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Response of extracellular polymeric substances to thermal treatment in sludge dewatering process☆

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ABSTRACT

Sludge dewatering is an important process in municipal wastewater treatment and critically influences the subsequent transportation and disposal. Thermal treatment coupled with other chemical processes has been widely used to improve sludge dewaterability. However, information about the response of sludge extracellular polymeric substances (EPS) to thermal treatment and its role in sludge dewatering is still limited. In this work, the effects of thermal treatment on anaerobic and aerobic sludges were investigated with an emphasis on the colloid properties of released EPS in sludge dewatering process. The results indicate that sludge dewaterability became deteriorated with the increased temperature in the range of 30–170 °C, which was ascribed to the disintegration of sludge flocs and change of EPS characteristics. Disintegrated sludge induced the release of the negatively charged EPS, resulting in the weakened bridging interaction and lower compactness. After thermal treatment, the EPS with a higher average molecular weight and stretched coil configuration retained more water. In addition, difference in dewaterability between anaerobic and aerobic sludges was found to be attributed to their different contents and structures of EPS components. These results provide an insight into thermal-dependent sludge dewatering process and are useful to facilitate water-sludge separation.

1. Introduction

A large amount of sewage sludge is produced as the byproduct of wastewater treatment process (Christensen et al., 2015). Dewatering is essential to reduce sludge volume and diminish transportation costs prior to further treatment such as anaerobic/aerobic digestion and co-incineration. Various methods have been used to dewater sludge, such as dose of chemicals (Neyens et al., 2004; Peeters et al., 2013; Ruiz-Hernando et al., 2013), ultrasound (Feng et al., 2009), Fenton's reagent (He et al., 2015), electrolysis (Yuan et al., 2011a) and acidification/alkalization (Chen et al., 2001). In these methods, a fraction of bound water is released and sludge dewaterability is improved after sludge flocs and microbial cells are partially destroyed.

Thermal treatment such as hydrothermal and microwave heating has received growing attention as an effective way to condition sludge. It could promote the hydrolysis of sludge (Neyens and Baeyens, 2003), release of extracellular polymeric substances (EPS) (Liu et al., 2016) and reduction of viscosity (Ruiz and Wisniewski, 2008), which are favorable to improve sludge dewaterability and facilitate sludge handling. Nevertheless, high energy consumption from heating requirement hinders its wide application. Thermal treatment begins to exhibit a positive effect only after temperature exceeds a threshold value (i.e., 120–150 °C), and dewaterability is significantly enhanced in the range of 180–210 °C (Wang et al., 2014). Below the critical temperature, dewaterability would be deteriorated by thermal treatment (Bougrier et al., 2008). Reaction time is also critical to the improvement of sludge dewaterability (Feng et al., 2014; Liu et al., 2012). As a result, thermal treatments and other chemical reagents such as acid/base, $CaCl_2$ and H_2O_2 have been coupled to intensify sludge dewatering at a lower temperature. Acid/base dose could promote solubility of total suspended solids (Ruiz-Hernando et al., 2013; Woodard and Wukasch, 1994); $CaCl_2$ could neutralize negative charge and compress sludge flocs (Guan et al., 2012).

EPS have been found to play an important role in sludge dewatering process (Mowla et al., 2013; Sheng et al., 2010). EPS govern

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sludge properties, like surface charge, hydrophobicity, bound water content and floc strength (Ruiz-Hernando et al., 2013; Neyens and Baeyens, 2003; Vaxelaire and Cezac, 2004). Sludge containing compact flocs without single cells and dissolved EPS had high dewaterability (Christensen et al., 2015). The release of excessive EPS showed a negative effect on sludge dewatering (Bougrier et al., 2008; Li and Yang, 2007). The protein-like polymers in EPS might be responsible for worse dewaterability after microwave treatment (Liu et al., 2016). It was also found that the characteristics of EPS were more important than their quantity in sludge dewatering (Neyens and Baeyens, 2003; Li and Yang, 2007).

Among the numerous characteristics of EPS, chemical properties, molecular weight and configuration structure of colloids affect the water entrapment and sludge compaction. However, the response of sludge EPS to thermal treatment and its role in sludge dewatering remain unclear. Therefore, thermal treatment of aerobic and anaerobic sludge was performed to investigate its effects on sludge dewaterability in this work. The principle objectives were to probe the response of released EPS and floc structure to thermal treatment in sludge dewatering process. The gel permeation chromatography (GPC) and laser light scattering were integrated to reveal the colloid properties of EPS. A deep insight into characteristics of released EPS and disintegration of sludge flocs would be favorable to understand the thermal-dependent sludge dewatering and develop new sludge dewatering technologies.

2. Materials and methods

2.1. Sludge samples

Aerobic sludge was collected from Wangtang Municipal Wastewater Treatment Plant in Hefei, China. Anaerobic sludge was sampled from an anaerobic reactor fed with excess sludge in Suzhou, China. The sludge samples were stored at 4 °C and used within two weeks. Their characteristics are shown in Table 1. The total solids (TS) contents, volatile solids (VS) contents, moisture content and pH were measured according to the standard methods (APHA, 2005). Zeta potentials and z-average size of sludge suspensions were measured using a Zetasizer Nano ZS instrument (Malvern Co., UK) at 25 °C.

2.2. Sludge dewaterability experiments

Anaerobic sludge was diluted with deionized water by 4 times to reach a similar TS content to aerobic sludge, which was directly used without pretreatment. Sludge solution of 200 mL was heated in a water bath at a pre-determined temperature (30, 45, 60, 75 and 90 °C) for 30 min. Another 200 mL sample was treated in an autoclave at 170 °C for 30 min. A Model 304B instrument (Triton Ltd., UK) equipped with an 18 mm diameter funnel and Whatman no. 17 chromatography-grade paper was applied to measure the capillary suction time (CST) of sludge. The specific resistance to filtration (SRF) of sludge suspensions was determined by filtration test (Wang et al., 2013). The filtrate passed through a filter paper in vacuum filtration and released EPS was collected for subsequent analysis.

Two additional experiments were designed to verify the effects of released EPS and floc disintegration on sludge dewaterability. Raw and thermal-treated sludge samples were filtered in a Buchner funnel and separated into supernatant and sludge pellets. EPS solution separated from the thermal-treated sludge at various temperatures was mixed with raw sludge pellets to examine the effects of released EPS on dewatering. The supernatant of raw sludge was added into the treated pellets in order to explore the effects of sludge disintegration on dewaterability. Two mixed solutions, defined as released EPS + raw pellets and treated pellets + raw supernatant, were directly measured for CST and SRF without thermal treatment. The detailed manipulation procedure was shown in Fig. S1.

Table 1
Physicochemical characteristics of sludge samples.

	Aerobic sludge	Anaerobic sludge
Moisture content (%)	99.0 ± 0.6	96.3 ± 0.9
TS (g/L)	10.1 ± 0.4	37.2 ± 0.1
VS (g/L)	6.8 ± 0.3	17.5 ± 0.2
pH	6.52	7.88
CST (s)	21.5 ± 1.2	91.3 ± 1.6
Z-average size (μm)	22.8 ± 3.2	19.2 ± 3.9

2.3. Characterization of released EPS

The supernatant of sludge sample was filtered through 0.45-μm filters before chemical analysis. The contents of polysaccharides in the released EPS were determined by the anthrone-sulfuric acid method with glucose as the standard (Frolund et al., 1996); the contents of proteins and humic substances were measured using the modified Lowry method with egg albumin and humic acid as the standards (Frolund et al., 1996). GPC (Waters Co., USA) equipped with Waters Ultrahydrogel 250, 500 and 2000 column in series coupled with UV absorbance and refractive index (RI) detectors was used to determine the average molecular weight. The column was calibrated by standard polyethylene oxide from Agilent Co. (Batch Number 0001024141) (Yuan et al., 2011b). The monosaccharides in the released EPS were analyzed using a gas chromatography (7890A, Agilent Co., USA) (Magnelli et al., 2002).

EPS were freeze-dried before infrared spectra (IR) analysis with a VERTEX 70 FT-IR (Bruker Co., Germany). All the spectra consisted of 128-scans interfergram with a 4 cm^{-1} resolution. The amide I region of protein spectrum at 1700-1600 cm^{-1} was analyzed further to determine the secondary structure of proteins (Yuan et al., 2011b).

Laser light scattering tests were conducted by an ALV/DLS/SLS-5022F spectrometer (ALV Co., Germany) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632.8$ nm) as the light source. Dynamic light scattering (DLS) and static light scattering (SLS) were combined to reveal the colloidal properties of EPS, which were represented by *z*-average root-mean-square radius of gyration ($<R_g>$) and mean hydrodynamic radius ($<R_h>$). In order to investigate the changes of EPS configurations at different temperatures, LLS analysis was carried out from 23 °C to 57 °C with an increase of about 10 °C. The detailed manipulation process and theoretical analysis could be found in a previous work (Wang et al., 2012).

3. Results and discussion

3.1. Changes of dewaterability and other properties of sludge

The sludge dewaterability exhibited a notable difference after the thermal treatments. As the temperature was increased from 30 °C to 170 °C, the CST values of both aerobic and anaerobic sludges increased (Fig. 1), suggesting a more difficult status for dewatering. In comparison with their original values of CST, the influence of thermal process on sludge dewaterability was more prominent for the anaerobic sludge than for the aerobic sludge. Similar variation trends were observed for the curve of SRF, confirming the negative effect of thermal treatment on dewaterability (Fig. 2).

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