Combination treatment of ultrasound and ozone for improving solubilization and anaerobic biodegradability of waste activated sludge

Guihua Xu, Shaohua Chen*, Jianwen Shi, Shumei Wang, Gefu Zhu

Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

ABSTRACT

The hydrolysis is known to be the rate-limiting step of biological sludge anaerobic degradation. The disruptions of sludge flocs and microbial cell walls by ultrasound combined with ozone treatment (US/O_3) were investigated in laboratory-scale experiments. The results showed that temperature, O_3 dose, US energy density and pH had a positive effect on the disintegration of sludge. The organic substrates were released into the liquor, which induced the increases of soluble chemical oxygen demand (COD_S) and turbidity in the aqueous phase. Accordingly, the biodegradability of sludge was improved. The COD_S increased from 1821 to 2513 mg/l after reaction for 30 min when $NaHCO_3$ was added, which indicated that the ozone molecule played a major role in the disintegration of waste activated sludge. The COD_S was 2483 mg/l after 60 min O_3 treatment followed by 60 min US treatment, and it changed into 3040 mg/l after 60 min US/O_3 treatment, which proved that US/O_3 induced a synergetic effect. The pH-drop of sludge from 6.8 to 5.21 might be attributed to the increase of volatile fatty acid from 61.35 to 111.96 mg/l during the US/O_3 treatment process.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Anaerobic digestion is well known as the green technique to treat the biological sludge. However, anaerobic digestion is a very slow process with a long retention time of 20–30 days [1], since the hydrolysis is the rate-limiting step [2]. In order to improve hydrolysis and anaerobic digestion performance, using cell lyse pretreatments is one possible and effective route. Therefore, several methods to solubilize or hydrolyze sludge cells prior to anaerobic digestion have been developed, which include mechanical [3], chemical [4–7] and thermal treatments [8,9].

For all methods mentioned above, ultrasonic technology, Fenton process and ozone oxidizing method are promising technologies for the disruption of sludge and the improvement of anaerobic digestion performance. The ultrasonic application on sludge before anaerobic digestion process has been extensively investigated in the recent 20 years [10–13]. Ultrasound (US) is well known to disrupt the sludge flocs and microbial cell walls, so US treatment can induce the release of soluble substances into aqueous phase. This produces more biogas and reduces the anaerobic digestion time. The COD_S, floc size, biodegradability, kinetic model and mechanism of US treatment have been studied extensively [14–18]. The effect of ultrasound treatment is mainly induced by acoustic cav-

itation, which is a combination of different phenomena, including chemical reactions using radicals, pyrolysis, combustion and shearing [18]. High frequency promotes oxidation by radicals, whereas low frequency improves mechanical. Furthermore, hydromechanical shear force produced by ultrasonic cavitations is predominantly responsible for sludge disintegration [14]. Fenton technology is one of the commonly used advanced oxidation processes (AOPs). Ferrous iron is used to initiate and catalyse the decomposition of H_2O_2 and produce hydroxyl radical ($\bullet OH$) in Fenton system [19]. Fenton's reagent has been mainly used to improve the dewatering property and reduce sludge production [20–22]. In the recent 2 years, Fenton process starts to be used for improving sludge anaerobic biodegradability [23,24]. In AOPs, the $\bullet OH$ reactions are responsible for the disruption of sludge [25]. The $\bullet OH$ with powerful oxidation abilities reacts with the whole sludge without any selective, leading to the mineralization of sludge solids. In addition, the H_2O_2 may increase the volume of sludge, and the ferrous iron may bring adverse effects on the next treatment process and sludge agricultural application. These reasons limit the application of Fenton regent. Ozone oxidation to disintegrate sludge cells also has been widely studied [4,5,26–28]. Due to the strong oxidative property of ozone, it can be used to disrupt the sludge flocs and lyse cells. The ozone oxidation reaction does not possess selective, so ozone reacts with the whole matter: soluble and particulate fractions, organic or mineral fractions [26]. Ozonation effectiveness is based on the multiple effects produced by the oxidative activity of ozone and ozone-derived oxidation species, such as hydroxyl radical. The optimal consumed

* Corresponding author. Tel.: +86 592 6190995; fax: +86 592 6190977.
E-mail address: shchen@iue.ac.cn (S. Chen).

dose of ozone ranges from 0.05 to 0.5 g O_3/g total solid (TS) [27]. A mineralization phenomenon will occur when ozone dose exceeds 0.18 g O_3/g TS [28]. Moreover, ozonation can modify viscosity, settlement and particle size of sludge [27,29].

Ozonation is scarcely applied on sludge because of the high energy consumption in O_3 production, and this problem also exists in the sludge disintegration by ultrasound. The majority of waste activated sludge (WAS) is water, which absorbs the ultrasonic energy. Therefore, the sound energy used for the WAS degradation is very little. Ozonation combined with sonolysis is an advanced oxidation process, which has been used for water and wastewater treatment, especially used for treating hard-degradation organics [30,31]. US/O_3 induces a synergetic effect, so US/O_3 is more effective than ozonation or sonolysis treatment alone. In the US/O_3 reaction process, ultrasonic radiation has been demonstrated to increase the mass transfer of ozone to solution via increasing volumetric mass transfer coefficient. Moreover, O_3 is decomposed to generate very reactive free radicals, and the decomposition of O_3 can be enhanced by ultrasound to generate more •OH [32].

US/O_3 has played obvious effects on water and wastewater treatment, and it is more effective compared with ozonation or sonolysis treatment alone. In most reports, US treatment and O_3 treatment were studied separately as the pretreatment methods of anaerobic digestion. Furthermore, few works has been devoted to the US/O_3 treatment on WAS. This study is aimed at investigating the modification of WAS characteristics by US/O_3 treatment and its effects on the anaerobic biodegradability. After the determination of optimal operating conditions, mechanism of US/O_3 treatment was also investigated.

2. Experimental

2.1. Waste activated sludge

The WAS in our experiments was collected from a local full-scale wastewater treatment plant (WWTP, Xiamen, China) that used the anaerobic-aerobic process, and was stored at 4 °C for use. The characteristics of the sludge were as follows: water content was 98.28%, pH was 6.8, COD_S was 82.77 mg/l, total COD (TCOD) was 17460 mg/l, suspended solids (SS) was 18218 mg/l and volatile solids (VS) concentration was 10065 mg/l. The low COD_S/TCOD ratio (0.05) implied that most COD existed in the solid phase.

2.2. Apparatus

2.2.1. US/O_3 apparatus setup

Fig. 1 shows the scheme of ultrasound combined with ozone treatment on WAS. The ultrasonic apparatus was an ultrasonic homogenizer Autotune 950 W (SCIENTZ-IID, Xinzhi Inc., China), worked with a probe with diameter of 8 mm and operating frequency of 21 kHz. The ultrasonic probe was dipped 10 mm into the sludge. The ultrasonic energy output was adjusted between 40 and 600 W under various test conditions; ozone was generated from pure oxygen using an ozone generator (NPA20, Nippon Inc., China), and ozone was released to sludge by a microporous diffuser. The concentration and flow rate of O_3 in gas phase, before and after reaction with sludge, were measured. Gas flow rate was adjusted from 1 to 4 l/min under various experimental conditions. For each batch experiment, 400 ml sludge was filled in a 7 cm × 25 cm (diameter × height) bottle. According to various experimental conditions, the pH and temperature of sludge were adjusted by 1 mol/l NaOH and a water bath, respectively.

2.2.2. Anaerobic biodegradability apparatus setup

Anaerobic digestion tests were carried out to compare methane production for different substrates with the same inoculum under
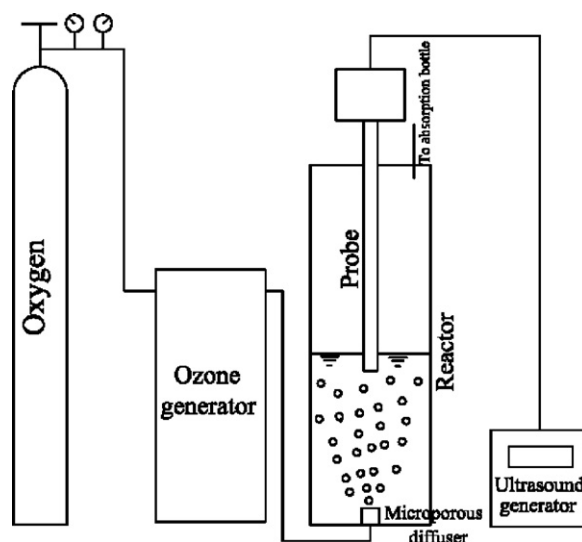

Fig. 1. Scheme of ultrasound combined with ozone treatment on waste activated sludge.

mesophilic (35 °C) conditions. The inoculum used was collected from the anaerobic digestion reactor in the same WWTP. The inoculum was diluted to 4 g/l of volatile suspended solids (VSS). By adding 1 mol/l HCl or 1 mol/l NaOH before feeding, the pH of sample was adjusted to 7.0. Treated or untreated sludge sample was added to 400 ml of inoculum, and 0.5 g COD/g VSS in the inoculum was introduced in every bottle. Glass bottles were agitated (200 rpm) in order to homogenize samples, and several control samples were realized: a blank (deionized water), a sodium acetate sample (completely biodegradable compound) and an untreated sample (raw sludge added).

2.3. Analytical methods

The TS, SS, VS, COD, temperature and water content of sludge samples were measured according to the standard methods [33]. For COD_S measurement, the samples were centrifuged (centrifugal force 10,000 × g) for 30 min, and the supernatant was removed for analysis by using the normalized method [33]. The COD solubilization (S_{COD}) represented the transfer of COD from the particulate fraction of the sludge to the soluble fraction. S_{COD} was calculated by using the difference between COD_S and the initial COD_S (COD_{S0}), comparing with the initial particulate COD (COD_{P0}).

$$S_{COD} = \frac{COD_S - COD_{S0}}{COD_{P0}} \times 100\% \tag{1}$$

The TS solubilization (S_{TS}) and VS solubilization (S_{VS}) represented the transfer of TS and VS from the particulate fraction of the sludge to the soluble fraction. The samples were centrifuged and removed the supernatant, and the left solids were used for measuring the TS and VS. For this paper, the TS and VS in the left solids were called TS_p and VS_p, respectively. Solids concentrations of the supernatant were deduced, and then matter solubilization (S_{TS} and S_{VS}) was calculated.

$$S_{TS} = \frac{TS_{p0} - TS_p}{TS_{p0}} \times 100\% \tag{2}$$

$$S_{VS} = \frac{VS_{p0} - VS_p}{VS_{p0}} \times 100\% \tag{3}$$

The pH value was measured with a PHS-3C instrument (Shanghai Precision &Scientific Inc., China). The turbidity was measured by a portable turbiscan apparatus (AQ4500, Orion). Particle size

was measured on a laser particle size analyzer (Mastersizer 2000, Malvern firm). The produced biogas was collected in a 100 ml calibrated glass cylinder [14], and the produced methane volumes were measured by movement of liquid (water, pH 14). The O_3 concentration was determined by using iodimetric method [34].

The volatile fatty acid (VFA) was detected by gas chromatography (GC) (7890A, Agilent) equipped with a flame ionization detector. A capillary HP-FFAP column (30 m × 0.32 mm i.d. × 0.25 μm film thickness) was used with nitrogen as the carrier gas at a constant flow rate of 2 ml/min. Splitless injection of 1 μl of the sample was automaticity conducted. The GC oven temperature was programmed from 60 °C (1 min) to 110 °C (0 min) at 5 °C/min, then to 200 °C at 30 °C/min and held for 1 min. The injector temperature was 200 °C and the detector temperature was 250 °C.

3. Results and discussion

3.1. Comparison of three processes (US, O_3 and US/O_3) for the disintegration of WAS

Comparison of US, O_3 and US/O_3 for the disintegration of WAS was presented in Fig. 2. At the end-point of the reaction (60 min), the COD_S was 797, 2347 and 3341 mg/l for US, O_3 and US/O_3 treatment, respectively. US/O_3 treatment made more COD release from the particulate fraction to the soluble fraction than US and O_3 treatment alone.

The combination of ultrasound with ozone resulted in a synergetic, which led to the increase in the overall rate of disintegration. In ozonation alone, O_3 transferred from the gas phase into the liquid phase and then either reacted directly with the substrate or indirectly with radicals generated by O_3 autodecomposition. As for sonolysis alone, reactions included shearing, pyrolysis and chemical reactions with radicals generated from the pyrolysis of H_2O in a cavitation bubble [18,35]. However, in the US/O_3 system, the above reaction pathways might be affected each other. For example, US could enhance the mass transfer of ozone to solution by
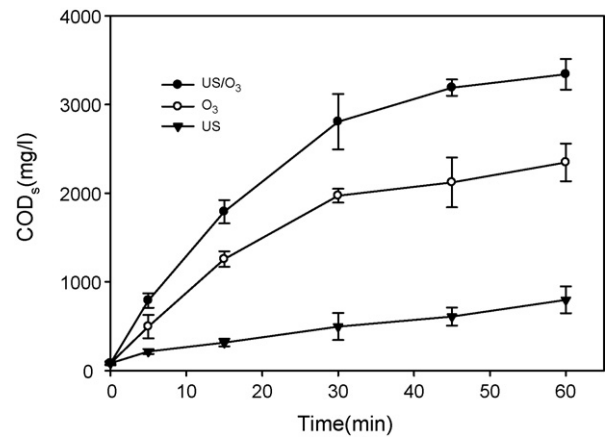

Fig. 2. Comparison of US, O_3 and US/O_3 for the disintegration of WAS: TS 10 g/l; pH 6.8; O_3 dose 1.0 g/h; US energy density 0.26 W/ml; temperature 27 °C.

means of increasing volumetric mass transfer coefficient, which might result in more O_3 being transferred to the solution. Furthermore, US could enhance the decomposition of O_3 to generate more •OH to react with the substrate [32,36]. On the other hand, the microbubbles of O_3 might act as cavitation nucleuses of sonolysis to produce more acoustic cavitations, which increased the efficiency of US treatment.

3.2. Effects of the US/O_3 operating conditions

3.2.1. Effect of pH

Fig. 3a shows the effect of initial pH on the disintegration of sludge as the pH changed from 6.8 to 12.4. At the 30 min reaction time-point, the S_{COD} was 11.99%, 21.34%, 27.58%, 28.54%, and 30.01% at pH 6.8, 8.1, 10.0, 11.1 and 12.4. At the end-point of the reaction (60 min), the S_{COD} was 17.02%, 25.99%, 32.35%, 34.25%, and 36.59%, respectively.
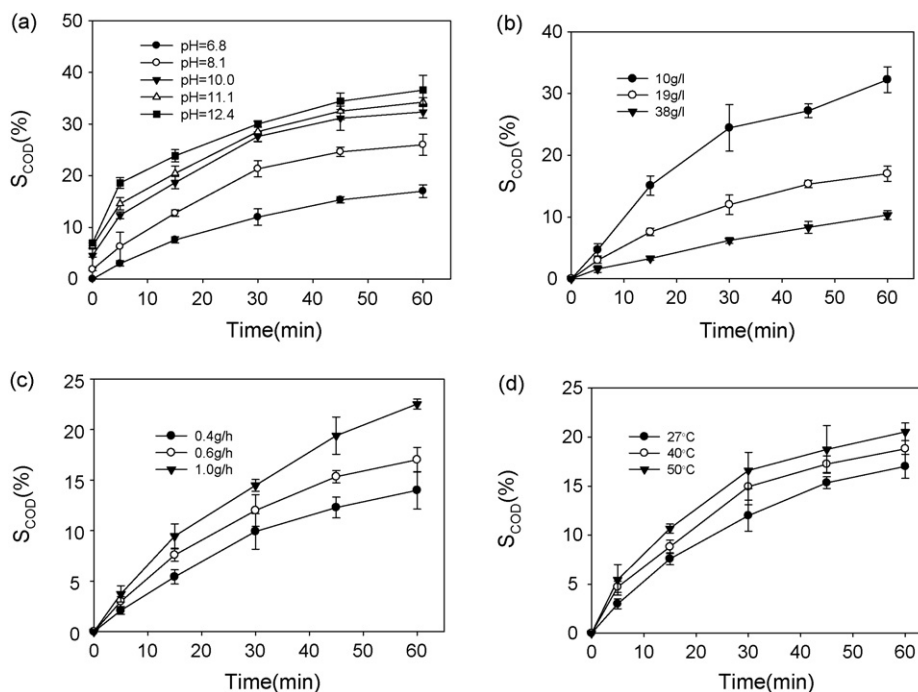

Fig. 3. Effect of process variables on the disintegration of WAS. (a) Effect of initial pH: TS 19 g/l; O_3 dose 0.6 g/h; US energy density 0.26 W/ml; temperature 27 °C. (b) Effect of initial TS concentration of WAS: pH 6.8; O_3 dose 0.6 g/h; US energy density 0.26 W/ml; temperature 27 °C. (c) Effect of O_3 dose: TS 19 g/l; pH 6.8;US energy density 0.26 W/ml; temperature 27 °C. (d) Effect of temperature: TS 19 g/l; pH 6.8; O_3 dose 0.6 g/h; US energy density 0.26 W/ml.

The S_{COD} increased with the increase of pH, which was not consistent with the previous reports that the degradation rate decreased at high pH values [30,31]. The reason was that the sludge became basic with the increase of pH, and the alkaline destroyed floc structures and cell walls by hydroxy anions. Moreover, the combination of alkaline and ultrasonic treatment enhanced the efficiency each other [6]. More O_3 decomposed to secondary oxidants when pH increased, such as the generation of more $^{\bullet}OH$ [37]. However, the added basic matters to adjust pH might produce new pollutions and increase treatment costs. In addition, high pH brought adverse effects on the next anaerobic digestion. So the optimal pH value should be set in light of the practice conditions.

3.2.2. Effect of initial TS concentration of WAS

The effect of the initial TS concentration of WAS on disintegration was examined and the results were shown in Fig. 3b. As it could be seen from Fig. 3b, the S_{COD} decreased with the increase of initial sludge concentration. At the 30 min reaction time-point, the S_{COD} was 24.44%, 11.99% and 6.2% at TS 10, 19 and 38 g/l. At the end-point of the reaction (60 min), the S_{COD} was 32.26%, 17.02% and 10.32%, respectively.

The overall disintegration rate of sludge depended on the concentration of O_3 molecule in aqueous, the power and frequency of ultrasound and the number of $^{\bullet}OH$ in aqueous phase. Our experiments were conducted under the same conditions, which indicated that the concentration of O_3 and the rate of production of $^{\bullet}OH$ in aqueous were almost constant. In addition, the power and frequency of ultrasound kept constant. So the amount of the disrupted sludge kept almost constant, and the COD_S increased a little with the increase of initial sludge concentration. These factors led to a decrease rate of disintegration with the increase of initial sludge concentration.

3.2.3. Effect of O_3 dose

In order to examine the effect of O_3 dose on the disintegration of WAS by US/O_3. The O_3 dose ranged from 0.4 to 1.0 g/h was investigated and the results were shown in Fig. 3c. It could be seen that the S_{COD} increased from 9.92% to 14.48% and from 13.99% to 22.53% with the O_3 dose ranged from 0.4 to 1.0 g/h for 30 and 60 min, respectively. The results showed that O_3 dose had a positive effect on the disintegration efficiency of US/O_3.

The increase in O_3 dose could improve the mass transfer of O_3 and increase the area of the gas–liquid interface, which resulted in an increase of ozone concentration and the formation of the free radicals in the solution [32]. However, when the O_3 dose was higher than the appropriate value, which would induce a mineralization phenomenon [28]. Therefore, the O_3 dose/TS ratio for sludge disintegration should be determined by further experiments for individual treatment systems.

3.2.4. Effects of temperature

The effects of temperature on disintegration of WAS by US/O_3 were studied in the range 27–50 °C as shown in Fig. 3d. The S_{COD} increased from 17.02% to 20.53% with temperatures ranged from 27 to 50 °C at 60 min. The results showed that the S_{COD} increased slowly with the increase of temperature. The effects of temperature were complex, which had positive and negative effects on US/O_3 treatment. The concentration of O_3 in aqueous solution decreased with the increase of temperature, and the increase of temperature reduced the intensity of bubbles collapse [38]. These factors hindered sludge disintegration. On the other hand, the increase of the temperature enhanced the rate of mass transfer during ozone dissolution [39]. These were the positive effects on the sludge disintegration. As a result from the obtained data, the improvement of mass transfer was superior to the unfavorable effects caused by
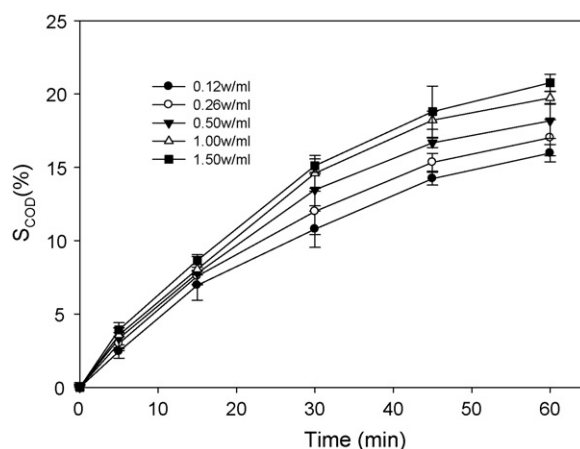

Fig. 4. Effect of US energy density: TS 19 g/l; pH 6.8; O_3 dose 0.6 g/h; temperature 27 °C.

the increase temperature, so the S_{COD} increased with the increase of temperature.

3.2.5. Effect of US energy density

The effect of US energy density on the disintegration of WAS by US/O_3 was presented in Fig. 4. As the US energy density increased from 0.12 to 1.5 W/ml, the S_{COD} varied from 10.78% to 15.11% at 30 min and from 15.96% to 20.76% at 60 min, respectively. The results indicated that the increase of US energy density had a little positive effect on the efficiency of disintegration. With the US energy density increasing, the cavitation bubble volume became very large, resulting in the insufficient collapse of bubbles. Therefore, more US energy was dissipated. In addition, the degassing rate of O_3 increased with the higher US energy density, which had an adverse effect on the concentrations of O_3 and radicals. On the other hand, the higher US energy density causing cavitation bubbles at a higher temperature were compensated for the increments of dissipated energy and the degassing rate of O_3 [31]. So the increment of the disintegration rate was slow with the increase of US energy density.

According to the above results, the operating conditions of the following experiments were set as follows: TS 19 g/l; pH 6.8; O_3 dose 0.6 g/h; US energy density 0.26 W/ml; temperature 27 °C.

3.3. The solubilization and anaerobic biodegradability of WAS treated by US/O_3

3.3.1. Particle size distribution and turbidity

The particle size distribution was examined during US/O_3 treatment process. It could be observed from Fig. 5a, for untreated samples, the particle size distribution ranged from 0.5 to 1261 μm. Volume distribution was centred in the 12–90 μm size intervals, with a mean diameter of 53.944 μm. For the treated sludge, the volume occupied by small particles was increased with the increase of treatment time. The 90% of the volume was occupied by particle with diameter size below or equal to 80 μm. Hence, the average particle size decreased to 18.12–38.99 μm. That was, US/O_3 treatments led the WAS to release matter into the aqueous medium. Moreover, the distributions of particle size at 30, 45 and 60 min were similar. It could be attributed to that most of WAS was disrupted after the first 30 min.

Fig. 5b shows the effect of treatment time on the turbidity of the aqueous phase. In the plot, since more particulate organic matter in solid media was released to the aqueous phase, the increasing of the supernatant turbidity with treatment time was obviously observed. The turbidity of supernatant also increased slowly after the first
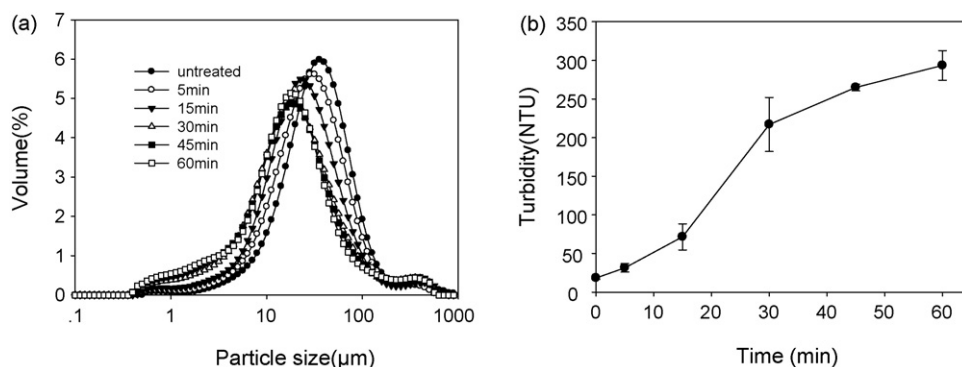
Fig. 5. US/O$_3$ effect on particulate matter. (a) Particle size distribution with treatment time. (b) Effect of treatment time on aqueous phase turbidity.

30 min treatment, which was consistent with the distribution of particle size and the change of COD$_S$.

3.3.2. Matter solubilization (S$_{TS}$ and S$_{VS}$)

US/O$_3$ treatment led to a transfer from particles to supernatant, and reduced the sludge volume. Fig. 6 presented results obtained in terms of TS and VS solubilization. The S$_{TS}$ and S$_{VS}$ increased with the treatment time: varied from 0% to 28% and 34%, respectively. US/O$_3$ treatment made particulate matter in WAS become small (Fig. 5a) and solubilize in the aqueous phase. Accordingly, SS and VS in the aqueous phase increased, and the WAS volume was reduced, which was consistent with the change of particle size.

During treatments, total COD, VS and TS concentrations remained almost constant (results were not shown), which showed that US/O$_3$ treatment did not lead to a mineralization phenomenon. At the beginning of treatments (5 min), the S$_{VS}$ was lower than the S$_{TS}$ about 1.6%. However, at 60 min, the S$_{VS}$ was more than the S$_{TS}$ about 6%. The above results showed that more particulate organic matter was released to aqueous phase than particulate mineral matter with the increase of treatment time. This phenomenon might be explained by the following reasons: US/O$_3$ treatment first disrupted the sludge flocs, and then disrupted microbial cell walls. Moreover, sludge flocs might have more mineral matter than organic matter, and most of the intracellular substances were organic matter. In conclusion, US/O$_3$ treatment was efficient in terms of matter solubilization and sludge reduction.

3.3.3. Effect of US/O$_3$ treatment time on batch anaerobic digestion

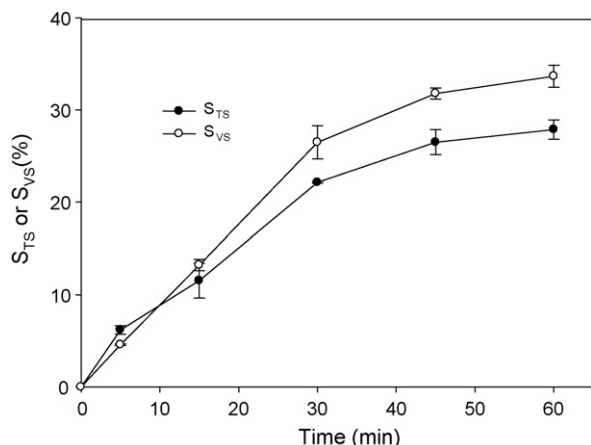The impact of US/O$_3$ treatment time on anaerobic digestion efficiency was evaluated by the accumulated amount of methane in anaerobic digestion tests. As shown in Fig. 7, the methane biogas productions of all treatments sludge were higher than that of untreated sludge, but were lower than acetic acid (totally biodegradable substrate). These results showed that the US/O$_3$ treatment obviously improved the sludge anaerobic digestibility. The methane biogas content of the sludge pretreated by US/O$_3$ at 120 min was lower than that at 30 and 45 min. It might be the reason that the overdose of ozone caused the formation of refractory compounds and decreased the biodegradability of sludge [27]. The optimal treatment time for improving anaerobic digestibility in this experiment was 30 min.

3.4. The possible mechanism of US/O$_3$ treatment

3.4.1. Effects of NaHCO$_3$

Fig. 8 shows the results of US/O$_3$ treatment with adding NaHCO$_3$ as a hydroxyl radical scavenger. After 10 and 100 mmol/l of NaHCO$_3$ were added, the COD$_S$ increased from 1821 to 2302 and 2513 mg/l, respectively. Compared to the sample without the addition of NaHCO$_3$, the COD$_S$ increased a little. The reason was that the added NaHCO$_3$ caused the sludge presented basic. Thus, it could be deduced from the results that the ozone molecules, not the radicals, played a major role in the disintegration of WAS, which was not consistent with some scholar's results [30,31]. In their results, the •OH played a major role in the oxidation of p-nitrotoluene and p-aminophenol [30,31]. The reason might be that the characteristics of treatment objects were different.

3.4.2. The reason of pH-drop

The changes of pH and VFA were investigated during US/O$_3$ treatment process. It could be observed from Fig. 9 that the pH val-
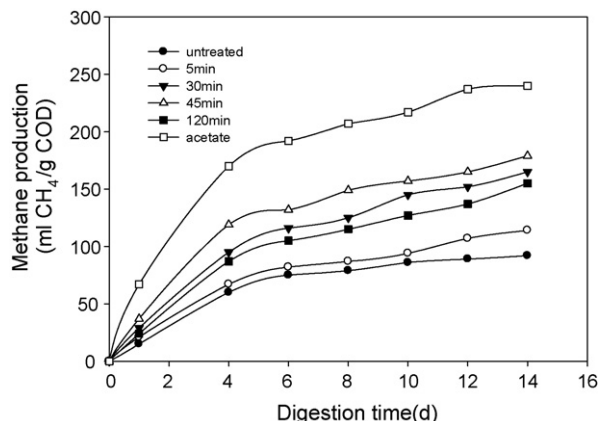

Fig. 6. US/O$_3$ effect on matter solubilization (S$_{TS}$ and S$_{VS}$).

Fig. 7. Batch anaerobic digestion tests at different US/O$_3$ treatment time.
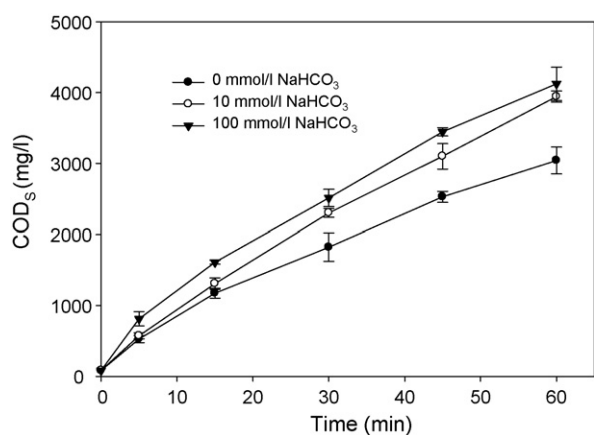
Fig. 8. Comparison of COD_S between $NaHCO_3$ adding and no $NaHCO_3$ addition.
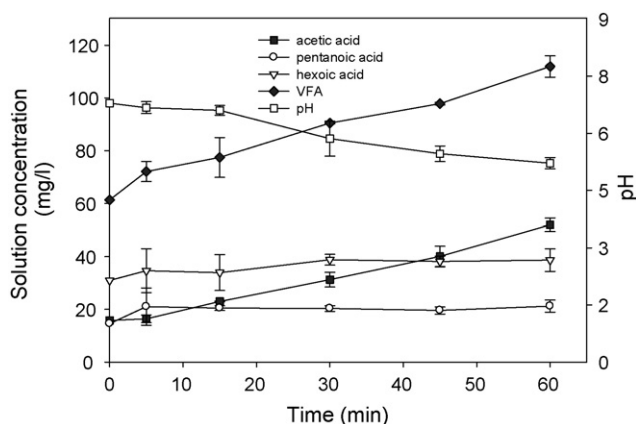

Fig. 9. The changes of pH and VFA before and after US/O_3 treatment.

ues decreased from 6.8 to 5.21 with the increase of VFA from 61.35 to 111.96 mg/l. The concentrations of acetic acid, pentanoic acid and hexoic acid increased from 15.8, 14.59 and 30.97 to 52.02, 21.24 and 38.7 mg/l at 60 min, respectively. Moreover, the propionic acid, butyric acid, isobutyric acid and isovaleric acid were undetected after the 60 min treatment by US/O_3. The pH-drop of sludge during the US/O_3 treatment process might be caused by the increases of VFA. Our results were consistent with the report that chemical
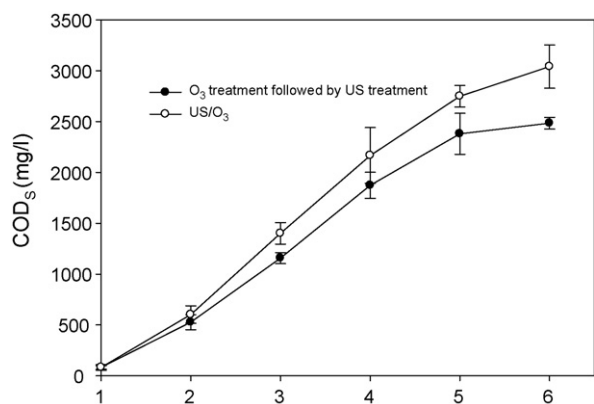

Fig. 10. Comparison of COD_S between US/O_3 treatment and O_3 treatment followed by US treatment in the same operating conditions. For US/O_3, 1, 2, 3, 4, 5 and 6 represented that WAS treated by US/O_3 for 0, 5, 15, 30, 45 and 60 min, respectively. For O_3 treatment followed by US treatment, 1, 2, 3, 4, 5 and 6 represented that WAS treated by O_3 firstly for 0, 5, 15, 30, 45 and 60 min, followed by US treatment for 0, 5, 15, 30, 45 and 60 min, respectively.
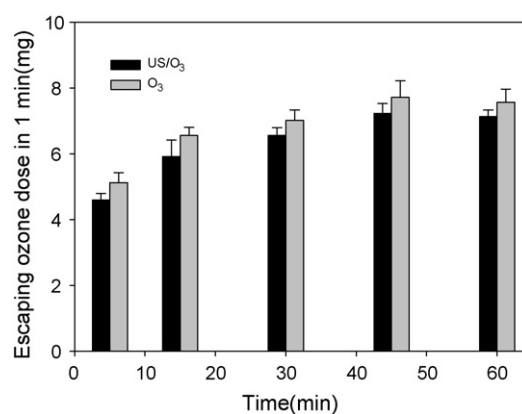

Fig. 11. Ozone escaping dose in 1 min for O_3 treatment alone and US/O_3 treatment at different treatment time.

or biological sludge solubilization produced a hydrolysate that was mainly constituted of VFA [40].

3.4.3. Comparison of COD_S and O_3 escaping dose

In order to testify the synergistic effect between ozonation and sonolysis, the comparison of COD_S between US/O_3 treatment and O_3 treatment followed by ultrasound treatment in the same operating conditions was conducted. It could be seen for Fig. 10 that the COD_S of sludge treated by US/O_3 was more than the COD_S of sludge treated by O_3 treatment and followed by US treatment (3040 and 2483 mg/l at 60 min, respectively), which obviously confirmed the enhancement between ozonation and sonolysis.

The escaping dose of O_3 treatment alone and US/O_3 treatment in 1 min at different treatment time was shown in Fig. 11. WAS treated by O_3 alone escaped more O_3 doses than that treated by US/O_3, so more O_3 reacted with sludge for US/O_3 treatment than the sludge treated by O_3 alone. It could be attributed to that ultrasonic radiation enhanced the mass transfer of ozone to the aqueous phase.

The results from Figs. 10 and 11 confirmed that ultrasound combined with ozone induced a synergetic effect, and US/O_3 was more effective than ozonation treatment or sonolysis treatment alone.

4. Conclusions

US/O_3 was an effective technology for improving the hydrolysis and anaerobic digestion performance, and was more effective than ozonation or sonolysis treatment alone. More works are needed to determine such as the toxicity, economical efficiency, kinetics models and reactor design. From the above experimental results and discussion, some interesting points could be concluded as follows.

The temperature, O_3 dose, US energy density and pH had a positive effect on the disintegration of sludge. However, the optimal operating conditions should be set in light of the individual treatment systems. US/O_3 technique led to solids solubilization, anaerobic biodegradability enhancement and sludge reduction. The COD_S and turbidity in the supernatant increased a lot. The reason was that the substances in the sludge flocs and cells were released into the aqueous phase. The methane biogas production of treated sludge was higher than that of untreated sludge, but the overdose of ozone caused the formation of refractory compounds and the decrease of biodegradability.

The ozone molecule direct reacted with WAS and the hydromechanical shear forces were responsible for sludge disintegration. US/O_3 induced a synergetic effect on the disintegration of WAS, and ultrasonic radiation enhanced the mass transfer of ozone to

solution. In addition, the probable reason of pH-drop was that the disrupted sludge produced VFA in the US/O_3 treatment process.

Acknowledgements

References

[1] S.G. Pavlostathis, J.M. Gossett, A kinetic-model for anaerobic-digestion of biological sludge, Biotechnol. Bioeng. 28 (1986) 1519–1530.

[2] T. Shimizu, K. Kudo, Y. Nasu, Anaerobic waste-activated sludge-digestion—a bioconversion mechanism and kinetic-model, Biotechnol. Bioeng. 41 (1993) 1082–1091.

[3] C. Schuster, Mechanical sewage sludge treatment, Chem. Ing. Tech. 79 (2007) 1871–1881.

[4] M. Weemaes, H. Grootaerd, F. Simoens, W. Verstraete, Anaerobic digestion of ozonized biosolids, Water Res. 34 (2000) 2330–2336.

[5] S. Deleris, E. Paul, J.M. Audic, M. Roustan, H. Debellefontaine, Effect of ozonation on activated sludge solubilization and mineralization, Ozone Sci. Eng. 22 (2000) 473–486.

[6] Y.Y. Jin, H. Li, R.B. Mahar, Z.Y. Wang, Y.F. Nie, Combined alkaline and ultrasonic pretreatment of sludge before aerobic digestion, J. Environ. Sci. 21 (2009) 279–284.

[7] I. Dogan, F.D. Sanin, Alkaline solubilization and microwave irradiation as a combined sludge disintegration and minimization method, Water Res. 43 (2009) 2139–2148.

[8] C. Eskicioglu, N. Terzian, K.J. Kennedy, R.L. Droste, M. Hamoda, Athermal microwave effects for enhancing digestibility of waste activated sludge, Water Res. 41 (2007) 2457–2466.

[9] D. Jolis, High-solids anaerobic digestion of municipal sludge pretreated by thermal hydrolysis, Water Environ. Res. 80 (2008) 654–662.

[10] K. Nickel, U. Neis, Ultrasonic disintegration of biosolids for improved biodegradation, Ultrason. Sonochem. 14 (2007) 450–455.

[11] G. Zhang, P. Zhang, J. Yang, Y. Chen, Ultrasonic reduction of excess sludge from the activated sludge system, J. Hazard. Mater. 145 (2007) 515–519.

[12] H. Li, Y.Y. Jin, R.B. Mahar, Z.Y. Wang, Y.F. Nie, Effects of ultrasonic disintegration on sludge microbial activity and dewaterability, J. Hazard. Mater. 161 (2009) 1421–1426.

[13] G.M. Zhang, J.G. He, P.Y. Zhang, J. Zhang, Ultrasonic reduction of excess sludge from activated sludge system II: urban sewage treatment, J. Hazard. Mater. 164 (2009) 1105–1109.

[14] A. Tiehm, K. Nickel, M. Zellhorn, U. Neis, Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization, Water Res. 35 (2001) 2003–2009.

[15] P.Y. Zhang, G.M. Zhang, W. Wang, Ultrasonic treatment of biological sludge: floc disintegration, cell lysis and inactivation, Bioresour. Technol. 98 (2007) 207–210.

[16] A. Gronroos, H. Kyllonen, K. Korpijarvi, P. Pirkonen, T. Paavola, J. Jokela, J. Rintala, Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion, Ultrason. Sonochem. 12 (2005) 115–120.

[17] F. Wang, Y. Wang, M. Ji, Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration, J. Hazard. Mater. 123 (2005) 145–150.

[18] C. Petrier, Y. Jiang, M.F. Lamy, Ultrasound and environment: sonochemical destruction of chloroaromatic derivatives, Environ. Sci. Technol. 32 (1998) 1316–1318.

[19] M. Kitis, C.D. Adams, G.T. Daigger, The effects of Fenton's reagent pretreatment on the biodegradability of nonionic surfactants, Water Res. 33 (1999) 2561–2568.

[20] M.-C. Lu, C.-J. Lin, C.-H. Liao, R.-Y. Huang, W.-P. Ting, Dewatering of activated sludge by Fenton's reagent, Adv. Environ. Res. 7 (2003) 667–670.

[21] N. Buyukkamaci, Biological sludge conditioning by Fenton's reagent, Process Biochem. 39 (2004) 1503–1506.

[22] R. Dewil, J. Baeyens, E. Neyens, Fenton peroxidation improves the drying performance of waste activated sludge, J. Hazard. Mater. 117 (2005) 161–170.

[23] H. Lee, M. Shoda, Stimulation of anaerobic digestion of thickened sewage sludge by iron-rich sludge produced by the Fenton method, J. Biosci. Bioeng. 106 (2008) 107–110.

[24] G. Erden, A. Filibeli, Improving anaerobic biodegradability of biological sludges by Fenton pre-treatment: effects on single stage and two-stage anaerobic digestion, Desalination 251 (2010) 58–63.

[25] M. Tokumura, M. Sekine, M. Yoshinari, H.T. Znad, Y. Kawase, Photo-Fenton process for excess sludge disintegration, Process Biochem. 42 (2007) 627–633.

[26] D. Cesbron, S. Deleris, H. Debellefontaine, M. Roustan, E. Paul, Study of competition for ozone between soluble and particulate matter during activated sludge ozonation, in: 9th French Chemical Engineering Congress, Saint Nazaire, France, 2003, pp. 1165–1170.

[27] C. Bougrier, C. Albasi, J.P. Delgenes, H. Carrere, Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability, Chem. Eng. Process. 45 (2006) 711–718.

[28] R. Goel, T. Tokutomi, H. Yasui, Anaerobic digestion of excess activated sludge with ozone pretreatment, Water Sci. Technol. 47 (2003) 207–214.

[29] A. Battimelli, C. Millet, J.P. Delgenes, R. Moletta, Anaerobic digestion of waste activated sludge combined with ozone post-treatment and recycling, in: 3rd IWA International Symoposium on Anaerobic Digestion of Solid Wastes, Garching, Germany, 2002, pp. 61–68.

[30] S. Song, M. Xia, Z. He, H. Ying, L. Bosheng, J. Chen, Degradation of p-nitrotoluene in aqueous solution by ozonation combined with sonolysis, J. Hazard. Mater. 144 (2007) 532–537.

[31] Z. He, S. Song, H. Ying, L. Xu, J. Chen, p-Aminophenol degradation by ozonation combined with sonolysis: operating conditions influence and mechanism, Ultrason. Sonochem. 14 (2007) 568–574.

[32] H. Destaillats, A.J. Colussi, J.M. Joseph, M.R. Hoffmann, Synergistic effects of sonolysis combined with ozonolysis for the oxidation of azobenzene and methyl orange, J. Phys. Chem. A 104 (2000) 8930–8935.

[33] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, 1995.

[34] IOA Standardisation Committee Europe, Iodometric method for the determination of ozone in a process gas, Brussels, 1987.

[35] L.K. Weavers, F.H. Ling, M.R. Hoffmann, Aromatic compound degradation in water using a combination of sonolysis and ozonolysis, Environ. Sci. Technol. 32 (1998) 2727–2733.

[36] V.O. Abramov, O.V. Abramov, A.E. Gekhman, V.M. Kuznetsov, G.J. Price, Ultrasonic intensification of ozone and electrochemical destruction of 1,3-dinitrobenzene and 2,4-dinitrotoluene, Ultrason. Sonochem. 13 (2006) 303–307.

[37] M. Muthukumar, D. Sargunamani, N. Selvakumar, Statistical analysis of the effect of aromatic, azo and sulphonic acid groups on decolouration of acid dye effluents using advanced oxidation processes, Dyes Pigments 65 (2005) 151–158.

[38] I.Z. Shirgaonkar, A.B. Pandit, Degradation of aqueous solution of potassium iodide and sodium cyanide in the presence of carbon tetrachloride, Ultrason. Sonochem. 4 (1997) 245–253.

[39] A. de, O. Martins, V.M. Canalli, C.M.N. Azevedo, M. Pires, Degradation of pararosaniline (C.I. Basic Red 9 monohydrochloride) dye by ozonation and sonolysis, Dyes Pigments 68 (2006) 227–234.

[40] J. Barlindhaug, H. Ødegaard, Thermal hydrolysis for the production of carbon source for denitrification, Water Sci. Technol. 34 (1996) 371–378.