition, relationship between protein and carbohydrate degradation and biogas production was also analyzed.

2. Methods

2.1. Sewage sludge

Sludge sample used in this experiment was collected from the secondary settling tank of a municipal wastewater treatment plant in Beijing, China. The sludge sample was thickened by gravity settling. Then, in order to maintain the sample freshness, it was stored at 4 °C prior to use. Characteristics of the sludge were as follows (average value): total chemical oxygen demand (TCOD) of 26,575 mg/L; soluble chemical oxygen demand (SCOD) of 137 mg/L; total solids (TS) of 28,767 mg/L; volatile solids (VS) of 19,767 mg/L; protein of 8312 mg/L; carbohydrate of 4816 mg/L; and pH of 7.15. Clearly, protein and carbohydrate counted for 2/3 of the total organics in the sludge. The inocula for anaerobic digestion were obtained from a mesophilic anaerobic digester in the same wastewater treatment plant.

2.2. Anaerobic digestion experiments

Batch anaerobic digestion tests were carried out using 1 L serum bottles. Each serum bottle was filled with 66 mL of inoculum and 200 mL of substrate. In order to facilitate analysis, 300 mL of Milli-Q water was added into each reactor. After the mixture of inocula and substrate, the reactor was flushed with N_2 gas for 10 min to establish an anaerobic condition. Then, all reactors were performed at 36 ± 1 °C in a water bath with agitation at a speed of 100 rpm.

2.3. Analytical methods

TS, VS and NH_4^+-N were analyzed according to the standard methods given in APHA (APHA, 2005). The pH and COD were measured by a pH tester and a COD meter (CTL-12, Huatong Inc., China), respectively. The sludge sample was centrifuged for 10 min at 12,000 rpm with a centrifuge (TGL16, Yingtai Inc., China) and immediately filtered through 0.45 μm membrane for analyzing SCOD. Before the TCOD determination, the sludge samples were treated with a 0.5 mol/L NaOH solution for 24 h, and then filtered through 0.45 μm membrane (Fang et al., 2014). Protein was measured according to the Bicinchoninic Acid (BCA) method (Lowry et al., 1951). Carbohydrate was analyzed using the phenol-sulfuric acid method (Dubois et al., 1956). Volatile fatty acid (VFA, including acetic acid, propionic acid, iso-butyric acid, butyric acid, iso-valeric acid and valeric acid) were measured by a gas chromatograph (SP-3420A, Beifenruili Inc., China). The operating temperatures for the injection port and the detector were 210 and 250 °C, respectively. The column temperature was 100 °C (1 min hold), increased at 10 °C/min to 210 °C (1 min hold). N_2 was the carrier gas at a flow rate of 30 mL/min. The biogas volume was measured by the displacement of HCl solution with pH of 3.

3. Results and discussion

3.1. Performances of sludge anaerobic digestion

The pH value is one of the most significant parameters during sludge anaerobic digestion. The appropriate pH value for fermentative microorganisms and methanogens is in the range of 5.0–8.5 and 6.5–7.8, respectively (Fang et al., 2014). As shown in Fig. 1a, the pH value remained in the range of 6.8–7.8 during most of digestion time.

Ammonia is an inhibitor during sludge anaerobic digestion. As shown in Fig. 1b, NH_4^+-N showed increasing trend during sludge anaerobic digestion due to the degradation of nitrogenous organic matters (Kayhanian, 1999). Concentrations of NH_4^+-N ranged from 45 to 285 mg/L in this study which were beneficial to the digestion process (Chen et al., 2008).

The VFA concentration is also a significant parameter during sludge anaerobic digestion. The VFA concentration increased significantly during the first 6 days as shown in Fig. 1c. This was due to micro-molecular organics transformation into VFAs by acidogenic micro-organisms. After 6 days digestion, VFA concentration decreased to a very low level since VFAs were transformed by methanogenic micro-organisms into CO_2 and CH_4.

The total cumulative biogas production and VS removal after sludge anaerobic digestion were 720 mL (Fig. 2) and 34.1%. Generally, VS reduction was in the range of 30–45% during sludge anaerobic digestion (Habiba et al., 2009). Moreover, the CH_4 and CO_2 contents in biogas ranged from 50% to 65% (v/v) and from 35% to 50% (v/v) during sludge anaerobic digestion, which were within the range reported by previous studies (Li et al., 2014; Zhang et al., 2012). These results indicated that the operational conditions were good (Appels et al., 2011) and the sludge anaerobic digestion was successful.

3.2. Protein and carbohydrate degradation during sludge anaerobic digestion

Fig. 3 shows the evolution of protein and carbohydrate concentrations during sludge anaerobic digestion. After sludge anaerobic