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A novel approach for improving the drying behavior of sludge by the appropriate foaming pretreatment

Jing Huang, Zhao-Hui Yang^{*}, Guang-Ming Zeng, Hui-Ling Wang, Jing-Wu Yan, Hai-Yin Xu, Cheng-Liu Gou

College of Environmental Science and Engineering, Hunan University, Changsha 410082, China

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ABSTRACT

Foaming pretreatment has long been recognized to promote drying materials with sticky and viscous behaviors. A novel approach, CaO addition followed by appropriate mechanical whipping, was employed for the foaming of dewatered sludge at a moisture content of 80-85%. In the convective drying, the foamed sludge at 0.70 g/mL had the best drying performance at any given temperature, which saved 35-41% drying time for reaching 20% moisture content compared with the non-foamed sludge. Considering the maximum foaming efficiency, the optimal CaO addition was found at 2.0 wt%. For a better understanding of the foaming mechanisms, the foamability of sludge processed with other pretreatment methods, including NaOH addition (0-3.0 wt%) and heating application (60 -120 °C), were investigated while continuously whipping. Their recovered supernatant phases were characterized by pH, surface tension, soluble chemical oxygen demand (sCOD), protein concentration, polysaccharide concentration and spectra of excitationemission matrices (EEM). These comparative studies indicated that the sludge foaming was mainly derived from the decreased surface tension by the surfactants and the promoted foam persistence by the protein derived compounds. Further, a comprehensive analysis of the sludge drying characteristics was performed including the surface moisture evaporation, the effective moisture diffusivity and the micromorphology of dried sludge. The results indicated that the drying advantages of foamed sludge were mainly attributed to the larger evaporation surface in a limited drying area and the more active moisture capillary movement through the liquid films, which resulted in longer constant evaporation rate periods and better effective moisture diffusivity, respectively.

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1. Introduction

The constituents removed from wastewater-treatment plants (WWTPs) include screenings, grit, scum, solids and biosolids.

The solids and biosolids are collectively referred to as "sludge" which is a mixture of excess biomass generated in the aerobic and anaerobic digestion of the organic constituents of municipal sewage and inorganic materials such as sand and metal oxides (Tchobanoglous et al., 2003; Ding et al., 2012). The

^{*} Corresponding author. Tel.: +86 731 88649168; fax: +86 731 88822829. E-mail address: yzh@hnu.edu.cn (Z.-H. Yang).

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sludge output has been continuously increasing with the rapid urbanization and the stringent environmental regulations for several years. Problems have arisen from the harmful constituents of sludge like heavy metals, toxic organics, pathogenic bacteria and viruses. That must be carefully treated, otherwise the constituents will cause secondary pollution, affect public sanitation and waste the efforts of WWTPs.

Correspondingly, various methods have been used to dispose or utilize the sludge, including incineration, landfilling, road surfacing, conversion to fertilizer, compression into building blocks and carbonization (Lundin et al., 2004). In order to reduce its costs of storing, transportation and handling prior to disposal or utilization, reduction of the sludge volume and quantity by water separation has become the principal part of sludge treatment (Zhao et al., 2010; Arlabosse and Chitu, 2007). In practice, several mechanical dewatering techniques including centrifuges, vacuum filters, belt filter presses and membrane filter presses have been alternatively employed in WWTPs (Chen et al., 2002).

The presence of organic components, mainly bacterial cells and extracellular polymer substances (EPSs), induce a high water retention and poor dewaterability due to the negatively charged polymer network and the highly colloidal and compressible nature (Saveyn et al., 2005; Citeau et al., 2011). Despite the technical improvements in recent years, a plateau value of 35% dry solids (DS) content seems to be the highest efficiency which can be reached by the commonly employed mechanical dewatering techniques (Tuan and Sillanpää, 2010; Mahmoud et al., 2011). Obviously, that value is not always sufficient and a more extended dewatering is often required.

Convective drying is a traditional and proven technique in drying industry, which enables a thorough dehydration of sludge and represents a potential intermediate unit operation for sludge drying. This technique has the advantages of providing volume reduction, stabilization through inactivation of pathogenic biological organisms and an increase of the energy value of the dry material (Peregrina et al., 2008). However, in most cases it is not cost-effective because of the high energy demands and the by-product status of sludge. Therefore, for the purpose of cost controlling, many studies have focused on the design of new thermal dryers, the optimization of thermal-drying operation and the use of renewable energy (Mathioudakis et al., 2009; Deng et al., 2009; Léonard et al., 2008; Slim et al., 2008; Bennamoun, 2012). In addition, some other studies have been concerned with the drying behavior of sludge with different properties (Ruiz et al., 2007; Wang et al., 2011).

No matter which energy sources such as fossil, solar, electric and biological are proposed, the nature and texture of sludge is definitely one of the key issues in the convective or conductive thermal-drying step. The water within sludge does not have similar properties in terms of vapor pressure, enthalpy, entropy, viscosity and density, which is widely dependent on its proximity to the solids (Vaxelaire and Cézac, 2004). In view of that, a large number of pretreatment methods have been proposed to improve the dewaterability of sludge, including the application of ultrasound, microwave, rapidfreezing, electrolysis, heat, as well as the addition of Fenton's reagent, acids, alkalis, ozone, surfactants or combination of these methods (Yuan et al., 2011; Gao, 2011). There is a general idea that those methods should disrupt the microorganism cell walls and change the water molecules-organic matter bonding. However, few methods have been developed for the purpose of improving the drying performance of the dewatered sludge. Only a few studies evaluated the influence of the sludge pretreatments on their drying behaviors (Dewil et al., 2005; Huron et al., 2010; Li et al., 2014).

Foam is a dispersion of gas in liquid or solid separated by thin liquid films or lamellaes (Heard et al., 2008). Foaming of liquid and semi-liquid materials has long been recognized as the method to process hard-to-dry materials, which shortens the drying time at a lower temperature and obtains products with desired properties in the industries such as food, chemicals and pharmaceuticals (Ratti and Kudra, 2006). During the thermal-drying step, the rapid drying rate is due to the large surface area of foams exposed for the moisture evaporation and the moisture movement of capillarity in the liquid films, which is suitable for the drying of materials with sticky and viscous behavior (Rajkumar et al., 2007). As the dewatered sludge is highly sticky and viscous, foaming pretreatment provides a potential solution for improving the drying behavior of sludge.

Based on the combination of foaming pretreatment and thermal-drying, three problems are raised regarding the source of foaming agent, the introduction of gas bubbles and the drying method. Generally, CaO is used as chemical conditioner to increase the dry solid content, to disinfect and to increase the drying rate of the dewatered sludge by the texturing effect (Huron et al., 2010). It also provides an alkaline environment that disrupts flocs and cells and releases the inner organic materials from the sludge, which may provide an intrinsic source for the foaming agents.

In this study, CaO addition followed by mechanical whipping, a simple and useful method, was developed for the foaming of dewatered sludge at a moisture content range of 80%–85%. Subsequently, convective drying was employed for drying the foamed sludge. Based on these methods, the objectives of this study were as follows: 1) To investigate the optimum foaming operation and the foaming characteristics for the dewatered sludge; 2) To analyze the mechanisms resulting in the sludge foaming; 3) To investigate the optimum drying conditions for the foamed sludge; 4) To evaluate the drying characteristics of foamed sludge and the micromorphology on the drying surface.

2. Materials and methods

2.1. Dewatered sludge

The dewatered sludge was collected after the process of belt filtration in a WWTP in Changsha, China. This plant treated 140,000 m³/d of wastewater using an Anoxic-Anaerobic-Carrousel process. The principal characteristics of the dewatered sludge are listed in Table 1.

The moisture content and the volatile solid content of the sludge were measured according to Chinese Standard methods (CJ/T 221-2005). Sludge density was determined by the mean ratio of measured weight and volume using two plastic conical measuring cylinders with the full-loaded

Table 1 $-$ The characteristics of the dewatered sludge.			
Dewatered sludge		Supernatant phase of sludge suspension	
Moisture content (wet basis %)	80—85	рН	7.07
Volatile solid (dry basis %)	54.2	Surface tension (mN/m)	65.3
Density (wet basis g/mL)	1.05	Emulsification activity (%)	0.0
Calorific value (dry basis MJ/kg)	13.04	sCOD (mg/L)	1740.0
		Protein (mg/L)	80.0
		Polysaccharide (mg/L)	5.1

volume of 46.7 mL and 206.6 mL, respectively. Transferring of the sludge samples was carried out gently to preserve their structure and to prevent trapping air voids when the conical measuring cylinder was filled up to the rim. Calorific value was measured by an oxygen bomb calorimeter (KSLR-4000, Kesheng, China).

2.2. Preparation of sludge foam

The dewatered sludge was premixed with different dosages of CaO ranging from 0 wt% to 3.0 wt% with 0.5 wt% increments in a portable cement mixer (JS140, JISHUN, China) at a rotation speed of 20 rpm for 30 min. The textures of dewatered sludge then changed from block mass to slurry flow with more homogeneous properties. The foam formation was conducted by whipping the premixed sludge using a cement mortar mixer (JJ-5, JIANYI, China) at the rotation speed of 140 \pm 5 rpm, and the revolution speed of 62 \pm 5 rpm. The densities of sludge foam were controlled by varying the duration of whipping.

2.3. Mechanisms of sludge foaming

2.3.1. Different pretreatment methods

Considering that the source of foaming agents might be mainly derived from the sludge, a series of comparative studies was conducted between the addition of CaO and other sludge pretreatment methods including the addition of NaOH and the application of heating. The dosages of NaOH were ranging from 0 wt% to 3.0 wt% with 0.5 wt% increments. The heating pretreatment was operated in an autoclave for temperatures ranging from 60 °C to 120 °C with 20 °C increments for 15 min. Foaming capacity and foam stability of the sludge were investigated after undergoing the different pretreatment methods.

2.3.2. Preparation and characterization of the sludge suspension

For a better understanding of sludge foaming, the sludge suspension was prepared by blending the pretreated sludge with distilled water in the mass ratio of 1:2, mixing for 30 min using the mechanical shaker, and centrifuging at 10,000 rpm for 10 min (Allegra 25R, Beckman Coulter, USA). The recovered supernatant phase was further characterized by pH, surface tension, soluble chemical oxygen demand (sCOD), protein concentration, polysaccharide concentration and spectra of excitation-emission matrices (EEM).

The pH and surface tension of the sludge suspension samples were measured by a pH-meter (PB-10, Sartorius, Germany) and a surface tensiometer (K100, Krüss, Germany), respectively.

For the determination of sCOD, the supernatant phase of the sludge suspension was filtered through a mixed cellulose esters membrane with micropores of 0.45 μ m. Part of the samples was further filtered through the membrane with micropores of 0.22 μ m for the determination of proteins and polysaccharides. The measurement of sCOD was based on the dichromate method according to Chinese Standard methods (GB 11914-89). The contents of proteins were determined by the Lowry-Folin method with bovine serum albumin (BSA) as standard (Lowry et al., 1951). Meanwhile, the polysaccharides were determined by the phenol-sulphuric acid colorimetry with glucose as standard (Dubois et al., 1956).

EEM spectra were obtained for the organic matters of the supernatant. In view of the high organic content, the supernatant was diluted 1:500 in deionized water. The total organic carbon (TOC) of the samples was diluted to 2.7 mg/L (original sludge), 5.7 mg/L (CaO addition) and 14.4 mg/L (NaOH addition), respectively (TOC-VCPH, Shimadzu, Japan), the pH of the samples was adjusted to 3.0 \pm 0.2 using 1.0 M HCl to minimize the potential for metal-binding and subsequent fluorescence quenching. EEM of the supernatant was recorded using a fluorescence spectrophotometer (F7000, Hitachi, Japan). Excitation and emission wavelength were set from 200 to 400 nm and 250-550 nm, respectively, at the sampling interval of 10 nm. Scan speed was set at 1200 nm/min, slit width was fixed at 5 nm, and photomultiplier detector voltage was fixed at 700 V. The fluorescence response of a blank solution consisting of deionized water with adjusted pH was examined and subtracted from the spectra of the samples in order to account for the effects of acid added to the samples and to remove Raman and Rayleigh scatter (Sanchez et al., 2013; Chen et al., 2003). All the experiments were conducted in triplicate.

2.4. Drying of sludge foams

2.4.1. Drying procedure

In the drying experiments, 5.00 g sludge sample was poured in a Petri dish (60 mm diameter and 12 mm height), and the thicknesses of the sludge foam mat depended on their density. The dishes were placed in the drying oven with different air temperatures of 30 °C, 40 °C, 50 °C and 60 °C, a relative humidity of 20% and a superficial air velocity of 0.2 m/s. The drying oven was pre-stabilized by passing hot air at the pre-set temperature for 30 min. Moisture loss of the samples was determined by the dish using an electronic balance (\pm 0.01) outside the drying oven every 20 min.

2.4.2. Drying curve and moisture diffusivity

During the drying procedure, the moisture content of the samples was calculated using its initial value and the mass loss in every interval. The drying curves were built to reveal the influence of the foaming pretreatment on the drying characteristics of the sludge. The calculation methods of the evaporation rate and the diffusion coefficient were shown in the supplementary appendix.

2.4.3. Micromorphology analysis

During the drying process, the morphology variation of thinlayer sludge foam was photographed every 20 s by a microscope (BX61, Olympus, Japan) equipped with a camera. Furthermore, an environmental scanning electron microscope (ESEM) (Quanta 200 FEI, USA) was used to study the microstructure of dried sludge with and without foaming in low vacuum mode at the acceleration potential of 20 kV.

3. Results and discussion

3.1. Sludge foamability and foam stability

The foamability can be evaluated by the measurement of the foam density. During the whipping process, a lower foam density indicates that more air is entrapped in the sludge foam. Fig. 1a shows the effects of whipping time and CaO addition on the foamability of sludge. The addition at the concentration of 0.5 wt% did not lead to sludge foam formation, whereas the sludge density was suddenly decreased as soon as the concentration reached 1.0 wt%. This phenomenon indicated that CaO addition had a significant effect on the formation of sludge foam. Further, in terms of the highest decreasing rate of sludge foam density, the optimal CaO

addition was found at 2.0 wt% which was low enough to avoid mass increase for the further disposal of sludge.

In most cases, foam formation is a sum effect of all the surface-active compounds present in the water (Schilling and Zessner, 2011). Undoubtedly, CaO does not belong to any kind of surface-active compounds. However, the alkaline environment can disrupt the flocs and cells, and release the sludge inner organic matters (Li et al., 2008). As shown in Fig. 2a, an increase of sludge pH is found with the increase of CaO addition. Meanwhile, the substantial increase of sCOD indicates that more organic matters are released into the supernatant phase of the sludge, which may provide an intrinsic source for the surface-active compounds.

In order to investigate the foaming mechanism of sludge by CaO pretreatment, we had conducted two comparative samples by the pretreatments of NaOH addition and Heating, respectively. For one thing, the NaOH and CaO both belong to the alkaline materials which hold the similar effects on releasing and activating the foaming agents from the sludge. For another, the heating pretreatment belongs to a physical method which can release the inner organic matters from the sludge and avoid introducing potential interfering substances.

The samples in CaO pretreatment and the NaOH pretreatment implied that the foamability of sludge indicated a certain relationship to the levels of sCOD. First, it is observed that the sludge foaming will be triggered when the sCOD reaches above 5000 mg/L regardless of the other foaming factors like pH, temperature, constituents, and so on. For example, comparing Fig. 1a with Fig. 2a, and Fig. 1b with



Fig. 1 – (a) to (c) Effects of the different pretreatment methods and the whipping time on the sludge foam density: (a) CaO addition including the pictures before and after foaming, (b) NaOH addition, (c) heating; (d) stability of the sludge foam after the whipping process with the pretreatment methods of CaO and NaOH addition, respectively. (The experiments were conducted in triplicate and presented in average.)



Fig. 2 – Effects of the different pretreatment methods on the pH and sCOD of the supernatant phase in sludge suspension: (a) CaO addition, (b) NaOH addition, (c) heating temperatures.

Fig. 2b, the sludge foaming is not observed when the sCOD is below 5000 mg/L. While CaO is at 1.0 wt% (Fig. 1a), and NaOH is at 0.5 wt% (Fig. 1b), their sCOD greatly increases to 5264 mg/L (Fig. 2a) and 5728 mg/L (Fig. 2b), respectively, and their sludge density suddenly decreased with the continuous whipping. However, the samples of heating pretreatment (Figs. 1c and 2c) are an exception to the above rule even though their sCOD goes up to 5424 mg/L and 6384 mg/L at the temperature of 100 °C and 120 °C, respectively. This phenomenon indicated that the foaming agents might be susceptible to the high temperature. Second, comparing the foaming samples shown



Fig. 3 – Effects of the different pretreatment methods on the surface tension and the protein and polysaccharide concentration of the supernatant phase in sludge suspension: (a) CaO addition, (b) NaOH addition, (c) heating temperatures.

in Figs. 1a and b, the sludge of NaOH pretreatment has a greater foamability than the CaO pretreatment.

Meanwhile, the sCOD values in the NaOH pretreatment are about 1.2–2.1 times higher than those in the CaO pretreatment shown in Fig. 2a and b. Consequently, sufficient organic matters released by the pretreatments may contain the surface-active compounds in proper concentration available for sludge foaming.

The stability of the foaming samples was further investigated. As shown in Fig. 1d, the sludge foam of CaO pretreatment has a greater stability than the NaOH pretreatment, which is the exact opposite to the foamability. In spite of the ingredients and levels of the surface-active compounds, the higher viscosity caused by the lower moisture content, the more particles derived from the Ca(OH)₂ precipitation and the bridging effect enhanced by the calcium ions all contribute to the stability of the sludge foam (Cooper and Kennedy, 2010; Schilling and Zessner, 2011; Ahmedna et al., 1999).

3.2. Surface tension and surfactants of the supernatant phase in the sludge

3.2.1. Surface tension

On reaching the critical micelle concentration (CMC) value, surface-active compounds or surfactants begin to selfassociate to form stable aggregates known as micelles, and the solution exhibits drastic changes in physical and chemical properties such as surface tension, electrical conductivity and detergent activity (Tan et al., 2010). Among them, the low surface tension makes the foam easier to form and maintains large interfacial area. Fig. 3a–c shows the variation of surface tension with the increase of CaO, NaOH and heating temperature, respectively. The dramatic decrease of surface tension indicated that certain surfactants were released into the supernatant phase of the sludge.

According to related studies (Becerra et al., 2010; Zhao et al., 2011), these surfactants were always due to the lipid compounds derived from the hydrolyzed lipid bilayer structure on the cell membrane. In this study, the correlation coefficient of -0.99, -0.94 and -0.98 in the pretreatment of CaO addition, NaOH addition and heating, respectively, demonstrated a good statistical correlation between sCOD and surface tension. Thus, the reduction of surface tension was associated with the extraction capacity of the pretreatment method which could be evaluated by the levels of sCOD. Further, the saponification of free lipids might induce a higher surface activity in an alkaline environment. Consequently, in the NaOH pretreatment, the alkaline environment and the highest sCOD of 12,064 mg/L facilitated the largest decline of surface tension from 68.9 mN/m to 44.7 mN/m, which might provide an exact reason for the greater foamability of sludge by NaOH pretreatment.

However, there was an interesting phenomenon that the surface tension occasionally deviated from the foamability in some of the samples. It can be seen from Figs. 1c and 3c that even though no sludge foaming has been observed in heating pretreatment, the decline of surface tension is not as small as we expected. For example, the surface tension in 100 °C and 120 °C heating pretreatment decreased to 53.3 mN/m and 52.3 mN/m, respectively. These values were very close to the lowest surface tension (at 53.1 mN/m) in CaO pretreatment (Fig. 3a), which got the best foamability in the CaO pretreatment group. However, the heating pretreatment at 100 °C and 120 °C did not induce the sludge foaming by persistent whipping. Generally, foamability relates to both foam formation and foam persistence, and surface tension lowering is necessary, but not sufficient. Thus, besides a lower surface tension, there must be other factors, especially concerning the foam persistence, contribute to the sludge foaming. This view was also supported by the sludge foamability and the surface tension in 0.5 wt% NaOH pretreatment. It can been seen from Fig. 1b that the sludge density in 0.5 wt% NaOH decreased to 0.66 g/mL after 10 min of whipping, and almost did not fluctuate in the following 30 min whipping. Meanwhile, its density curve was obviously differentiated from the other foaming samples in the NaOH pretreatment group whose plateau

phase of the decreasing density was always associated with the insufficient whipping. Indeed, with the sludge volume increasing, the rotated mixer paddles would be gradually immersed into the foam, and could not introduce the air effectively. Thus, considering the insufficient foaming in 0.5 wt% NaOH pretreatment, the invalid whipping factor could be eliminated. The plateau phase in this case might be attributed to an undesired foam persistence which was difficult to resist the shear in whipping and sustain a lower foam density.

3.2.2. Principal organic components

Most of the surfactants used to stabilize foams and emulsions fall into two categories: the low molar mass species (such as lipids, phospholipids) and the high molar mass species (such as protein and polysaccharides). Comparing these two categories, the latter surfactants are less effective at reducing interfacial tension, but they can contribute to the viscoelasticity of the foam lamellae, reduce the liquid drainage rates and provide a barrier to foam coalescence (Schramm, 2005). Coincidently, the principal organic components in the sludge are polysaccharides and proteins, in pure form or in association with other compounds (glycoproteins, lipopolysaccharides, etc.), which are potentially suitable as surfactants (Becerra et al., 2010; Kim et al., 2010). The alkaline agents could ionize the charged groups in proteins and polysaccharides, increase repulsion among polymeric matrix components, and increase their solubility (Chen et al., 2007). As shown in Fig. 3a and b, with the CaO and NaOH addition, the protein concentration significantly increases by 1742 mg/L and 4019 mg/L, respectively, and the polysaccharide concentration increases by 236 mg/L and 836 mg/L, respectively. No matter which pretreatment was applied, the protein and polysaccharide increasing trends could be divided into a rapid phase and a moderate phase, which were similar to that of sCOD shown in Fig. 2a and b. In particular, the curve of the protein was almost parallel with that of sCOD. This phenomenon demonstrated that the protein was a principal component in the organic matters released by the CaO and NaOH pretreatment. Considering its high level of content, some of the studies have focused on the protein recovery from sludge for its use as animal feed, foam extinguishing agent, and so on (Hwang et al., 2008).

In practice, the relatively non-specific foaming of denatured proteins was commonplace and widely exploited in food technology and other processes (Cooper and Kennedy, 2010). The sludge foaming process in this study was similar to the non-specific foaming of proteins, which usually required much higher protein concentrations (typically > 10 mg/L) and much more vigorous physical treatment (whipping or sparging) than the case with the specialized surfactant (Cooper and Kennedy, 2010). Furthermore, in several cases, it was found that the partial heat denaturation and the subsequent formation of soluble protein aggregates had a positive effect on the foam stability. However, the excessive heat denaturation could form the large insoluble protein aggregates which might decrease the amount of soluble proteins available for the foam stabilization, and reduce their diffusion coefficient on the proliferated interfacial area (Wierenga and Gruppen, 2010). These views on foams from protein solution

explained why the sludge foaming was not observed when the heating temperature was equal or higher than 100 °C. In view of that, the protein might be a critical factor on the foam persistence for the sludge foamability.

3.2.3. EEM fluorescence spectroscopy

The EEM fluorescence spectroscopy was employed to characterize the organic matters in the supernatant phase of the foaming samples. According to the classification scheme by Chen et al. (Chen et al., 2003), horizontal and vertical lines were drawn to divide the EEM into five regions (Fig. 4a-c). Compared with the sample without pretreatment (Fig. 4a), two peaks were readily identified from the spectra of the samples by 2.0 wt% CaO and 2.0 wt% NaOH pretreatment (Fig. 4b and c), respectively. The first main peak was identified at excitation/ emission wavelengths (Ex/Em) of 225-235/310-340 nm (Peak A), while the second main peak was identified at Ex/Em of 275-285/330-360 nm (Peak B). Peak A was stretched across the regions I (aromatic protein) and II (aromatic protein), and Peak B was located in region IV (soluble microbial by-productlike). These two peaks were associated to the compounds derived from proteins in which the fluorescence implied the presence of aromatic amino acids such as tyrosine and tryptophan. A third peak was identified at Ex/Em of 320-330/ 400-430 nm (Peak C) located around region V in which the fluorescence was due to the presence of humic acid-like compounds. The appearance of humic acid-like compounds is always associated with a stronger extraction method, and the alkaline treatment has been commonly employed to extract the bound EPS from the active sludge in wastewater treatment. Overall, the quantity and location of the main fluorescence peaks in the foaming samples were similar to that of the other studies concerning the components of EPS extracted from the sludge (Sheng and Yu, 2006; Domínguez et al., 2010).

According to the contours shown in Fig. 4b and c, the fluorescence peaks intensity of the protein derived compounds in the NaOH pretreatment was about 2.0 times higher than that of CaO pretreatment, which was coincident with their concentration levels shown in Fig. 3a and b. In addition, the intensity ratios of Peak A/Peak B (Fig. 4a-c) are the



Fig. 5 – Schematic depiction of the mechanisms for sludge foaming.

following: without pretreatment 1.25; CaO pretreatment 0.87; NaOH pretreatment 0.87. Commonly, the intensity of Peak A was higher than that obtained for Peak B in the case of loosely bound EPS (LB-EPS). On the contrary, the tightly bound EPS (TB-EPS) showed higher intensity for Peak B than for Peak A (Domínguez et al., 2010). Consequently, the organic matters released by the CaO and NaOH pretreatment are mainly derived from the TB-EPS in the sludge, and are dominated by the protein derived compounds.

3.3. Mechanisms of sludge foaming

Overall, regarding this complicated three-phase (air-watersolid) foaming system, the mechanisms of sludge foaming was mainly derived from two aspects (Fig. 5). First, the reduction of surface tension induced by the surfactants in low molar mass species made the foam easier to form. Second, the high molar mass species adsorbed on the foam lamellae, reduced the liquid drainage rates and promoted the foam



Fig. 4 – EEMs for the supernatant phase in the sludge suspension: (a) without pretreatment, (b) CaO addition, (c) NaOH addition. White lines divide EEMs into five regions (I-V).

persistence. Especially, the high level of protein derived compounds in proper molecular forms was a crucial factor for the sludge foaming in the CaO pretreatment. The partial unfolding of the protein molecule and the exposure of hydrophobic groups increased the hydrophobic interactions and enhanced the foam formation. Similarly, foam persistence could be enhanced by the adsorption of such protein fractions because the liquid drainage rates in the foam lamellae could be reduced by the steric mechanisms which were defined as the stabilization of dispersed species induced by the interaction of absorbed chains (Nicorescu et al., 2008).

3.4. Drying characteristics of foamed sludge

3.4.1. Drying curves

The influence of sludge foam density, convective drying temperature and drying time on the decreasing of moisture content were studied. Fig. 6 shows the changes of moisture content versus drying time at various temperatures (30 °C, 40 °C, 50 °C and 60 °C). From Fig. 6a–d, the total drying times required for attaining the equilibrium moisture content successively reduce with the increase of drying temperature. Obviously, the higher drying temperature implied more energy input to the system in the same time duration, which increased the heat transfer between the air and the sludge, and accelerated the moisture diffusion in the sludge. Therefore, drying temperature was one of the most important factors effecting on the drying time of sludge.

Meanwhile, as expected, the sludge samples pretreated by the foaming process required a shorter time to approach the equilibrium moisture content than the non-foamed sludge at 1.05 g/mL. The foamed sludge held the principal advantages of foam-mat drying including lower temperatures and shorter drying times in the same type of the dryer (Ratti and Kudra, 2006). However, a lower density of sludge foam did not always imply a shorter drying time in the same drying conditions. As shown in Fig. 6, the foamed sludge at 0.70 g/mL reveals the best drying performance at any given temperature, and compared with the non-foamed sludge 35-41% drying time is saved for reaching 20% moisture content. On the one hand, the shorter drying time primarily resulted from the larger surface area exposed to the drying air; on the other hand, the lower thermal conductivity of foams than liquids seemed to have a negative effect on the heat transfer. Thus the drying performance of sludge will not be improved by foaming pretreatment infinitely.

3.4.2. Evaporation rates

The evaporation rate was expressed as the amount of the evaporated moisture over time, which was always employed to evaluate the patterns of drying and the classification of moisture in the materials. For a clear demonstration of evaporation rate curves, four representative densities of the sludge (1.05 g/mL, 1.06 g/mL, 0.70 g/mL, 0.40 g/mL) were selected. As shown in Fig. 7, the profile of the curves is classically encountered when drying sludge in a convective



Fig. 6 – Drying curves of sludge at different densities and drying temperatures: (a) 30 °C; (b) 40 °C; (c) 50 °C; (d) 60 °C. (1.05 g/mL is dewatered sludge without foaming process; 1.06 g/mL is dewatered sludge with CaO addition but whipping; 0.90 g/mL – 0.40 g/mL are foamed sludges).



Fig. 7 – Evaporation rate curves of sludge at different densities and drying temperatures: (a) 30 °C; (b) 40 °C; (c) 50 °C; (d) 60 °C. (1.05 g/mL is the dewatered sludge without foaming process; 1.06 g/mL is the dewatered sludge with CaO addition but whipping; 0.70 g/mL – 0.40 g/mL are the foamed sludges).

system (Léonard et al., 2008). The curves could be roughly divided into three phases including the increasing phase, the plateau phase and the decreasing phase.

In the increasing phase, after an initial period of preheating, the evaporation rate of sludge progressively reached the maximum value. According to Fig. 7, the change in the drying air temperature from 30 °C to 60 °C leads to an increase of 200% in the maximum evaporation rate approximately. Obviously, the maximum value of evaporation rate was always higher when processing with a higher air temperature. In the plateau phase, the relatively constant evaporation rate periods were observed for majority of the curves at the moisture content range of 80%-60%. This phase typically corresponded to the loss of freely available water at the surface of the material, and mainly depended on the external conditions including the air temperature, velocity and humidity (Vaxelaire and Cézac, 2004). This also explained exactly why the plateau phase gradually narrowed down with the increasing temperature from Fig. 7a-d. Interestingly, at any drying temperature, the plateau phase of foamed sludge at 0.70 g/mL was extended to a wider range of moisture content, and distinguished from the others significantly. This phenomenon directly indicated that the best drying performance of 0.70 g/mL was mainly derived from its long constant evaporation rate periods. For one thing, the alkaline pretreatment supplied sufficient free water for surface evaporation by weakening the water retention of the sludge solid matrices and changing the water from bound type into free type. For another, the structure of sludge foam gradually opened due to the mechanical ruptures as shown in Fig. 8a–f. Thus, the increased interfacial area compensated the increased internal resistance to moisture transfer, which might be sufficiently enough to maintain the evaporation rate in certain constant value for a longer time. In the decreasing phase, the surface evaporation began to be less important with the reduction of moisture content, and the moisture diffusion finally became the most important factor in the drying process.

3.4.3. Effective moisture diffusivity

The effective moisture diffusivity characterizes the intrinsic mass transport property of moisture which includes molecular diffusion, liquid diffusion, vapor diffusion, hydrodynamic flow and other mechanisms (Karathanos et al., 1990). Fig. 9 shows the effective moisture diffusivity versus the moisture content of the sludge samples with different initial density at various temperatures (30 °C, 40 °C, 50 °C and 60 °C). The value of effective diffusivity increased with the reduction of moisture content, which arose from the factors controlling the moisture transport in the sludge drying process. At the initial stage of drying, the dominated moisture transport was liquid diffusion, for the sludge mat containing the highest quantity of moisture. As drying progresses, the surface of the sludge mat was dried gradually, and the diffusion might give an additional option in vapor form (Celma et al., 2012). At the final stage of the drying, cracks appeared throughout the depth of



Fig. 8 – Micrographs of the foamed sludge in the drying process at regular intervals: (a) 20 s; (b) 40 s; (c) 60 s; (d) 80 s; (e) 100 s; (f) 120 s.

the mat as a result of the increased water vapor pressure, which was beneficial for the moisture transport to the surface. In addition, from Fig. 9a–d, the increasing trend of slope demonstrates that a higher temperature accelerates the migration of moisture in the sludge mat directly. At any given temperature, the foamed sludge at the lowest density of 0.4 g/ mL got the highest value of effective diffusivity in each phase of the moisture content, while the sludge at 0.70 g/mL did not exhibit the best value anymore. This phenomenon mainly attributed to the enhanced capillary movement of moisture through the liquid films. The foams were relatively stable. For avoiding film rapture, the moisture flowed to the evaporation surface in the drying process (Ratti and Kudra, 2006; Rajkumar et al., 2007). Consequently, sludge foam in lower density



Fig. 9 – Effective moisture diffusivity of sludge at different densities and drying temperatures: (a) 30 °C; (b) 40 °C; (c) 50 °C; (d) 60 °C. (1.05 g/mL is dewatered sludge without foaming process; 1.06 g/mL is dewatered sludge with CaO addition but whipping; 0.70 g/mL – 0.40 g/mL are foamed sludges).



Fig. 10 – Environmental scanning electron microscope graphs of dried sludge: (a), (b), (c) are foamed sludge at the magnification of $200\times$, $500\times$, $1000\times$, respectively; (d), (e), (f) are non-foamed sludge at the magnification of $200\times$, $500\times$, $1000\times$, respectively.

implied that more bubbles, namely larger areas of liquid film, were employed to transport the moisture, and enhance the effective moisture diffusivity.

Nevertheless, the moisture diffusivity was just one of the factors determining the drying performance of foamed sludge. Actually, as mentioned above, the excessive foaming of sludge offset the saved drying time and resulted in extended drying time, because the dryer does not permit higher throughputs.

3.5. Environmental scanning electron microscope analysis

Fig. 10 shows ESEM micrographs of dried sludge in the form of foamed (a-c) and non-foamed (d-f), respectively. The gas bubbles in the sludge foam were nearly spherical (shown in Fig. 8) in contrast to the distorted polyhedral structure of dried sludge shown in Fig. 10a-c, which was probably due to the stress formation in the drying process. In any case, the opened porous structure of the foamed sludge obviously provided a larger evaporation surface than the non-foamed sludge in a limited drying space. In addition, the pores also changed the multilayer structure of non-foamed sludge shown in Fig. 10d-f, which decreased the internal resistance to moisture transfer drastically. Finally, the dried sludge mat was lightweight, loose and compressible because of the porous structure. These features were helpful for the further storage, transportation and disposition of sludge.

4. Conclusions

The CaO addition releases the organic matters into the supernatant phase of the sludge, which contains the surface-

active compounds in proper concentration available for sludge foaming. In the whipping operation, the optimal CaO addition is 2.0 wt%.

The reduction of surface tension in the supernatant phase of the sludge is associated with the extraction capacity of the pretreatment method. However, the low surface tension is not sufficient, and the foam persistence is another key factor contributed to the sludge foaming. The protein derived compounds dominate the principal component in the organic matters, which may be a crucial mechanism for promoting the foam persistence.

The foamed sludge at 0.70 g/mL has the best drying performance which is mainly derived from its longest constant evaporation rate periods. Overall, an appropriate foaming pretreatment provides a larger evaporation surfaces in the limited drying area, leads to a higher value of effective moisture diffusivity and improves the drying behavior of sludge drastically.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.10.036.

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