The one-stage autothermal thermophilic aerobic digestion for sewage sludge treatment: Stabilization process and mechanism

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Batch experiment was carried out in a simulated thermophilic aerobic digester to investigate the digestion process of one-stage autothermal thermophilic aerobic digester and to explore the sludge stabilization mechanism. Volatile solids removal was 38.4% at 408 h and 45.0% at 552 h. Chemical oxidation demand, total nitrogen, and ammonia nitrogen in supernatant increased rapidly up to 168 h, and all of them fluctuated moderately after 360 h. Volatile fatty acid (VFA) accumulated rapidly up to 24 to 168 h, then declined sharply, reaching a low concentration after 312 h. Propionic, iso-valeric, and isobutyric acids, in addition to acetic acids, were also the major components of VFA. As the biochemical metabolic process was inhibited under oxygen-deficiency condition, the digestion system can produce acetic, propionic, butyric acids and other VFA constituents to meet the demand for NAD+ and maximize ATP generation. The ORP affected the VFA production and depletion as well as sulfate levels.

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1. Introduction

In recent years, much attention has been paid to the treatment and disposal of sewage sludge due to the expansion of municipal wastewater treatment and increasingly stringent regulations. To reduce and stabilize sewage sludge, anaerobic and aerobic digestion processes are commonly used in wastewater treatment plants (WWTPs). Anaerobic digestion is employed worldwide as the oldest and most important process for sludge stabilization, and it is almost universal in large WWTPs because a considerable amount of methane can be recovered. However, aerobic digestion is more suitable for medium- and small-sized WWTPs where anaerobic digestion process is no longer economic. Autothermal thermophilic aerobic digestion (ATAD) is a promising aerobic process that can produce Class A biosolids from a wide range of organic sludge such as swine waste, sewage sludge, and food wastes (USEPA, 1990; Juteau, 2006). ATAD systems can successfully achieve thermophilic digestion due to the insulation and abundant heat produced by the microbial degradation of organic matter in the sludge, and have the advantage of rapid biomass degradation, short sludge retention time (SRT), and efficient pathogen inactivation compared to anaerobic digestion (Layden et al., 2007). The ATAD process has been adopted by a number of medium- and small-sized WWTPs in Europe and North America since it was first introduced in the early 1970s (Kelly and Mavinic, 2003). Recently, more investigations on ATAD process have payed attention to mathematical model (Gomez et al., 2007), bacterial function and community structure of thermophiles (Kim et al., 2002; Hayes et al., 2011), and dewatering performance of the digested sludge (Zhou, 2003).

ATAD systems are normally two-stage or multi-stage processes in order to achieve fast reduction of volatile solids (VS) and efficient pathogen inactivation. With continuous innovation of ATAD technology, one-stage ATAD has received attention in recent years. In China, simple one-stage ATAD devices occupying small area have been developed and patented (Zhu et al., 2005), and experimental results (Cheng, 2006; Liu et al., 2011a) have indicated that the one-stage ATAD process can achieve the same stabilization as two-stage ATAD systems. However there is still no full-scale one-stage ATAD process in operation due to its unclear stabilization mechanism and insufficient guidelines for practical operation. To better understand the sludge stabilization process, some researchers have investigated the microbial diversity in the simulated one-stage ATAD digester, finding that thermophilic digestion showed low level biodiversity, with the predominant microbes including anaerobic or facultative bacteria in addition to aerobic bacteria (Liu et al., 2010, 2011b). The feature of bacterial consortia in one-stage ATAD system showed high similarity with that in two-stage ATAD system (Staton et al., 2001; Hayes et al., 2011).

In view of the fact that short-chain volatile fatty acid (VFA) can affect the degradation of VS and the metabolic process in anaerobic digestion (Gottschalk, 1979; Wang et al., 1999), some researchers...
(Chu et al., 1997; Fothergill and Mavinic, 2000) have begun to pay more attention to the analysis of VFA in thermophilic aerobic digestion. Though VFA is an important indicator closely related to the sludge stabilization process, it has not received enough attention in one-stage ATAD system. To elucidate the stabilization process and mechanism for one-stage ATAD process, this work analyzed the variation of carbon, nitrogen, phosphorus, and sulfate, in addition to the digestion effectiveness in terms of VS removal and pathogen inactivation. Based on the obtained results and fundamental theories of aerobic and anaerobic digestions, a biochemical model was proposed to gain deeper insight into substrate metabolism in one-stage ATAD system.

2. Methods

2.1. Sewage sludge sample

Sewage sludge was sampled from the sludge thickening tank of a municipal wastewater treatment plant in Shanghai, China in which anaerobic–anoxic–oxic process was applied to domestic wastewater and primary and secondary sludges were both discharged into a sludge thickening tank. Prior to use, the sludge was sieved manually to remove matter coarser than 0.5 mm, then centrifuged at 2200 g for 3 min to obtain a total solid (TS) level between 5% and 6% (Staton et al., 2001; Liu et al., 2011a). As seen in Table 1, the ratio of VS/TS in the sludge was 62.7%, much lower than that in Europe and North America where it is usually 70–85% (Cheng, 2006).

2.2. Startup of the digestion process

Batch-mode experiment was carried out in a simulated autothermal thermophilic aerobic digester (Fig. 1). The total volume of the cylindrical stainless steel digester was 6.3 L, with the effective volume being 5 L due to potential foaming. The digester was filled with 5-L sludge sample, and then soaked in the water bath to maintain a certain digestion temperature. The water bath temperature was raised from 30 °C to 55 °C at a rate of 2.5 °C every 12 h, and then kept at 55 °C for 432 h afterward. Continuous aeration was supplied with an air flow rate of 0.10–0.12 L min−1 (Cheng et al., 2009) through microporous diffuser, with a constant stirring rate of 30 revolutions per minute. The pH in the digestion system was not regulated. Evaporation losses were made up with deionized water before each sampling.

During the entire digestion process, the pH and oxidation reduction potential (ORP) were monitored every 12 h, and sludge samples were collected every 48 h after digestion time for 24 h to determine TS and VS, as well as other indicators (SCOD, TN, and VFA).

2.3. Analytical methods

TS and VS were analyzed in accordance with the Standard Methods (APHA et al., 2005) in triplicate. All the following indicators except pathogen and heavy metal concentrations were determined twice. The pH and ORP of the sludge was measured by a pH meter (pHS-3C, Leici Co. Ltd. Shanghai) and an ORP meter (ORP-502, Ruo- sull Technology Co., Ltd. Shanghai), respectively.

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The sampled sludges were centrifuged for 15 min at 12,000g, and then filtered through 0.45-μm mixed cellulose ester membranes. The filtrate was collected to measure SCOD, total organic carbon (TOC), TN, NH4-N, NO3-N, NO2-N, orthophosphate (ortho-P), and SO42-. SCOD was analyzed by the standard reflux titrimetric method (SEPAC, 2002a), whereas TOC and TN were determined by a TOC/TN analyzer (Analytik jena multi N/C 3000, Germany). The concentration of NO3-N, NO2-N, ortho-P, and SO42- were determined by ion chromatography (MIC Dionex DX Series, Metrohm Corp., Switzerland), whereas NH4-N was measured by the distillation–boric acid absorption–titration method (SEPAC, 2002a) due to the complex composition of the sludge supernatant.

To quantify VFA (including acetic, n-butyric, iso-valeric and n-valeric acid), 1-mL filtrate sample was collected in a 1.5 mL gas chromatography (GC) vial and acidified with 100-μL of 3% H3PO4 to approximately pH 4.0 (Chen et al., 2007) before being assayed on an Shimadzu GC-2010 with a flame ionization detector and DB-FFAP column (30 m × 0.25 mm × 0.25 mm). The sample injection volume was 1.0 μL. Nitrogen was the carrier gas with a flux of 25 mL min−1. The injection port and the detector were maintained at 200 and 250 °C, respectively. The GC oven was programmed to begin at 120 °C for 2 min, next increase at 13 °C min−1 to 200 °C, and then to hold at 200 °C for an additional 2 min. The measured VFA constituents were expressed in mg L−1 COD (e.g. 1 mg L−1 acetic acid is 1.07 mg L−1 COD, and 1 mg L−1 butyric acid is 1.82 mg L−1 COD).

The collected sludges were dried at 60 °C for 24 h and then crushed. The resulting powder was then subjected to Inductively Coupled Plasma (ICP) analysis (Iris-Advantage1000, USA) to determine the concentrations of key metal elements.

Fecal coliform and Salmonella sp. bacteria were determined on a wet weight basis as pathogen indicators. Bacteria were tested in accordance with the Analytical and Monitoring Methods of Water and Wastewater (SEPAC, 2002a). Fecal coliform was initially identified using lactose peptone broth, and confirmed on EC broth. Salmonella sp. bacteria was initially identified on tetraionate broth and confirmed on Bismuth Sulphite (BS) agar, then followed by biochemical tests. If present, salmonella serotyping was used.

3. Results and discussion

3.1. Digestion effectiveness of the simulated one-stage ATAD system

The ATAD process reduced sludge by destroying VS to produce a stabilized final product suitable for disposal or reuse, and the VS removal efficiency is related to both reactor temperature and sludge retention time (USEPA, 1990). Fig. 2 presents the removal efficiency of VS in the one-stage ATAD system. VS removal reached 38.4% at 408 h, with its concentration decreasing from 34.6 g L−1 at 0 h to 21.3 g L−1. At the end of the digestion period (i.e. at 552 h), VS removal was 45.0%, VS concentration correspondingly decreased to 19.0 g L−1, and the ratio of VS/TS decreased from 62.7% at 0 h to 46.8%. Compared with the normal two-stage ATAD process with a minimum SRT of 8 d and a maximum SRT of 15 d (Staton et al., 2001; Kelly and Mavinic, 2003), 408 h (i.e. 17 d) were required for the simulated one-stage ATAD system to exceed 38% VS removal, mainly due to the batch-mode operation. The ratio of VS/TS in this study was lower than that in Europe and North America, inevitably requiring a longer SRT for the ATAD system.
to achieve the same VS reduction, due to more non-biodegradable or recalcitrant materials in the sludge. Since the bacterial diversity in the one-stage ATAD process showed no clear difference from the two- or multi-stage ATAD processes (Liu et al., 2010; Hayes et al., 2011), the thermophilic digestion temperature played the key role for the degradation of organic substrates. As a result, the one-stage ATAD system also had efficient VS removal as favorable as for the two-stage ATAD process.

Though the untreated sludge had 2.5 $\times$ 10$^7$ MPN fecal coliform per gram TS and 19 MPN Salmonella sp. bacteria per four gram TS. Both fecal coliform and Salmonella sp. bacteria in the digested sludge decreased sharply after digestion for 552 h, becoming too low to be detected, completely in line with the Class A sludge definitions in Part 503 of the USEPA 40 CFR (USEPA, 1993). As a result, the one-stage ATAD system was fully able to meet the pasteurizing requirements for land application.

ICP analysis for the raw and digested sludges (Table 2) indicated that the content of inorganic elements in the digested sludge increased moderately. However, the concentrations of heavy metals such as Cr, Ni, and Pb were all far lower than the threshold values stipulated by GB 18918-2002 of the People’s Republic of China (SEPAC, 2002b), indicating that the digested sludge met the requirements for application to agricultural land.

### 3.2. Carbon transformation and the speculation of metabolic pathways

The thermophilic aerobic digestion process resulted in abundant organic matter rapidly releasing lipids, polysaccharides, proteins, and nucleic acid into the supernatant and contributing to the concentration of SCOD (van Loosdrecht and Henze, 1999; Liu et al., 2010). Fig. 3A shows that both SCOD and TOC increase rapidly during the early digestion period (up to 120 h), and maintained high values from 120 to 216 h, with the highest concentrations of 8400 and 3220 mg L$^{-1}$, respectively. SCOD and TOC began to decline after 216 h, but both showed a small increase from 456 to 552 h. During the entire digestion process, the TOC/SCOD ratio ranged from 36.2% to 43.2%, remaining nearly constant.

In the initial digestion of sewage sludge, less temperature-tolerant microorganisms die and some thermostable enzymes such as proteases are released by cell lysis, in turn enhancing sludge degradation (Bomio et al., 1989; Li et al., 2009). As a result, the system maintained efficient removal of VS, consistent with the sharp increase of SCOD in the first 96 h. As digestion continued, thermophilic microbes can make full use of the released compounds to achieve rapid growth and developed predominant populations in the digestion system (Liu et al., 2010). Thus the organic substrates in the digester degraded rapidly, and SCOD and TOC began to decline after 216 h. In the late digestion period, the digester only achieved moderate VS removal (Fig. 2), and a stable bacterial population predominated in the digester.

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zn</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sludge (0 h)</td>
<td>575</td>
<td>19</td>
<td>1.3</td>
<td>49</td>
<td>146</td>
<td>45</td>
<td>39</td>
<td>–</td>
</tr>
<tr>
<td>Digested sludge (552 h)</td>
<td>806</td>
<td>22</td>
<td>2.2</td>
<td>65</td>
<td>207</td>
<td>48</td>
<td>58</td>
<td>–</td>
</tr>
<tr>
<td>Threshold value$^a$</td>
<td>2000</td>
<td>75</td>
<td>5</td>
<td>600</td>
<td>800</td>
<td>100</td>
<td>300</td>
<td>5</td>
</tr>
</tbody>
</table>

$^a$ Threshold value is stipulated by GB18918-2002 according to pH < 6.5.
In the ATAD process, the oxygen demand of the system is higher than the aeration capacity due to rapid VS degradation, usually resulting in microaerobic conditions prevailing and partial oxidation of substrates in the ATAD digester (Chu et al., 1996; Staton et al., 2001; Liu et al., 2011b). In an ATAD digestion process, abundant organic substrates can be released into the supernatant under thermophilic conditions due to cell lysis, and microaerobic conditions are responsible for the VFA production (Chu et al., 1997; Mavinic et al., 2001). As the NADH (nicotinamide adenine dinucleotide) is produced by oxidation of substrates or tricarboxylic acid cycle (TCA cycle) in ATAD digestion process, the oxidized form of NADH (NAD+) can not be generated in a timely manner by the operation of the respiratory chain under the oxygen limiting condition, and the further oxidation of substrates is inhibited. Chu et al. (1996) proposed a biochemical model to explain the substrate metabolism in thermophilic aerobic digestion. This model suggests that the bacteria could employ substrate level redox reactions to reduce the accumulation of NADH and maximize ATP production by shuttling acetyl-CoA through an acetyl-phosphate intermediate to acetate in response to the limited capacity of the respiratory chain. The model reveals that excess acetyl-CoA can be converted to acetate under microaerobic condition in the ATAD process. However, it is unable to explain the formation of propionic, butyric, and valeric acid.

A biochemical model of substrates metabolism for one-stage ATAD system is proposed, based on fundamental theories of aerobic and anaerobic digestions (Fig. 4). As the electron transport chain is inhibited by the limited oxygen in the ATAD system, the microorganisms regulate other metabolic pathways to meet the demand for NAD⁺ and maximize ATP generation. Converting acetyl-CoA to acetate can only generate ATP; however, the formation of propionic and butyric acid not only enhances the ATP production, but also favors reoxidation of NADH. Butyric acid production is often coupled with that of acetic acid. It is formed from two molecules of acetyl-CoA yielding acetoacetyl-CoA, which is then converted, via the intermediates β-hydroxybutyryl-CoA and crotonyl-CoA, to butyryl-CoA (Gottschalk, 1979). In metabolism process, pyruvate and methylmalonyl-CoA can yield propionyl-CoA and oxaloacetate. The latter can be converted to succinate via intermediate malate and fumarate; as propionyl-CoA is coupled with succinate, propionic acid is generated, and the produced succinyl-CoA is further converted to methylmalonyl-CoA to facilitate the propionate formation. The formation of n-valeric and iso-valeric acid is largely associated with Stickland fermentation of protein (Table 3). This view is supported by the finding of Weimer (2011) that carbohydrates yielded primarily acetic and propionic acid, whereas proteins yielded a more favorable product mix (longer chain and branched chain VFA). It has been reported that the content of protein can reach 40–60% (Tanaka et al., 1997; Chen et al., 2007) and proteolytic activity is the main enzymatic activity in an aerobic thermophilic sewage sludge treatment process (Bomio et al., 1989; Li et al., 2009). After amino acids are produced due to enzymatic hydrolysis of protein, n-valeric and iso-valeric acid can be formed through reductive deamination of single amino acid.
or by oxidation–reduction between pairs of amino acids via the Stickland reaction (McInerney, 1988).

The accumulation of VFA in the ATAD supernatant was not only related to their production, but also depended on their degradation or utilization. \( n \)-Butyric and \( n \)-valeric acid degraded via \( \beta \)-oxidation to acetate and acetate + propionate, respectively, and iso-butyric and iso-valeric acid degraded more slowly than their normal forms. Wang et al. (1999) investigated the degradation of VFA in anaerobic digestion and found that \( n \)-butyric acid degraded faster than \( n \)-valeric acid, not only by \( \beta \)-oxidation but also by isomerization. These between butyric and valeric acid are helpful in explaining the order of VFA concentration: iso-valeric acid > iso-butyric acid > (\( n \)-butyric or \( n \)-valeric acid) (Fig. 3B). As for propionic acid, on the one hand it generated more than butyric acid under oxygen-limited condition due to more NAD+ being produced (Fig. 4) and facilitated the digestion system. On the other hand, the high concentration of acetate adversely affected on the degradation of propionic acid, but not butyric acid (Gorris et al., 1989). Hence propionic acid became a main constituent of VFA, second only to acetic acid (Fig. 3B).

The biochemical model of substrate metabolism is closely related to the oxidation and reoxidation of NADH, which significantly affects the ORP variation in the ATAD system as aeration is constantly supplied. Staton et al. (2001) pointed out that the ATAD systems need variable oxygen supply due to the shift in the hydrolysis process. As SCOD rapidly increased in the first 168 h (Fig. 3A), the biochemical metabolic process was inhibited by the oxygen-limited condition, resulting in production of VFA. However the reductive NADH was still present at a relative surplus, making the ATAD system obtain a low ORP of less than \(-130\) mV (Fig. 3C). As thermophilic digestion continued from 168 to 216 h, VS removal remained high, reaching 4.7% (Fig. 2), SCOD had a corresponding increase (Fig. 3A), but VFA declined sharply (Fig. 3B), indicating that most of the

Table 3

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Empirical formula</th>
<th>C4 and C5 product</th>
<th>Stickland role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Histidine</td>
<td>C6H9O2N3</td>
<td>n-Butyrate</td>
<td>Uncoupled</td>
</tr>
<tr>
<td>Lysine</td>
<td>C6H14O2N2</td>
<td>n-Butyrate</td>
<td>Donor</td>
</tr>
<tr>
<td>Threonine</td>
<td>C6H13O2N</td>
<td>iso-Butyrate</td>
<td>Donor</td>
</tr>
<tr>
<td>Valine</td>
<td>C6H13O2N</td>
<td>iso-Butyrate</td>
<td>Acceptor</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>C5H9O4N</td>
<td>n-Valerate</td>
<td>Acceptor</td>
</tr>
<tr>
<td>Arginine</td>
<td>C6H13O2N</td>
<td>iso-Valerate</td>
<td>Acceptor</td>
</tr>
<tr>
<td>Leucine</td>
<td>C6H13O2N</td>
<td>iso-Valerate</td>
<td>Donor</td>
</tr>
<tr>
<td>iso-Leucine</td>
<td>C6H13O2N</td>
<td>neo-Valerate</td>
<td>Donor</td>
</tr>
<tr>
<td>Proline</td>
<td>C5H9O2N</td>
<td>n-Valerate</td>
<td>Acceptor</td>
</tr>
</tbody>
</table>
accumulated intermediate metabolic substrates were rapidly degraded by the TCA cycle (Fig. 4). The TCA cycle produced a large amount of NADH, so that more oxygen was consumed to meet the requirement for NAD\(^+\). As a result, the digestion system still showed low ORP at this time (Fig. 3C). After 360 h, the ORP value remained above 0 mV, in line with a previous investigation (Cheng et al., 2009) which found that the ORP in a continuously aerated ATAD system can exceed 0 mV. For later digestion times, VFA presented little accumulation, and SCOD showed a moderate decline, implying that the aeration had met the demand for oxygen and that the sludge began to achieve stabilization.

3.3. Nitrogen transformation in digestion process

The changes of TN and NH\(_4\)-N in the supernatant are shown in Fig. 5A. TN and NH\(_4\)-N varied in similar manner. In the first 168 h, the concentration of TN and NH\(_4\)-N rose continuously, reaching 1630 and 1010 mg L\(^{-1}\), respectively. Next TN and NH\(_4\)-N decreased rapidly from 168 to 312 h and then fluctuated mildly after 360 h. The ratio of NH\(_4\)-N/TN decreased from 72.6% at the outset to 62.0% at 216 h, then fluctuated from 57.4% to 48.4% between 264 and 552 h.

During the thermophilic digestion process, abundant nitrogen was released to the supernatant due to the degradation of protein in the extracellular polymeric substance and the decay of less temperature-tolerant cells (Li et al., 2004; Li et al., 2009), resulting in a rapid increase of TN in the initial 168 h. In this simulated ATAD digester, the concentration of NO\(_3\)-N and NO\(_2\)-N (Fig. 5B) was always less than 3.0 and 0.8 mg L\(^{-1}\), respectively, indicating that nitrification and denitrification were inhibited. Therefore ammonia was released to the supernatant due to deamination of the peptide and amino acid products following protein hydrolysis. The released ammonia could solubilise in the bulk sludge water of the digester and achieve dynamic equilibrium due to the reaction: NH\(_3\)+H\(_2\)O→NH\(_4\)+OH\(^-\). As a result, the rising concentration of ammonia in supernatant was accompanied by an increase in the pH of the digestion system, as indicated in Fig. 5C where pH increased from 6.9 at 0 h to 7.7 at 48 h. However pH maintained low from 48 to 168 h, mainly related to the rapid accumulation of VFA during this period (Fig. 3B). This indicates that the pH not only depends on the release of ammonia, but also on the production of VFA.

In the ATAD system, ammonia stripping represents the only way for TN to decrease because ammonia can be stripped from the digestion system due to continuous aeration (Liu et al., 2010). After 168 h, the concentration of VFA began to decrease, and the pH tended to be alkaliescent. As a result, both TN and NH\(_4\)-N declined sharply due to continuous ammonia stripping. As digestion continued, VS removal increased only moderately, so that TN and NH\(_4\)-N did not change significantly after 360 h due to the approximate equilibrium between release of nitrogen and stripping of ammonia. This result is also supported by previous investigations (Cheng, 2006; Liu et al., 2010) showing that a batch-operation ATAD system maintained steady TN and NH\(_4\)-N during the later digestion period.

3.4. Variation of orthophosphate and sulfate in the supernatant

Fig. 6A shows the variation of ortho-P with the digestion time. The digested sludges (except for digestion time of 0 h) had less ortho-P than the raw sludge. As the sludge was digested for 120 h, it showed relatively high ortho-P, up to 79 mg L\(^{-1}\), in the supernatant. However this value was still less than 104 mg L\(^{-1}\) at 0 h. After 216 h, ortho-P in the digestion system began to fluctuate from 33 to 41 mg L\(^{-1}\). As noted above, the ATAD process resulted in rapid cell lysis of less temperature-tolerant microorganisms, causing some phosphorus to be released, enhancing the concentration of ortho-P. However ortho-P in this study did not increase, but showed small decline compared with the raw sludge. As mentioned above, the ATAD system exhibited oxygen-deficiency condition when abundant organic matter was released to the supernatant during the initial digestion time (Fig. 3A), resulting in the electron transport chain being inhibited to some degree. Therefore the digestion system shifted from the TCA cycle to other pathways to maintain the redox balance. As seen in Fig. 4, the production of acetic, propionic, and butyric acid not only reoxidized NADH to NAD\(^+\) to maintain the redox balance, but also maximized ATP production by substrate level redox reactions. Accompanying with this metabolic pathway, some ortho-P was consumed to meet the requirement for ATP formation. As a result, the concentration of ortho-P in the supernatant remained lower, even though the ORP remained low during the first 168 h. As digestion continued, the ATAD system reached a higher ORP than during the first
digestion period. For example, the ORP value exceeded $-4$ mV after 312 h (Fig. 3C). At this time, the TCA cycle was the main metabolic pathway as the electron transport chain became smoother. The NADH produced during oxidation of substrates can be reoxidized by oxygen, and ATP is generated by oxidative phosphorylation of respiratory chain (Fig. 4). As a result, ortho-P maintained a low concentration at later digestion times. As noted above, the aeration made the ortho-P of the digested sludge less than that of the raw sludge. Therefore the total phosphorus in the digested sludge could increase substantively due to lack of gaseous phosphorous release and the reduction of sludge.

The concentration of sulfate in this study clearly increased after a digestion time of 552 h (Fig. 6B). Sulfate showed little increase within the first 24 h, then rapidly increased from 3.8 mg L$^{-1}$ at 24 h to 1260 mg L$^{-1}$ at 168 h. It fluctuated moderately between 168 and 264 h, and then increased slowly from 264 h to the end of digestion time. At a digestion time of 24 h, the temperature in the digester was 35 °C, and SCOD increased to 2180 mg L$^{-1}$ (Fig. 3A); however VFA (Fig. 3B) and NH$_4^-$-N (Fig. 5A) only increased moderately, indicating that most of the released organic matter consisted of macromolecular compounds and that hydrolysis of organic matter (including protein) to soluble substances remained the rate-limiting step. As a result, few sulfur-containing proteins (the existing form of organic sulfur) degraded, and sulfate showed no distinct increase. As digestion time shifted from 24 to 120 h, the digestion temperature increased sharply from 35 to 55 °C, where thermophilic digestion caused the rapid degradation of organic matter. The degradation of sulfur-containing amino acids resulted in the production of hydrogen sulfide, which can be oxidized to sulfate. Though oxygen-limiting conditions led to VFA production from 24 to 168 h, sulfate still increased rapidly (Fig. 6B), indicating that the microaerobic condition in an ATAD system had less inhibition on the formation of sulfate. Sulfate can combine with alkali metals to produce precipitates, due to their low solubility, which resulted in sulfate not showing a distinct increase between 168 and 264 h. After 264 h, the ORP increased from $-85$ to $+68$ mV, and the aeration began to meet the oxygen requirement of the ATAD system. Thus, sulfur-containing compounds could be completely converted to sulfate, contributing to the slow increase of sulfate at later digestion times. As the sludge was digested for 552 h, the concentration of sulfate increased by a wide margin, allowing a considerable fraction of the alkali metals to be precipitated into the digested sludge. This conclusion is well supported by the ICP results (Table 2) which show that the concentrations of inorganic elements in the digested sludge were higher than in the raw sludge.

4. Conclusion

VS removal in the simulated one-stage ATAD digester reached 38.4% at 408 h and 45.0% at 552 h. Both VS reduction and pathogen inactivation could meet with the requirements of Class A sludge. Based on the variation of VFA and the fundamental theories of aerobic and anaerobic digestions, a biochemical model was proposed. The digestion system could regulate its metabolic pathways to produce VFA (such as propionic, butyric acid) or completely degrade the substrate according to the changed digestion process. The pH depends on the relative equilibrium between ammonia and VFA, and ORP is closely related to both VFA and sulfate.

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