Characteristics of Organic Matters During Anaerobic Digestion of Ultrasonically Pretreated Sludge and the Effects on Sludge Dewaterability

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1. INTRODUCTION

MORE and more excess sludge is produced in biological wastewater treatment (BWT) systems in recent years. Normally, the excess sludge handling and disposal account for 50–60% of the total construction and operation costs of whole wastewater treatment plants (WWTPs) [1]. Anaerobic digestion and dewatering of sludge are two widely used methods to reduce the volume of excess sludge [2,3]. Whereas, the digestion efficiency was limited and the sludge dewaterability would become poor because of the increase in fine particle part during anaerobic digestion [4]. In order to improve the anaerobic digestion efficiency, ultrasound as the pretreatment for digestion had been studied previously [5]. However, information regarding the sludge dewaterability of anaerobic digestion followed by the ultrasound pretreatment is still largely lacking.

Size exclusion chromatography (SEC) technique was previously applied to investigate the compositions and characteristics of dissolved organic matters (DOM) from nature water or landfill leachate or aquatic and terrestrial systems [6,7]. To the best of our knowledge, no previous work has yet been done to evaluate the sludge dewaterability by this technique. The purposes of this work were to investigate the variations of organic matters and sludge dewaterability during anaerobic digestion and further explored the relationship between the sludge dewaterability and molecular weights (MW) in the different fractions of sludge flocs.

2. MATERIALS AND METHODS

2.1. Sludge Sample

The activated sludge sample was collected from the aerated basin of a municipal WWTP in Shanghai, China. This plant treats 75,000 m³/d of wastewater (93% from domestic and 7% from industrial origin) using anaerobic-anoxic-oxic process. They were transported to the laboratory within 30 min after sampling and settled for 1.5 h at 4°C with supernatant decant, then the sludge sediments were collected and screened through a 1.2-mm screen and subsequently centrifuged at 1500 r/min for 10 min with supernatant decant again. The sediments were pretreated using an ultrasonic reactor (FS-600, Shanghai Sonxi Co., Ltd., China) operated at the condition of 20 kHz, 480 W and 10 min [8,9].

ABSTRACT: The present study evaluated the sludge dewaterability and further explored the relationship between the sludge dewaterability and the molecule weights (MW) of organic matters in the different fractions of sludge flocs. The sewage sludge was sampled and fractionated into four fractions: (1) slime, (2) loosely bound extracellular polymeric substances (EPS) (LB-EPS), (3) tightly bound EPS (TB-EPS), and (4) pellet. The results show that proteins (PN) and polysaccharides (PS) were mainly distributed in the TB-EPS and pellet fractions (75.1%), fewer in the slime and LB-EPS fractions. The sludge dewaterability was improved during anaerobic digestion, and the normalized CST correlated with PN, PS, and MW in the LB-EPS fraction. The results suggest that the size exclusion chromatography (SEC) technique could be an effective method to be potentially applied as an indicator to sludge dewaterability.
transducer was immersed 10 mm into 50 ml sludge samples, and the temperature was maintained at about 25°C in an ice water bath to prevent possible temperature effects. At last, the sonicated sludge was inoculated by anaerobic sludge sampled from our laboratory, the ratio of inoculated sludge to sonicated sludge was about 1:20. The TSS and VSS of mixed sludge were 19.14 ± 0.08 mg/L and 6.87 ± 0.52 mg/L, respectively.

2.2. Anaerobic Digestion

Anaerobic digestion was carried out in an airtight vessel with a working volume of 4.0 L. 3.0 L of sludge were encased and pH was adjusted automatically between 6.8 and 7.5 by 6 M HCl and NaOH solutions during anaerobic digestion. Oxygen in the vessels was removed by nitrogen gas (N₂) sparging for 2 min. The vessels were then sealed up with rubber stoppers, keeping the environment temperature at 37 ± 1°C. About 100 ml of sludge samples were collected at regular intervals and used for the stratification extraction and other analysis.

2.3. Sludge Structure and Stratification Protocol

Sludge stratification protocol was modified according to our previously described method [8,9]. Extracellular polymeric substances (EPS) in sludge flocs are composed of soluble EPS (i.e., slime) and bound EPS. The latter exhibits a dynamic double-fractioned structure and can be classified as loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS) based on the extraction methodology. After the EPS is extracted, the cells in the residue form a pellet. Hence, from the outer surfaces to the cores, the sludge flocs possess a multifractioned structure consisting of slime, LB-EPS, TB-EPS, and pellet.

2.4. Analytical Methods

The chemical analyses were carried out in duplicate using chemicals of analytical grade. PN was determined by the modified Lowry method [10], using casein (Shanghai Sangon Biotechnology Co., Ltd, China) as the standard. PS was measured by the Anthrone method [11], with glucose as the standard. CST has been widely accepted for the evaluation of sludge dewaterability due to the simple equipment required, and a high value of CST usually implies a poor dewaterability [12]. In order to measure the dewaterability potential of sludge flocs, the CST values were normalized by dividing them by the initial TSS concentration and then expressed in units of seconds per liter per gram TSS. The MW of organic matters in the different fractions were determined by a SEC (LC-10ADVP, Shimadzu, Japan) equipped with a differentiator detector (RID-10A) and a TSK gel column (G4000PWXL, TOSOH Co., Japan), the mobile phase was Milli-Q water. Polyethylene glycol/oxides (MW at 1,169 kDa; 771 kDa; 128 kDa; 12 kDa; 4 kDa; 620 Da; 194 Da) were used as reference molecules for the calculation. Other sludge parameters, including total suspended solids (TSS) and volatile suspended solids (VSS), were analyzed following the standard methods [13]. The statistical analysis was carried out using the software SPSS version 11.0 for Windows (SPSS, Chicago, IL, USA). Pearson’s coefficient is always between −1 and +1, where −1 denotes a perfect negative correlation, +1 denotes a perfect positive correlation, and 0 denotes the absence of a relationship. The correlation was considered statistically significant at a 95% confidence interval (p < 0.05).

3. RESULTS

3.1 The Variations of PN and PS during Anaerobic Digestion

Figure 1 depicts the variations of PN and PS with time during the anaerobic digestion. The process could be separated into three phases according to the anaerobic digestion time: phase 1 (digestion time < 5 d), phase 2 (5–27 d) and phase 3 (> 27 d). The total PN and PS concentration followed the order: phase 2 > phase 1 > phase 3. It is well known that the anaerobic digestion consists of three stages: hydrolysis, acidification and methanation. Hydrolysis of the sludge flocs can be described as the breakdown of organic matters, resulting in the fragment of cell wall and the release of intracellular compounds [14], and it happened mainly at phase 1 and partly at phase 2, so the phase 2 had the highest concentration of PN and PS. Chen et al. [15] also reported that the concentration of organic matters increased significantly under not only acidic but also alkaline conditions. The organic matters at phase 3 would be the sludge remaining mainly consisting of non-biodegradable fractions and inorganic matters [2].

The initial PN and PS concentrations in the loosely bound fractions (slime and LB-EPS) were 159.5 ± 3.0 mg/g-VSS and 37.2 ± 8.9 mg/g-VSS, respectively.
Subsequently, they decreased to 46.3 ± 1.4 mg/g-VSS and 23.0 ± 3.3 mg/g-VSS at 42nd day. While in the tightly bound fractions (TB-EPS and pellet), the PN concentration increased from the initial 458.4 ± 1.4 mg/g-VSS to 487.9 ± 3.0 mg/g-VSS at 42nd day, and PS concentration decreased from 135.3 ± 16.0 mg/g-VSS to 95.9 ± 13.4 mg/g-VSS. In other words, the organic matters in the loosely bound fractions were easily degraded when compared with those in the tightly bound fractions, suggesting that the organic matters in the tightly bound fractions were mainly large molecule matters or colloids that were not easily decomposed.

3.2 The Sludge Dewaterability during Anaerobic Digestion

Figure 2 presents the variation of normalized CST during anaerobic digestion. The initial normalized CST was 50.6 s L/g-TSS, it rapidly decreased to 28.3 s L/g-TSS at 10th day and slowly fell to 7.73 s L/g-TSS at 34th day, then approached the plateau value until the end of test period. Some researchers had reported that the anaerobic digestion would deteriorate the sludge dewaterability [4,16]. However, we interestingly found that the sludge dewaterability was improved during the anaerobic digestion followed by ultrasound pretreatment.

3.3 The Transformation of Molecular Weights during Anaerobic Digestion

SEC reveals a wide range of molecular weights (MW). For the sake of further discussion, the MW distributions of organic matters in different EPS fractions could be categorised into two groups according to the retention time: MW > 210 kDa (retention time < 13 min) and MW < 210 kDa (retention time > 13 min). The anaerobic digestion could convert the complex organic matters into low molecular weight organic matters [4], we took the LB-EPS fraction for example [Figure 3(b)], the large molecule matters (MW > 210 kDa) occupied 100% at 0th day, they decreased to 36.0%, 25.4%, and 22.3% at 10th day, 27th day, and 34th day, respectively. While the small molecule matters (MW < 210 kDa) increased from none to 64.0%, 74.6%, and 77.7% at 10th day, 27th day, and 34th day, respectively. Hence, complex organic matters in the LB-EPS fraction were mainly degraded (78.7%) into less complex organic matters during anaerobic digestion. The organic matters in the TB-EPS and pellet fractions [Figures 3(c) and 3(d)] also had the similar degradation tendency as
in the LB-EPS fraction. However, the organic matters in the slime fraction mainly consisted of less complex matters (52.1% < 210 kDa) and the MW of organic matters varied fluctuately during anaerobic digestion [Figure 3(a)].

4. DISCUSSION

4.1 Correlation Analyses between the Normalized CST and PN and PS

Table 1 shows the Pearson correlations between the normalized CST and the PN and PS in the different fractions of sludge flocs. The normalized CST only correlated with PN ($R^2 = 0.92, p = 0.005$) and PS ($R^2 = 0.95, p = 0.011$) in the LB-EPS fraction, there was no correlation with PN ($R^2 < 0.98, p > 0.09$), or PS ($R^2 < 0.97, p > 0.14$) in other fractions.

Several studies have been aimed at investigating the effects of EPS and their compositions on sludge dewaterability. Novak et al. [17] reported that the digested sludge dewaterability was directly affected by the amount of biopolymers released into the solution during the anaerobic process. Higgins and Novak [18] found that PN was of more significance than PS to sludge dewaterability, the degradation of PN by protease resulted in poorer dewaterability, while the degradation of PS had no noticeable effect on sludge dewaterability. Li and Yang [19] reported that the LB-EPS (corresponding to slime and partly LB-EPS in this study) played a greater role than the TB-EPS on sludge dewaterability. Owing to the complicated matrix of sludge structure, those results above did not identify which parts or which compositions of EPS were the strongest determinants to the sludge dewaterability. The present study demonstrated that the organic matters in the LB-EPS fraction had more important influence on the sludge dewaterability.

![Figure 3. The SEC profiles in the different fractions of sludge flocs. (a) slime; (b) LB-EPS; (c) TB-EPS; (d) pellet.](image-url)

<table>
<thead>
<tr>
<th>Fractions (Layers)</th>
<th>PN</th>
<th>PS</th>
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<tr>
<td>Slime</td>
<td>0.89</td>
<td>0.091</td>
</tr>
<tr>
<td>LB-EPS</td>
<td>0.92</td>
<td>0.005</td>
</tr>
<tr>
<td>TB-EPS</td>
<td>0.95</td>
<td>0.224</td>
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<tr>
<td>Pellet</td>
<td>0.98</td>
<td>0.470</td>
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</table>
4.2 Correlation Analyses between Sludge Dewaterability and Molecular Weights

As mentioned above, the SEC technique was widely applied in many domains [6,7]. However, they were mostly qualitative analysis, and no previous work has yet been done to evaluate the sludge dewaterability by this technique. In this study, we for the first time found that there was a strong positive correlation between the sludge dewaterability and the MW of the organic matters in the LB-EPS fraction ($p = 0.027$), suggesting that the organic matter in the LB-EPS fraction was a significant contributor to the sludge dewaterability. So we could detect the MW of organic matters in the LB-EPS fraction to predict the sludge dewaterability. This would be a simple and effective technique for the environmental researchers to better understand the organic substance properties and the sludge dewaterability and could help to design and optimize the sludge/wastewater treatment facilities.

5. CONCLUSIONS

The sludge dewaterability during anaerobic digestion followed by ultrasound pretreatment was evaluated and the correlation between the sludge dewaterability and the organic matters in the different fractions of sludge flocs was explored. The organic matters in the sludge flocs were mainly distributed in the TB-EPS and pellet fractions, fewer in the slime and LB-EPS fractions. The sludge dewaterability was improved during the anaerobic digestion, and the normalized CST significantly correlated with organic matters in the LB-EPS fraction. In this study, we for the first time reported that there was a strong positive correlation ($p = 0.027$) between the sludge dewaterability and the MW of organic matters in the LB-EPS fraction. The results suggest that the SEC technique could be an effective method to be potentially applied as an indicator to the sludge dewaterability.

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