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The molecular weight distribution of dissolved organic carbon after application off different sludge disintegration techniques

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ABSTRACT

The effect of sludge disintegration on molecular weight distribution of dissolved organic carbon (DOC) is demonstrated by size exclusion chromatography with online organic carbon detection (SEC-OCD). Ozone, ultrasound and sodium hydroxide were used to disintegrate excess sludge. Significant differences on the molecular weight distribution of the released DOC were found for the different treatments. Ozonation did not change the DOC distribution based on the molecular size, compared to untreated sludge. Small molecular weight compounds were the dominant constituents solubilized by sodium hydroxide treatment. Ultrasound disintegrated the sludge flocs and dissolved large molecules into the sludge liquid phase. Especially for sodium hydroxide and ultrasound treatment the analysis with SEC-OCD clearly shows the preferential fractions of organic carbon, which are more quickly transferred to methane in batch anaerobic experiments. For sodium hydroxide, it is the small molecular weight fraction as for ultrasound treatment the degradation is evenly distributed throughout all weight fractions.

1. Introduction

In wastewater treatment, anaerobic stabilization of excess sludge is one of the favored biological processes. The main benefits of this process are reduction of sludge solids and production of biogas as a renewable energy [1–3]. To stabilize the sludge in anaerobic digestion the first step is destruction of the sludge flocs, release of large molecular weight compounds and make them more accessible to anaerobic bacteria to hydrolyze them into smaller molecules. However, hydrolysis of large molecular weight compounds is often assumed the rate-limiting step in anaerobic digestion, which governs biodegradability of organic matter and finally methane production [4,5]. To accelerate the hydrolysis step several sludge pre-treatment methods have been proposed. Among these methods ultrasound, ozone, alkaline treatment with sodium hydroxide or a combined thermo-chemo-sonic disintegration have been reported to be the very promising techniques [6–10].

Ultrasound, ozone and alkaline treatment have different sludge disintegration mechanisms. Previous studies mainly focused on determining the optimum range of ultrasound specific energy, ozone consumption and sodium hydroxide concentration, which could enhance methane production [11–14]. Kavitha et al. compared different disintegration technics by using the energy input as parameter, they found COD solubilization between 11.6 and 34% for a range of specific energy between 7.4 and 24.6 kJ/g TS [15]. Most studies dealing with disintegration have assessed sludge pretreatment performance by analyzing sum parameters such as increase of the SCOD (soluble chemical oxygen demand) or decrease of total solids (TS) of the sludge. Due to the different sludge disintegration mechanisms, released organic carbon would have different characteristics, which could not be explained by sum parameters. Molecular weight of organic compounds present in excess sludge is an important parameter and might highly influence the reaction rate of hydrolysis. Size exclusion chromatography (SEC) is a method in which molecules are separated by their size [16]. In principle, the retention times obtained for SEC columns are inversely correlated with the molecular size and in good approximation with the molecular weight of the eluted substances. Application of this chromatographic technique provides additional information on the differences in the molecular weight distribution of dissolved organic carbon (DOC) released after different sludge disintegration methods and would help to understand better the effect of each pretreatment method on methane production. However, few studies have investigated sludge solubilization with emphasis on the molecular weight of the released organic compounds. Tian et al. studied molecular weight distribution of solubilized substances after the application of ultrasound and ozone [17]. The results demonstrated that both treatments solubilized high molecular weight (HMW) compounds into the liquid phase. On the

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other hand, ozonation of sonicated sludge resulted in degradation of HMW compounds to smaller molecules contributing to increase the methane production. Furthermore, Tian et al. used SEC to differentiate the fractions, which can be dissolved from excess sludge by hydrolysis and ultrasound [18]. The authors showed that a combination of alkaline-ultrasound treatment was beneficial for the subsequent anaerobic digestion. This improvement was attributed to hydrolysis of macromolecules to smaller organic compounds by alkaline treatment [19]. Xiao et al. used SEC combined with the extraction of extracellular polymeric substances (EPS) to identify the molecular weight distribution of dissolved organic carbon (DOC) after treatment of activated sludge with ultrasound and acidification [20]. In 2017 the same group observed two fractions of proteins (0–20 kDa and > 20 kDa) with SEC after treatment of activated sludge [21]. They found the low molecular size fraction to be dominant for ultrasound, alkaline and thermal treatment. Another group applied membrane filtration with a range of different molecular weight cut-off to separate the products from microwave irradiation and conventional heating (96 °C) of activated sludge. The different fractions were then used to identify the contribution of different molecular weight compounds to methane production during anaerobic treatment [22]. Due to the complexity of excess sludge, there is still a relative lack of knowledge on the molecular weight distribution of DOC released after different disintegration mechanisms. Besides, changes in molecular weight distribution of DOC during anaerobic digestion and its influence on methane production has not been reported in previous studies.

The aim of this study is to compare the solubilization of organic carbon due to sludge disintegration by ozone, sodium hydroxide and ultrasound, with respect to molecular weight distribution of the released DOC. Size exclusion chromatography with online organic carbon detection (SEC-OCD) was conducted to separate the released organic carbon based on the molecular size. The effect of each pretreatment method on the performance of anaerobic digestion was assessed by analyzing the biodegradability of the dissolved organic carbon and methane production during five days. In parallel, the removal of the different fractions of dissolved organic carbon was monitored during the anaerobic digestion with SEC-OCD.

2. Material and methods

2.1. Sludge sources

Experiments were carried out with excess sludge obtained from a municipal wastewater treatment plant in Heidelsheim, Germany. The plant works on the principle of conventional activated sludge. Excess sludge is characterized by the total solids (TS) of 6 ± 1 g/L and total chemical oxygen demand (TCOD) of 6.3 ± 1 g/L. The samples were collected weekly and stored in refrigerator at 4 °C until use within 24 h. The anaerobic digested sludge (inoculum) was collected from the anaerobic digester working under mesophilic conditions (37 °C). TS and TCOD of the inoculum were 21 ± 1 g/L and 23 ± 6 g/L respectively.

2.2. Sludge disintegration methods

Ozone was generated from pure oxygen (99.5% purity) with an Ozomat COM ozone generator (ANSEROS Company, Germany). 0.5 L of sludge sample was placed in a reactor (V = 1.5 L) and ozonated for different time intervals from 0 to 120 min. To provide an effective contact between ozone and sludge flocs as well as favoring the oxidation of organic matter, a diffuser was installed on the bottom of the reactor. Ozone gas with a concentration of 40 mg/L and a flow rate of 45 L/h was fed to the reactor. The ozone concentration in the gas phase after a certain time of reaction with sludge was measured with the UV (ultra violet) analyzers. Ozone consumption was calculated from the difference for ozone at the inlet and outlet of the reactor per dry weight of initial TS in the sludge. To evaluate the performance of sludge ozonation, excess sludge was disintegrated under different ozone consumptions varied from 0.005 to 0.16 g O_3/g TS. The optimum ozone consumption was determined based on the sludge solubilization and mineralization.

Sonication was performed with ultrasound of type SONOPULS Ultrasonic homogenizer HD 3200 (Bandelin electronic GmbH & Co.KG, Germany). A Rosett cell RZ5 was used for an intensive and uniform sonication of the sample (Bandelin electronic GmbH & Co.KG, Germany). The sludge (V = 0.5 L) was filled in the cell, ultrasound probe was placed in the center and immersed 1 cm into the sample. Sludge was pretreated for 7 min at 20 kHz frequency with the input power of 120 W resulted in specific energy input of 16.8 kJ/g TS.

Sodium hydroxide was dissolved in deionized water to make a solution of 0.1 mol/L. 200 mL of the solution was introduced to 0.5 L of sludge resulting in 0.2 g NaOH/g TS concentration or 0.03 mol/L dosage at pH = 12.5. The sludge was mixed at around 200 rpm and the duration of treatment was 2 h. Prior to sample analyses and methane production, pH of the alkalized sludge was adjusted to about seven, using hydrochloric acid. The latter is necessary to properly run the SEC.

2.3. Anaerobic digestion

An automatic methane potential test system (AMPTSII, Bioprocess Control AB, Sweden) was conducted for anaerobic digestion experiments. A detailed description of the system can be found in Badshah et al. [23]. Untreated sludge and disintegrated sludge (substrate) were centrifuged at 8000 rpm for 10 min, 300 mL of the supernatant from each substrate was mixed with 100 mL anaerobic digested sludge (inoculum) in a reactor. The inoculum was pre-incubated for 5 days at test temperature (37 °C) to deplete residual biodegradable organic matter present in it [24]. The experiments were carried out in triplicates for each substrate under mesophilic conditions (37 °C). The methane production was monitored daily for 5 days. To study the effect of each disintegration method on the biodegradability of the released organic carbon and on the methane production, samples were taken from each reactor at the beginning, after one and after five days of anaerobic digestion and were analyzed with SEC-OCD. For the supernatant of untreated and ozonated sludge anaerobic digestibility experiments were repeated four times and for the supernatant of the sludge pretreated with sodium hydroxide and ultrasound two times. The entire scheme of sludge disintegration and anaerobic digestion experiments together with size exclusion chromatography and online organic carbon detection (SEC-OCD) is shown in Fig. 1.

2.4. Analytical methods

TS were measured according to the DIN 38 414 [25]. To analyze dissolved organic carbon (DOC), sludge samples were centrifuged at 8000 rpm for 10 min and the supernatant of the sludge was filtered through 0.45 µm polyether sulfone (PES) membrane filter. To determine sludge solubilization, DOC of the samples was analyzed using TOC-VCSN (Shimadzu, Japan). Sludge solubilization is represented by the amount of DOC released after disintegration per amount of ozone consumed by TS in the sludge and calculated as follows:

$$\text{Sludge solubilization, mg } DOC_{released}/\text{g O3 g TS} = \frac{DOC_{O_3} - DOC_0}{O_3 \cdot TS \cdot V}$$

where DOC_{O3} and DOC_0 are the DOC of the filtered supernatant of ozonated sludge and untreated sludge (mg/L). O_3 is the amount of ozone consumed by sludge during the disintegration process (g), TS is the total solid of sludge before ozonation (g/L) and V is the volume of the sludge (L).

Total chemical oxygen demand (TCOD) was measured according to the German DIN ISO 15705 [26]. Due to the oxidation effect of ozone, there is a reduction in TCOD, which is represented as sludge mineralization and calculated as follows: