Bioresource Technology 200 (2016) 579–586

Contents lists available at ScienceDirect

Bioresource Technology

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

Alkali-solubilized organic matter from sludge and its degradability in the anaerobic process

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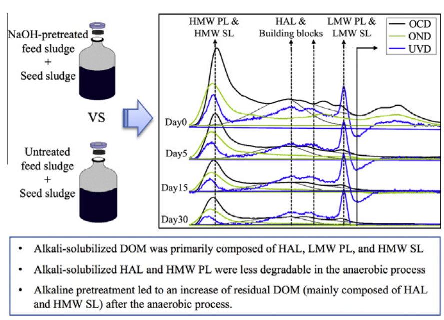
HIGHLIGHTS

- DOM composition of pretreated sludge defines its anaerobic biodegradability.
- Alkaline pretreatment was effective at releasing dissolved organic matter (DOM).
- Alkaline pretreatment improved the anaerobic degradability of DOM.
- Humic-acid-like (HAL) and high MW protein-like substances were more refractory.
- Alkaline pretreatment led to an increase of residual DOM in the anaerobic process.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 August 2015
Received in revised form 24 October 2015
Accepted 26 October 2015

Keywords:
Dissolved organic matter
Anaerobic degradability
LC-OCD-OND
EEM–FRI
FT-IR

ABSTRACT

This study investigates alkali-solubilized dissolved organic matter (DOM) and its fate in the anaerobic treatment process. DOM was fractionated into high molecular weight (HMW) protein-like substances (PL), HMW saccharide-like substances (SL), low molecular weight (LMW) PL, LMW SL, and humic acid-like substances (HAL). The results indicate alkali-solubilized DOM is primarily composed of LMW PL, HMW SL, and HAL. Alkaline pretreatment improved the overall anaerobic degradability of DOM in sludge (removal efficiency of total DOM increased by 28.4%). However, certain DOM fractions (mainly HMW PL and HAL) exhibited low degradability during anaerobic treatment, primarily caused by the low degradability of aromatic groups (such as aromatic amine groups from tryptophan-like PL). Alkaline pretreatment also resulted in an increase of residual DOM, which is mainly composed of HAL (52.9%) and HMW SL (49.9%).

1. Introduction

Anaerobic processes have been widely applied for the mineralization of sludge and recovery of energy (Bruni et al., 2010). However, anaerobic degradation of sludge is limited by the rupture of microbial cells, solubilization of dissolved organic matter (DOM), and decomposition of high molecular weight (HMW) DOM (Carrère et al., 2010; Müller et al., 2004). Alkaline pretreatment is an efficient method to solubilize DOM and enhance methane generation (Li et al., 2015). However, the characteristics of alkali-solubilized DOM and its transformation and degradation are still ambiguous. Alkali-solubilized DOM represents the biodegradability of sludge as it contains the readily usable carbon

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http://dx.doi.org/10.1016/j.biortech.2015.10.083
0960-8524/

source which can be directly converted by microorganisms to methane (Xue et al., 2015). On the other hand, some refractory DOM may affect the process efficiency or form toxic by-products in anaerobic processes (Carlsson et al., 2012; Tran et al., 2015). Hence, characterization of DOM could largely improve the understanding of the impacts of alkaline pretreatment on anaerobic treatment of sludge and could be used to predict methane generation, process efficiency, residual composition, and effluent toxicity in anaerobic processes.

In previous studies, alkali-solubilized DOM has been investigated by various analytical methods (Zhang et al., 2015). However, most of these studies provided inadequate or inaccurate information. For instance, protein assay could be interfered by humic acid-like compounds (HAL), peptides, amino acid, and other low molecular weight (LMW) compounds (Vakondios et al., 2014), but most previous studies have neglected such interference (Kunacheva and Stuckey, 2014). In addition, previous studies mainly focused on the characteristics of overall DOM without prior fractionation (Carlsson et al., 2012). This could limit the understanding of the fate of DOM. For instance, the degradability of alkali-solubilized refractory DOM was largely affected by its molecular weight (Monlau et al., 2013). Hence a prior fractionation of DOM based on its molecular weight is necessary. Size-exclusion chromatography (SEC) can fractionate DOM based on differences in molecular weights (MW) (Stewart et al., 2013). However, traditional detection units (such as UV detector) for SEC provide very limited information on the chemical characteristics of DOM (Kunacheva and Stuckey, 2014).

Recently, new methods have been developed based on the Lowry method and Frølund modification for simultaneous measurement of proteins and humic matter, where interference of HAL on the quantification of protein-like compounds (PL) was minimized (Vakondios et al., 2014). SEC coupled with organic carbon detection and organic nitrogen detection (SEC-OCD-OND, or LC-OCD-OND) have been applied to measure the concentration of biopolymers, HMW PL, HMW SL (such as polysaccharides), HAL, building blocks, LMW DOM, and total dissolved organic carbon (DOC) (Stewart et al., 2013). By combining spectrophotometric measurements of PL, HAL, and SL and SEC-OCD-OND, the concentrations of HMW PL, HMW SL, LMW PL, and LMW SL can be estimated. The excitation–emission matrix coupled with fluorescence regional integration (EEM–FRI) technique can semi-quantify several DOM sub-fractions (such as tyrosine-like proteins, tryptophan-like proteins, fulvic acid-like materials, microbial byproduct-like materials, HAL, etc.) and provide insights into the transformation of DOM in sludge treatment processes (Chen et al., 2003). Fourier transform infrared spectroscopy (FTIR) can qualify and semi-quantify the specific functional groups of DOM (Li et al., 2014). Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) can trace the fate of each individual DOM (Schneider and Riedel, 2010). These methodologies can help to develop a better understanding of the fate of alkali-solubilized DOM in the anaerobic process.

The objectives of this study are to investigate the alkali-solubilized dissolved organic matter (DOM) and its fate in the anaerobic process. Combined SEC-OCD-OND and spectrometric measurement of PL, SL, and HAL, and the fate of several DOM fractions were also looked into. In addition, the transformation of DOM in the anaerobic process was investigated by EEM–FRI, FT-IR, and MALDI-TOF-MS. This study can help develop better understanding of the mechanism, merits and demerits of alkaline pretreatment, and help in the design of more efficient sludge treatment and post treatment processes. In addition, the methodology applied in this study can be expanded to investigate the fate of DOM fractions arising from other sludge treatment processes.

2. Methods

2.1. Feed sludge and seed sludge

The feed sludge (FS) was dewatered sludge from an industrial wastewater treatment plant. The anaerobic seed sludge (SS) was obtained from a mesophilic anaerobic digester at a local municipal wastewater treatment plant. The degassing and storage of SS were performed based on a previous study (Li et al., 2015). Physicochemical parameters of the FS and degassed SS are listed in Table 1.

2.2. Pretreatment of sludge

Alkaline pretreatment was carried out based on a previous study (Li et al., 2015). The NaOH dosage was set to 0.1 g NaOH per g feed volatile solids (g-NaOH/VS).

2.3. Anaerobic treatment experiment

The anaerobic treatment tests were performed based on previous studies (Li et al., 2015). Briefly, the total volume of a serum bottle was 300 mL, with 200 mL working volume and 100 mL headspace. The organic loading ratio was 1.5 g total feed chemical oxygen demand per g seed volatile suspended solids (g-TCOD/g-VSS). Samples were collected at day 0, day 5, day 15, and day 30 of the anaerobic process test. Control tests were carried out with unpretreated FS. Experiments were carried out in triplicate.

2.4. Sample characterization

2.4.1. PL, HAL, and CL measurements by spectrophotometric method

Total SL (both HMW SL and LMW SL) concentration measurement was performed in accordance with the Phenol–Sulphuric Acid method (Dubois et al., 1956), where Glucose was used as the standard. Total PL (HMW PL and LMW PL) and HAL concentrations were measured using the modified Lowry method (Frølund et al., 1995). Commercially supplied bovine serum albumin (BSA) (Sigma–Aldrich® Co. LLC, UK) was used as standard. This method was based on the fact that the addition of Cu (II) ion increased the absorbance of PL solution at 750 nm by a factor of about 5, while absorbance of HAL solution would not be affected. Two different measurement methods for each sample were employed. Accordingly, the relationships between absorbance of standard samples (A_{WithCu} and $A_{WithoutCu}$), PL concentration (C_{PL}), and HAL concentration (C_{HAL}) could be established (Frølund et al., 1995). Based on the assumption that the general chemical formulae of SL, PL, and HAL are represented by $(C_6H_{10}O_5)_n$ (Staff, 1996), $C_{52.5}$-$H_{6.65}N_{16.0}O_{21.5}S_{2.0}$ (Satyanarayana, 2014), and $C_{48.3}H_{6.8}N_{7.2}O_{37.1}S_{0.9}$-$Ash_{1.7}$ (Amir et al., 2010), 1.000 g of SL, PL, and HAL shall be equal to 0.444, 0.497, and 0.435 g of equivalent carbon respectively.

2.4.2. Size-exclusion chromatography-organic carbon detection-organic nitrogen detection

A size-exclusion chromatography-organic carbon detection-organic nitrogen detection (LC-OCD-OND) system (DOC-LABOR,

Table 1
Physicochemical characteristics of FS and SS.

Characteristics	Seed sludge, g/L	Feed sludge, g/kg
TCOD	15.5	52
SCOD	0.3	2
Total solids (TS)	15.8	58
Volatile solids (VS)	11.5	54
Total suspended solids (TSS)	14.5	NIL[a]
Volatile suspended solids (VSS)	11.0	NIL[a]

[a] These values are not available, as feed sludge was in solid state.