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Insights into anaerobic transformation of key dissolved organic matters produced by thermal hydrolysis sludge pretreatment

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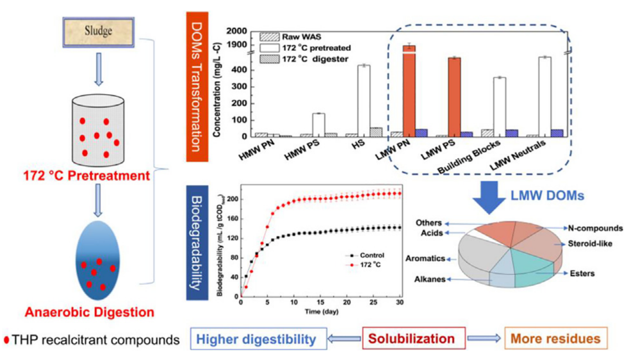
GRAPHICAL ABSTRACT



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ABSTRACT

The detailed dissolved organic matters (DOMs) profile by thermal hydrolysis pretreatment and their transformation during anaerobic digestion (AD) were investigated. Among the temperature tested, 172 °C treatment showed the best sludge solubilization and the maximum methane production. The study revealed that high temperature sludge pretreatment mainly improved the release of low molecular weight (LMW) proteins, LMW neutrals and LMW polysaccharides. Notably, the effluent from thermal treated sludge digesters contained more DOMs residues. The predominant residual DOMs were humic substances, LMW proteins and LMW neutrals. At the molecular level, over 50% of the residual LMW components were slowly biodegradable or nonbiodegradable steroid-like compounds and aromatics. Further profiling of the higher MW compounds detected the recalcitrant or inhibitory compounds, e.g. benzenoids, flavonoids, pyridines and their derivatives. It is recommended that polishing step should be considered to further reduce the refractory residues in AD liquor.

1. Introduction

Sewage sludge generated from the wastewater treatment plants (WWTPs) has been a big issue due to the limited treatment techniques and strict environmental regulations for sludge disposal (Eshtiaghi et al., 2013). The operation cost for sludge treatment is up to 50% of the total investment in WWTPs (Hii et al., 2014; Kroiss, 2004). To compensate the high cost, anaerobic digestion (AD) has been implemented to stabilize sludge and recover energy (Coelho et al., 2011). As an environmentally friendly method, AD can effectively remove the odor,

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pathogens and organics, as well as generate biogas energy. However, the rate-limiting step of hydrolysis introduces the inevitable drawbacks of the process, which needs very long sludge retention time (large reactor volume) and thus hinders the application of AD technology (Ruiz-Hernando et al., 2014).

To accelerate the hydrolysis efficiency thus improve the subsequent AD performance, various pretreatment methods prior to AD have been studied, such as thermal hydrolysis, mechanical, chemical and biological pretreatment (Kim et al., 2010; Park and Kim, 2015; Wilson and Novak, 2009). Among them, thermal hydrolysis pretreatment (THP) has been successfully installed at the full scale for more than a decade (Pilli et al., 2014). Generally, THP can be categorized into high temperature hydrolysis pretreatment and low temperature thermal pretreatment. It is reported that AD performance and sludge dewaterability were likely to be enhanced with the elevated high temperature from 100 to 180 °C (Li et al., 2017a). One of the well-known high temperature THP processes is CAMBI, where sludge is heated up to around 170 °C by direct steam injection (Han et al., 2017). It has various inherent merits in sludge treatment, e.g. higher volatile solids (VS) reduction, enhanced biodegradability, improved dewaterability and reduced viscosity (Carrere et al., 2008; Ennouri et al., 2016; Li and Noike, 1992). Temperature above 180 °C is not favorable which may produce more refractory compounds and reduce the sludge biodegradability (Abe et al., 2013; Bougrier et al., 2008; Stuckey and McCarty, 1984). Meanwhile, the low temperature pretreatment (below 100 °C) has also been developed considering the concerns of huge energy consumption (Appels et al., 2010). Certainly, different temperature will have different treatment mechanisms on sludge. It was proposed that solubilization of exo-polymeric substances (EPS) may be dominant under the lower temperature ($<$ 121 °C) while liberation of intracellular components may become prevalent under high temperature ($>$ 121 °C) with the elevated percentages of cells rupture (Ennouri et al., 2016). However, the true mechanisms and the profiles of solubilized organic matters under different temperature have not yet been confirmed. This study selected low, medium and high temperature (70, 121 and 172 °C) thermal treatment methods for comparison.

THP is particularly effective in treating waste activated sludge (WAS), which consists of considerable not easily biodegradable bacterial cells (Barber, 2016). These cells have a sturdy structure of EPS which protects the cells from the hydrolytic enzyme and other attacks from outside (Toreci et al., 2009). The major components of EPS, i.e. proteins (PN), polysaccharides (PS) and humic acid (HA), amount differently in different sludge flocs layers, and EPS in these layers can be characterized as soluble EPS (SB EPS), loosely bound EPS (LB EPS) and tightly bound EPS (TB EPS). Yu et al. (2008) reported that the location of the dominate EPS components in different EPS fractions will affect their accessibility and biodegradability.

Dissolved organic matters (DOMs) of sludge are directly accessible to bacteria in comparison with particulates. It is known that DOMs generated with different sludge pretreatment methods may have different distributions and fate. However, previous studies mainly focused on either qualitative or semi-quantitative characterization of the overall DOMs in EPS matrix, without a comprehensive analysis of the specific key compounds. Further, the transformation of solubilized DOMs during thermal pretreatment and subsequent AD process is not clear.

Hence, this study aimed to analyze the generation of DOMs with low, medium and high temperature thermal pretreatment, investigate the transformation of these compounds during AD process, and identify the residual compounds after AD process. The solubilization and biodegradability of WAS with different thermal treatments were compared and discussed. Characterization of DOMs was carried out using size exclusion chromatography (SEC) coupled with organic carbon detection and organic nitrogen detection (LC-OCD-OND) (DOMs sub-fractions analysis), Gas Chromatography–Mass Spectrometry (GC–MS) (volatile low molecular weight (LMW) components analysis), and Ultra Performance Liquid Chromatography–Mass Spectrometry (UPLC-MS) (unbiased comprehensive untargeted analysis of the higher MW organics). This study provided fresh insights of thermal pretreatment prior to AD with respect to the fate and transformation of DOMs in sludge treatment process.

Table 1
Characteristics of raw sludge and seed sludge.

	Units	Seed sludge	Raw sludge
Total solids (TS)	g/L	15.02 ± 0.25	13.13 ± 0.15
Volatile solids (VS)	g/L	11.24 ± 0.13	10.65 ± 0.21
Total suspended solids (TSS)	g/L	14.12 ± 0.20	12.27 ± 0.12
Volatile suspended solids (VSS)	g/L	10.60 ± 0.21	10.21 ± 0.16
Total chemical oxygen demand (tCOD)	g/L	15.17 ± 0.23	14.37 ± 0.29
Soluble chemical oxygen demand (sCOD)	g/L	0.26 ± 0.11	0.24 ± 0.10
Protein (PN)	mg/L	96.24 ± 2.47	89.91 ± 3.43
Polysaccharide (PS)	mg/L	54.43 ± 1.12	45.06 ± 1.75
pH	1	7.44 ± 0.02	6.46 ± 0.02

2. Materials and methods

2.1. Sludge source

The WAS from a local wastewater treatment plant in Singapore was collected as the feed sludge. It was concentrated and stored at 4 °C before use. Anaerobic sludge from the same plant was used as the seed sludge for AD. The properties of sludge samples are presented in Table 1.

2.2. Reagent and chemicals

Acetone, n-hexane, chloroform and dichloromethane (GC–MS grade) were purchased from Merck KGaA (Germany). Isopropanol, acetonitrile, methanol and water (LC-MS grade) were purchased from Sigma-Aldrich (US). Ammonium formate and formic acid were purchased from Sigma-Aldrich (US). The alkane standard mixture of C10–C40 (50 mg/L) was purchased from Sigma-Aldrich (US). Ultrapure water was obtained from a Milli-Q water process (Millipore Advantage A10, Merck, France).

2.3. Sludge pretreatment

The pretreatment at 70 °C was carried out in a water bath for 30 min. The pretreatment at 121 °C was carried out in a vertical pressure steam sterilizer (HG-50, Hirayama Manufacturing Corporation, Japan) for 30 min. The pretreatment at 172 °C was carried out in a pressure reactor (Model 4534, Parr Instrument Company, US), where the temperature was controlled at 172 ± 3 °C for 30 min. All the pretreated sludge was cooled down to the room temperature before DOMs characterization and use in AD. Triplicates were conducted for each temperature pretreatment and each replicate was characterized separately. The three replicates were then mixed together and used as feed sludge for AD.

2.4. Anaerobic digestion process

An automatic methane potential test system (AMPTS II, Bioprocess Control Company, Sweden) was used to carry out AD experiments. 1.5 g $tCOD_{feed}$/g VSS_{seed} was chosen as the optimal organic loading. Each reactor had a working volume of 400 mL and a headspace of 150 mL. All reactors with sludge were purged with nitrogen gas for 10 min and sealed immediately to induce the anaerobic environment. The AD reactors were all operated at 35 °C for about 30 days with the semi-continuous stirring. Control reactors were conducted with raw sludge as the feed sludge. Blank reactors with only seed sludge and deionized