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Influence of alkyl sulfates on waste activated sludge fermentation at ambient temperature

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Abstract

Alkyl sulfates (AS), such as sodium dodecyl sulfate (SDS), are widely used in household and industrial products, and can be found in some wastewater and waste activated sludge (WAS). The effect of SDS on the fermentation of WAS at ambient temperature was investigated in this paper. Experimental results showed that the concentrations of protein and carbohydrate in aqueous phase increased with the amount of SDS. The concentrations of both NH_4^+-N and PO_4^{3-}-P in fermentation liquor also increased in the presence of SDS. In addition, it was observed that the fermentative short-chain fatty acids (SCFAs) concentration was affected by SDS. With the increase of SDS dosage, the maximum SCFAs concentration increased, and the fermentation time before reaching the maximum SCFAs concentration also increased. Further investigation showed that the produced SCFAs consisted of acetic, propionic, *n*-butyric, *iso*-butyric, *n*-valeric and *iso*-valeric acids, and acetic, *iso*-valeric and propionic acids were the three main products. The influence of SDS on methanogenesis was also investigated, and the inhibitory effect of SDS on methanogens activity was observed.

Keywords: Waste activated sludge (WAS); Fermentation; Short-chain fatty acids (SCFAs); Methane; Alkyl sulfates

1. Introduction

Surfactants are widely used in household cleaning detergents, personal care products, textiles, paints polymers, pesticide formulations, pharmaceuticals, mining, oil recovery and pulp and paper industries [1]. The world production of synthetic surfactants amounts to 7.2 million tonnes annually [2]. Because of their amphiphilic nature, surfactants can adsorb to the surface of sewage sludge. Typically, 25% of surfactants entering a sewage treatment plant are physically separated during the primary settling step with the sludge which goes to the sludge settling tank [3].

Large amount of sludge (including primary sludge and waste activated sludge) are produced due to the widespread use of biological wastewater treatment. Anaerobic fermentation is generally used to stabilize organic matters of these sludges and thereby reduce odor production and the release of harmful chemicals into environment. Short-chain fatty acids (SCFAs), especially acetic and propionic acids, are the intermediate products of sludge fermentation and are also the preferred carbon source for biological nitrogen and phosphorus removal microbes [4–6]. Usually, three steps, hydrolysis, acidification and methanogenesis, are involved in sludge fermentation process, and the initial hydrolysis of particulate organic matter to soluble substance is believed to be the rate-limiting step of anaerobic fermentation [7]. In the literature, it has been reported that surfactants can disrupt the performance of anaerobic digester due to its inhibition to methanogenesis [8–11]. However, the effects of surfactants on sludge hydrolysis and acidification have not been documented.

Alkyl sulfates (AS), a kind of anionic surfactant, are among the most widely used surfactants. In some cases, such as in textile finishing industry, AS are used in quite large amount [12]. Sludge produced from such kind of wastewater treatment plants contains high concentration of AS. And this high loading rates of AS might give influence on sludge hydrolysis and acidification as well as methanogensis. Also, during sludge fermentation the nitrogen and phosphorus have been observed to

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release from sludge. Thus, the purpose of this study was to investigate the effect of high AS concentrations on sludge protein and carbohydrate solubilization, nitrogen and phosphorus release, and SCFAs and methane production during the fermentation of waste activated sludge (WAS). Sodium dodecyl sulfate (SDS) was chosen as a model compound of AS in this study.

2. Experimental

2.1. Source of WAS

The WAS used in this study was obtained from the secondary sedimentation tank of a municipal wastewater treatment plant in Shanghai, China. The sludge was concentrated by settling at 4 °C for 24 h, and its characteristics after settlement are summarized in Table 1. As seen in Table 1, protein and carbohydrate accounted for, respectively, 66.3% and 7.3% of sludge total COD (TCOD).

2.2. Batch fermentation tests

The investigation on SDS affecting WAS fermentation at ambient temperature were carried out in 12 identical reactors, in which 6 reactors were used for liquid sampling and the duplicate 6 for methane sampling. All reactors were made of plexiglass and each had a liquid volume of 2.0 L. They were equipped with stainless steel stirrers with blades for mixing the contents, and were maintained at 21 ± 1 °C for 21 days. The ratio of SDS dosage to dry sludge in the batch reactors was 0, 0.05, 0.1, 0.2, 0.25 and 0.3 g/g, respectively, and the reactor with no SDS addition was set to be the blank test.

2.3. Analysis

After sampling, the sludge was immediately filtered through a Whatmann GF/C glass microfiber filter with 1.2 μm pore size. The filtrate was analyzed for carbohydrate, protein, NH_4^+-N, PO_4^{3-}-P and SCFAs, and the filter was assayed for TSS and VSS. PO_4^{3-}-P, NH_4^+-N, TSS and VSS were measured according to Standard Methods [13]. Soluble carbohydrate was assayed by the phenol–sulfuric method with glucose as standard [14]. Soluble protein was determined by the Lowry–Folin method with bovine serum albumin (BSA) as standard [15]. Sludge lipid was extracted by the Bligh–Dyer method from the acidified sample, and was then measured gravimetrically after the solvent was evaporated at 80 °C [13]. The total protein content of sludge (in the form of COD) was calculated from the corresponding Total Kjeldahl Nitrogen (TKN) concentration by subtracting the inorganic nitrogen concentration and dividing the difference by 0.16, multiplying the result by 1.5 finally [16].

For the quantification of SCFAs, the filtrate was collected in a 1.5 mL gas chromatography (GC) vial, and acidified with 3% H_3PO_4 before assayed on a HP5890 GC with flame ionization detector and CPWAX52CB column (30 m × 0.32 mm × 0.25 mm). Nitrogen was the carrier gas and the flux was 50 mL/min. The injection port and the detector was maintained at 200 and 220 °C, respectively. The oven of GC was programmed to begin at 110 °C and to remain there for 2 min, then to increase at a rate of 10 °C/min to 200 °C, and to hold at 200 °C for an additional 2 min. The sample injection volume was 1.0 μL.

Methane was measured by a by a gas chromatograph (GC-14B, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD) and a 3-m stainless column. The temperature of the injection, column and detector was set at 40, 50 and 90 °C, respectively. Nitrogen was used as the carrier gas at a flow rate of 30 mL/min.

3. Results and discussion

3.1. Effect of SDS on sludge protein and carbohydrate solubilization at different fermentation times

Tanaka et al. [17] observed that protein, carbohydrate and lipid are the main constituents of domestic sludge. In this study, as seen in Table 1 protein was the largest constituent of the WAS, and lipid which accounted for only around 1% of sludge TCOD could be neglected. Hydrolysis of WAS causes sludge protein and carbohydrate released in aqueous phase, and the variations of soluble protein and carbohydrate concentrations at different SDS dosages were therefore investigated.

Fig. 1 describes the effect of SDS on the soluble protein concentration at different fermentation times. As seen in Fig. 1, the protein concentration increased with the

Table 1
Partial characteristics of the concentrated WAS used in this investigation

Parameter	Mean	S.D.[a]
pH	6.86	0.16
TSS (total suspended solids) (mg/L)	11,036	151
VSS (volatile suspended solids) (mg/L)	9,531	97
SCOD (soluble chemical oxygen demand) (mg/L)	118	17
TCOD (total chemical oxygen demand) (mg/L)	14,890	560
Carbohydrate (mg COD/L)	1,085	105
Protein (mg COD/L)	9,874	431
Lipid and oil (mg COD/L)	152	6
Soluble NH_4^+-N (mg/L)	23.5	0.7
Soluble PO_4^{3-}-P (mg/L)	19.8	0.4

[a] S.D., standard deviation.

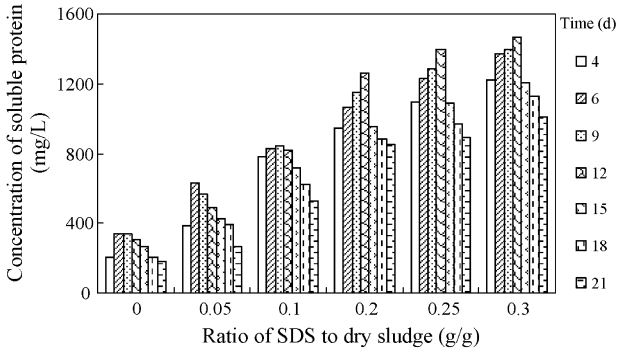

Fig. 1. Effect of SDS on soluble protein concentration at different fermentation times.

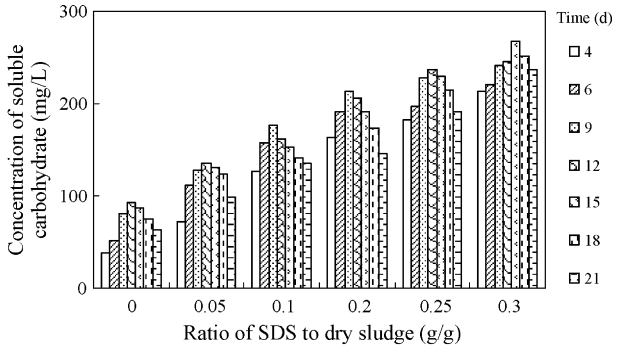

Fig. 2. Effect of SDS on soluble carbohydrate concentration at different fermentation times.

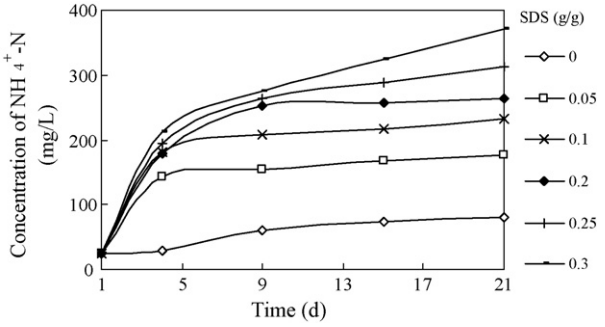

Fig. 3. Variations of the observed NH_4^+-N concentration during fermentation at different SDS dosages.

dosage of SDS. During the initial 6 days of fermentation the soluble protein concentration at different SDS dosages was as follows: 1372.91 mg/L (0.3 g SDS/g TSS) > 1227.05 (0.25 g/g) > 1060.13 (0.2 g/g) > 827.73 (0.1 g/g) > 631.44 (0.05 g/g) > 341.81 (blank test). Further investigation revealed that on the 6th day the soluble protein concentration linearly increased with SDS dosage in the range of 0–0.3 g/g ($Y_{\text{soluble protein concentration}} = 3597.3X_{\text{SDS dosage}} + 341.81$, $R^2 = 0.96$). These observations could be made at any other fermentation time (linear equations not shown). SDS had the same effect on soluble carbohydrate as on soluble protein (see Fig. 2). For example, on the 6th day the carbohydrate concentration in aqueous phase increased linearly from 51.59 mg/L in the blank test to 220.98 mg/L at SDS 0.3 g/g.

The possible reason for the increased soluble protein and carbohydrate concentrations in the presence of SDS was that SDS significantly increased the solubilization of both sludge protein and carbohydrate. It is well known that sludge components are cemented together by extracellular polymeric substances (EPS), which are mainly composed of microbially produced biopolymers, such as carbohydrate and protein [18]. Usually, these sludge protein and carbohydrate are absorbed in sludge surface, but they can be solubilized by SDS and dissolve into water because surfactant has the feature of solubilization [19]. The enhanced solubilization of EPS in the presence of SDS would also cause the break-up of sludge matrix, and then the sludge macromolecules organic compounds previously protected from hydrolytic enzyme attack were exposed and could be easily degraded by hydrolytic enzymes. The improvement of the solubilization of sludge protein and carbohydrate by surfactant has also been observed in our previous studies [20]. Thus, SDS efficiently accelerated the hydrolytic rate of WAS and improved the hydrolysis of WAS.

As also seen in Figs. 1 and 2, the concentrations of both soluble protein and carbohydrate increased gradually in the initial stage of fermentation, but decreased in the latter fermentation time. Apparently, the initial release rates of these two substrates were higher than their degradation, which made their accumulations temporarily increased. But in the latter stage of fermentation the release rates slowed down and were exceeded by degradation, which resulted in the decrease of observed soluble protein and carbohydrate concentrations.

3.2. Effect of SDS on NH_4^+-N and PO_4^{3-}-P releases at different fermentation times

Fermentation of WAS resulted in significant releases of NH_4^+-N (Fig. 3) and soluble phosphorus (PO_4^{3-}-P) (Fig. 4). Similar to soluble protein and carbohydrate, both observed NH_4^+-N and PO_4^{3-}-P concentrations in the fermentation liquor also increased due to the effect of SDS. As seen from Fig. 3, the observed NH_4^+-N concentration in fermentation liquor kept increasing during the whole fermentation time no matter SDS was utilized or not. It can also be seen in Fig. 3 that the observed NH_4^+-N concentration increased with the amount of SDS at any fermentation time. On the 4th day of fermentation, the observed NH_4^+-N concentration in the fermentation liquor increased from 29.67 mg/L in the blank test to 213.15 mg/L at SDS 0.3 g/g. It was interesting to note that instead of increasing gradually as NH_4^+-N during fermentation, the observed PO_4^{3-}-P concentration decreased with further increasing time after reaching the maximum value when SDS was used (see Fig. 4), but the observed PO_4^{3-}-P concentration in the blank test increased with time during fermentation. The reason is still unclear, and need to be further explored in the coming investigations.

Also it can be seen from Figs. 3 and 4 that the observed NH_4^+-N release was greater than PO_4^{3-}-P in most cases. This may be attributed to the fact that the particulate nitrogenous materials are readily degraded during the acid phase of anaerobic digestion [21].

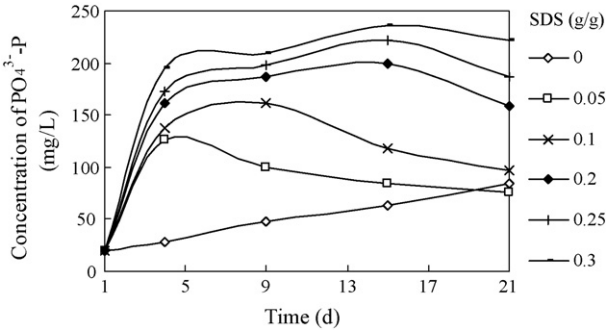

Fig. 4. Variations of the observed PO_4^{3-}-P concentration during fermentation at different SDS dosages.

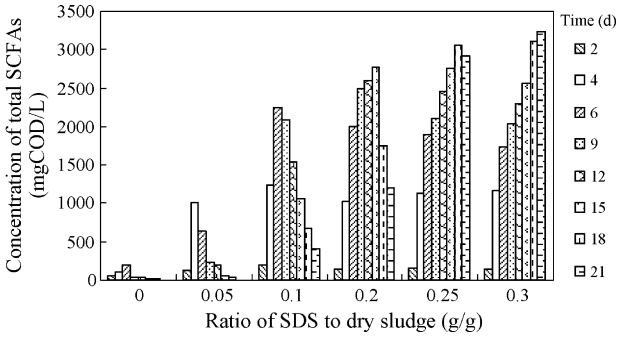

Fig. 5. Effects of SDS dosage and fermentation time on total SCFAs concentration.

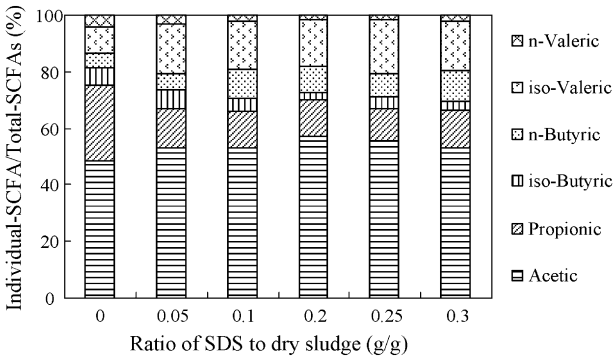

Fig. 6. Composition of SCFAs at different SDS dosages on the 6th day of fermentation.

3.3. Effect of SDS on SCFAs formation at different fermentation times

It was observed that SCFAs were produced during sludge fermentation. The detectable SCFAs in this investigation included acetic, propionic, *n*-butyric, *iso*-butyric, *n*-valeric and *iso*-valeric acids. In this paper, the individual SCFA concentration was expressed by mg COD/L by using appropriate conversion factors [7], and the sum of individual SCFA was recorded as the amount of total SCFAs. The effects of SDS on total SCFAs concentration during the whole fermentation time are shown in Fig. 5. Apparently, significant amount of SCFAs were accumulated in the presence of SDS, and the maximum SCFAs concentration increased gradually as the ratio of SDS to dry sludge increased from 0 to 0.3 g/g. The fermentation time before reaching the maximum SCFAs concentration also increased with SDS dosage. As seen in Fig. 5, the maximum SCFAs concentration was respectively 1000.74 mg COD/L at SDS 0.05 g/g and fermentation time of 4 days, 2243.04 at 0.1 g/g and 6 days, 2780.36 at 0.2 g/g and 15 days, 3066.23 at 0.25 g/g and 18 days, and 3234.95 at 0.3 g/g and 21 days, while it was only 191.10 mg COD/L in the blank test at fermentation time of 6 days. After reaching their respective maximum value, the SCFAs concentration at SDS dosage less than 0.2 g/g decreased sharply with further increasing time (see Fig. 5). This might be due to the participation of SCFAs consumers, such as methanogens. However, during the 21-day fermentation time, higher SDS dosages, such as 0.25 and 0.3 g/g, could reduce or inhibit the methanogens activity, which will be discussed in the following text.

Fig. 6 shows the percentage of individual SCFA accounting for total SCFAs at different SDS dosages when fermentation time was 6 days (almost the same observation was made at other fermentation time, data not shown). The data in Fig. 6 indicated that acetic acid was the most prevalent product no matter SDS was utilized or not. It was observed that in the blank test the fraction of acetic > propionic > *iso*-valeric, which has also been observed by other researchers [22]. Wang et al. [22] found that the individual SCFA concentration in WAS digestion process was in the following order: acetic > propionic > *iso*-valeric > *iso*-butyric > (*n*-valeric, *n*-butyric), no matter which type of sludge pretreatment method (ultrasonic, thermal, freezing) was used. However, the different observation was made when SDS was used in this study. As seen in Fig. 6, in the presence of SDS *iso*-valeric acid was the second major product, which was followed by propionic acid. Acetic, *iso*-valeric and propionic acids represented more than 80% of the total SCFAs in all experiments.

Under anaerobic conditions the microbial degradation of SDS via β-oxidation can also produce SCFAs [23], which indicated that some of the SCFAs produced during WAS fermentation in the presence of SDS might come from SDS degradation. Right now, however, it is quite difficult to distinguish which SCFAs were produced from WAS or from SDS degradation even if the ^{14}C-labeled SDS test were conducted, because there is only one carbon labeled in the available ^{14}C-labeled SDS from the market. After the first β-oxidation of ^{14}C-labeled SDS, ^{14}C would be in an acetic acid molecular, and then ^{14}C could not give any more information about the degradation of the residual SDS molecular. Thus, experiments on the anaerobic degradation metabolism of SDS during WAS fermentation need to be further investigated in the future.

3.4. Effect of SDS on methanogens activity at different fermentation times

The effect of SDS on methanogens activity expressed by methane production is shown in Fig. 7. The addition of lower dosage SDS, such as 0.05 g/g, caused only slight decrease of methane production with no significant lag-time appeared. However, the lag-phase of methane generation increased from 2 days at SDS 0.1 g/g to 12 days at SDS 0.25 g/g. The lag-phase was so

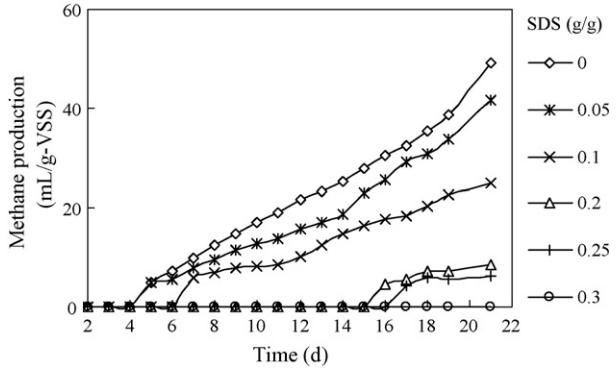

Fig. 7. Methane production at different SDS dosages during the entire fermentation time.

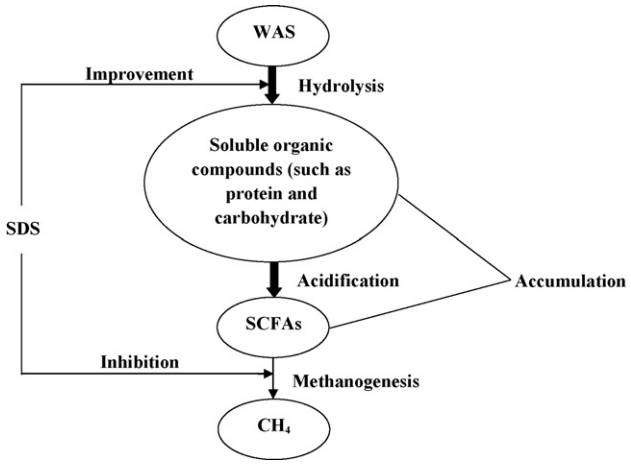

Fig. 8. Simple representation of the influence of SDS on WAS fermentation.

long that there was no methane detectable at SDS 0.3 g/g even on the last day of fermentation. As shown in Fig. 7 the methane production decreased sharply with the increase of SDS. Apparently, the activity of methanogens was inhibited by surfactant, which has also been reported by other researchers [8–11].

Usually, hydrolysis, acidification and methanogenesis all occur in sludge fermentation. SCFAs, the products of acidification, are the substrates for methanogenesis and can be easily metabolized to methane by methanogens under proper conditions. Data in Fig. 7 demonstrate that methane was actually produced in the presence of SDS. Also, it can be seen from Figs. 5 and 7 that the decrease of methane always coincides with the increase of SCFAs production, which indicates that one main reason for improved SCFAs accumulation in WAS fermentation was due to the decreased SCFAs consumption by methanogens. Due to the measurement of SCFAs and methane carried out in two separated reactors (one for liquid sampling and another for methane sampling, see Section 2), the observed starting time of SCFAs decrease in Fig. 5 did not exactly coincide with that of methane appearance in Fig. 7. For example, methane in the blank test and at SDS 0.25 g/g showed up earlier in the gas sampling reactor than in the liquid sampling reactor.

From the above experiments results, it can be seen that the influence of SDS on WAS fermentation lies in the following two aspects: the improvement of WAS hydrolysis, which provided more soluble organic compounds (such as soluble protein and carbohydrate) for fermentation, and the inhibition of methanogenesis, which reduced the consumption of produced SCFAs. Thus, the intermediate products of WAS fermentation, SCFAs was largely accumulated. The effects of SDS on WAS fermentation are simply illustrated in Fig. 8.

4. Conclusions

The performance of WAS fermentation was influenced by SDS at ambient temperature. In the presence of SDS, the concentrations of protein and carbohydrate in aqueous phase were increased, and the concentration of SCFAs was significantly enhanced. Also it was observed that the maximum SCFAs concentration increased with the dosage of SDS. Further study showed that higher SDS dosage inhibited the activity of methanogens. The lag-phase of methane generation increased with the dosage of SDS, and methane production decreased sharply at higher SDS dosage. At SDS dosage below 0.05 g/g, the influence of SDS on methane production was slight with no lag-phase appeared. Thus, the performance of anaerobic sludge digester would not be seriously affected by SDS with its dosage below 0.05 g/g.

Fermentation of WAS caused the release of NH_4^+-N and PO_4^{3-}-P. The concentrations of both NH_4^+-N and PO_4^{3-}-P in fermentation liquor also increased in the presence of SDS. If the SCFAs-rich effluent from fermentation of WAS were used as supplementary carbon source for BNR (biological nutrient removal), NH_4^+-N and PO_4^{3-}-P released would increase the nutrient load of wastewater treatment plants. Therefore, it is desirable to remove NH_4^+-N and PO_4^{3-}-P from fermentation liquor of WAS before being fed to BNR plants.

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