Influence of surfactants on anaerobic digestion of waste activated sludge：acid and methane production and pollution removal

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Abstract

The objective of this study is to summarize the effects of surfactants on anaerobic digestion of waste activated sludge. The increasing amount of waste activated sludge has caused serious environmental problems. Anaerobic digestion (AD), as the main treatment for waste activated sludge containing three stages (i.e., hydrolysis, acidogenesis and methanogenesis), has been widely investigated. Surfactant addition has been demonstrated to improve the efficiency of AD. Surfactant, as an amphipathic substance, can enhance the efficiency of hydrolysis by separating large sludge and releasing the encapsulated hydrolase, providing more substance for subsequent acidogenesis. Afterwards, the short chain fatty acids (SCFA), as the major product, have been produced. Previous investigations revealed that surfactant could affect the transformation of SCFA. They changed the types of acidification products by promoting changes in microbial activity and in the ratio of carbon to nitrogen (C/N), especially the ratio of acetic and propionic acid, which were applied for either the removal of nutrient or the production of polyhydroxyalkanoate (PHA). In addition, the activity of microorganisms can be affected by surfactant, which mainly leads to the activity changes of methanogens. Besides, the solubilization of surfactant will promote the solubility of contaminants in sludge, such as organic contaminants and heavy metals, by increasing the bioavailability or desorbing of the sludge

Keywords: *Surfactant*; *Sludge*; *Anaerobic digestion*; *Contaminants removal*

1. Introduction

Nowadays, more and more contaminants existing in water need to be remediated adequately. One of the most widely used means for contaminant removal is activated sludge process [1]. As a kind of biological wastewater treatment, large amounts of waste activated sludge (WAS) are produced in wastewater treatment [2]. The amount of WAS increases with the quantitative dilatation of municipal and industrial wastewater [3]. The increasing quantity of WAS has become an environmental problem which needs to be solved urgently [4]. For example, the quantity of WAS in China is expected to increase to 34 million tons (at a moisture content of 80%) in 2018, and more than 75% would be handled insecurely [5]. Therefore, an efficient sludge treatment technique is strongly desired for WAS treatment [6], converting the easily biodegradable organic matters into relatively stable substances, and keeping the residues below the standard values [7-9].

To solve the problems of sludge over quantification, many techniques have been used. In developed countries, concentration and anaerobic digestion are the most common methods for WAS treatment. The corresponding cost for WAS treatment accounts for 60% of the total running cost of wastewater treatment plants (WWTPs) [10], which suggests that the method of concentration and anaerobic digestion cannot be widely accepted. Other methods such as landfill and ocean dumping technology, due to their negative impacts on the environment-spread of toxic substances in soil and low-cost utilization of land, are being used rarely [10]. Currently, the re-utilization of sludge resources is generally expected [11, 12]. Anaerobic digestion, a method consisting of three stages, i.e., hydrolysis, acidogenesis and methanogenesis, has been widely applied for sludge stabilization. Pollution control and energy recovery can be fulfilled at the same time, which is one of the advantages of anaerobic digestion [13]. In addition, stabilizing organic matters of the sludge and hindering the harmful chemicals into environment can be achieved concurrently [4]. Moreover, getting biogas or short chain fatty acids from this process can also be achieved [8, 14]. The main component of the biogas is methane which can be used as the resource, and SCFA can be applied to generate polyhydroxyalkanoates or used as a preferable carbon source to remove nutrient during wastewater treatment [15, 16]. The characteristics including production of renewable sources, concepts of integrated biorefining and advanced waste treatment, will make it possible for anaerobic digestion to be widely used in the future [17]. Therefore, more and more researchers have studied to improve the efficiency of anaerobic digestion [18]. However, the disadvantages of long reaction period and low efficiency limit its development.

Surfactant, possessing both hydrophobic groups and hydrophilic groups, is now widely studied and used [19, 20]. The classification of surfactants is generally divided into chemical surfactants (CSF) and biological surfactants (BSF); or divided into cationic, anionic, nonionic, and zwitterionic surfactants [21, 22]. The chemical surfactants, for instance, sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), linear alkylbenzene sulphonates (LAS), and Triton X-100 etc., are widely used in practical applications [23]. However, CSFs are commonly toxic to the environment and easily accumulated in the environment [24]. BSFs, such as rhamnolipid (RL), saponin (SP), surfactin (SF) and glycolipid, have advantages such as biodegradability, efficiency at harsh temperature or pH, and lower toxicity compared to the chemical counterparts [14, 25]. Surfactant can be adsorbed on the interface, reduce surface tension, or form micelles. The insoluble substance gets into the micelles and enhances its solubility [26-28].

In process of anaerobic digestion, surfactant can enhance solubility of organic matter in the sludge in order to improve the efficiency of hydrolysis and remediation [29, 30]. Different surfactants can lead to different amounts of acetic and propionic acid (short chain fatty acids), and can also affect the growth of polyphosphate accumulating organisms (PAO), glycogen accumulating organisms (GAO) and methanogens. In addition, surfactant can influence some characteristics of the sludge. For example, surfactant can change the pH and the structure of the sludge component such as proteins and carbohydrates. Moreover, surfactant can alter sludge floc diameter which is closely related to anaerobic digestion of sludge [31, 32]. Furthermore, surfactants also have a good performance in the removal of pollutants during the anaerobic digestion process [33]. Two kinds of organic pollutions are discussed generally in the sludge-organic pollution, hydrophobic organic compounds and heavy metal pollutants [34]. It is concluded that the removal mechanisms about organic contaminants by surfactant can be summed up into three aspects: emulsification of liquid pollutant, micellar solubilisation, and facilitated transport. All mechanisms are designed to increase microbial contact with pollutants and improve the efficiency of microbial treatment [27]. In order to promote the removal of metal ions from the sludge, surfactant may act in two ways, i.e., ion exchange and complexing with metal ions [24].

Recently, some investigations have found the advances in utilization of surfactants during the dewatering of sludge. But the process of anaerobic digestion has been neglected, which will be summaried in this article. The surfactants can work in two aspects: improving anaerobic digestion effciency and enhancing removal of contaminants, which will be discussed in this paper. In addition, this review expounds the theory direction and future prospect.

2. Influence of surfactants on properties of WAS

2.1 Effect on physicochemical properties

In the process of anaerobic digestion, pH value is a significant impact factor, and its effect runs through the whole anaerobic digestion process. At pH 6.5-7.2, the process of methane production is optimized; while at pH 4.0-8.5, it is optimized for fermentative process [8]. Different pH values also have different influences on acidification process. When pH is higher than 8, the products obtained in the process of acidification are gradually shifted from acetic and butyric acids to acetic and propionic acids [8]. The addition of surfactants can change the pH value of sludge. It was reported that with an increase of SDS dosage in the sludge from 0 to 50 mg/g SS of SDS, the sludge pH increased from 6.1 to 7.1 [3, 35]. The effect of another chemical surfactant, SDBS, on the pH of the sludge is different from SDS. When 20-50 ppm SDBS was added into WAS, the pH dropped from 7.4 to 6.0 within 20 days [36, 37]. However, the alkaline condition is better than the acid condition to promote the anaerobic digestion process [8].

Generally, the main constituents of sludge are proteins, carbohydrates and lipids [14]. The chemical surfactants, which are more toxic than biological surfactants, may lead to changes in the structure of the sludge. The surfactant can lead to denaturation of proteins via tertiary structure unfolding in the sub-micellar and chain expansion [38]. The micelle-like cluster composed of surfactants will form in the presence of proteins. Chen et al. (2013) found that with the existence of SDBS, the fluorescence peak intensity of proteins decreased from 5.14×10^6 to 2.88×10^6, indicating that SDBS was the main contributor to the denaturation of protein. The monomers of SDS binding to protein by hydrophobic interactions lead to unfold of the tertiary structure at the sub-CMC concentration. However, when SDS concentration is above CMC, the micelles nucleate on the hydrophobic patches of the protein chain cause it to expand [38]. The most important conclusion obtained from the experiment is that when a variety of interactions between proteins and surfactants are compared, specific ion interactions are greater than nonspecific hydrophobic interactions, indicating that the details of the process depend on the type of surfactant [39, 40]. The anionic surfactants, such as SDS and SDBS, owning to longer alkyl chain, having more strongly protein fluorescence. The different head groups of different anionic surfactants do not show distinct difference. However, the nonionic surfactants, such as TX-100, surfactin and saponin, show less interaction with protein because of non-mainstream type of reaction [40, 41].

Morphology is the characterization parameter investigated generally for sludge. Generally, the addition of surfactant is accompanied by the occurrence of saponification [42, 43], which would cause the fast reduction of mean projected area, diameters and alter the flocs shape expressed as circularity index. In consideration of the influence of morphology by SDS addition, two ranges of concentrations can be discriminated: 0.0025–0.025 g/L and 0.25–2.5 g/L. It was increased by 8% for mean projected area after 24 h without SDS addition. However, this parameter was reduced about 30%

in the run containing SDS at concentrations 0.0025-0.025 g/L and >55% at concentrations of 0.25-2.5 g/L. In addition, other factors including diameter, convex perimeter, ferret diameter and perimeter were also enhanced about 8-9% after 24 h in the control run; while decreased in the run with SDS about 10-15% for concentrations at 0.0025-0.025 g/L, and 30-40% for concentrations at 0.25-2.5 g/L [42]. At present, this phenomenon has not been systematically elaborated and the mechanism has not been fully expounded, which also provides a reference for future research.

However, there is few papers clearly indicating that the BSF has any observed effects on the pH and its constituents as well as morphology, which suggests that the direction is worth studying in depth.

2.2 Impact on biological properties

The microbial elements of sludge play very important role in the anaerobic digestion process, and thus the microbiological factors should be focused [44]. The microorganisms contained several groups are complicated and delicate in the process of anaerobic digestion. The whole microbe-process requires the design of the optimal method because the optimal operation conditions of different microbes cannot be completely overlapped [8]. The complex microbial community usually consists of a large number of bacteria and archaea populations, which are usually related to hydrolysis, acidification, biogas production and pollutant removal [45].

The core groups of bacteria in anaerobic digesters consist of *Chloroflexi*, *Betaproteobacteria*, *Bacteroidetes*, and *Synergistetes*. However, *Methanosarcinales*, *Methanomicrobiales*, and *Arc I phylogenetic groups* are mainly archaeal community [14, 46]. The effects of surfactant on the characteristics and structure of microbes deserve the attention of researchers [47].

Generally, surfactant can transform cell structure of microorganism via making materials on cell surface depart from the attached site and dissolved in aqueous solution [4]. Specifically, as amphipathic surfactant combines the proteins with hydrophilic groups, surfactants could impair the function and integrity of biological membranes, thereby causing native structure disturbing [48]. Whereas the hydrophobic groups combine with lipids, causing the liquefaction of membranes and impairment of their barrier properties [49]. In the comparison between chemical surfactants and biological surfactants, the biological surfactants show better biocompatibility. With the addition of the same dosage of 40 mg/g TSS of SDS, SDBS, and RL to the sludge, the percentage of *Proteobacteria* decreased to 46.1% in control, 35.6% with SDBS, 34.7% with SDS, and 43.2% with RL after 8 days, respectively, and the same tendency was also found for *Bacteroidetes* and *Chloroflexi* [50]. However, for *Firmicutes*, a critical participant in hydrolysis and acidification, the percentage was the highest (in relative abundance) in SDS about 26.9%, higher than that in RL about 24.4%, and were found to be lower in SDBS about 6.7% and the lowest in Control about 4.2% [31, 51, 52]. However, the exact mechanism of SDS enhancing the abundance of *Firmicutes* is still unknown. In addition, RL shows better biocompatibility, which allows highly active hydrolysis and is favorable to functional microbe for further interaction in anaerobic digestion [51]. The effects of different biosurfactants are different. Previous experiments showed that the negative effects of SF and RL on diversity of metabolic and species were conforming. However, SP showed much fewer block on diversity of metabolic and species than RL and SF, and exhibited better biocompatibility, even if possessed inferior surface activity than SF and RL [45, 46, 53]. The reasons may be related to the difference of characteristic between anionic surfactants (SP and RL) and nonionic surfactants (SP). The influences of the addition of surfactants on microbes are shown in Fig. 1.

In general, microorganisms and enzymes are always complementary to the biological characteristics of the sludge [54]. In this complex enzyme system, the various processes in which the enzymes involved are protease and α-glucosidase during hydrolysis, acetatekinase during acidification, coenzyme F_{420} during methanation, and dehydrogenase about microorganisms [15]. Among them, the composition of the hydrolase is more complex. Four kinds of hydrolases, i.e., a-glucosidase, alanine-aminopeptidase, esterase, and dehydrogenase, play important roles in hydrolysis [55]. A-glucosidase can degrade starch, while alanine-aminopeptidase is responsible for the degradation of proteins. For esterase activity, measuring as hydrolysis fluorescein diacetate (FDA), does not produce information about specific substances degradation. Whereas, dehydrogenase activity has been found to correlate with substrate removal in sludge [56-59]. These enzymes organically form an important part of the enzyme system, which can promote the disintegration of large particles and produce more surface for attaching of microbes, leading to a high efficiency degradation [11].

The effects of surfactants on enzyme activity have also been investigated. SDS suppresses the ATPase activity of P-glycoprotein at low concentrations [60]. However, it stimulates protease and amylase activities. The increased amount can be attributed to destruction of the sludge matrix and release of the enzymes immobilized on the floc structure [3, 26, 35]. When the dose increases to a certain level, it will have a hindrance. Another chemical anionic surfactant, SDBS, has the analogous effects on enzymes. It can enhance the activity of protease and a-glucosidase, but the exact reasons for this phenomenon are still unclear [2]. When the dose of additional SF, RL, and SP was 50, 50, 100 mg/g DS, respectively, the biosurfactant RL was the most powerful one compared to others which gained the activities of neutral protease and α-glucosidase to 4.07 and 5.73 times, respectively. SF and SP had the same effects, but the increase was less than that of RL. Furthermore, the addition of RL made the activity of coenzyme F_{420} decrease by 40%. RL also possessed a violent negative impact on the dehydrogenase and acetate kinase activities. SF also had a wicked effect on the activity of the coenzyme F_{420}, dehydrogenase and acetate kinase, but the effects were weaker than that of RL. For example, the activity of acetate kinase was 73% after SF addition, but it was 26% after RL addition. When it came to methane production, SF addition slightly reduced with the increase of dose in the original period, but the throughput gradually raising and outstripping the control test after 6 d. In contrast, RL invariably showed powerful inhibition of methanogenesis which was probably attributed to the decrease of coenzyme F_{420} activity [15]. SP addition had not shown any inhibition, methane yield in the test with each dose of SP remaining the same to the control test which indicated that methanogenesis was not influenced by SP addition [15]. In general, researches have summed up that the influence of enhancing or inhibiting by surfactants may depend on the length of alkyl chain, but there is no specific experiment to prove it, which could be an in-depth point [26, 61, 62].

3. Impact on anaerobic digestion

Anaerobic digestion, containing hydrolysis, acidification, and methanogenesis, is a complex biochemical process. Surfactant, owing to special characteristics, may have some effects on sludge during anaerobic digestion. Hence, the effect of surfactants on the three stages of anaerobic digestion will be discussed, respectively.

3.1 Hydrolysis

The mechanisms of the increment of hydrolysis by surfactant can be summed up in two aspects: sludge components and enzyme activity (Fig. 2). The sludge blocks will be dispersed, and the hydrolase will be released from the sludge, which increase the efficiency of hydrolysis. And the latter has been discussed in the second chapter. Extracellular polymeric substances (EPS) is the main part of sludge components [44]. The main fractions of EPS are proteins and carbohydrates [63]. Surfactant can cause the break-up of sludge substance, especially the EPS, which releases more proteins and carbohydrates [16, 64]. The existence of the electrostatic interaction between enzymes and extracellular polymer substances leads to the complexes of extracellular polymer substance-enzyme, which traps enzymes in substrate. Therefore, the activity of enzymes have increased due to the release of enzymes by surfactant addition [65, 66]. In addition, surfactants enhance solubility of material particles by reducing surface tension or forming micelles, which can also improve the hydrolysis efficiency [14]. As one of the most widely used chemical surfactant, the impact of SDS was discussed previously. With the addition of SDS, the thicknesses of protein and carbohydrate all increased. In a fermentation experiment, the thicknesses of protein and carbohydrate reached 0.3418 and 0.5159 g/L in the control test, 0.8277 and 0.1576 g/L with 100 mg/g SDS, and 1.3729 and 0.2209 g/L with 300 mg/g SDS dosage, respectively, in the sixth day of fermentation [1]. Ji et al. (2010) found that by adding 20 mg/g of SDBS in fermentation system, the maximal proteins and carbohydrates released were 1.7 and 1.9 times of those from the control in the sixth day of fermentation, respectively. As for biosurfactant, alkyl poly glycosides (APG), a kind of widely used surfactant, its influence has been investigated. In previous experiments, the maximal concentrations of proteins and carbohydrates were 3.3020 and 0.6580 g/L in WAS+SDS system with SDS dose of 200 mg/g TSS, respectively, whereas the corresponding concentrations were 1.6870 and 1.2060 g/L in WAS+APG system with APG dose of 200 mg/g TSS, respectively, indicating that SDS enhanced the protein production, and APG enhanced the carbohydrate production [26]. This appearance can be attributed to the hindrance of composing of the enzymes involved in protein hydrolysis [67]. For the other biosurfactants, it has been confirmed that the concentration of proteins increased with the addition of RL, SF and SP during the initial 60 mins, which was related to the dose. Comparing with SP, however, SF as well as RL had a preferable impact on the solubilization of EPS [68]. The essence of this phenomenon is partly because of the weaker surface activity of SP than RL and SF; and the other part is because of the degradation of

SP, and this degradation is not observed for RL and SF [15, 69, 70].

3.2 Acidification

Generally, SCFAs, the products of acidification, are the designation of a series of acids, including acetic acid, propionic acid, and butyric acid, etc. [71]. Wherein, acetic acid and propionic acid are the two kinds of acids with the largest amount, and their proportion has a profound effect on the properties of SCFAs. For different purposes of production, there are different requirements for the intermediate products. The ultimate purpose of acidification is promoting more methane production. Therefore, a higher proportion of acetate is required, which is attributed to the direct degradation of acetic acid by methanogens [72] and other SCFAs should be converted into acetic acid before being used to produce methane [73]. However, if the purpose of acidification is to enhance the efficiency of biological nutrient removal (BNR), one feasible means of supplying PAO with a selective advantage over GAO is through operating the carbon source composition. Investigation has suggested that PAO activity with propionate is greater as compared to acetate, so it is required that obtaining higher proportion of propionic [74]. The increasing efficiency of BNR by propionic could be attributed to the different characteristics between PAOs and GAOs [75]. Both PAO and GAO can consume SCFA to obtain energy, but only PAO can hydrolyze polyphosphate. Therefore it is necessary to inhibit the activity of GAO, and then promote the polyphosphate hydrolysis by enhancing PAO activity [76, 77]. Acetate, as a kind of SCFA, can easily be adsorbed and consumed by GAO and PAO. However, the consumption of propionic acid is distinct. The rate of propionic consumption by GAO is slower than that by PAO. Moreover, PAO has been proven to be more accommodable when carbon source changes as compared to GAO [78, 79]. Therefore, more proportion of propionic can enhance the activity of PAO and baffle the activity of GAO, leading to the enhancement of biological nutrient removal efficiency.

The most influential factor in the composition of short chain fatty acids is pH. With the increase of pH value, the amount of acetate, butyrate, and iso-butyrate all increased, and the same trend has been observed for amount of higher weight molecular, such as valerate, iso-valerate, and caproate [80, 81]. However, the optimal amount interval of propionate is between 6.0-9.0 and its optimal proportion can up to 50% [74]. In addition, the C/N also has definite impact on product of SCFA. Generally, both carbon and nitrogen originate from the product of hydrolysis-protein and carbohydrate. The improvement of C/N of digestive matrix was favorable to the production of propionate [82]. Hence, with a high content of protein, the enhancement of nitrogen elements content has been caused. Therefore, the C/N of digestive matrix becomes excessively small and the production of propionic is limited, and the addition of carbohydrate matter is indispensable [74]. Nevertheless, excessively large C/N also results in some negative phenomenon. The production of PHA requires the nitrogen-limited condition, whereas high C/N prevent the merisis of active biomass for close connection between nutrition and cell merisis. Nevertheless, Jiang et al. (2009) have found that enhancing feed degree or optimizing process factors can achieve high production of PHA even without nitrogen-removal [83]. The maximum permissible value of C/N is 50, and this value exceeding 50 may cause the cessation of process [84, 85].

The addition of surfactant may improve acidification efficiency. SCFA yield was enhanced by SDS [86]. Jiang et al. (2007) found that, in the sixth day of zymolysis, the concentration of SCFA was 2243.04 mg COD/L with 100 mg/g SDS, whereas it was merely 191.10 mg COD/L in the control. However, with higher concentration of SDS being added, less SCFA was produced during the original stage of zymolysis, which could be ascribed to the negative influence of SDS. For instance, the destruction of microbial protein structure and accumulation in the environment to produce toxic byproducts [87]. The rank of the composition SCFAs was in the order of acetic > propionic > iso-valeric in the control. However, the addition of SDS changed the array to acetic >iso-valeric> propionic. The results showed that the production of SCFA was enhanced remarkably in the presence of SDBS. At 6 days of fermentation time, the maximum SCFA was 2599.1 mg COD/L with 20 mg/g SDBS addition, whereas it was 339.1 mg COD/L in the control test without sodium dodecyl benzene sulfonate addition [2]. The same situation was observed when the dose of sodium dodecyl benzene sulfonate was higher than 200 mg/g. After all, the inhibition of microorganism caused by SDS and SDBS cannot be neglectable. However, the rank of all kinds of SCFAs was different from that with SDS addition. During the original 6-day fermentation, there was no doubt that acetic acid was the most universal component, but the propionic acid was the sub major products, their percentages were acetic acid about 27.1%, and propionic acid about 22.8%, respectively. The maximum SCFA concentration reached 800 mg COD/L in the fifth day in the control without biosurfactants. Its production enhanced with the increasing dose of SF or RL (ranging from 23 to 50 mg/g DS), and the maximum concentration was nearly 3.3 g COD/L. However, SCFA production was distinctly improved when the dose of SP varied from 20 to 100 mg/g DS, and the maximum concentration of SCFA was 3.1 g COD/L. There was no significant enhancement for higher dosage of SP, RL, and SF [2]. In the aspect of transformation of SCFA components, the emphasis is on the changes in the content of acetic and propionic acid. With SP, RL and SF addition, the percentage of acetic, propionic and n-butyric acid were enhanced in pace with the augmenting dose of the biosurfactants. However, the proportion of acetic acid to propionic acid in reactors with SF or RL addition was higher than that with SP and in the control [16]. In fact, the propionic acid was the main product during the acidification of glucose, whereas the ratio of acetic acid was high when protein was degraded [88], which was probably correlated to the influence of surfactant addition. However, the effect of surfactant degradation on the production of SCFA is also worthy to discuss. There are two mechanisms to enhance SCFA generation, i.e., biological effect and chemical effect. The latter particularly depended on the degradation of surfactant itself. However, in terms of some surfactants that have been discussed, SP possessed a analogical enhancement of SCFA production by its degradation, although its surface ability was lower than SF and RL [15]. Whereas in the case of SDS, SDBS, RL, and SF, the improved yield of SCFA was primarily caused by biological impact rather than chemical impact [26].

3.3 Methanogenesis

Methanogenesis, the last step of anaerobic digestion, is defined as the process of converting acetate and hydrogen from acidification to methane and carbon dioxide by methanogenic bacterial [89, 90]. Generally, a significant SCFA consumption was observed in the fermentation of WAS, assumably be attributed to the consumers participation, for instance, methanogens [26]. The order of SCFA consuming is acetate, butyrate, and propionate during the methanogenesis [64], which indicates that a higher proportion of acetic acid is accompanied by a larger amounts of methane production. Two parameters are of great significance in the process of methane production, i.e., pH and activities of methanogenic bacteria.

During the whole period of fermentation, the methane yield enhanced with pH increasing from 4.0 to 6.0, and declined when pH further increased to 10.0 [91]. Apparently, the highest methane production was achieved at pH 7.0 during fermentation time, which indicated that both the higher and lower pH could decrease the activity of methanogenic bacteria [92]. Previous investigation showed that the production rate of biogas general tended to accord with sigmoid function (S curve), indicating that the methane production can be split into three stages: lag phase, decomposition phase, and flattening phase [3]. Methane production is lentitude at the start and end of curve, suggesting that the methane generated in reactor corresponds to specific growth rate of methanogenic microbe [93]. To enhance the methanation efficiency and biogas production, various efforts have been made. Preatment efforts contains physical, chemical, and biological treatment. However, different purposes lead to different consequences. Supposing that the purposes were SCFA accumulation and PHA production, the methods reducing methane production had to be adopted.

In specific surfactants, SDS was observed to affiliate with the inhibition of methanogens activity during the sludge fermentation [26]. It has been reported that the SDS would inhibit the methanogens acitivities in the period of sludge fermentation. With the dose of SDS raised from 20 to 300 mg/g, the hindrance ratio of methane yield augmented definitely from 3% to 100% [94]. Another anionic surfactant SDBS also prevented the process of methanogenesis. Total gas yields and methanogenesis from glucose were decreased to half maximal rates at 20 to 50 ppm SDBS during the original period of fermentation [36]. It has shown that the surfactants with aromatic and cyclic, such as SDBS, were found to be the most hazardous compounds for anaerobic acetoclastic methanogenesis [49]. However, SDS is one of the few surfactants with minimal toxicity to methanogens [49]. The inhibition of methane production by saponins is the smallest, which is attributed to the negligible effects of methanogenic bacteria activity after saponins addition. Actually, RL possessed serious antibacterial activity to methanogenic bacteria and some related enzymes. As mentioned above, the addition of RL made the activity of coenzyme F_{420}, a methane related enzyme, decreased by 40%. In addition, it was confirmed that the RL not only prevent the methanogenesis, but also retard the metabolism of other microbes, which might cause the destruction of biological activity of sludge [94].

4. Effects of surfactant addition on contaminant removal

During waste water treatment, activated sludge process produces a large number of waste activated sludge, which contains a lot of pollutants [95, 96]. They might shift to the different compartments involving atmosphere, soli, and surface water via pinpoint or diffuse inputs [97]. The most discussed contaminants, including hydrophobic organic matter (HOC) and heavy metals [98, 99]. The removal of these pollutants has always been a hot issue. The influences of surfactant on representative HOC contaminants have been summarized in Table 1.

Surfactants have a great potential of solubilization. Generally, there are three influence mechanisms for the advancement of HOC biodegradation by surfactants addition (Fig. 3). The first mechanism is forming micelle shaped by surfactant and encasing the HOC. Therefore microorganisms are able to adsorb the contaminant from the micelles core. In the second mechanism, surfactants enhance the mass transfer of contaminants to the aqueous phase for further degrade by microorganisms, which is attributed to the reduced surface tension by surfactant [100]. And for the third mechanism, the cell hydrophobicity has been changed by the addition of surfactants, resulting in the direct contact between cells and contaminants [101-103]. In addition, there is another mechanism that has been conjectured, in which surfactants promote microorganisms to be adsorbed to sludge surface sites occupied by contaminants [104].

Because of the application of various kinds of metals in industry, there are also various heavy metal ions in the wastewater, which causes the sludge filled with heavy metal ions [105, 106]. Heavy metals cannot be biodegraded. On the contrary, they can only be transformed from one configuration to another, which can change their mobility and toxicity

[107]. Some forms of heavy metals can be transformed by process of redox or by alkylation. There were two main mechanisms for desorption of heavy metals from sludge by surfactant addition (Fig. 4). Firstly, the cationic surfactant can permute the same charged metal ions by rivalry for some but not all negatively charged surface, because of the interaction of repulsion between cationic surfactant and heavy metals. Secondly, the anionic surfactants form nonionic complexes with heavy metal by ionic bonds which are stronger than the bonds of metal with sludge [108, 109] . The metal-surfactant complexes are desorbed from sludge substance to aqueous due to the decrease of the surface tension [110-112]. In general, the two mechanisms can be concluded in ion exchange and counterion binding.

5. Conclusion and future prospects

This review summarized the utilization of surfactant in the process of anaerobic digestion, including the influences on sludge properties, and conversion process of hydrolysis, acidification and methanogenesis. In addition, due to the excellent solubilization of surfactant, the removal of organic pollution and heavy metals might also be affected by surfactant addition. Surfactants, as an amphiprotic compound, have characteristic of solubilization via reducing interface tension or forming micelles, when the concentration of surfactant is under or above CMC, respectively. In the process of anaerobic digestion, due to the rate-limiting influence of hydrolysis, enhancing its efficiency will lead to the increment of acidification substrate. Therefore, the increased SCFA production can be applied to remove nutrient and produce PHAs. Surfactant can not only affect the proportion of various SCFA, but also influence the activities of certain microorganisms, which have significant roles in anaerobic digestion.

Notably, future investigations can be paid attention to the following aspects: i) Establishing technological process for the production of biosurfactant for industrial production. Although the toxicity and risk of biosurfactant are smaller than those of chemical surfactant, the price of biosurfactant is higher than chemical surfactants, which limits its wide application. ii) Establishment of models to describe the influence surfactant addition on different microorganisms. Due to the complex constitution of microorganism involved in anaerobic digestion, as well as the dual character of surfactant, the quantify effects of surfactant need specific model. iii) Process improvement of producing PHAs from SCFA. The production of PHAs is in the theoretical stage. In order to achieve the consummate craft of waste resources re-utilization, it is worth investigating how to establish a systematic process for PHAs production.

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