

# Effectiveness of Waste Activated Sludge Solubilization Treated by Sonication, Thermal and Acid-Alkali Adjustment

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Solubilization performance using sonication, thermal and acid-alkali adjustment in batch treatment of waste activated sludge (WAS) samples were evaluated. By sonication, the organics (measured as COD) and nutrient releases from waste activated sludge increased with treatment time (up to 60 min) and intensity (0.167, 0.330 and 0.500 W/mL); while, by thermal treatment, the releases increased with treatment time (up to 3 h) and temperature (50, 70 and 90 °C). Organic-N of the supernatant accounted for most of the total nitrogen released from the waste activated sludge, followed by NH<sub>3</sub>-N and trace amounts of nitrate and nitrite; orthophosphorus. was the predominant form of the released total phosphorus. The molecular weight distribution of soluble organics, BOD<sub>5</sub>/COD and C/N data of the supernatant suggest that it can be returned to the biological aerobic unit for treatment without any negative effect. The sludge treatment by adjusting pH to 3-10 was unable to cause substantial release of organic and nutrient species; at a higher pH of 12 for 4 h, the releases were still too few to result in a significant reduction of the waste activated sludge volume. Among the three treatments, sonication shows an attractive process for waste activated sludge solubilization.

Keywords: Waste activated sludge (WAS); Sludge solubilization; Sonication; Thermal treatment; Acid-alkali adjustment.

# INTRODUCTION

Various forms of the aerobic activated sludge process are employed in more than 700 municipal wastewater treatment plants (WWTPs) in China with a combined treatment capacity of about 2534 ×  $10^4$  m<sup>3</sup>/day<sup>1</sup>. The large amount of waste activated sludge (WAS) generated from those WWTPs presents a significant environmental problem. To minimize the production of waste activated sludge, many new sludge reduction treatment processes have been proposed, including mechanical treatment<sup>2</sup>, ultrasonic treatment (sonication)<sup>3-6</sup>, ozonation<sup>7,8</sup> and chemical treatment<sup>9,10</sup>; among them, sonication and ozonation are attractive because they are environmentally benign and controllable.

Ultrasound is a pressure wave that propagates through a medium with a vast amount of energy dissipation generating numerous gas and vapor bubbles which may grow and then collapse violently at high speeds to cause acoustic cavitation. Cavitation occurs more readily at a frequency of 20-40 kHz<sup>11</sup>. High temperature and pressure developed inside the collapsing bubbles may produce many physico-chemical effects<sup>12</sup>. Under sonication, large and stable activated sludge flocs are disinte-

grated<sup>13</sup> and that a portion of the insoluble organic matter may be dissolved<sup>14</sup>. Sonication of waste activated sludge is capable of destroying the flocs holding extracellular polymeric substances (EPS) to result in much smaller flocs due to the hydro-mechanical shear force created in the reactor<sup>15</sup> and also producing highly oxidative ·OH in the amount that increases with treatment time and intensity<sup>16</sup>. Some literature reports have documented that sonication would cause different degrees of cell lysis and releases of organic and nutrient species when it is performed on waste activated sludge of different forms of activated sludge process<sup>17,18</sup>. During thermal treatment of excess sludge, organics, nutrients and some metal cations like Mg<sup>2+</sup> and K<sup>+</sup> could be released in abundance and in the temperature range of 40-70 °C, more total phosphorus (TP), total nitrogen (TN) and total organic carbon (TOC) would be released from sludge at higher temperature<sup>19</sup>. It has been well known that under acid or alkaline condition the microorganism activity may be restrained and that the cell wall would be dissolved with the concurrent release of its organic constituents into water. Many documents about alkaline and acid pretreatment improving excess sludge anaerobic fermentation have been reported<sup>20,21</sup>. Xiao *et al.*<sup>22</sup> has found alkaline treatment can increase the soluble chemical demand oxygen (SCOD) by releasing the organic materials from cells to water and converting the insoluble ones to soluble ones and remove volatile solid (VS) and total solid (TS) when the pH value was 13. Sludge size reduced with the increase of pH value. Sludge concentration, pH value and treatment time were three important factors of alkaline treatment.

Such treatments cause waste activated sludge floc disintegration and cell lysis with the concurrent release of many of its organic, nitrogen and phosphorus constituents. Recycling of the treated sludge to the existing biological treatment unit might therefore increase its organic, nitrogen and phosphorus loadings. Although the release of organic constituents of waste activated sludge has been well documented, the release of nutrient species in waste activated sludge treatment has not been properly covered in the literature. Given the more stringent requirements for nutrient removal, a comprehensive understanding of nitrogen and phosphorus releases during waste activated sludge treatment is essential for a successful waste activated sludge reduction program. There have been few reports comparing the effectiveness of different waste activated sludge treatment processes on the basis of organic, nitrogen and phosphorus release from waste activated sludge<sup>23</sup>. Fractionating the organic constituents of the liquid phase to different molecular weight (MW) size fractions would provide detailed information about their characteristics helpful for selecting effective treatment technologies<sup>24,25</sup>. An experimental study was therefore conducted to determine the effects of the treatment conditions of sonication, thermal treatment and acidalkali adjustment on the release of the waste activated sludge organic, nitrogen and phosphorous constituents and to propose an innovative and effective sludge reduction process.

## **EXPERIMENTAL**

Waste activated sludge (WAS) samples: A lab anaerobic/ oxic (An/O) biological phosphorus removal system (valid volume = 32 L) was operated during the study period to provide the waste activated sludge samples for the batch sludge treatment experiments. The influent was 120 L/d, containing glucose, acetate, amylum as the main organic substrates and NH<sub>4</sub>Cl, KH<sub>2</sub>PO<sub>4</sub> as the nutrients, with a chemical oxygen demand (COD) concentration of 450-500 mg/L, total nitrogen concentration of 40-48 mg/L and total phosphorus concentration of 6.8-8.0 mg/L. To avoid nitrification in the oxic reactor, 20 mg/L of allythiourea was also added to the influent. An average 5.3 L of mixed liquor, having a mixed liquor suspended solids (MLSS) concentration of 1800-2500 mg/L, was removed daily to maintain the designed sludge age of 6 d for the anaerobic/ oxic system.

After the start-up period of about two months, the An/O system exhibited a stable and good biological phosphorus removal capability. The waste activated sludge samples were then prepared by settling of the removed mixed liquor to the desired density for the comparative sludge treatment experiments. The waste activated sludge's total phosphorus content was 4.6-6.8 % of its total solids based on the average of five replicate measurements. Characteristics of the waste activated sludge samples are listed in Table-1. COD, total nitrogen and total phosphorus of the whole waste activated sludge sample (overall) were measured after it was completely mixed using a magnetic stirrer; COD, total nitrogen, NH<sub>3</sub>-N, total phosphorus and orthophosphorus were measured for the supernatant (liquid phase) after the sample centrifugation at 4000 rpm for 20 min. All measurements were conducted within 2 h after sampling to simulate the fresh waste activated sludge sample of a wastewater treatment plant. Reported values are averages of the duplicates; the experimental data were within  $\pm 8$  % of the average values.

**Sludge treatment methods:** The ultrasonic apparatus used was a homogeneous sonicator (JYD-650L, Shanghai Zhixin Inc., China), consisted of the ultrasound generator and a probe (10 mm diameter), with an operating frequency of 20-25 kHz and a maximum power input of 650 W. Batch treatment runs without temperature regulations were carried out in 400 mL beaker containing 300 mL of the waste activated sludge sample in each under mixing of a magnetic stirrer. The tip of the probe was 15 mm below the sample surface. During the treatment, the sonication intensity was controlled at 0.167, 0.330 and 0.500 W/mL, respectively and the treatment time was from 10 to 60 min. During the treatment, the temperatures increased in the samples at different sonication intensities were measured, which were changed from 6 to 33 °C.

In this study, a temperature controlled shaking water bath was employed for the thermal and acid-alkali adjustment treatment runs. The thermal treatments were performed at the controlled temperatures of 50, 70 and 90 °C and the treatment time (holding time) was up to 3 h. The heating times for waste activated sludge samples from room temperature (20-22 °C) to controlled temperature were in the range of 9-20 min. During the acid-alkali adjustment runs, the temperature was maintained at the room temperature and the initial pH was adjusted to 3, 5, 10 and 12 by adding 1:1 diluted  $H_2SO_4$  or 4 M NaOH. The treatment times were up to 4 h. The shaking was maintained at 120 rpm during the treatment runs. At the end of

TABLE-1 CHARACTERISTICS OF THE WASTE ACTIVATED SLUDGE SAMPLES (UNIT: mg/L, EXCEPT pH AND VOLATILE SOLID/TOTAL SOLIDS)						
Parameter	eter Value Parameter Value					
Liquid phase (supernatant)		Whole sample (overall)				
pH	$7.29 \pm 0.2$	Total solids	$6470 \pm 720$			
Chemical oxygen demand	$86.0 \pm 6.8$	Volatile solid /Total solids	$0.73 \pm 0.04$			
Total nitrogen	$31.1 \pm 4.3$	Chemical oxygen demand	$7440 \pm 590$			
NH <sub>3</sub> -N	$29.3 \pm 9.8$	Total nitrogen	$429.4 \pm 44.9$			
Total phosphorus	$0.26 \pm 0.09$	Total phosphorus	$348.6 \pm 56.3$			
Orthophosphorus	$0.17 \pm 0.09$	-	-			

treatment, the pH values of waste activated sludge samples had been measured.

After the treatment, the waste activated sludge samples were centrifuged at a speed of 4000 rpm for 20 min and concentrations of organic, nitrogen and phosphorus species of the supernatant were measured.

**Analyses:** Measurements of COD, biological oxygen demand (BOD<sub>5</sub>), total nitrogen, NH<sub>3</sub>-N, NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N, total phosphorus, orthophosphorus, total solids and volatile solid were performed according to the Standard Methods<sup>26</sup>. TOC was measured by a TOC analyzer (Liqui TOC, Elementar Analysensyteme Co., Germany) and pH by pH analyzer (Delta 320, Mettler Toledo Co.).

Molecular weight distribution of the TOC constituents of the liquid phase before and after sonication was determined using UF membranes (SCM model) with MW cut-offs of 2 kDa and 100 kDa. Membranes were first rinsed several times with ultra-pure water in a beaker 12 h before use. Nitrogen gas (99.999 %) pressure was controlled at 0.15-0.25 MPa to promote filtration. After rinsing, filtrate of the primary filter (0.45  $\mu$ m) before and after sonication was pressurized; the permeate was collected from each MW cut-off for TOC measurement. The results were expressed as percentage of the total TOC for each of its three fractions (MW = 2 kDa, 2 kDa < MW =100 kDa and MW >100 kDa).

The percentage of released COD was calculated by:  $(COD_i - COD_o) \times 100/COD_s$ , where COD<sub>i</sub> and COD<sub>o</sub> were COD of the liquid phase after and before treatment and COD<sub>s</sub> was COD of the waste activated sludge sample. The release percentages of total nitrogen and total phosphorus were calculated similarly to COD.

Ultrasonic treatment: It was well known that sonication can disintegrate the structure of sludge flocs and solubilize some of the cellular organic substances. The changes in organic concentration of the liquid phase during sonication (COD release profiles) at three sonication intensities are listed in Table-2. It is obvious that COD of the supernatant increased almost linearly with time at the three sonication intensities. 3040, 3670 and 4120 mg/L of COD (42, 45.6 and 54.1 % of the total waste activated sludge COD) was released from the waste activated sludge after 1 h treatment at 0.167, 0.330 and 0.500 W/mL, respectively. Such results were much higher than those reported by Chu et al.3 showing that 20 % of the waste activated sludge COD was released after 2 h of sonication (20 kHz, 0.44 W/mL). Even the intensity increased three folds from 0.167 W/mL to 0.500 W/mL, the accumulative percent of released COD increased only 28.8 %. The sonication treatment reduced the sludge concentration; the final total solids were 4.32, 3.39 and 3.31 g/L (66.8, 52.4 and 51.2 % of the original sludge total solids) after 1 h at 0.167, 0.330 and 0.500 W/mL, respectively. Such results have validated sonication as an effective technology for waste activated sludge volume reduction.

To ensure the sonicated waste activated sludge can be recycled to the biological aerobic unit, the BOD<sub>5</sub>/COD ratios of the liquid phase before and after sonication treatment were investigated. The higher BOD<sub>5</sub>/COD ratios of the sonicated samples (0.38-0.50 *vs.* 0.02-0.10) suggest that most of the organic species released will be biodegradable in the existing biological treatment unit of the WWTP. To further characterize

TOC FROM THE WASTE ACTIVATED SLUDGE DURING THE SONICATION TREATMENT						
	Sonication time (min)					
	10	20	30	40	50	60
	Intensity: 0.167 W/mL					
Accumulative COD in supernatant (mg/L)	856	1558	1946	2519	2672	3044
Released COD (%)	11.6	21.3	26.7	34.7	36.9	42.0
Released TOC (mg TOC/g TS)	7.6	9.9	15.6	21.4	24.2	33.7
$MW \le 2kDa \ (\%)$	50.2	50.9	72.0	59.6	56.8	86.5
2kDa < MW ≤ 100kDa (%)	7.0	24.8	2.0	1.1	11.9	13.4
MW > 100kDa (%)	42.8	24.3	26.1	39.4	31.4	0.0
			Intensity:	0.330 W/mL		
Accumulative COD in supernatant (mg/L)	1079	2039	2547	3341	3539	3666
Released COD (%)	12.7	24.9	32.9	41.4	43.9	45.6
Released TOC (mg TOC/g TS)	13.1	22.2	30.4	58.4	85.0	95.7
$MW \le 2kDa \ (\%)$	45.3	63.8	68.6	53.2	69.7	70.8
2kDa < MW ≤ 100kDa (%)	32.7	21.5	24.3	19.0	21.3	17.4
MW > 100kDa (%)	22.1	14.7	7.2	27.8	9.0	11.8
	Intensity: 0.500 W/mL					
Accumulative COD in supernatant (mg/L)	1568	2352	3107	3463	3757	4117
Released COD (%)	20.4	30.8	40.7	45.5	49.4	54.1
Released TOC (mg TOC/g TS)	21.1	33.1	59.5	82.1	102.8	104.0
$MW \le 2kDa (\%)$	58.6	81.5	78.5	75.0	74.1	76.1
2kDa < MW ≤ 100kDa (%)	31.3	10.3	18.3	5.6	15.6	22.1
MW > 100kDa (%)	10.1	8.3	3.2	19.4	10.3	1.8

#### TABLE-2 SPECIFIC AMOUNT OF ORGANIC AND MOLECULAR WEIGHT DISTRIBUTION OF THE RELEASED TOC FROM THE WASTE ACTIVATED SLUDGE DURING THE SONICATION TREATMENT

the released organic species, series of filtration runs were conducted to obtain distributions of organic fractions (MW = 2 kDa, 2 kDa < MW =100 kDa and MW >100 kDa) released by sonication. Table-2 shows specific amount of released TOC (mg TOC/g total solids) from the waste activated sludge samples and the distribution of the three TOC fractions during sonication under three intensities. 33.7, 95.7 and 104.0 mg TOC/g total solids were released from waste activated sludge after 1 h sonication at 0.167, 0.330 and 0.500 W/mL, respectively, showing the specific amount of released TOC increased with sonication time and intensity; Organic species of MW = 2 kDa were most abundant in all samples and that they are expected to be more biodegradable than the higher MW organic constituents<sup>27</sup>.

Alongwith the release of the organic compounds, many nitrogen species were also released during sonication of the waste activated sludge samples. The accumulative release profiles of total nitrogen of the liquid phase are shown in Fig. 1(a) and the accumulative percent of released total nitrogen profiles are presented in Fig. 1(b). Similar to the COD release pattern, the accumulative released total nitrogen increased gradually and after 1 h treatment liquid phase total nitrogen concentrations of all sonicated samples were in the range of 180-210 mg/L relative to the initial total nitrogen (TN) reached 37.8, 48.4, 47.2% at 0.167, 0.330 and 0.500 W/mL, respectively. Organic-N accounted for most of the released total nitrogen. The ratio of organic-N to total nitrogen of the liquid

phase increased to 55.2-75.8 % after 1 h treatment, while the ratio of NH<sub>3</sub>-N to total nitrogen declined to 24.0-44.8 % (Fig. 1(c) and 1(d)). Contributions of nitrate and nitrite were negligible (< 0.50 mg N/L).

It has been stated that the extra nitrogen loading resulting from the recycling of supernatant of the treated waste activated sludge would have no adverse effect on the biological nitrogen removal performance if COD/TKN of the combined influentrecycle stream<sup>28</sup> is over 9. In this study, the sonication resulted in a rapid increase in COD/TKN of the liquid phase (from 1.1 to 2.8 before the treatment) although the rate of increase slowed down after 20 min. The COD/TKN ratios for all liquid phase samples were higher than 15 at 20 min and after 1 h treatment the values were 17, 17 and 21 at 0.167, 0.330 and 0.500 W/mL, respectively. Therefore, with the necessary modifications, the existing biological treatment unit can accommodate the extra organic and nitrogen loadings of the recycled supernatant of the sonicated waste activated sludge. Since most domestic wastewaters have a rather low C/N ratio in southern part of China, such recycling may in fact enhance the biological treatment performance since it will result in a more favorable C/N ratio for the influent. Optimization studies should be performed if sonication treatment of waste activated sludge is considered for the WWTP.

The accumulative release profiles of total phosphorus of the liquid phase are shown in Fig. 2(a) and the accumulative per cent of released total phosphorus profiles are presented in Fig. 2(b). 180, 214.9 and 203.7 mg/L of total phosphorus



Fig. 1. Nitrogen release profiles of the liquid phase during sonication treatment: (a) accumulative total nitrogen (TN) concentration, (b) accumulative percent of released total nitrogen, (c) organic-N/TN, and (d) NH<sub>3</sub>-N/TN



Fig. 2. Phosphorus release profiles of the liquid phase during sonication treatment: (a) accumulative total phosphorus (TP) concentration, (b) accumulative per cent of released total phosphorus, (c) specific amount of released total phosphorus, and (d) orthophosphorus/total phosphorus

concentration in the supernatant, corresponding to 59.5, 68.7 and 68.1 % of released total phosphorus, were observed after 1 h treatment at 0.167, 0.330 and 0.500 W/mL, respectively. Fig. 2(c) illustrates that the specific amount of the released total phosphorus (total phosphorus released per total solids) increased with sonication time during the treatment, reaching 27.8, 33.2 and 31.5 mg/g total solids after 1 h sonication treatment at 0.167, 0.330 and 0.500 W/mL, respectively.

According to the principle of removal of biological phosphorus, direct recycle of the sonicated waste activated sludge would significantly increase the phosphorus loading and may result in a high phosphorus concentration in effluent exceeding the discharge limit. Such an adverse effect has been reported for the SBR system after the sonicated sludge was included in the feed<sup>29</sup>. In this study, orthophosphorus was the predominant form [71.9-92.1 % of total phosphorus, Fig. 2(d)] of the released total phosphorus from waste activated sludge, due most likely to its high density of phosphorus accumulating organisms (PAOs), making it possible for the phosphate recovery by precipitation or crystallization. The extra loading of orthophosphorus released from sonication of a high total phosphorus waste activated sludge should be substantially reduced before recycling the treated waste activated sludge or its supernatant to the biological unit.

**Thermal treatment:** The COD release profiles of the waste activated sludge at three temperatures are listed in Table-3. It is obvious that the COD of the supernatant increased sharply within the first 0.5 min; 616, 1744 and 2230 mg/L of COD (7.1, 23.6 and 28.8 % of the total waste activated sludge COD) were released from waste activated sludge after 0.5 h treatment at 50, 70 and 90 °C, respectively. However after 3 h, the respective COD concentrations of the supernatant were 1390, 2150 and 2607 mg/L (17.9, 29.4 and 33.9 % of the total waste activated sludge COD); the increase was smaller for the same temperature increment from 70 to 90 °C. During the 3 h of thermal treatment at 50, 70 and 90 °C, total solids declined to 5.35, 4.46 and 4.44 g/L (82.7, 68.9 and 68.6 % of the original sludge total solids ), respectively.

The BOD<sub>5</sub>/COD ratios of the liquid phase before and after thermal treatment were also tested. The higher ratios of the treated samples than those after sonication treatment (0.43-0.68 vs. 0.38-0.50) suggest that most of the organic species released will be much more biodegradable in the existing biological treatment unit of the WWTP. Table-3 also shows specific amount of released TOC from the waste activated sludge samples and the distribution of the three TOC fractions during thermal treatment at three temperature conditions. Specific amount of the released TOC increased with time and temperature; 39.0, 71.8 and 90.4 mg TOC/g total solids were

#### TABLE-3 SPECIFIC AMOUNT OF ORGANIC AND MOLECULAR WEIGHT DISTRIBUTION OF THE RELEASED TOC FROM THE WASTE ACTIVATED SLUDGE DURING THE THERMAL TREATMENT

	Treatment time (Holding Time) (h)			
	0.5	1	2	3
	Temperature: 50 °C			
Accumulative COD in supernatant (mg/L)	616	901	1156	1390
Released COD (%)	7.1	11.1	14.7	17.9
Released TOC (mg TOC/g TS)	15.9	21.2	35.6	39.0
MW ≤ 2kDa (%)	68.7	88.3	94.1	93.8
2kDa < MW ≤ 100kDa (%)	15.7	5.1	3.7	4.4
MW > 100kDa (%)	15.6	6.6	2.2	1.9
		Temperatur	e: 70 °C	
Accumulative COD in supernatant (mg/L)	1744	1866	1906	2150
Released COD (%)	23.6	25.3	25.9	29.4
2kDa < MW ≤ 100kDa (%)	6.6	12.5	5.7	7.8
MW > 100kDa (%)	38.9	28.6	35.9	26.5
	Temperature: 90 °C			
Accumulative COD in supernatant (mg/L)	2230	2362	2481	2607
Released COD (%)	28.8	30.6	32.2	33.9
$2kDa < MW \le 100kDa$ (%)	1.6	0.1	0.2	10.4
MW > 100kDa (%)	5.6	5.0	9.8	1.4

released from waste activated sludge after 3 h of thermal treatment at 50, 70 and 90 °C, respectively. Similar to sonication treatment, organic species of MW = 2 kDa were most abundant in all samples.

During thermal treatment of the waste activated sludge samples, many nitrogen species were also released. The accumulative concentration of total nitrogen of the liquid phase is shown in Fig. 3(a). At 70 and 90 °C, the initial release of nitrogen



Fig. 3. Nitrogen release profiles of the liquid phase during thermal treatment: (a) accumulative total nitrogen (TN) concentration, (b) accumulative NH<sub>3</sub>-N concentration, (c) organic-N/TN, and (d) NH<sub>3</sub>-N/TN

species was fast, relative to the initial total nitrogen of 31.1 mg/L, 158.6 and 220.6 mg/L of total nitrogen (30.4 and 47.1 % of the total waste activated sludge total nitrogen) were released respectively from waste activated sludge after 0.5 h treatment; the release rate then slowed down. The corresponding NH<sub>3</sub>-N releases were much lower as shown in Fig. 3(b). The nitrogen species distribution pattern was found to be dependent on thermal temperature. At 70 and 90 °C, organic-N accounted for most of the released total nitrogen; the ratio of organic-N to total nitrogen of the liquid phase increased to 64.1-77.1 %, while the ratio of NH<sub>3</sub>-N to total nitrogen declined to 21.6-35.4 % (Fig. 3(c) and 3(d)). At 50 °C, little total nitrogen was released (Fig. 3(a)) and NH<sub>3</sub>-N was the major nitrogen species (> 73 % of total nitrogen). Contributions of nitrate and nitrite during thermal treatment were negligible (< 4.2 mg N/L).

The thermal treatment resulted in an increase in COD/ TKN of the liquid phase. The values of all waste activated sludge samples were higher than 10 after 1 h thermal treatment at the three temperature conditions, showing that the recycling of the supernatant would have no adverse effect on the biological nitrogen removal performance.

The accumulative release profiles of total phosphorus of the liquid phase are shown in Fig. 4(a) and the accumulative

per cent of released total phosphorus profiles are presented in Fig. 4(b). Similar to the COD release patterns, the accumulative released total phosphorus increased sharply in the first 0.5 h treatment and the rate of increase slowed down later. 126.7, 194.8 and 260.4 mg/L of total phosphorus concentration in the supernatant, corresponding to 33.8, 50.8 and 66 % of the released total phosphorus, were observed after 0.5 h treatment at 50, 70 and 90 °C, respectively. Fig. 4(c) illustrates that the specific amount of the released total phosphorus (total phosphorus released per total solids) increased with time and temperature, reaching 19.5, 30 and 40 mg/g total solids after 0.5 h treatment at 50, 70 and 90 °C, respectively.

Fig. 4(a) and 4(d) show that orthophosphorus was the predominant form (orthophosphorus/total phosphorus 81.0-97.8 %) of the released total phosphorus from waste activated sludge, making it possible to recover the phosphate by precipitation or crystallization. Although such results differ from that of Kuroda *et al.*<sup>30</sup> showing polyphosphate (poly-P) was the predominant form (85-90 mg/L or 87 % of released total phosphorus) after 1 h thermal treatment at 70 °C, our results are consistent with literature reports by Xue *et al.*<sup>19</sup>.

Acid-alkali adjustment: In this study, the accumulative release profiles of COD, total nitrogen and total phosphorus of the liquid phase during acid-alkali adjustment treatments



Fig. 4. Phosphorus release profiles of the liquid phase during thermal treatment: (a) cumulative total phosphorus (TP) concentration P, (b) accumulative percent of released total phosphorus, (c) specific amount of released total phosphorus, and (d) accumulative orthophosphorus concentration

are listed in Table-4. At an initial pH of 3, 5 and 10, only small amounts of COD, total nitrogen and total phosphorus were released after 4 h. Much more releases were observed for treatment at an initial pH of 12. The concentration of COD, total nitrogen and total phosphorus of the supernatant increased with time as expected from the disintegration of waste activated sludge. 1520, 94.2 and 205.9 mg/L of COD, total nitrogen and total phosphorus were found in the supernatant, corresponding to 24.7, 25.3 and 50.1 % of COD, total nitrogen and total phosphorus release after 4 h at an initial pH of 12. During the same time period, total solids of the treated waste activated sludge went down from 6.47 to 4.93 g/L, while solution pH also declined to 10. Orthophosphorus accounted only for 26.7-37.7 % of total phosphorus in the supernatant, suggesting that precipitation will be ineffective in reducing its total phosphorus.

TABLE-4						
ACCUMULATIVE RELEASE AMOUNT OF ORGANIC AND						
NUTR	NUTRIENT DURING ACID-ALKALI ADJUSTMENT					
TREATMENT (UNIT: MG/L)						
	pH = 3	pH = 5	pH = 10	pH = 12		
		COD				
1 (h)	240	200	165	1131		
2 (h)	200	202	154	1440		
4 (h)	399	240	133	1520		
		TN				
1 (h)	24.4	21.3	51.1	80.3		
2 (h)	30.5	24.8	52.9	88.2		
4 (h)	29.2	22.6	54.8	94.2		
TP						
1 (h)	61.4	43.7	11.2	129.8		
2 (h)	68.6	40.6	26.5	177.1		
4 (h)	79.0	75.9	41.7	205.9		

The phospholipid bilayers of the cell could be dissolved readily under the highly alkaline condition, the sludge disintegration was thus more complete at pH of 12 relative to those at the lower pHs. The above observations are consistent with the findings of Xiao and Liu<sup>22</sup> showing that the alkaline treatment below the critical pH of 11 would destroy only sludge floc structure rather than cell structure, therefore the release of cellular constituents would be insignificant.

Comparison of the waste activated sludge treatment methods: From the results obtained in three treatment methods, it is obvious that the acid-alkali adjustment was unable to accomplish the desired extent of waste activated sludge treatment to result in a meaningful volume reduction. To allow for the comparison between sonication and thermal treatment, effects of the energy input (kJ/g total solids initial) on the organic and nutrient releases were determined. Based on the relative release percents of COD, total nitrogen and total phosphorus, as illustrated in Fig. 5 and the relative total solids reduction data discussed earlier, sonication is expected to be more effective to result in waste activated sludge volume reduction than thermal treatment. Combining sonication with phosphorus removal in an integrated sludge treatment process is effective for reducing waste activated sludge production and recycling of the treated waste activated sludge or its supernatant may even improve the biotreatment efficiency in a biological unit.



Fig. 5. Effectiveness of energy input on organic and nutrient releases during sonication and thermal treatments

#### Conclusions

(1) During the sonication treatment, the release of organic, nitrogen and phosphorus species increased with treatment time and sonication intensity. After 1 h treatment at 0.167, 0.330 and 0.500 W/mL intensities, 42, 45.6 and 54.1 % of the organic content (measured as COD) of the waste activated sludge were released, respectively. It also resulted in the releases of 37.8, 48.4 and 47.2 % of total nitrogen and 59.5, 68.7 and 68.1 % of total phosphorus, respectively. Most of the released total nitrogen was organic-N (55.2-75.8 %), followed by NH<sub>3</sub>-N (24.0-44.8 %) and the much smaller amounts of nitrate and nitrite. Orthophosphorus was the predominant form (71.9-92.1 %) of the released total phosphorus; it is possible to accomplish phosphate recovery from the liquid phase by lime precipitation or crystallization. The molecular weight distribution pattern of the soluble TOC species, BOD<sub>5</sub>/COD and C/N of the post treatment in the supernatant suggest that it may be recycled to the biological unit without any adverse effect.

(2) During thermal treatment, the release of organic, nitrogen and phosphorus species increased with time and temperature; after initial fast release of COD and total phosphorus, the release rates went down after the first 0.5 h of treatment. For the treatment performed at 50, 70 and 90 °C, the COD releases after 0.5 h were 7.1, 23.6 and 28.8 %, respectively and the corresponding total phosphorus releases were 33.8, 50.8 and 66.0 %. Most of the soluble TOC was the organics of low MW and that most of total phosphorus released was orthophosphorus (81.0-97.8 %). The total nitrogen release at 50 °C was very low; while it was much higher at 70 and 90 °C in manners similar to the releases of COD and total phosphorus. Organic-N accounted for the most released total nitrogen (64.1-77.1 %), followed by NH<sub>3</sub>-N (21.6-35.4 %) and much smaller amounts of nitrate and nitrite.

(3) The acid-alkali adjustment treatment at pH of 3, 5 and 10 did not result in substantial releases of the organic and nutrient constituents of the waste activated sludge. Although treatment at an initial pH of 12 was much more effective, the release efficiency was much lower than the corresponding releases of treatment by sonication and thermal treatments. Most of the released total phosphorus can not be removed or

recovered since orthophosphorus contributed a much smaller total phosphorus component (26.7-37.7 %).

(4) Sonication showed the most effectiveness of the three treatment methods to accomplish significant waste activated sludge volume reduction. Combining sonication with lime precipitation for phosphorus removal in an integrated sludge treatment process is expected for reducing waste activated sludge production. The recycling of the treated waste activated sludge or its supernatant may even improve the biotreatment efficiency of the biological unit of wastewater total phosphorus.

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