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Experimental and theoretical analyses on the impacts of ionic surfactants on sludge properties

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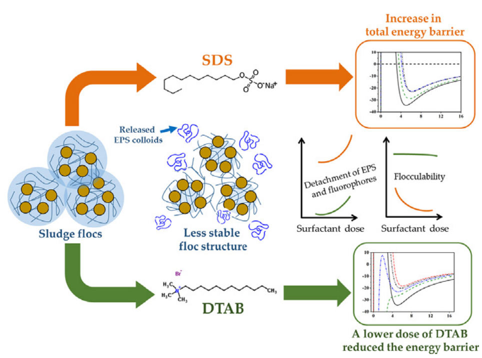
HIGHLIGHTS

- Surfactants affect the surface characteristics and microstructure of sludge.
- Dose of anionic SDS resulted in more release of EPS than cationic DTAB did.
- Surfactant dose and total EPS contents were correlated to sludge flocculability
- The integrated approach can track surfactant-assisted sludge dewatering process

GRAPHICAL ABSTRACT



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ABSTRACT

A large amount of excess waste activated sludge is produced in municipal wastewater treatment plants and should be further disposed to avoid environmental pollution. Ionic surfactants are being widely used for sludge conditioning, but how and to what extent ionic surfactants change the sludge properties remain unclear. In this work, the impacts of two typical ionic surfactants on the flocculability and stability of sludge were investigated by using experimental and theoretical analyses. The treatment of anionic sodium dodecyl sulfate (SDS) resulted in more detachment of extracellular materials and fluorophores from sludge compared to the treatment of cationic trimethyl ammonium bromide (DTAB). Fourier transform infrared spectra analysis indicates the promoted release of proteins and polysaccharides induced by the surfactants. Deteriorated flocculability of sludge was observed for the SDS-treated sludge, while treatment of DTAB slightly affected the overall sludge flocculability. The sludge floc structure became less stable after treatments of both surfactants, as confirmed by the elevated dispersed mass concentration of small particles in shearing tests. The relationship between the content of extracellular polymeric substances, surfactant dose and sludge properties were evaluated and the roles of released extracellular polymeric substances and surfactant dose in affecting sludge flocculability were examined. Extended DLVO approach was adopted to explore the stability of sludge. By using such an integrated approach, the impacts of ionic surfactants on sludge flocculability and stability were revealed, which is useful in understanding the mechanisms of sludge conditioning by surfactant treatment.

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1. Introduction

Municipal wastewater treatment plants have produced a huge amount of excess waste-activated sludge (Mahmoud et al., 2006; Hanotu et al., 2014; Guan et al., 2017), which inevitably leads to great economic burdens (Mowla et al., 2013). To date, numerous works have been conducted to enhance the sludge flocculability and dewaterability by using chemicals or adjusting sludge properties, aiming to accelerate the sludge reduction rate and efficiency. Salt addition, pH adjustment or electrolysis treatments are found to promote sludge compressibility (Qi et al., 2011; Yuan et al., 2011c; Raynaud et al., 2012). Conventional chemical additives include aluminum sulfate, ferric chloride, polyelectrolyte, enzymes and surfactants etc. (Neyens et al., 2004; Ruiz-Hernando et al., 2013; Zhang et al., 2016). In these methods, the surface properties of sludge are partially altered and a fraction of bound water is released from sludge flocs. The improved sludge flocculability and dewaterability after treatments could bring benefits to subsequent sludge disposal.

Surfactants are one of the most versatile chemical products and their additions into excess sludge can lower the surface tension by modifying the interface characteristics between liquid/liquid or liquid/solid (Rosen, 2004). The presence of surfactants could also alter cell structures by detaching extracellular polymeric substances (EPS) from sludge and thus affect the sludge properties (Mikkelsen, 2001; Sheng et al., 2010; Yuan et al., 2011a). We previously found that the destruction of sludge flocs and the release of bound water occurred owing to the effects of the cationic surfactants such as dodecyl trimethyl ammonium bromide (DTAB) (Wang et al., 2014a). While anionic sodium dodecyl sulfate (SDS) played an opposite role in sludge dewatering by increasing both negative charge and repulsive forces between released EPS, or called soluble-EPS (S-EPS) and sludge flocs (Wang et al., 2014b). By combining use surfactants and additional approaches, e.g., acid/alkaline (Chen et al., 2001; Chen et al., 2004; Hong et al., 2015), Fenton's reagent (Hong et al., 2017), flocculants (Sun et al., 2014) or electrolysis (Yuan et al., 2011a; Yuan et al., 2011b), promotion in cell destruction, EPS detachment, bound water release and superior flocculability/dewaterability could be achieved. For activated sludge, the double-layered EPS structure is comprised of loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS). LB-EPS generally lead to a worse sludge flocculability/dewaterability compared to TB-EPS (Li and Yang, 2007). Although the physicochemical properties of sludge and the amount/properties of EPS affect the flocculability of sludge flocs (Mikkelsen and Keiding, 2002; Liu and Fang, 2003), the effects of ionic surfactants on the LB-EPS/TB-EPS fractions are less studied and the relationship between sludge surface properties and sludge flocculability induced by ionic surfactants remains unrevealed.

The aggregation of sludge is primarily governed by interactions between sludge cells and could be described by the extended-DLVO theories (Liao et al., 2002; Sheng and Yu, 2006). The classical DLVO theory involves the estimation of the energy due to the overlap of electric double layers and the van der Waals energy in terms of interparticle distance. The DLVO and extended-DLVO theories have been applied to explore the aggregation of sludge flocs (Xu and Li, 2016). The loosely bound EPS show a positive effect on the sludge aggregation, while the interaction energy of tightly bound EPS is depending on the separation distance between cells (Liu et al., 2010). However, the effects of ionic surfactants on the sludge aggregation by using the theoretical approach have not been well documented.

In this work, we aimed to examine the changes of sludge flocculability and aggregate stability induced by typical ionic surfactants, i.e., SDS and DTAB. The characteristics of released EPS, surface characteristics and microstructure of sludge after treatment were measured and compared. The flocculability and floc stability of sludge in the presence of surfactants were examined by using flocculation and shearing tests. In order to reveal the surfactant-tuned flocculability/stability, the extended-DLVO theory was applied to evaluate the effects of surfactant treatments on total energy barriers. This work would provide more insights into how and to what extent ionic surfactants alter the surface properties and stability of sludge.

2. Materials and methods

2.1. Treatment of sludge

Activated sludge samples were harvested from Wangtang Municipal Wastewater Treatment Plant, Hefei, China. The pH and the mixed liquor suspended solids (MLSS) of the samples were 6.93 ± 0.08 and 5214 ± 261 mg L^{-1}, respectively. The initial sludge was initially centrifuged at 3000 rpm for 4 min. The pellets were washed with NaCl solution (0.9%) and then re-suspended with the same solution to its original volume. SDS (99% purity, Shanghai Chem. Co., China) and DTAB (99%, Aldrich Co.) were used as model surfactants. A preset amount of surfactants was dosed into each 100 mL sludge sample. The mixture was stirred at 300 rpm for 1 min, followed by slow vibration at 170 rpm for 5 min using a magnetic stirrer. The sludge samples after surfactant treatments were centrifuged at 2000 g for 15 min and the supernantant was collected and defined as the released EPS. The sludge pellets left in the centrifuge tube was re-suspended in 0.05% NaCl solution to its original volume. The sludge was centrifuged at 5000 g for 15 min and the organic matter in the supernatant was defined as the LB-EPS. To extracting LB-EPS, the pellets were re-suspended in 0.05% NaCl solution to the original volume again and heated to 60 °C in a water bath for 30 min. The readily extracted fractions were regarded as the TB-EPS (Li and Yang, 2007). The polysaccharides (PS) in EPS fractions were determined by anthrone-sulfuric acid method, while the concentrations of proteins (PN) and humic substances (HS) were measured using the modified Lowry method (Frolund et al., 1996). All the treatments and analytical measurements were carried out in duplicate.

Luminescence spectrometry (LS-55, Perkin-Elmer Inc., USA) was used to obtain excitation–emission matrix (EEM) fluorescence spectra recorded at excitation wavelengths of 200–450 nm by 10-nm increments and at emission wavelengths of 300–560 nm by 0.5–nm. Parallel factor (PARAFAC) analysis was used to separate the actual fluorescence spectra from the raw spectra (Li et al., 2008). The supernatant after surfactant treatments were filtered through 0.45 μm cellulose acetate membrane and lyophilized. Fourier transform infrared (FTIR) spectra were collected on Vertex 70 (Bruker Co., USA) with KBr pellets to identify the characteristic functional groups of the released EPS, surfactants and raw sludge. The Zeta potential and zero point of charge of each sample were recorded using a Zetasizer Nano ZS Instrument (Malvern Co., U.K.) at 25 °C. The surface thermodynamic properties of sludge, such as the surface free energy, were estimated using a contact angle approach as described previously (Liu et al., 2007).

2.2. Shear testing and flocculating ability analysis

A 1-L baffled paddle-mixing chamber was used in the shearing test. A reactor baffle (10 mm width × 12 mm height) was placed in the inner surface of the cylinder and sheared at an intensity of G = 800 1/s by stirring with a flat paddle mixer (JJ-4, JCGS Instrument Co., China). The stability of sludge flocs was characterized by the supernatant turbidity at equilibrium. Supernatant of 3 mL was taken from the reactor at given time intervals. The samples were centrifuged at 2200 rpm for 2 min and the absorbance at 650 nm was measured using a spectrophotometer (UV751GD, Analytical Instrument Co., China) as the supernatant turbidity. Since the mass concentrations of detached primary particles are low, it is difficult to accurately measure the value of the SS of the detached particles based on the standard method (Mikkelsen and Keiding, 1999; Mikkelsen and Kelding, 2002). Thus, the turbidity of sludge supernatant was alternatively measured and converted to mass concentration (Wahlberg et al., 1994). The value of $m_{d,t}$ was calculated using the turbidity/SS-concentration conversion factor of 1.2 mg SS/1/