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Assessment of the correlation between odors release and dewaterability of sludge in sludge dewatering process under different conditioning methods

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ABSTRACT

In this paper, we assessed the correlation between odors release and dewaterability of sludge in sludge dewatering process under different sludge conditioning methods. In experiments, four sludge conditioning methods were adopted, such as polyaluminum chloride, $FeCl_3$ cooperates with CaO ($FeCl_3$ + CaO), acidizing conditioning and Fenton conditioning. The purpose of the study was to investigate the influence factors of odors release, and what conditioning method was the best to be used for sludge dewatering of Xiaohongmen WWTP in Beijing. According to the conditioning experiments, qualitative and quantitative analysis of odors and the correlation analysis between odors concentration and characteristics of sludge, we found that Fenton conditioning showed the best dewaterability of sludge. Moreover, soluble EPS (SEPS) content in the supernatant was the most with Fenton conditioning and consists of tryptophan protein-like substances, aromatic protein-like substances, humic acid and fulvic acid. The amount of H_2S release and the amount of NH_3 release were the most under Fenton conditioning. And the amount of volatile organic compounds (VOCs) release was the most with $FeCl_3$ + CaO conditioning. There was the positive correlation between odors release and SEPS. And hydrocarbon was the main factor causing the total amount of VOCs change. Fenton conditioning as the best conditioning method for sludge dewatering, promoted a large number of odors gas to release. Odors gas was gathered to the subsequent resource utilization. Meanwhile, the weight of raw sludge was reduced, and raw sludge as a kind resource was used to produce odorous gases. Finally, a new resource concept, chemical raw materials derived from odors, was submitted.

Keywords: Sludge conditioning methods; Odors release; Dewaterability of sludge; SEPS; Correlation analysis

1. Introduction

Odor is a gaseous substance, which stimulates the human olfactory organs and damage the living environment. In the earth, there are more than 2.0 million different compounds, in which one-fifth of them can produce a foul odor and main odorous substances are about 10,000 types [1]. In production and daily life, the common odorous substances are also very much, such as ammonia (NH_3), hydrogen sulfide (H_2S), trimethylamine, styrene, thiols, lower fatty acids, etc. Odorous substances always are multicomponent mixtures with low concentration. Owing to the acute sense of smell, humans can perceive the trace level of odorous substances.

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Therefore, odorous substances directly influence the living environment and health of human. According to the sources of odor substances, there are natural sources and artificial sources. Since 1990, CIM (commercial, industrial and municipal) sources have been researched in many countries, which contained municipal wastewater treatment, landfills and industrial emissions. Then studies on the low carbon organic matters (e.g., methyl mercaptan, methyl sulfide, dimethyl sulfide, dimethyl disulfide, trimethylamine) have been carried out and relevant emission standards were set in some countries.

In China, many studies are focused on the technology and engineering application of odors treatment. However, there are few studies on the reaction of atmospheric chemistry. In recent years, a few reports focus on the present situation of air environmental quality and temporal/spatial distribution of pollutions. Tang et al. [2] had studied the composition and content of malodor volatile organic compound (MVOC) in the different sewage treatment units and surrounding ambient air at a typical municipal wastewater treatment plant (WWTP) in Guangzhou. According to the analysis on the source emission characteristics, molecular markers and activity of atmospheric chemistry, they had established MVOC source component. Wang et al. [3] elaborated the source, main compositions and concentrations of odor in the WWTP, and further summarized the present situation of malodor pollution. Finally, they put forward the evaluation system of malodor pollution in China WWTP. Due to differences in each process, there are much different in types and concentrations of odors [4]. According to the distribution of odor release in process units of WWTP, many researchers considered the odors concentration in sludge dewatering unit was the most, which was about 50% of total odors concentrations in WWTP [5]. Gao et al. [6] reported that H_2S emission in sludge conditioning with different inorganic salt coagulants was influenced by sludge properties. Kurade et al. [7] reported that the biogenic flocculants can reduce the moisture content of sludge to 70% and also reduced the unpleasant odor. Liu et al. [8] examined the effects of ultrasound, Fenton oxidation and ultrasound coupled with Fenton oxidation pre-treatments (prior to anaerobic digestion) on the elimination of odorous compounds. There have been some studies on the removal of malodorous gases in the WWTP [9–11]. However, there are rarely published researches on the correlation between odors and sludge conditioning or sludge dewatering technology. And transfer behavior of odorous pollutants in wastewater sludge system under typical chemical conditioning processes for dewaterability enhancement is also little.

In this paper, we assessed the correlation between odors release and dewaterability of sludge in sludge dewatering process under different chemical conditioning methods. In experiments, four sludge conditioning methods were adopted, such as polyaluminum chloride (PAC), $FeCl_3$ cooperates with CaO ($FeCl_3$ + CaO), acidizing conditioning and Fenton conditioning. The purpose of the study was to investigate the influence factors of odors release. Meanwhile, the paper examined that the best balance point between sludge conditioning methods, odorous gases and dewaterability of sludge.

2. Materials and methods

2.1. Materials

2.1.1. Raw sludge

The raw sludge was activated sludge from secondary clarifier (SC) in Xiaohongmen WWTP. It treats approximately 600,000 m^3 of wastewater daily, which is treated by anaerobic–anoxic–oxic (A/A/O). The sample was stored at 4°C and was analyzed within 7 d after sampling. The characteristics of the sludge are listed in Table 1.

2.1.2. Chemical agents

PAC, $FeCl_3$, CaO, sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2) and ferrous sulfate ($FeSO_4$) were used in the study. PAC was produced by a local factory (Beijing Millions Water Cleaning Agent Co., China). Other coagulants and chemical agents (e.g., CaO, sulfuric acid [H_2SO_4], and hydrogen peroxide [H_2O_2]) were produced by Sinopharm Group Chemical Reagent Co. Ltd. The Al_2O_3 content of PAC is 10%, and the mass concentration of $FeCl_3$ is 38%.

2.2. Experiments

2.2.1. Sludge conditioning experiment

Sludge conditioning experiments with different conditioning methods were used as a source of odors. First, 100 mg of SC sludge was weighed and put into a 200 mL beaker. After that, the experiments were started at a rapid mixing of 200 rpm and chemical agents were quickly added separately. The equipment was shown in Fig. S1 (sludge sampling part).

In the chemical agents adding of the experiment, the dosage of PAC was 10% (g g^{-1} DS). In $FeCl_3$ + CaO conditioning, 15% (g g^{-1} DS) $FeCl_3$ was added and blended for 5 min, then 30% (g g^{-1} DS) CaO was added. In acidizing conditioning, the pH value of sludge was adjusted to 2–3 using 50% H_2SO_4 solution. In Fenton conditioning, the pH value of sludge was adjusted to 2–3 using 50% H_2SO_4 solution first, then 10% (g g^{-1} DS) $FeSO_4$ was added and blended for 5 min, finally 30% H_2O_2 was added 2–3 mL.

2.2.2. Odors sampling experiment

When the sludge conditioning experiments were started, vacuum air pump was opened and odors sampling was collected using bubble absorption tube (to sample H_2S and NH_3) and the carbon rod (to sample VOCs). The gas flow

Table 1
Characteristics of waste sludge

Indicator	Sludge
Moisture content (%)	97.24
pH	7.01
TOC (mg g^{-1} dry solid [DS])	149.06
SRF ((10^{12} m kg^{-1})	51.76

was set at 1.0 L min^{-1}. The equipment was shown in Fig. S1 (odors sampling part).

2.3. Analytical methods

2.3.1. Odor test

Methylene blue Spectrophotometric Method (GB/T11742-1989) was used for the measurement of hydrogen sulfide (H_2S).

Sodium hypochlorite-salicylic acid method (GB/T14679-1993) was used for determining ammonia (NH_3).

GC-MS (6890GC/5973MSD, Agilent Co., USA) was used for analyzing and identifying VOCs.

2.3.2. Ammonia-N test

Salicylate-hypochlorous acid photometric method (GB7481-1987) was used for determining ammonia–N (NH_3–N).

2.3.3. Specific resistance of sludge and moisture content

Specific resistance of sludge (SRF) was measured with the standard Buchner funnel test using a quantitative filter paper. It can be obtained by Eq. (1) as follows:

$$r = \frac{2PA^2b}{\mu\omega} \tag{1}$$

where P (kg m^{-2}) denotes pressure, A (m^2) is filtration area, μ (kg s m^{-2}) is kinetic viscosity, w (kg m^{-3}) denotes dry solid weight per unit volume sludge on the filtrate media, b is slope of filtration equation $t/V = bV + a$, and t (s) is time, V (m^3) denotes volume of filtrate. The raw sludge and conditioned sludge were separately poured into a Buchner funnel with a 0.45 μm cellulose acetate membrane to filter, and the pressure of vacuum filtration was 0.6 MPa. The weight of filtrate was recorded every 10 s using electronic scale before surface cracking was observed. The equipment is shown in Fig. S2.

2.3.4. Extracellular polymeric substances analysis

First, the concentration of dissolved organic carbon (DOC) of the sample was diluted below 10 mg L^{-1} before test. Three-dimensional excitation–emission matrix (3-DEEM) spectra were measured by a fluorescence spectrophotometer (F-4500, Hitachi, Japan) with an excitation range from 200 to 400 nm at 10 nm sampling intervals and an emission range from 220 to 550 nm at 10 nm sampling interval. The spectra were recorded at a scan rate of 12,000 nm min^{-1}, using excitation and emission slit bandwidths of 10 nm. Each scan had 37 emission and 27 excitation wavelengths.

2.3.5. Statistical analysis

Statistical Program for Social Sciences (Version 21.0, Systat Software of IBM) was used to resolve the correlation analysis. Pearson's correlation coefficient (R) was used to evaluate the linear correlation between characteristics of sludge, odors release and physicochemical indicators.

2.3.6. Other analytic methods

DOC of soluble extracellular polymeric substances (SEPS) was analyzed using TOC analyzer (Shimadzu, Kyoto, Japan). pH was measured by a pHS-3C (Shanghai, China) pH meter.

3. Results and discussion

3.1. Influence of chemical conditioning on dewaterability of sludge

3.1.1. Influence of chemical conditioning on SRF and moisture content

There have been studies highlighting the sludge dewatering. SRF and moisture content of the cake (MC) are the two main indexes of dewaterability of sludge [5]. Barker and Stuckey [12], thought that sludge can be classified into three types, for example, bad dewaterability (>10^{12}–10^{13} m kg^{-1}), medium dewaterability ((5–9) 10^{11} m kg^{-1}) and good dewaterability (<4 10^{11} m kg^{-1}). According to the value of SRF in Table 1, the raw sludge was bad dewaterability. The raw sludge was excess activated sludge containing a large amount of organic matter. As shown in Fig. 1a, the values of SRF with different conditioning methods were greatly less than the SRF of raw sludge. And the value

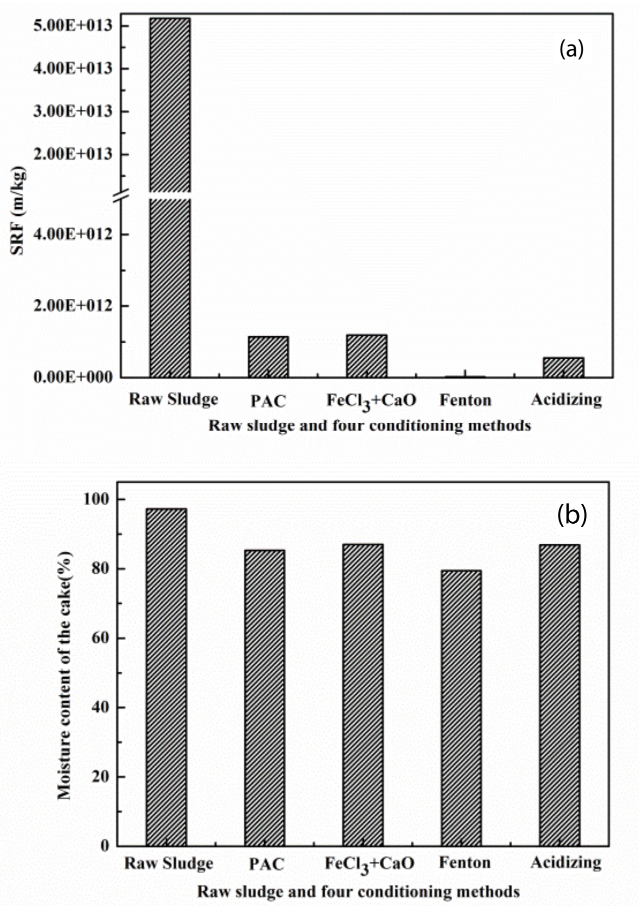

Fig. 1. Effect of four conditioning methods on (a) SRF and (b) moisture content of the cake.

of SRF with Fenton conditioning is the least in Fig. 1a. From Fig. 1b, the MC with Fenton conditioning also was the least. Obviously, inorganic coagulants could eliminate the negative surface charge of the sludge particles by charge neutralization and interparticle bridging, resulting in particle destabilization and aggregation [13]. Then OH· oxidation in Fenton conditioning was more effective to convert bound water into the free water by destructing EPS. So Fenton conditioning expressed excellent effect in dewaterability of sludge.

3.1.2. Influence of conditioning methods on soluble EPS

There have been studies highlighting the significant effect of EPS in the sludge on sludge dewaterability [14]. Gao et al. [6,15] reported that there is some relationship between odors emission and SEPS in the sludge. Therefore, it was necessary to research the soluble EPS (SEPS) before investigating odors emission. Fig. 2 presents the effect of four conditioning methods on SEPS content. Compared with the concentration of SEPS in the raw sludge, the concentration of SEPS under different conditioning methods were all greatly changed in Fig. 2. However, the concentrations of SEPS were as follows: Fenton > acidizing ≈ $FeCl_3$ + CaO > raw sludge > PAC. Based on the curve of pH values under different conditioning methods (shown as Fig. S3), it indicated that acidizing conditioning could break the barriers of EPS resulting in a large number of SEPS created and dissolved in the water. Instead, PAC conditioning greatly decreased the concentration of SEPS which even was less than the SEPS content in raw sludge. It was probably because PAC could not break the EPS structure, at the same time, coagulation of PAC could reduce the EPS content.

There have been many studies on the 3D-EEM spectroscopy application in the wastewater treatment systems [16]. Chen et al. [17] and Hudson et al. [18] reported that 3D-EEM spectrum was able to accurately respond the chemical compositions of SEPS. According to the peaks of EEM fluorescence spectra on the SEPS, the main compositions of SEPS were aromatic protein-like substances (APN), tryptophan protein-like substances (TPN), humic acids (HA) and fulvic acids (FA). APN was always an indication of organic contaminants in wastewater, and TPN was related to the microbial activity. Fig. 3 provides the effect of four conditioning methods on components of SEPS. From Fig. 3a, HA has the most concentration in SEPS of raw sludge, followed by TPN, APN and FA. After treated by four conditioning methods, the concentrations of TPN, APN, and HA were greatly changed, and it has little difference in the concentrations of FA. From Fig. 3b, acidizing and Fenton conditioning both promote humic acid class generating, meanwhile, TPN and APN reducing remarkably. From Fig. 3, it is possible to infer that TPN and APN were broken down into other low-molecular-weight organics.

3.2. Effect of four conditioning methods on H_2S and NH_3 release

Generally, odorous pollutants are divided into inorganic gaseous and volatile organic compounds (VOCs) in the WWTP. Of these, inorganic gaseous mainly are studied on H_2S gas and NH_3 gas. It is well known that H_2S gas and NH_3 gas both come from biochemical reactions of substances

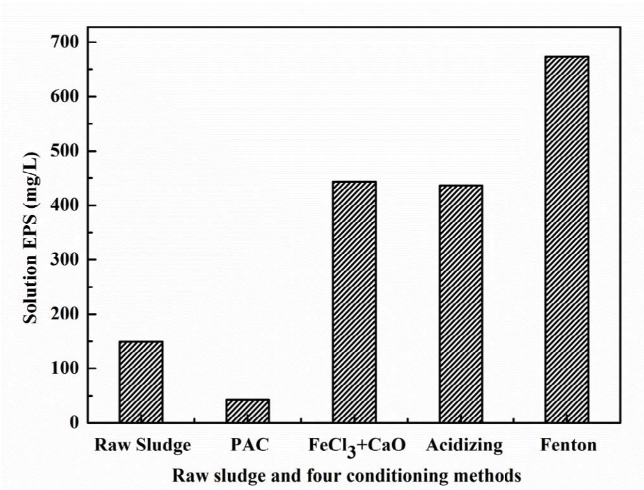

Fig. 2. Effect of four conditioning methods on SEPS.

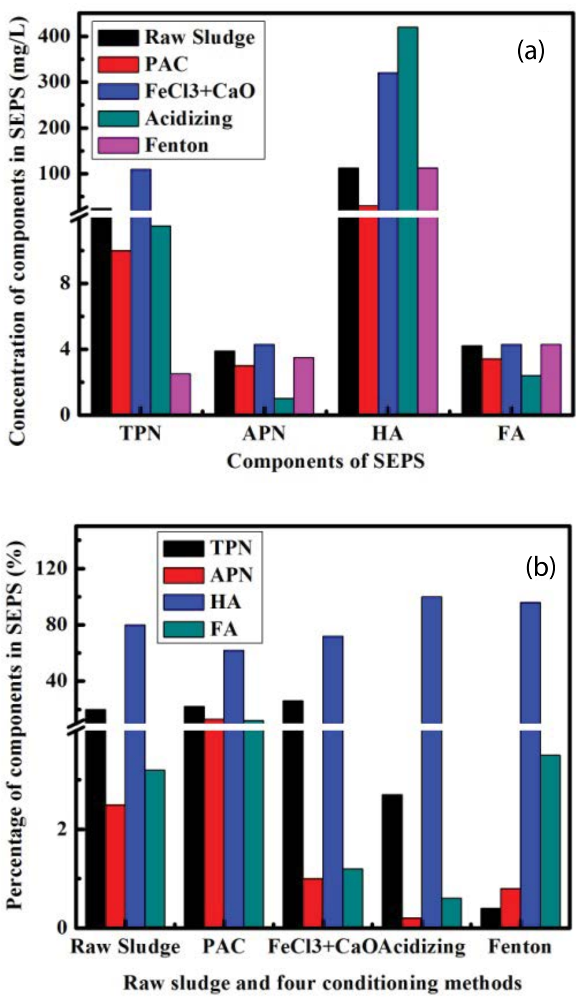

Fig. 3. Effect of four conditioning methods on components of SEPS: (a) concentration of components in SEPS and (b) percentage of components in SEPS.

containing sulfur and nitrogen. Sulfate ions can be converted into H_2S by sulfate-reducing bacteria (SRB) under anaerobic conditions [19]. In the process, small molecules of organic matters are oxidized either completely to CO_2 and/or some intermediate compounds. Meanwhile, there happens to be the nitrate respiration and ammonification acting on the ammonium and nitrate by bacterial and fungal. Then nitrate reductase (NR) played an important role. NO_3^- is reduced by NR to NO_2^-, which the reaction forms and physiological effect are the similar to aerobic respiration. Along with denitrification of NO_3^- turning to N_2 gas under gram-negative nonspore-bearing bacillus, small molecule of non-nitrogen organic matter is oxidized to CO_2. Moreover, organic nitrogen compounds are degraded into NH_4^+ by ammonification microorganisms. And NO_2^- is also reduced to NH_4^+ by alienation of nitrite reduction bacterium.

As described in Fig. 4a, the amount of H_2S release increased evidently using four conditioning methods. The contents of H_2S released were as follows: $H_2S_{Fenton} > H_2S_{Acidizing} > H_2S_{PAC} > H_2S_{FeCl_3+CaO} > H_2S_{Raw\ sludge}$. Akgul et al. [20] reported metal addition could be an effective way to control odors from toxic volatile sulfur compounds, pathogens and to improve dewaterability during anaerobic digestion. Yang et al. [21] also reported that sulfide and sulfate reducing bacteria as sulfur inhibitors effectively achieved sulfur suppression in the process of anaerobic digestion of sludge. In addition, the effect of Fenton was far superior to other conditioning methods in regard to the H_2S release. This indicated that acidic condition promotes the H_2S release, but excessive acidification inhibits the H_2S release (Fig. S3). Fig. 4b shows the amount of H_2S released using four conditioning methods in different time periods. From Fig. 4b, the amount of H_2S release using PAC, $FeCl_3$ + CaO and acidizing conditioning methods mainly increased in the first 20–30 min, following time expanding and then decreased. However, the amount of H_2S release using Fenton conditioning mainly decreased following time expanding.

As described in Fig. 5a, the amount of NH_3 release increased evidently using four conditioning methods. The contents of NH_3 released were as follows: $NH_{3Fenton} > NH_{3Acidizing} > NH_{3PAC} > NH_{3FeCl_3+CaO} > NH_{3Raw\ sludge}$. This indicated that acidic condition promotes the NH_3 release, but excessive acidification inhibits the NH_3 release. It was because that NO_3^- was reduced by NR to NO_2^- under the acid condition and excessive acid could fix NH_3. Andreev et al. [22] thought that ammonium content increased due to urea hydrolysis. Fig. 5b

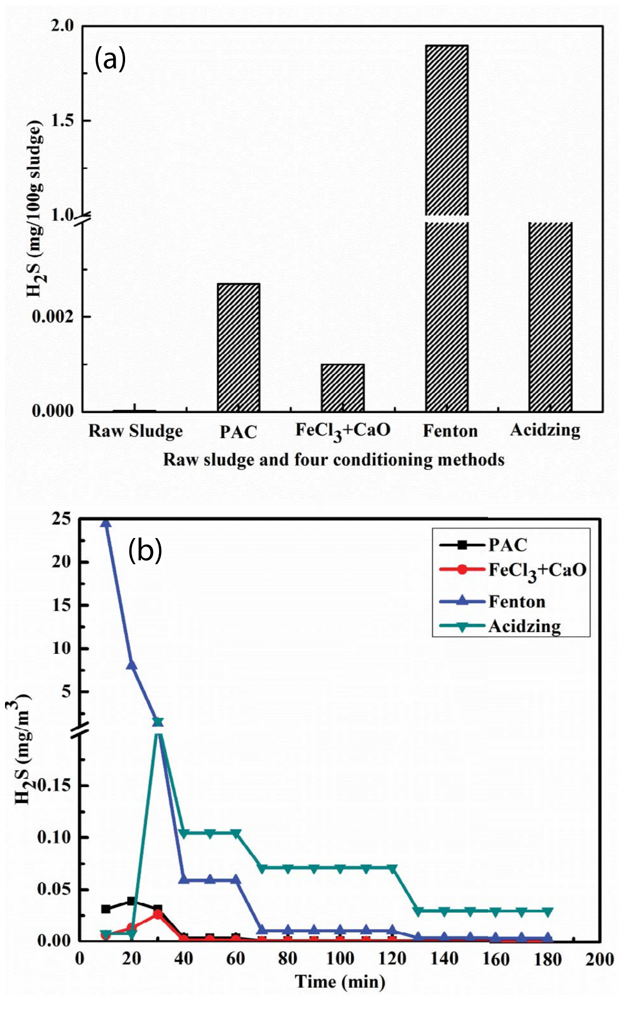

Fig. 4. Effect of four conditioning methods on the amount of H_2S release.

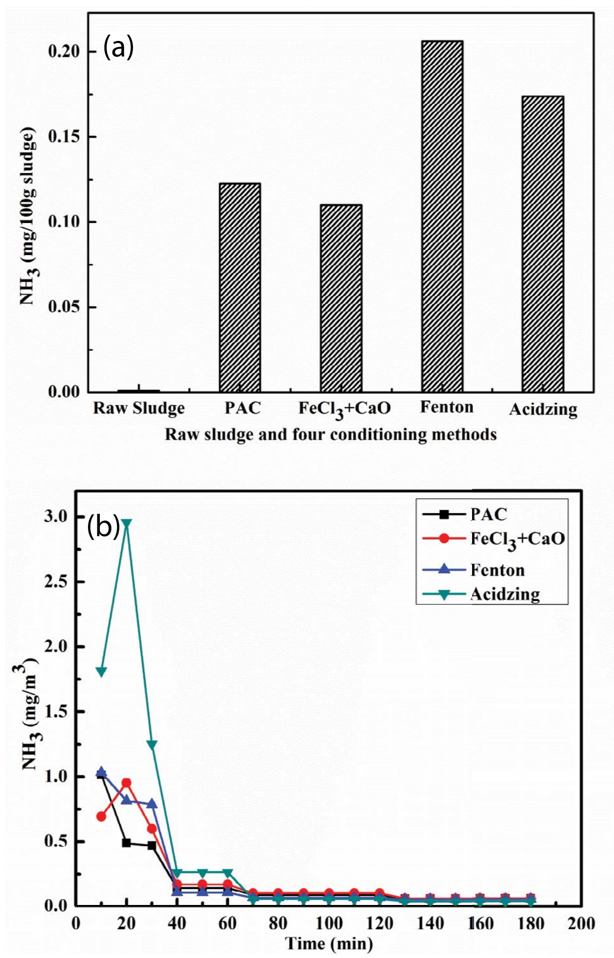

Fig. 5. (a) The amount of NH_3 release from sludge with different conditioning methods and (b) the amount of NH_3 release using four conditioning methods in different time periods.

shows the amount of NH_3 released using four conditioning methods in different time periods. From Fig. 5b, the amount of NH_3 release using $FeCl_3$ + CaO and acidizing conditioning methods mainly increased in the first 10–20 min, following time expanding and then decreased. However, the amount of NH_3 release using PAC and Fenton conditioning methods mainly decreased following time expanding.

Compared with H_2S, NH_3 emission was much lower. Many researchers reported that NH_3 was not considered as a main odors source in the WWTP [23,24]. However, NH_3 emission was significantly intensified under chemical conditioning processes.

3.3. Distribution of odorous substance in the different conditions

In the study, the amount of VOCs release was influenced by four conditioning methods. As described in Fig. 6, VOCs emission was evidently increased under different chemical conditioning processes. The total VOCs concentrations were 0.18, 39.78, 40.82, 40.23, and 40.29 ug m^{-3} for raw sludge, PAC, $FeCl_3$ + CaO, acidizing and Fenton conditioning, respectively. The contents of VOCs released were as follows: $VOCs_{FeCl_3+CaO} > VOCs_{Fenton} > VOCs_{Acidizing} > VOCs_{PAC} > VOCs_{Raw\ sludge}$. 32 VOCs could be detected by GC-MS under sludge conditioning. Dibromochloromethane, tetrachloroethane, 1,2-dibromoethane, ethylbenzene, o-xylene, m-xylene and *p*-xylene were the main compounds in VOCs. According to the different types of organic matters, VOCs were divided into BTEX, halogenated benzene (HB), and hydrocarbons (H). As can be seen from Fig. 6, BTEX were 20.46 and 20.27 ug m^{-3} for Fenton and acidizing conditioning, which was more than other two conditioning methods. There was no obvious difference in the amounts of HB released for four conditioning methods. H emission in $FeCl_3$ + CaO conditioning was more than that under other three conditioning methods. This indicated that the release of BTEX is effected by the pH of the sludge and the acidic conditions contribute to the release of BTEX. The amount of HB was substantially free from any conditions. However, H emission obviously was influenced by alkaline conditions. In a word, BTEX was the most amount in the VOCs, but H was the main factor causing the total amount of VOCs change.

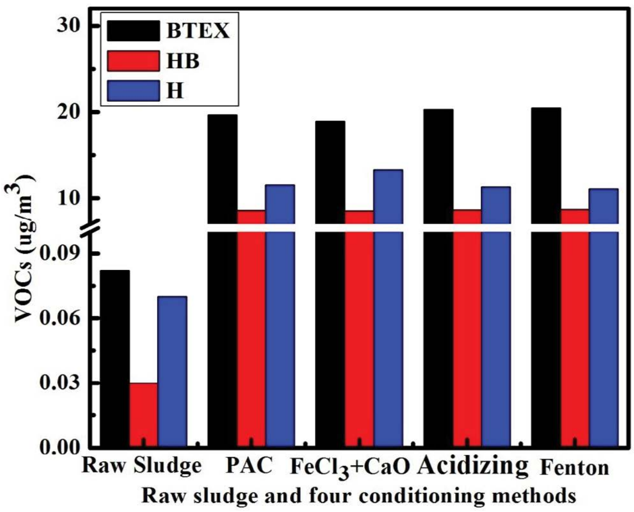

Fig. 6. Amount of VOCs release of sludge before and after four conditioning methods.

3.4. Correlation analysis between odors concentration and characteristics of sludge

To identify the relationship between odors concentration and characteristics of sludge during chemical conditioning for excess activated sludge dewatering from secondary clarifier with four representative conditioning methods (PAC, $FeCl_3$ + CaO, Fenton, and acidizing), Statistical Program for Social Sciences (SPSS) was used to resolve the correlation analysis. The correlation analysis was performed to get insight into the relationship between odors concentration, SEPS properties and sludge dewaterability under conditioning. As described by correlation analysis, the significant correlation was found between odors concentration (H_2S, NH_3, and VOCs) and MC, SRF, SEPS, pH. Analyzing details further, the components of SEPS were TPN, APN, FA, and HA, and the components of VOCs were BTEX, HB, and H.

From Table 2, the strong correlations existed between H_2S concentration and MC (R^2 = –0.974, p < 0.05). It was because that MC decreased and supernatant liquid increased, in which H_2S concentration increased. And H_2S was easily spilled under acidic condition. The positive correlations existed between H_2S concentration and SEPS (R^2 = 0.708), H_2S concentration and BTEX (R^2 = 0.631), H_2S concentration and HB (R^2 = 0.887). SEPS as the external organic matter of EPS, constantly dissolved into supernatant liquid in the conditioning process, and simultaneously H_2S was produced. Zhang et al. [13], Niu et al. [25], and Zhang et al. [26] pointed out that EPS played an important role in sludge dewatering process. The more the SRF concentration in the supernatant liquid , the less the SRF of sludge. Thus the negative correlations existed between H_2S concentration and SRF (R^2 = –0.863). Similarly, the strong negative correlations existed between NH_3 concentration and SRF (R^2 = –0.992, p < 0.01). Moreover, the positive correlations existed between NH_3 concentration and SEPS content (R^2 = 0.690), NH_3 concentration and HA content (R^2 = 0.886). HA was the main component in SEPS.

The negative correlations existed between NH_3 concentration and MC content (R^2 = –0.735), NH_3 concentration and TPN content (R^2 = –0.928), NH_3 concentration and pH (R^2 = –0.842). It was because that MC decreased and supernatant liquid increased, in which NH_3 concentration increased. And NH_3 was easily spilled under alkaline condition. There were strong positive correlations existing between NH_3 concentration and HB content (R^2 = 0.987, p < 0.05), and negative correlations existed between NH_3 concentration and H content (R^2 = –0.764). It might only be mathematically relevant. The positive correlations existed between NH_3 concentration and H_2S content (R^2 = 0.804). It was because denitrifying sulfur bacteria use nitrate to oxide sulfur and reduce nitrate. SRB also used nitrogen in amino acid as nitrogen source on one condition. A few SRB get nitrogen through dissimilatory reduction reaction from nitrate and nitrite.

Table 2
Pearson correlation analysis between odors release and characteristic of sludge under four conditioning methods

	H_2S	NH_3	VOCs	BTEX	HB	H
pH	–0.404	–0.842	0.499	–0.963*	–0.770	0.915
MC	–0.974*	–0.735	0.173	–0.618	–0.834	0.551
SRF	–0.863	–0.992**	0.064	–0.887	–0.994**	0.697
SEPS	0.708	0.690	0.607	0.395	0.695	–0.060
TPN	–0.540	–0.928	0.079	–0.897	–0.856	0.699
APN	–0.431	–0.532	–0.739	–0.250	–0.493	–0.110
HA	0.595	0.886	0.230	0.746	0.827	–0.464
FA	–0.556	–0.406	–0.823	–0.060	–0.429	–0.277
H_2S	1.000	0.804	0.010	0.631	0.887	–0.486
NH_3	0.804	1.000	–0.148	0.935	0.987*	–0.764
VOCs	0.010	–0.148	1.000	–0.464	–0.150	0.747
BTEX	0.631	0.935	–0.464	1.000	0.902	–0.935
HB	0.887	0.987*	–0.150	0.902	1.000	–0.744
H	–0.486	–0.764	0.747	–0.935	–0.744	1.000

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

The positive correlations existed between VOCs concentration and SEPS ($R^2 = 0.607$). Gao et al. [17] considered that VOCs were inclined to adsorb on EPS through hydrophobic interactions. Thus EPS was broken by chemistry conditioning causing the concentration of SEPS increased, and adsorbed VOCs released. However, the negative correlations existed between VOCs concentration and APN ($R^2 = –0.739$), VOCs concentration and FA ($R^2 = –0.832$). It might be because APN and FA were broken down into volatile low molecular weight organics in the conditioning process. Considering the components of VOCs, the positive correlations existed between VOCs concentration and H ($R^2 = 0.747$), which demonstrated that H was the main factor causing the total amount of VOCs change (in section 3.3).

In the process of multivariate correlation analysis, the partial correlation coefficient described the correlation coefficient between any two variables when the other variables are fixed. The partial correlation coefficient reflected the real correlation of the two variables which is suitable for the relationship between the design variables and the design requirements. Therefore, the partial correlation coefficient was selected to determine the degree of correlation between the design variables and the design requirements in the next discussion.

Considering the influence of pH on the conditioning, there was the partial correlation analysis between odors release and characteristics of sludge under four conditioning methods when control variable was pH (as shown in Table 3).

Table 3
Partial correlation analysis between odors release and characteristics of sludge under four conditioning methods (control variable was pH)

	H_2S	NH_3	VOCs	BTEX	HB	H
MC	–0.970	–0.828	–0.023	–0.999*	–0.915	0.537
SRF	–0.942	–1.000**	–0.574	–0.857	–0.985	–0.021
SEPS	0.680	0.890	0.888	0.521	0.793	0.482
TPN	–0.444	–0.723	–0.982	–0.257	–0.587	–0.711
APN	–0.389	–0.680	–0.992	–0.198	–0.537	–0.752
HA	0.479	0.750	0.974	0.295	0.619	0.683
FA	–0.640	–0.864	–0.911	–0.475	–0.759	–0.528
H_2S	1.000	0.940	0.267	0.980	0.986	–0.314
NH_3	0.940	1.000	0.580	0.853	0.984	0.029
VOCs	0.267	0.580	1.000	0.070	0.424	0.831
BTEX	0.980	0.853	0.070	1.000	0.933	–0.497
HB	0.986	0.984	0.424	0.933	1.000	–0.152
H	–0.314	0.029	0.831	–0.497	–0.152	1.000

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

From Table 3, the obviously strong correlations exist between NH_3 concentration and SRF ($R^2 = -1.000$, $p < 0.01$), BTEX concentration and MC ($R^2 = -0.999$, $p < 0.05$). Obviously, the absolute value of correlation coefficients all increased and approached 1.000.

In section 3.1.2, Fig. 3 infers that TPN and APN were broken down into other low molecular weight organics. These low molecular weight organics were decomposed into odors (H_2S, NH_3, and VOCs) under microorganism and chemistry conditioning. Ding et al. [27] reported that odor concentration had a close relationship with emission of sulfur-containing compounds, amines and total volatile organic compounds. And the main VOCs released were benzene series and organic acid. Therefore, the obviously positive correlation existed between BTEX concentration and HA ($R^2 = 0.974$), and the obviously negative correlation existed between BTEX concentration and TPN/APN ($R^2 = -0.982/R^2 = -0.992$). Whether various odors concentration (H_2S, NH_3 and VOCs) or concentrations of VOCs components (BTEX, HB, and H), there was the negative correlation between these gases concentration and TPN/APN concentration. Dentel and Gossett [28] thought that the addition of iron and aluminum could reduce the bioavailability of protein and other molecules through complexation. It also could infer that protein might be a resource of VOCs under biological action. It meant that the protein could be degraded into VOCs under chemical action and biological action. Especially, the impact of hydrocarbons (H) was more pronounced. These indicated that the correlation between the various malodorous gas and the characteristics of the sludge is reliable. Fenton conditioning, as the best conditioning method for sludge dewatering, promoted a large number of odors gas to release. Odors gas was gathered to the subsequent resource utilization. Meanwhile, the weight of raw sludge was reduced, which made the reduction of dry sludge emissions. In addition, raw sludge as a kind resource was used to produce odorous gases.

4. Conclusions

In this paper, we assessed the correlation between odors release and dewaterability of sludge in sludge dewatering process with different conditioning methods. In experiments, four sludge conditioning methods were adopted, such as PAC, $FeCl_3$ + CaO, acidizing conditioning, and Fenton conditioning. The purpose of the study was to investigate the influence factors of odors release, meanwhile, dewaterability of sludge was the best using fit conditioning method for sludge dewatering of Xiaohongmen WWTP in Beijing. According to the conditioning experiments, qualitative and quantitative analysis of odors and the correlation analysis between odors concentration and characteristics of sludge, conclusions of the study were as follows:

- Fenton conditioning showed the best dewaterability of sludge. Moreover, SEPS content in the supernatant was the most using Fenton conditioning and consists of TPN, APN, HA, and FA.
- The amount of H_2S release and the amount of NH_3 release were the most under Fenton conditioning. And the amount of VOCs release was the most under $FeCl_3$ + CaO conditioning.
- There was the positive correlation between odors release and SEPS. And hydrocarbon was the main factor causing the total amount of VOCs change.

All that said, Fenton conditioning, as the best conditioning method for sludge dewatering, promoted a large number of odors gas to release. Odors gas was gathered to the subsequent resource utilization. Meanwhile, the weight of raw sludge was reduced, which was conducive to the reduction of dry sludge emissions. In addition, raw sludge as a kind resource was used to produce odorous gases.

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Supplementary Information

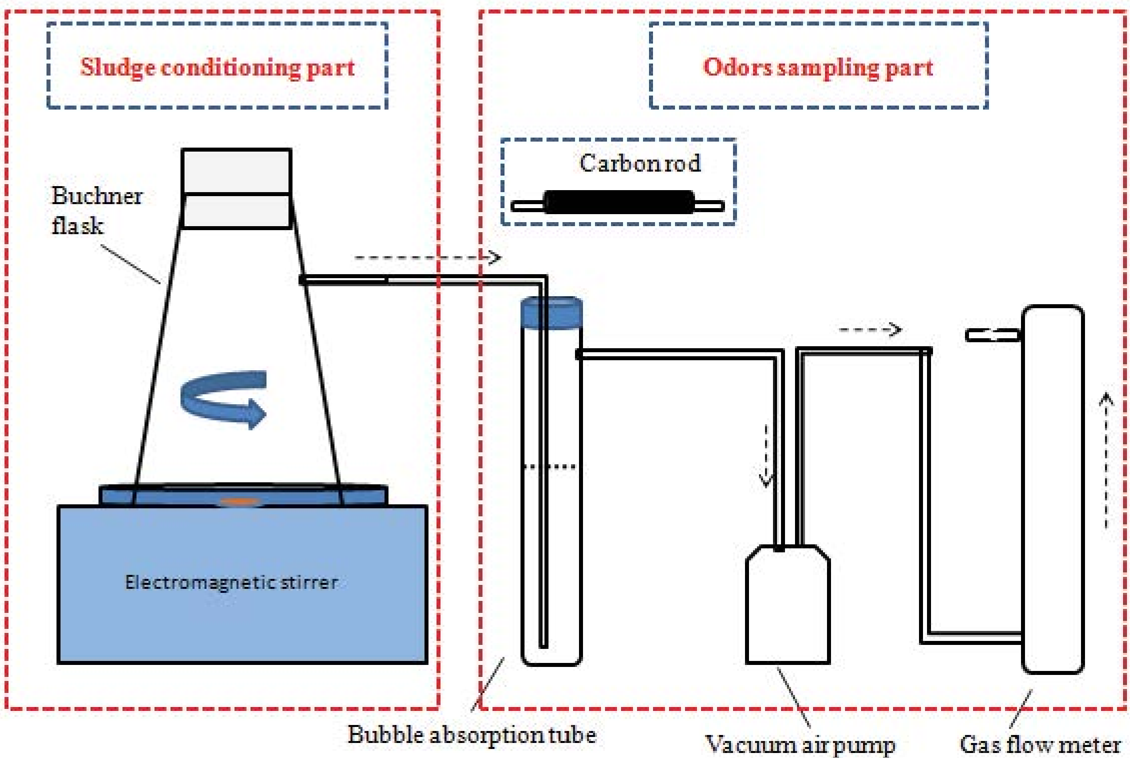

Fig. S1. Experimental process of sludge conditioning and odors sampling.

Fig. S2. SRF equipment.

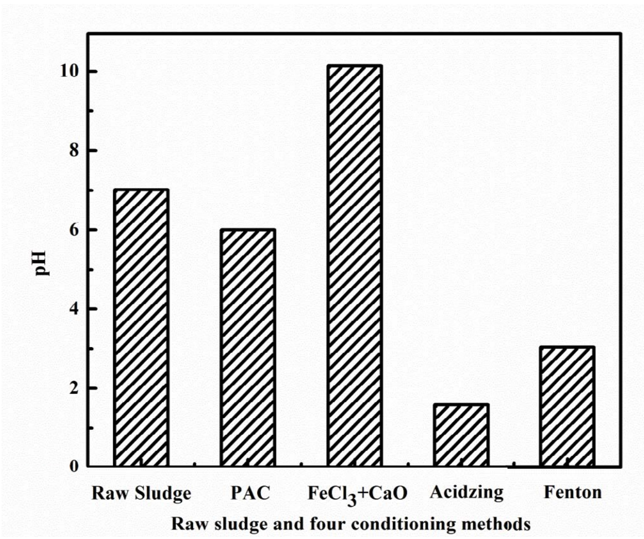

Fig. S3. pH of sludge before and after four conditioning methods.