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Emission characteristics of nitrogen- and sulfur-containing odorous compounds during different sewage sludge chemical conditioning processes

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HIGHLIGHTS

- NH_3, SO_2, H_2S and COS are emitted during different sludge conditioning processes.
- H_2S and SO_2 generation increase in the acidic environment created by H_2SO_4.
- Fenton peroxidation facilitates the formation of COS.
- CaO can reduce sulfur-containing gases emission via generation of calcium sulfate.
- CaO leads to the conversion of free ammonia or protonated amine to volatile NH_3.

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ABSTRACT

Chemical conditioners are often used to enhance sewage sludge dewaterability through altering sludge properties and flocs structure, both affect odorous compounds emissions not only during sludge conditioning but also in subsequent sludge disposal. This study was to investigate emission characteristics of ammonia (NH_3), sulfur dioxide (SO_2), hydrogen sulfide (H_2S) and carbonyl sulfide (COS) generated from sewage sludge conditioned by three representative conditioners, i.e., organic polymers, iron salts and skeleton builders, F-S (Fenton's reagent and skeleton builders) composite conditioner. The results demonstrate that polyacrylamide (PAM) has an insignificant effect on emission characteristics of nitrogen- and sulfur-containing odorous compounds, because the properties, sulfur and nitrogen speciations are similar in PAM-conditioned sludge and raw sludge (RS). Significant increases of SO_2 and H_2S emissions in the H_2SO_4 conditioning process were observed due to the accelerated decomposition of sulfur-containing amino acids in acidic environment. Fenton peroxidation facilitates the formation of COS. CaO can reduce sulfur-containing gases emission via generation of calcium sulfate. However, under strong alkaline conditions, free ammonia or protonated amine in sludge can be easily converted to volatile ammonia, resulting in a significant release of NH_3.

1. Introduction

Odorous compounds from sewage sludge are difficult to control [1–3] and the odor emission can pose significant challenges to environmental regulation and public health. Numerous researches have been carried out to clarify or investigate the types and strengths of odorous compounds during sludge production, digestion, drying, composting, landfill, incineration or other disposal processes [3–10]. In fact, there are many types of odorous compounds, especially nitrogen- and sulfur-containing ones, generated during sludge generation, treatment and disposal process. Reduced sulfur and nitrogen compounds have been identified as common odorous compounds released by sewage sludge [4]. Ammonia (NH_3) emission passed through three stages, i.e., rising rate, constant rate and decreasing rate stages during sludge drying [5]. Hydrogen sulfide (H_2S) and dimethyl sulfide (DMS) are probably released during anaerobic digestion as byproduct in biogas [6]. In some disposal processes, e.g., incineration and composting, the emissions are characterized with relatively high concentrations of sulfur dioxide (SO_2) and nitrogen oxides (NO_x), due to the high sulfur and nitrogen content of sewage sludge [2,3,7,8]. Despite the increasing importance of intensified attention being given to odorous compounds emitted from sewage sludge, little effort has been directed at the odors releasing during sludge chemical conditioning, which is an essential process in sludge treatment and disposal.

As water content in sewage sludge is usually higher than 95%, reducing the sludge volume by mechanical dewatering is economically favorable [11,12]. However, the colloidal and compressible

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Table 1
Proximate and ultimate analyses of RS and CF.

Materials	Proximate analysis (wt%)[a,b]				Ultimate analysis (wt%)[b]			
	M	V	A	FC	C	H	N	S
RS	7.56	40.13	59.68	0.19	20.35	3.30	2.64	0.83
Shenhua bituminous CF	6.41	32.61	7.90	59.49	45.72	3.84	34.78	0.81

[a] M, V, A and FC are moisture, volatile matter, ash and fixed carbon.
[b] Dry basis except for moisture in air-dried basis.

natures of sewage sludge apparently hamper the dewatering process [13]. Thus, pre-dewatering chemical conditioning is commonly used to improve the sludge dewaterability. Flocculation of sludge with organic polymers (polyelectrolytes) is a conventional method, which, with subsequent centrifuge or belt press dewatering, can only achieve a water content level of 75–85% [14,15]. This fails to meet the requirements of incineration or landfill disposal in China. In order to further reduce the water content of sludge cake, iron salts combined with physical conditioners, often known as skeleton builders, e.g., lime, fly ash or coal fines (CF), were practically used to enhance the sludge dewatering performance by forming a shell of precipitate around the sludge flocs [12,16]. However, the dewatered sludge cake produced in this process may still not be sufficient to realize the deep dewatering at low conditioner dosages. With increasing regulating intensity on sludge treatment and disposal, many researchers committed to explore other sludge treatment alternatives by applying innovative and more efficient conditioners to reform the sludge structure [14]. The combination of Fenton's reagent and skeleton builders (referred to as F-S composite conditioner) has been proven to be a viable option in our previous study [17].

When different conditioners are used to enhance sludge dewatering, sludge properties change differently which may have a great effect on subsequent sludge disposal. In addition, sludge properties are closely associated with odorant compounds generation during conditioning. Therefore, the emphases of this study were placed on (a) investigating and comparing emission characteristics of main nitrogen- and sulfur-containing odorous compounds generated from sludge conditioned by organic polymers, iron salts and skeleton builders, and F-S composite conditioner, and (b) identifying the mechanism of odor emission during conditioning through investigation on variations of properties, nitrogen and sulfur speciations of the conditioned sludge.

2. Materials and methods

2.1. Materials

Raw sludge (RS) used in this study was a mixture of sludge primary and secondary of a municipal wastewater treatment plant in Wuhan, China. Samples were collected and stored at 277 K in polypropylene bottles. The water content and chemical oxygen demand (COD) of the RS were 97.0% (w/w) and 18,700 mg L^{-1}, respectively. The results of the proximate and ultimate analyses of RS (dried at 378 K) are shown in Table 1.

Cationic polyacrylamide (PAM) prepared at 0.1% (w/w) was chosen as a representative of organic polymers while $FeCl_3$ as that of iron salts. Sulfuric acid was used to adjust pH of the sludge samples. Fe^{2+} in Fenton's reagent was prepared by mixing $FeSO_4{\cdot}7H_2O$ with H_2O_2 (30 wt%). All the chemicals used including CaO were of analytical grade (Sinopharm Chemical Reagent, China). Shenhua bituminous coal was milled and sieved to less than 0.5 mm in particle size. The proximate and ultimate analyses of CF are also presented in Table 1.

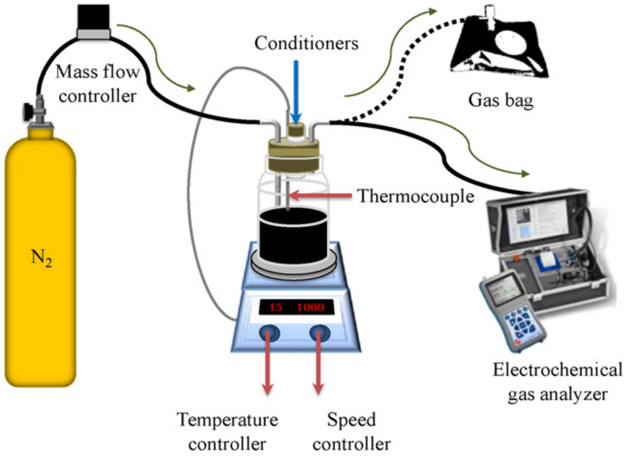

Fig. 1. Experimental set-up.

2.2. Experimental methods

At beginning, 500 mL sludge sample was transferred to a 1000 mL reactor at room temperature and atmospheric pressure as shown in Fig. 1, and conditioned in accordance with the procedures listed in Table 2. Mixing and temperature control were achieved by a magnetic stirrer (RET basic package2, IKA Inc., Germany). With 1 L min^{-1} N_2 as the carrier gas, volatile odorous compounds outleted. Nitrogen-containing odors in gaseous samples were continuously measured by an electrochemical gas analyzer (Ecom J2KN, rbr Messtechnik GmbH, Germany), which was calibrated before and after testing at the temperature of the tested atmosphere by using fresh outdoor air (20.9% oxygen). When sludge conditioning was performed again, gaseous samples were collected using 5-L gas bags with the first one being used for 1 min, the second for 4 min and others for 5 min. Sulfur-containing odors in 8 gas bags were measured by HC-5 trace sulfur analyzer. The analyzer was calibrated before the experiments using "Standard Gas"

Table 2
Sludge conditioning schemes.

No.	Conditioning methods
0	Control (**Sample 0**)
1	PAM (35 mg g^{-1} DS) → Mixing (40 min) (**Sample 1-1**)
2	$FeCl_3$ (65 mg g^{-1} DS) → Mixing (5 min) (**Sample 2-1**) → CaO (500 mg g^{-1} DS) → Mixing (35 min) (**Sample 2-2**)
3	$FeCl_3$ (65 mg g^{-1} DS) → Mixing (5 min) (**Sample 3-1**) → CaO (100 mg g^{-1} DS) → Mixing (5 min) (**Sample 3-2**) → CF (400 mg g^{-1} DS) → Mixing (30 min) (**Sample 3-3**)
4	H_2SO_4 (2 mg g^{-1} DS) → Mixing (1 min) (**Sample 4-1**) → $FeSO_4$ (40 mg g^{-1} DS) → Mixing (4 min) (**Sample 4-2**) → H_2O_2 (32 mg g^{-1} DS) → Mixing (25 min) (**Sample 4-3**) → CaO (500 mg g^{-1} DS) → Mixing (10 min) (**Sample 4-4**)
5	H_2SO_4 (2 mg g^{-1} DS) → Mixing (1 min) (**Sample 5-1**) → $FeSO_4$ (40 mg g^{-1} DS) → Mixing (4 min) (**Sample 5-2**) → H_2O_2 (32 mg g^{-1} DS) → Mixing (25 min) (**Sample 5-3**) → CaO (100 mg g^{-1} DS) → Mixing (5 min) (**Sample 5-4**) → CF (400 mg g^{-1} DS) → Mixing (5 min) (**Sample 5-5**)

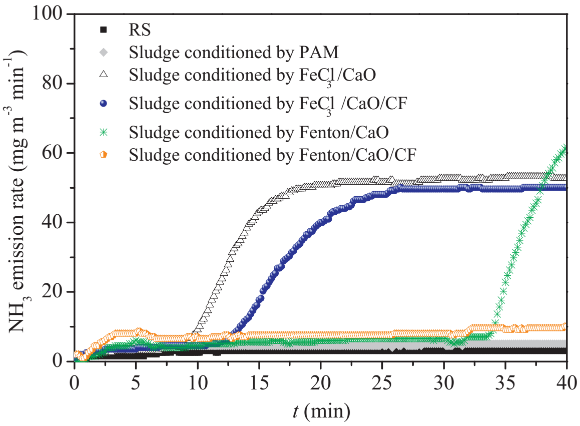

Fig. 2. Effect of different conditioners on emission characteristics of ammonia.

of known concentrations, which is specially mixed by a supplier to the customer's specifications to match component gasses that they would be testing for.

After gas analysis was completed, the conditioning test was performed the third time. When the conditioner was added into the sludge and reaction was completed, the sludge samples were collected. These samples were named as 0 to 5-5, as listed in Table 2. The pH values of sludge in each stage of conditioning were measured by a pH meter (Model pH S3, Shanghai, China).

To stop the biochemical reactions in sludge timely and reduce the loss of volatile constituents, raw and conditioned sludge samples were freeze-dried instead of being thermal dried for subsequent analyses. All the samples were milled and sieved to less than 45 μm in particle size. Proximate analysis of dry sludge was conducted by using a TGA2000 (Las Navas Company, Spain) proximate analyzer while elemental analysis by a Vario Microcube (Elementar Company, Germany) elemental analyzer. The nitrogen and sulfur speciations of freeze-dried samples surface were investigated by X-ray photoelectron spectroscopy (XPS) using a VG Multilab 2000 X-ray photoelectron spectrometer. The software (Avantage) was applied in statistic processing, with the relative element contents in different speciations calculated by integration of the peak area. Supposing that different forms of elements in the samples are equally distributed, the actual quantity of element in a certain form is the result of the total amount of that element in sludge multiplied by the relative surface element content in that speciation. Experiments were conducted three times to determine the validity and reproducibility of the results.

3. Results and discussion

3.1. Odors production

Our experimental results showed that NH_3 was the only detectable nitrogen-containing odorous compounds emitted from different conditioned sludge samples. The average results are shown in Fig. 2, and the deviations did not exceed 10% of the total. The amount of NH_3 released from the RS was relatively small and addition of PAM did not change the ammonia emissions. After the sludge was conditioned by $FeCl_3$, the CaO addition caused a significant NH_3 emission. Moreover, addition of 500 mg g^{-1} DS CaO resulted in greater NH_3 emission compared with that of 100 mg g^{-1} DS. When using the F-S composite conditioner, a small amount of NH_3 was emitted from the samples even there is no CaO addition. The presence of CaO at dosage of 500 mg g^{-1} DS resulted in a large amount of NH_3 emission.

The total amount of NH_3 emission was estimated by integrating NH_3 emission rates over conditioning time, as summarized in Table 3. The results show that during each conditioning process, NH_3 emission exceeded the threshold 1.1 mg m^{-3} (1.5 ppm, v/v) [18]. And the largest total amount of NH_3 emission was obtained when sludge was conditioned by $FeCl_3$ and CaO.

Three types of sulfur-containing odorous compounds were detected by the trace sulfur analyzer during different conditioning processes. And the total amount of each sulfur-containing compound emission was calculated by plusing the results of emission rate in each condition stage multiplied by conditioning time, as listed in Table 3. As illustrated in Fig. 3a and Table 3, PAM could prevent hydrogen sulfide (H_2S) from being released to some extent. But H_2S emission still exceeded the threshold of 0.00062 mg m^{-3} (0.00041 ppm, v/v) [18]. Little H_2S was released when the sludge was conditioned by $FeCl_3$ and skeleton builders, especially after the addition of CaO. In contrast, the amount of H_2S emitted increased sharply with the addition of the F-S composite conditioner until CaO participated in the conditioning process. According to Fig. 3b, the emission of SO_2 only occurred in the initial mixing of RS and was higher than the threshold of 2.5 mg m^{-3} (0.87 ppm, v/v) [18]. PAM as well as combination of $FeCl_3$ and skeleton builders could both effectively inhibit the release of SO_2. In the case of the F-S conditioning, the pH was adjusted by adding H_2SO_4 in the first 1 min, which promoted the emission of SO_2. When adding H_2O_2 into the sludge, SO_2 release stopped immediately. As shown in Fig. 3c and Table 3, carbonyl sulfide (COS) was detected only in the Fenton reaction period of the F-S composite conditioning process, and its emission exceeded the threshold of 0.15 mg m^{-3} (0.055 ppm, v/v) [18].

3.2. Variations in sludge properties

Chemical conditioners mentioned above can enhance the sludge dewaterability through charge neutralization [13,16], interparticle bridging [13,19], rigid structure formation [20] and/or oxidation [17]. Different reactions lead to different sludge properties. The emission characteristics of nitrogen- and sulfur-containing odorous compounds relate to or associate with the characteristics of the sludge, especially the nitrogen and sulfur speciations. Table 4 tabulates the results of the proximate and ultimate analyses of the freeze-dried samples. Compositions of sludge samples conditioned with different chemicals differ. Volatile matters, ash and the element contents of RS and PAM-treated sludge are similar, resulted in similar odors release pattern. In the second and third sets of the experiments, the addition of 500 mg g^{-1} DS CaO decreased the sludge volatile matter, nitrogen and sulfur content. This might be connected with the increasing amount of sludge dry solids and decomposition or hydrolysis of organic matter under strong alkaline conditions. The addition of 100 mg g^{-1} DS and 400 mg g^{-1} DS coal fine caused a decrease in volatile matter content but slight increase in nitrogen and sulfur content. For F-S reagents conditioning, nitrogen content also decreased with the addition of skeleton builders. This is because H_2SO_4 and $FeSO_4$ were applied to adjust sludge pH and provide Fe^{2+}. The sludge sulfur content was substantially increased, which provided basis for a large amount of sulfur-containing gas emissions.

As illustrated in Table 4, CaO addition raised pH values to over 11.65 in samples 2-1, 3-2, 3-3 and 4-4. The higher pH values are consistent with the increased NH_3 emissions. Similar phenomena about nitrogen-containing gases were found by other researchers. Kim et al. [21] attributed the amine odor trimethylamine generation to increased pH and temperature caused by lime addition. Chang et al. [3] believed that the product organic amines volatilized mostly noticeably due to the high pH of lime-added sludge. In our

Table 3
The total amounts of NH_3, H_2S, SO_2, COS emissions.

No.	Samples	Total amounts of emissions (mg, for 1 m^3 sludge)			
		NH_3	H_2S	SO_2	COS
0	RS	109.2	518.7	4.5	0
1	Sludge conditioned by PAM	178.5	452.1	2.9	0
2	Sludge conditioned by $FeCl_3$/CaO	1452.0	5.3	0	0
3	Sludge conditioned by $FeCl_3$/CaO/CF	1198.5	4.6	0	0
4	Sludge conditioned by Fenton/CaO	423.6	839.4	16.5	11.5
5	Sludge conditioned by Fenton/CaO/CF	306.0	827.6	15.5	9.7

experiments, temperatures were maintained at 288 ± 1 K. Therefore, it is pH, not temperature that contributed to NH_3 generation.

The results from XPS data suggest the significant differences in the observed relative ratios of S and N among the samples, as shown in Figs. 4 and 6. The N 1s peak is resolved into three component peaks which achieved an acceptable fit in the XPS spectra. The binding energy values at 401.5 ± 0.6 eV, 400 ± 0.2 eV, 398.6 ± 0.2 eV can be assigned to N—H in ammonia or protonated amine, N—O/C—N in amide or amine, and nitrogen in amine groups (=N—), corresponding to N_1, N_2, N_3, respectively [22–24].

Fig. 5 demonstrates that nitrogen in raw and conditioned sludge mainly exists in the form of amide or amine. This is because sewage sludge flocs consist of micro-organisms (mainly bacteria) [25], containing a large number of organic macromolecules such as protein, which is a kind of natural polymers linked by amide —CO—NH— bond (or peptide bond). Nitrogen species distribution in PAM conditioned sludge is similar to those in RS, leading to almost the same nitrogenous gases emission characteristics (Fig. 5a and b). When skeleton builders, 500 mg g^{-1} DS or 100 mg g^{-1} DS CaO combined with 400 mg g^{-1} DS CF, were added into $FeCl_3$-treated sludge, less nitrogen in amide or amine and no nitrogen in ammonia or protonated amine could be detected (Fig. 5c and d). The decrease in amide and amine might be associated with protein degradation and the increased amount of dry solids in sludge. Strong alkaline conditions (Table 4) are favorable for the solubilization of sludge proteins and their biodegradation [26]. The transformation of N speciation can be explained by these reactions:

$$\text{R-CONH}_2 + \text{OH}^- \rightarrow \text{R-COO}^- + \text{NH}_3 \quad (1)$$

$$\text{R-CONHR'} + \text{OH}^- \rightarrow \text{R-COO}^- + \text{NH}_2\text{R'} \quad (2)$$

$$\text{R-CN} + 2\text{OH}^- \rightarrow \text{R-COO}^- + \text{NH}_3 \quad (3)$$

Meanwhile, abundant OH^- could drive the reaction (4), thus free ammonia or protonated amine is easily converted to volatile ammonia, resulted in a significant increase in ammonia emission.

$$\text{NH}_4{}^+ + \text{OH}^- \leftrightarrows \text{NH}_3 + \text{H}_2\text{O} \quad (4)$$

For the F-S conditioning process, Fenton peroxidation is capable of decomposing a number of organic substances via strong oxidation, thus the amount of organic nitrogen (N_2 and N_3) decreases while that of inorganic one (N_1) increases. In this case, 500 mg g^{-1} DS CaO also leads to the conversion of almost all the N in ammonia or protonated amine to N in volatile NH_3. However, pH value of the sludge after treated by 100 mg g^{-1} DS CaO and 400 mg g^{-1} DS CF is 10.82, partially causing the reaction discussed above.

Comparing with nitrogen, sulfur composition is more complex, as illustrated in Fig. 6. Six component peaks were detected,

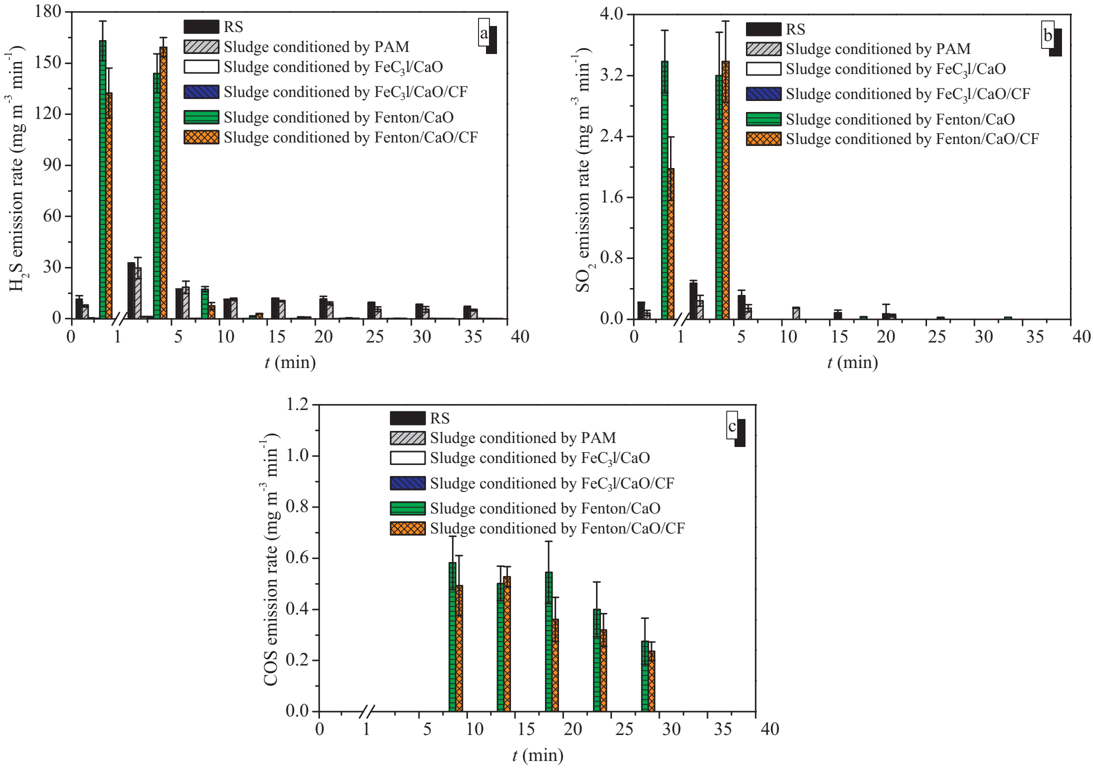

Fig. 3. Effect of different conditioners on emission characteristics of (a) hydrogen sulfide, (b) sulfur dioxide and (c) carbonyl sulfide.

Table 4
Sludge properties.

No.	Samples	Conditioners	Proximate analysis (wt%)[a,b]				Ultimate analysis (wt%)[b]				pH
			M	V	A	FC	C	H	N	S	
0	RS	Control	5.13 ± 0.85	42.26 ± 0.20	57.72 ± 0.21	0.02 ± 0.01	20.53 ± 0.03	3.19 ± 0.17	3.30 ± 0.02	0.93 ± 0.02	6.83 ± 0.03
1-1	Sludge conditioned by PAM	PAM	1.83 ± 0.66	44.54 ± 0.41	54.59 ± 0.34	0.87 ± 0.07	20.89 ± 0.40	3.23 ± 0.44	3.26 ± 0.02	0.94 ± 0.01	6.86 ± 0.05
2-1	Sludge conditioned by $FeCl_3$/CaO	$FeCl_3$	6.29 ± 0.95	39.23 ± 0.33	59.70 ± 0.42	1.07 ± 0.10	19.97 ± 0.37	3.46 ± 0.13	3.46 ± 0.01	0.71 ± 0.02	6.41 ± 0.03
2-2		$FeCl_3$/CaO	4.51 ± 0.21	35.04 ± 0.51	64.93 ± 0.47	0.03 ± 0.04	13.82 ± 0.19	3.09 ± 0.17	1.78 ± 0.02	0.29 ± 0.09	11.96 ± 0.02
3-1	Sludge conditioned by $FeCl_3$/CaO/CF	$FeCl_3$	5.99 ± 0.89	39.08 ± 0.82	60.57 ± 0.61	0.35 ± 0.21	18.97 ± 0.28	3.53 ± 0.04	3.38 ± 0.08	0.77 ± 0.05	6.40 ± 0.02
3-2		$FeCl_3$/CaO	7.60 ± 0.34	39.45 ± 0.64	59.47 ± 0.75	1.08 ± 0.11	18.30 ± 0.60	3.30 ± 0.18	2.45 ± 0.01	0.65 ± 0.04	11.7 ± 0.01
3-3		$FeCl_3$/CaO/CF	6.03 ± 0.47	48.85 ± 0.35	50.25 ± 0.35	0.90 ± 0.71	29.67 ± 0.01	3.46 ± 0.11	2.21 ± 0.01	0.66 ± 0.05	11.69 ± 0.02
4-1	Sludge conditioned by Fenton/CaO	H_2SO_4	4.85 ± 0.69	44.02 ± 0.74	54.84 ± 0.08	1.14 ± 0.82	19.35 ± 0.01	3.41 ± 0.05	3.34 ± 0.01	1.76 ± 0.13	5.09 ± 0.02
4-2		H_2SO_4/Fe_2SO_4	6.02 ± 0.48	46.19 ± 0.30	53.22 ± 0.31	0.59 ± 0.01	18.29 ± 0.11	3.33 ± 0.02	3.10 ± 0.07	2.95 ± 0.13	4.84 ± 0.02
4-3		H_2SO_4/Fe_2SO_4/H_2O_2	7.48 ± 0.45	43.48 ± 0.45	55.45 ± 0.64	1.07 ± 0.18	17.13 ± 0.06	3.33 ± 0.10	3.36 ± 0.04	3.17 ± 0.11	4.04 ± 0.02
4-4		H_2SO_4/Fe_2SO_4/H_2O_2/CaO	6.38 ± 0.64	32.42 ± 0.82	66.62 ± 0.88	0.96 ± 0.06	13.04 ± 0.16	3.01 ± 0.04	1.83 ± 0.05	1.50 ± 0.20	11.94 ± 0.04
5-1	Sludge conditioned by Fenton/CaO/CF	H_2SO_4	2.90 ± 0.42	45.31 ± 0.07	54.00 ± 0.14	0.69 ± 0.21	20.57 ± 0.47	3.43 ± 0.08	3.37 ± 0.07	1.71 ± 0.18	5.17 ± 0.03
5-2		H_2SO_4/Fe_2SO_4	7.12 ± 0.40	45.44 ± 0.62	53.95 ± 0.07	0.61 ± 0.55	17.84 ± 0.25	3.36 ± 0.03	3.19 ± 0.01	2.72 ± 0.12	4.64 ± 0.03
5-3		H_2SO_4/Fe_2SO_4/H_2O_2	6.04 ± 0.21	44.94 ± 0.48	54.47 ± 0.75	0.59 ± 0.27	18.98 ± 0.137	3.60 ± 0.22	3.37 ± 0.01	2.91 ± 0.06	3.95 ± 0.05
5-4		H_2SO_4/Fe_2SO_4/H_2O_2/CaO	6.79 ± 0.72	36.97 ± 0.89	61.54 ± 0.76	1.49 ± 0.13	17.23 ± 0.168	3.22 ± 0.05	2.48 ± 0.02	2.73 ± 0.06	10.35 ± 0.01
5-5		H_2SO_4/Fe_2SO_4/H_2O_2/CaO/CF	4.63 ± 0.24	47.74 ± 0.06	51.38 ± 0.25	0.88 ± 0.31	29.79 ± 0.192	3.56 ± 0.37	2.00 ± 0.05	2.02 ± 0.11	6.83 ± 0.07

[a] M, V, A and FC are moisture, volatile matter, ash and fixed carbon.

[b] Dry basis except for moisture in freeze-dried basis.

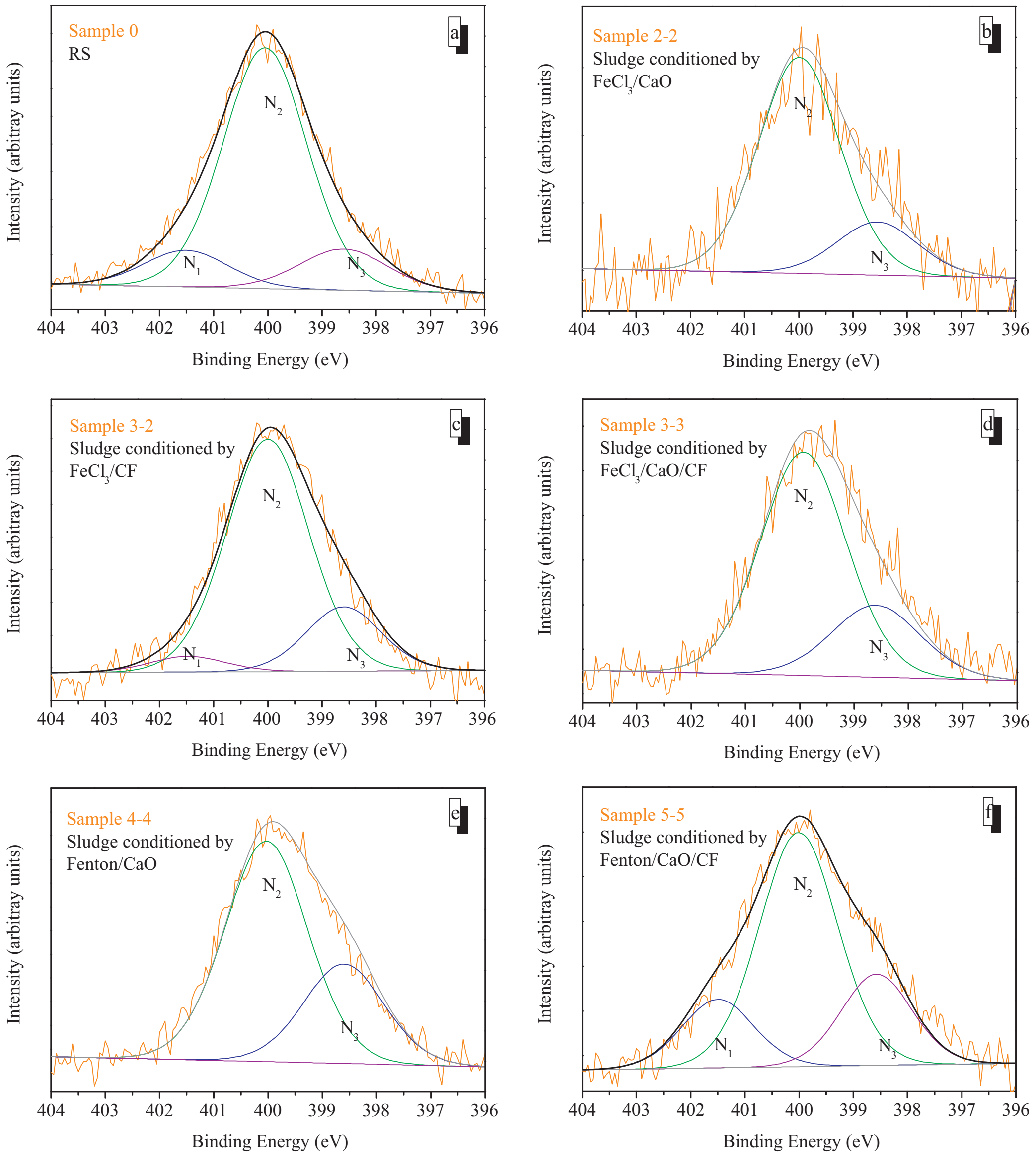

Fig. 4. XPS spectra of N 1s for different sludge.

achieving an acceptable fit in the S 2p XPS spectra. The binding energy values at 170.0 ± 1.0 eV, 168.2 ± 0.2 eV, 166.0 ± 0.5 eV, 164.1 ± 0.2 eV, 163.3 ± 0.4 eV, and 162.2 ± 0.6 eV can be assigned to sulfate, sulfonic acid, sulfoxide, aromatic sulfur, aliphatic sulfur, and inorganic sulfides, corresponding to $S_1, S_2, S_3, S_4, S_5, S_6$, respectively [27–33].

It can be clearly seen from Fig. 7a and b that PAM addition has little effect on the total sulfur content, but strong impacts on forms of sulfur undergone chemical or physical transformation. After PAM conditioning, the total content of inorganic sulfate increases slightly, demonstrating that the partial nomadic SO_2 and H_2S are fixed in sludge flocs by charge neutralization or inter-particle bridging. As illustrated in Fig. 7c and d, when using $FeCl_3$ and skeleton builders were used as the conditioners, the total sulfur content declined due to the expanded sludge dry solids. It is noteworthy that Fe^{3+} could eliminate the generation of H_2S (Fig. 3a) since there would be a transfer of electrons between Fe^{3+} and S^{2-} in an oxidation-reduction reaction. Sulfur presented in $FeCl_3$-treated sludge is mainly sulfonic acid and aliphatic sulfur. After CaO addition, H_2S is absorbed into alkaline sludge to form hydrosulfide (Eq. (5), HS^-, referred to as "sulfide") [34], followed by complete oxidation to sulfate, which has been identified by the increased sulfates content (shown in Fig. 6b and c).

$$H_2S(aq) + OH^- \leftrightarrows HS^- + H_2O \qquad (5)$$

Meanwhile, low SO_2 generation might be related with the formation of calcium sulfate. Fig. 7e and f display a significant increase in total sulfur content of each sample in the F-S composite conditioning process, with sulfate and sulfonic acid as the predominant sulfur species. The acidic environment created by H_2SO_4 accelerates the decomposition of sulfur-containing amino acids oxidation of inorganic sulfides, resulted in an increase in H_2S and SO_2 generation. But the addition of $FeSO_4$ appeared to prohibit reaction (6), causing decreased H_2S emission and increased content of sulfides.

$$FeS + H_2SO_4 \leftrightarrows FeSO_4 + H_2S \qquad (6)$$

During the Fenton reaction, highly reactive hydroxyl radicals facilitate the oxidation and decomposition of sulfur proteins and other organic macromolecules in sludge. The increase in the content of sulfoxide as well as decrease in the content of aromatic and aliphatic sulfur might be connected with the oxidation of aromatic thioethers and aliphatic thioethers. The reaction products including

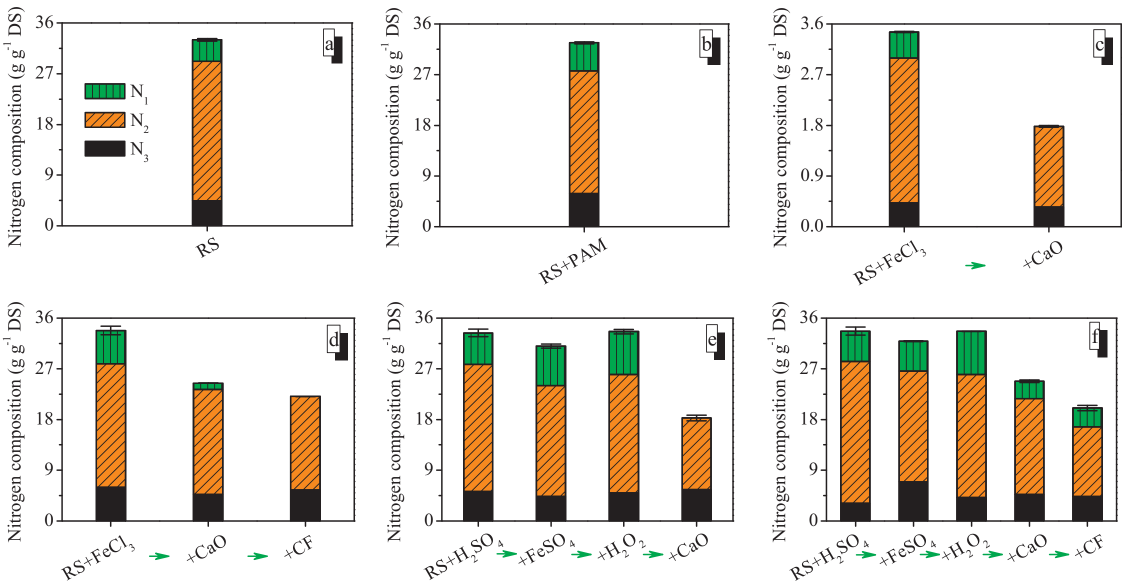

Fig. 5. Nitrogen composition of raw and conditioned sludge determined by XPS.

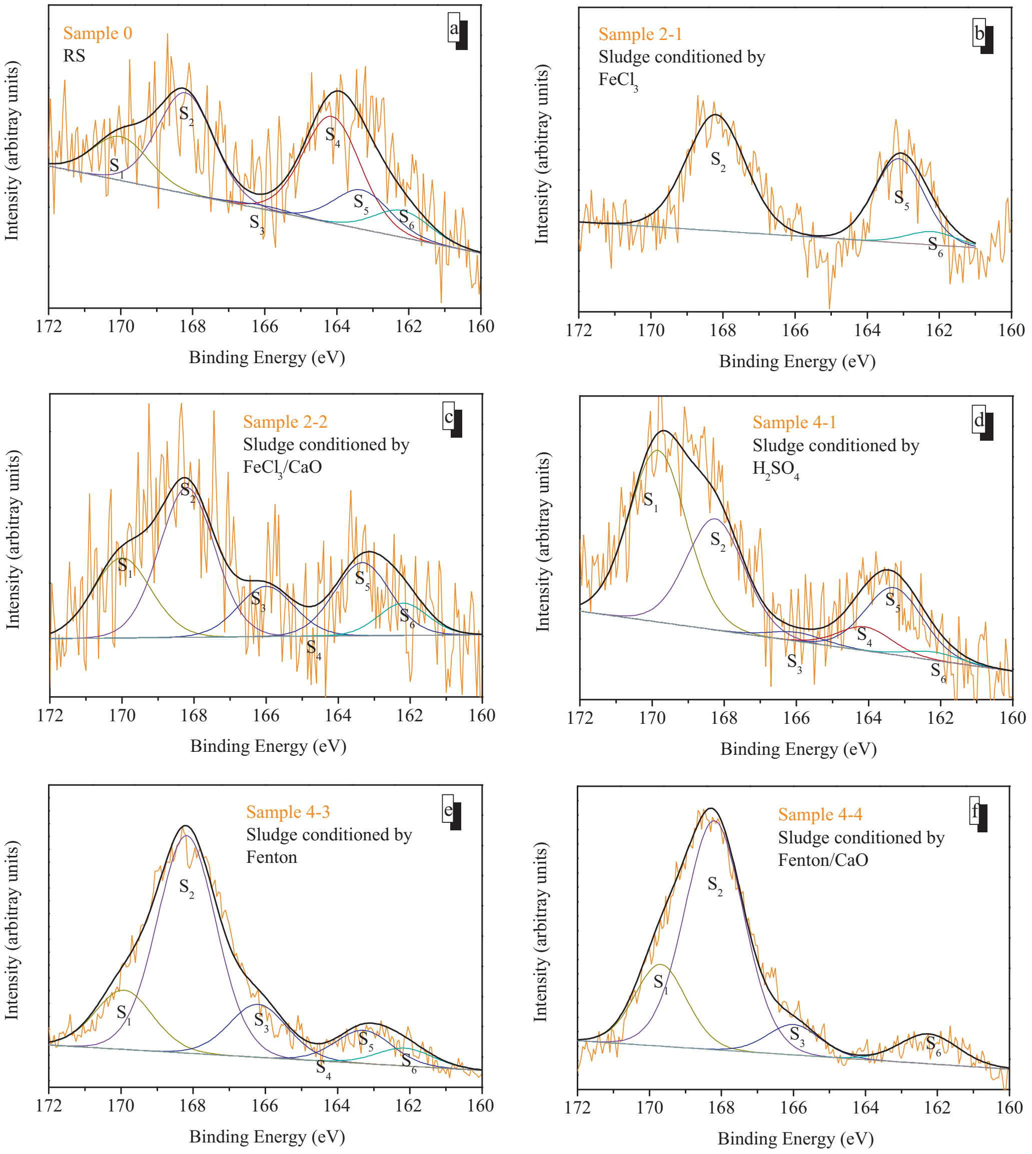

Fig. 6. XPS spectra of S 2p for different sludge.

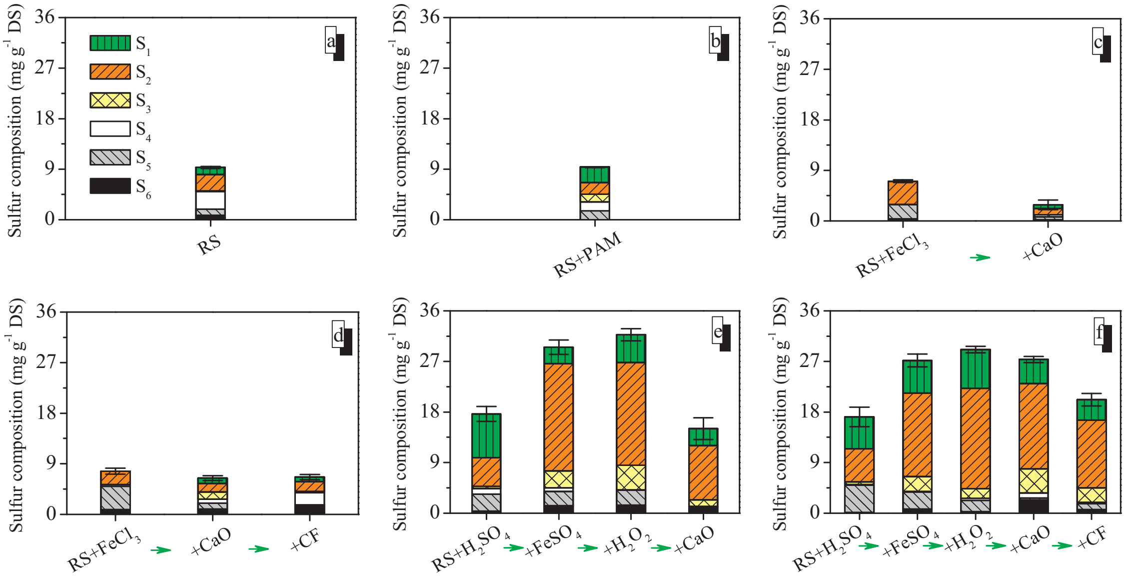

Fig. 7. Sulfur composition of raw and conditioned sludge determined by XPS.

sulfoxide, aromatic and aliphatic sulfur may further decompose with COS production under strong oxidizing conditions, which is consistent with the emission characteristics of COS shown in Fig. 3c.

4. Conclusions

Emission characteristics of main nitrogen- and sulfur-containing odorous compounds generated from sewage sludge conditioning using three representative conditioners were investigated. NH_3, SO_2, H_2S and COS were detected during sludge conditioning. The results indicate that PAM has little effect on emission characteristics of these four odorous gases. Significant increases of SO_2 and H_2S releasing were observed in acidic environment due to the accelerated decomposition of sulfur-containing amino acids. Fenton oxidation facilitates the generation of COS probably because sulfur proteins were decomposed, followed by further decomposition of the reaction products. CaO can reduce emission of sulfur-containing odorous compounds via formation of calcium sulfate. However, CaO also leads to a significant release of NH_3 because free ammonia or protonated amine in sludge is converted to volatile ammonia under strong alkaline conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2012.07.060.

References

[1] R.M. Stuetz, R.A. Fenner, G. Engin, Assessment of odors from sewage treatment works by an electronic nose, Water Res. 33 (1999) 453–461.
[2] P. Gostelow, S.A. Parsons, R.M. Stuetz, Odors measurements for sewage treatment works, Water Res. 35 (2001), 579-497.
[3] J.S. Chang, M. Abu-Orf, S.K. Dentel, Alkylamine odors from degradation of flocculant polymers in sludges, Water Res. 39 (2005) 3369–3375.
[4] C. He, J.H. Yan, X.Z. Li, V.K. Sharma, S.Y. Li, Elimination of sludge odor by oxidizing sulfur-containing compounds with ferrate(VI), Environ. Sci. Technol. 43 (2009) 5890–5895.
[5] W.Y. Deng, J.H. Yan, X.D. Li, F. Wang, X.W. Zhu, S.Y. Lu, K.F. Cen, Emission characteristics of volatile compounds during sludges drying process, J. Hazard. Mater. 162 (2009) 186–192.
[6] B.R. Dhar, E. Elbeshbishy, H. Hafez, G. Nakhla, M.B. Ray, Thermo-oxidative pretreatment of municipal waste activated sludge for volatile sulfur compounds removal and enhanced anaerobic digestion, Chem. Eng. J. 174 (2011) 166–174.
[7] W.Y. Deng, J.H. Yan, X.D. Li, F. Wang, Y. Chi, S.Y. Lu, Emission characteristics of dioxins, furans and polycyclic aromatic hydrocarbons during fluidized-bed combustion of sewage sludge, J. Environ. Sci. 21 (2009) 1747–1752.
[8] C. Hort, S. Gracy, V. Platel, L. Moynault, Evaluation of sewage sludge and yard waste compost as a biofilter media for the removal of ammonia and volatile organic sulfur compounds (VOSCs), Chem. Eng. J. 152 (2009) 44–53.
[9] L. Fraikin, T. Slmon, B. Herbreteau, J.P. Levasseur, F. Nicol, M. Crine, A. Léonard, Impact of storage duration on the gaseous emissions during convective drying of urban residual sludges, Chem. Eng. Techol. 34 (2011) 1172–1176.
[10] J.A. Cusido, L.V. Cremades, M. Gonzalez, Gaseous emissions from ceramics manufactured with urban sewage sludge during firing processes, Waste Manage. 23 (2002) 273–280.
[11] F. Colin, S. Gazbar, S.K. Dentel, Distribution of water in sludges in relation to their mechanical dewatering, Water Res. 29 (1995) 2000–2005.
[12] C. Chen, P.Y. Zhang, G.M. Zeng, J.H. Deng, Y. Zhou, H.F. Lu, Sewage sludge conditioning with coal fly ash modified by sulfuric acid, Chem. Eng. J. 158 (2010) 616–622.
[13] H. Saveyn, S. Meersseman, O. Thas, P.V.D. Meeren, Influence of polyelectrolyte characteristics on pressure-driven activated sludge dewatering, Colloids Surf. A 262 (2005) 40–51.
[14] E. Neyens, J. Baeyens, M. Weemaes, B. De heyder, Pilot-scale peroxidation (H2O2) of sewage sludge, J. Hazard. Mater. B 98 (2003) 91–106.
[15] M. Citeau, O. Larue, E. Vorobiev, Influence of salt, pH and polyelectrolyte on the pressure electro-dewatering of sewage sludge, Water Res. 45 (2011) 2167–2180.
[16] S. Deneux-Mustin, B.S. Lartiges, Ferric chloride and lime conditioning of activated sludges: an electron microscopic study on resin-embedded samples, Water Res. 35 (2001) 3018–3024.
[17] H. Liu, J.K. Yang, Y.F. Shi, Y. Li, S. He, C.Z. Yang, H. Yao, Conditioning of sewage sludge by Fenton's reagent combined with skeleton builders, Chemosphere 88 (2012) 235–239.
[18] Y. Nagata, N. Takeuchi, Measurement of odor threshold by triangle odor bag method, Bull. Jpn. Environ. Sanit. Center 17 (1990) 77–89.
[19] M.C.Lo. Irene, C.K.Lai. Keith, G.H. Chen, Salinity effect on mechanical dewatering of sludge with and without chemical conditioning, Environ. Sci. Technol. 35 (2001) 4691–4696.

[20] J. Zall, N. Galil, M. Rehbun, Skeleton builders for conditioning oily sludge, J. Water Pollut. Control Fed. 59 (1987) 699–706.

[21] H. Kim, S. Murthy, C. Peot, M. Ramirez, M. Strawn, C.H. Park, S. McConnell, Examination of mechanisms for odor compound generation during lime stabilization, Water Environ. Res. 75 (2003) 121–125.

[22] B.Q. Liao, H.J. Lin, S.P. Langevin, W.J. Gao, G.G. Leppard, Effects of temperature and dissolved oxygen on sludge properties and their role in bioflocculation and settling, Water Res. 45 (2011) 509–520.

[23] Y. Jin, P. Ling, Y. He, L. Chen, J. Chen, T. Zhang, Preparation, characterization and anti-*Helicobacter pylori* activity of Bi^{3+}-hyaluronate complex, Carbohydr. Polym. 74 (2008) 50–58.

[24] X.F. Sun, S.G. Wang, W. Cheng, M.H. Fan, S.H. Tian, Enhancement of acidic dye biosorption capacity on poly(ethylenimine) grafted anaerobic granular sludge, J. Hazard. Mater. 189 (2011) 27–33.

[25] A. Zita, M. Hermansson, Effects of bacterial cell surface structures and hydrophobicity on attachment to activated sludge flocs, Appl. Environ. Microbiol. 63 (1997) 1168–1170.

[26] H. Liu, J. Wang, X.L. Liu, B. Fu, J. Chen, H.Q. Yu, Acidogenic fermentation of proteinaceous sewage sludge: effect of pH, Water Res. 46 (2012) 799–807.

[27] M. Kozłowski, XPS study of reductively and non-reductively modified coals, Fuel 83 (2004) 259–265.

[28] S.R. Kelemen, C.C. Walters, P.G. Kwiatek, H. Freund, M. Afeworki, M. Sansone, W.A. Lamberti, R.J. Pottorf, H.G. Machel, K.E. Peters, T. Bolin, Characterization of solid bitumens originating from thermal chemical alteration and thermochemical sulfate reduction, Geochim. Cosmochim. Acta 74 (2010) 5305–5332.

[29] F. Liu, W. Li, H.K. Chen, B.Q. Li, Uneven distribution of sulfurs and their transformation during coal pyrolysis, Fuel 86 (2007) 360–366.

[30] P.S. Li, Y. Hu, W. Yu, Y.N. Yue, Q. Xu, S. Hu, N.S. Hu, J. Yang, Investigation of sulfur forms and transformation during the co-combustion of sewage sludge and coal using X-ray photoelectron spectroscopy, J. Hazard. Mater. 167 (2009) 1126–1132.

[31] T. Grzybek, R. Pietrzak, H. Wachowska, X-ray photoelectron spectroscopy study of oxidized coals with different sulphur content, Fuel Process. Technol. 77-78 (2002) 1–7.

[32] S.P. Marinov, G. Tyuliev, M. Stefanova, R. Carleer, J. Yperman, Low rank coals sulphur functionality study by AP-TPR/TPO coupled with MS and potentiometric detection and by XPS, Fuel Process. Technol. 85 (2004) 267–277.

[33] H.K. Chen, B.Q. Li, J.L. Yang, B.J. Zhang, Transformation of sulfur during pyrolysis and hydropyrolysis of coal, Fuel 77 (1998) 487–493.

[34] P.L.F.V.D. Bosch, M.D. Graaff, M. Fortuny-Picornell, R.C.V. Leerdam, A.J.H. Janssen, Inhibition of microbiological sulfide oxidation by methanethiol and dimethyl polysulfides at natron-alkaline conditions, Appl. Environ. Biotechnol. 83 (2009) 579–587.