

## Effects of Mixture Ratios on Co-Fermentation of Primary Sludge and Waste Activated Sludge under Alkaline Condition

Gao-qiang Su<sup>1</sup>, Bing-yu Zheng<sup>1</sup>, Zhi-guo Yuan<sup>1,2</sup>, Shuying Wang<sup>1</sup>, Yong-zhen Peng<sup>1\*</sup>

<sup>1</sup>Key laboratory of Beijing Water Quality Science and Water Environment Recovery Engineering, Beijing University of Technology, Beijing 100124, China

<sup>2</sup>Advanced Water Management Center, The University of Queensland, QLD 4072, Australia

**Abstract:** Primary sludge (PS) or waste activated sludge (WAS) can produce a large amount of volatile fatty acids (VFAs) under alkaline conditions, and the VFAs can be supplied for the wastewater treatment plants to enhance nitrogen and phosphorus removal. However, how VFAs production will be affected by co-fermenting PS and WAS under alkaline condition is rarely reported. This study investigated the effects of mixture ratios on co-fermentation of PS and WAS at pH = 10. The best fermentation time for sludge solubilisation and VFAs production was 4 days for any mixture ratio investigated. Acetic acid was the prevalent VFA for all mixture ratios investigated. With the ratio of WAS increasing, the acetic acid percentage decreased, while the *n*-butyric acid percentage and *n*-valeric acid percentage both increased. Co-fermentation demonstrated equivalent, sometimes even higher hydrolysis and acidification abilities compared with separately-fermentation.

**Key words:** Waste activated sludge, primary sludge, alkaline condition, co-fermentation, volatile fatty acids

### 1 Introduction

Primary sludge (PS) and waste activated sludge (WAS) are two different types of sludge generated in the wastewater treatment plants (WWTPs). The chemical constituents of PS and WAS are mainly protein, carbohydrate and lipids, which can be utilized to produce volatile fatty acids (VFAs) in the hydrolysis and acidification process [1], [2], and VFAs can be used for nitrogen and phosphorus removal. Compared with acid or neutral condition, alkaline conditions can enhance PS and WAS hydrolysis and suppress the activities of methanogens, which can induce a significant amount of VFAs production [2], [3]. Nevertheless, VFAs produced by PS alone are usually not adequate for enhancing nitrogen and phosphorus removal in the WWTPs, so adding VFAs produced by WAS will be beneficial [4].

There are two ways to produce VFAs by fermenting PS and WAS. One way is separately-fermenting PS and WAS, the other way is co-fermenting PS and WAS. Obviously, more reactors are required by the first way, and the second way may be economical. However, how VFAs production will be affected when PS and WAS are co-fermented under alkaline conditions is rarely reported. The objective of this study was to study whether it is efficient to produce VFAs by co-fermenting PS and WAS at pH 10.

### 2 Materials and Methods

#### 2.1. Sources of PS and WAS

The PS used in this study was obtained from Gaobeidian WWTP in Beijing, China. The WAS was taken from a pilot-scale sequencing batch reactor (SBR) at the sedimentation phase in our laboratory. VSS

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\*Gaoqiang Su. Tel.: +86 10 67392627; Fax: +86 10 67392627.  
E-mail address: sugaoqiang1985@emails.bjut.edu.cn

concentrations of PS and WAS were adjusted to the same value by centrifuging. The characteristics of the sludge are presented in table 1.

TABLE I. SLUDGE CHARACTERISTICS

	PS*	WAS*
pH	6.87 (0.03)	6.96 (0.02)
TSS (total suspended solid )(mg/ L)	12593 (392)	8693 (132)
VSS (mg/L)	7863 (163)	7863 (164)
SCOD (soluble COD) (mg/ L)	115 (0.9)	48 (0.5)
TCOD (Total COD) (mg/L)	8502 (187)	10518 (47)
soluble protein (mg/L)	29 (0.6)	8 (2.8)
soluble carbohydrate (mg/ L)	19 (0.2)	12 (2.4)
C/N	9 (0.5)	5 (0.3)

\*The standard deviations in triplicate tests are shown in brackets.

## 2.2. Operational conditions

Experiments were conducted in seven tests. These tests were carried out in wide-mouth reagent bottles, which were made of glass and each had a working volume of 0.9 L. The PS to WAS ratio were 100:0, 80:20, 60:40, 50:50, 40:60, 20:80 and 0:100 (v:v) for the seven tests, respectively. All the reactors were sealed by rubber stoppers and purged by nitrogen gas for 3 minutes to remove oxygen. pH values of all the reactors were controlled at  $10 \pm 0.2$  by adding 4 M sodium hydroxide (NaOH) and 4 M hydrochloric (HCl). Temperature was controlled at 35 °C. Each reactor was mixed by magnetic stirrer at  $100 \pm 10$  rpm (rotations per minute). Samples were taken every four days. All tests were conducted in triplicate.

## 2.3. Analytical methods

Sludge samples from the reactors were centrifuged at 4000 rpm for 20 min and then filtrated by 0.45 µm cellulose membrane. The filtrate was analyzed for SCOD, protein, carbohydrate, VFAs. The analyses of TCOD, SCOD, TSS, VSS were conducted in accordance with standard method (APHA, 1998) [5]. pH was monitored by WTW, pH/oxi340i (WTW Company, Germany). Protein was measured by Lowry-Folin method with bovine serum albumin as standard [6]. Carbohydrate was measured by the phenol-sulfuric method with glucose as standard [7]. VFAs were analyzed by an Agilent 6890 N GC. Total carbon (TC) and total nitrogen (TN) of the sludge were analyzed by multi N/C 3000 analyzer (Jena, Germany). Each sample was measured for three times, the average was used as the experimental data.

## 3 Results and Discussion

### 3.1. SCOD solubilisation and acid production

Sludge solubilisation can be expressed by the changes of SCOD concentrations [1]. Acetic, propionic, n-butyric, iso-butyric, n-valeric and iso-valeric acids were the main types of acids produced during the sludge fermentation [1]. The concentrations of the six types of acids were converted to COD to demonstrate the sludge acidification process. Fig. 1(a) and (b) shows the effects of mixture ratios on SCOD solubilisation and acid production at different fermentation time. It can be found that SCOD and VFA concentrations increased quickly from 0 d to 4 d, and then became stable, which indicated that the best fermentation time were all 4 d for any mixture ratio investigated.

Furthermore, with the ratio of PS decreasing SCOD and VFA concentrations increased in most cases, which meant that co-fermenting PS with WAS could release more SCOD and produce more VFA than fermenting PS. Ji et al. [8] also found that SCOD released and VFA production by the mixture of PS and WAS was higher than that released by PS under pH uncontrolled condition. But this phenomenon contradicted to the results of Yuan et al. [9], which indicated that PS could release more SCOD and produce more VFA than WAS. This might be that TCOD of PS was less than that of WAS in this study.

### 3.2. Compositions of VFAs

Compositions of VFAs influenced significantly on nitrogen and phosphorus removal. Acetic acid and propionic acid were the optimal acids for nutrient removal [10], [11]. Fig. 1. (c) shows the compositions of VFAs under different mixture ratios at 4 d.

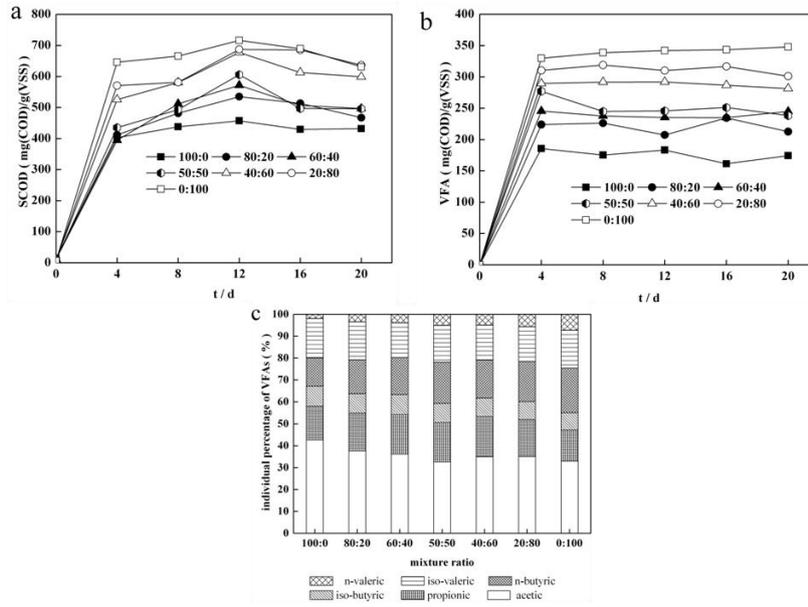


Fig.1: effects of mixture ratios on (a) SCOD solubilisation, (b) VFA production, (c) compositions of VFAs at 4-day fermentation time

It was obvious that acetic acid was the prevalent acid under any mixture ratio investigated, and it accounted for 33~43% for all the conditions. While *iso*-valeric acid, which only accounted for 2~7%, was the least acid produced. Furthermore, with the ratio of WAS increasing, the acetic acid percentage decreased, whereas the *n*-butyric and *iso*-valeric acids percentages both increased. The propionic, *iso*-butyric and *iso*-valeric acids percentages were insignificantly influenced by mixture ratio, which accounted for 14~18%, 8~9%, 16~18% at any mixture ratio investigated, respectively. More protein was released by WAS (data not shown), and the production of valeric acid was mainly related to protein fermentation, so this might be the reason why the valeric acid percentage increased with the ratio of WAS [12].

### 3.3. Hydrolysis and acidification abilities of co-fermented sludge and separately-fermented sludge

Fig. 2 demonstrates the hydrolysis and acidification abilities of co-fermented sludge and separately-fermented sludge.  $SCOD_{\text{experiment}}$  and  $VFA_{\text{experiment}}$  were the amount of SCOD and VFAs detected in the experiment.  $SCOD_{\text{theoretical}}$  and  $VFA_{\text{theoretical}}$  were the theoretical amount of SCOD and VFAs, which can be calculated by equations (1) and equation (2):

$$SCOD_{\text{theoretical}}(t) = r_{\text{PS}} \times SCOD_{\text{PS}}(t) \times 7.863 + r_{\text{WAS}} \times SCOD_{\text{WAS}}(t) \times 7.863 \quad (1)$$

$$VFA_{\text{theoretical}}(t) = r_{\text{PS}} \times VFA_{\text{PS}}(t) \times 7.863 + r_{\text{WAS}} \times VFA_{\text{WAS}}(t) \times 7.863 \quad (2)$$

$r_{\text{PS}}$  and  $r_{\text{WAS}}$  were the ratios of PS and WAS in the mixture,  $t$  was the fermentation time.  $SCOD_{\text{PS}}(t)$  and  $SCOD_{\text{WAS}}(t)$  were the SCOD concentrations released by PS and WAS at fermentation time  $t$ .  $VFA_{\text{PS}}(t)$  and  $VFA_{\text{WAS}}(t)$  were the acid yields of PS and WAS at fermentation time  $t$ . 7.863 was the VSS concentration of MS.

From Fig. 2, it can be found that  $SCOD_{\text{experiment}}$  were nearly the same with  $SCOD_{\text{theoretical}}$  at any mixture ratio investigated. Sometimes  $SCOD_{\text{experiment}}$  were even higher than  $SCOD_{\text{theoretical}}$ . The results meant that mixing PS with WAS sometimes could enhance the hydrolysis process. Yuan et al. [9] also found that  $SCOD_{\text{experiment}}$  was 35% higher than the  $SCOD_{\text{theoretical}}$  when co-fermenting PS with WAS. The difference between this study and the results of Yuan et al. [9] might be that SCOD release in their study mainly depended on biological effects of enzymes, whereas in this study SCOD release mainly depended on the chemical effects of sodium hydroxide. Under pH uncontrolled conditions there were a large amount of compounds in PS which couldn't be released into water due to low hydrolysis enzyme activity. When PS was mixed with WAS, the hydrolysis enzyme produced by WAS could enhance the hydrolysis ability of PS. However, PS and WAS released more compounds into water under alkaline conditions [1], [2], and the compounds left in the PS were refractory, which resulted that the biological effects were not so obvious as

those in pH uncontrolled conditions when PS was mixed with WAS. Therefore, the percentage of SCOD increment was lower in this study.

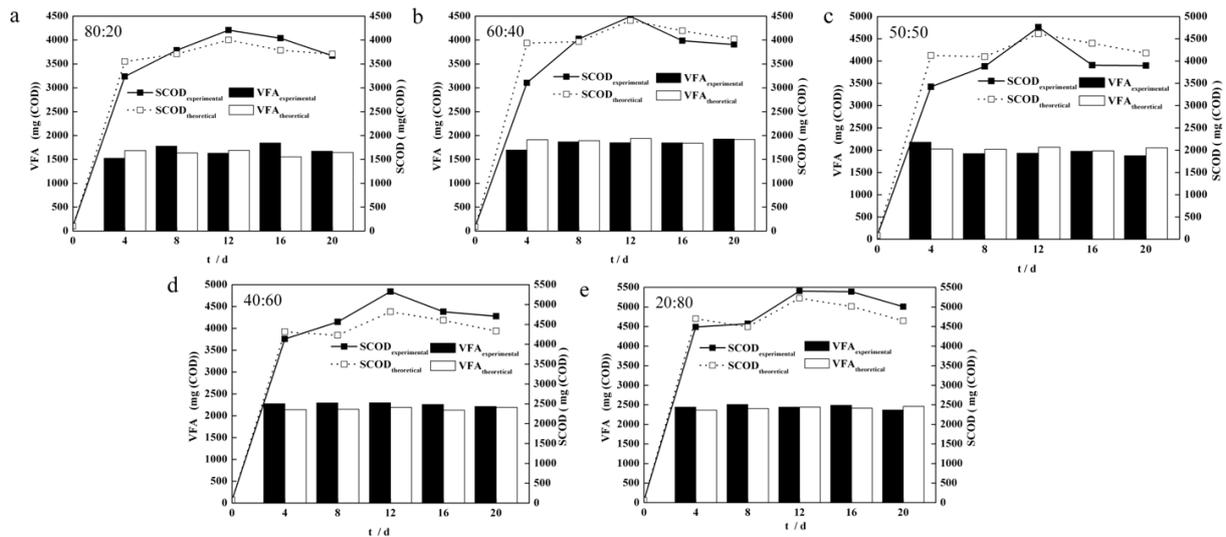


Fig.2: the hydrolysis and acidification abilities of co-fermented sludge and separately-fermented sludge

In addition,  $VFA_{\text{experiment}}$  and  $VFA_{\text{theoretical}}$  were also similar at any mixture ratio investigated, and  $VFA_{\text{experiment}}$  were a little higher than  $VFA_{\text{theoretical}}$  on occasion. At 4 d, the  $VFA_{\text{experiment}}$  were 153, 137, 77 mg (COD) higher than  $VFA_{\text{theoretical}}$  when the mixture ratios were 50:50, 40:60, 20:80. This phenomenon implied that mixing PS and WAS didn't hinder the VFAs production, sometimes it could improve VFAs production. Feng et al. [13], also indicated that co-fermentating food wastes with WAS could enhance VFA production. The optimal C/N ratio for anaerobic digestion is in the range of 20:1~30:1[14]. In the study of Feng et al. [13], the C/N ratio was improved from 9:1 to 13.1:1 when WAS was mixed with food waste. Contrary to those studies, the C/N ratios of MS were in the range of 5.4~8.6:1 in this study, obviously these values were far less than the optimal value for anaerobic digestion. Thus, this might be the reason why  $VFA_{\text{experiment}}$  were not so much higher than  $VFA_{\text{theoretical}}$  at any mixture ratio investigated in this study. From the study of Feng et al. [13], it can be inferred that the  $VFA_{\text{experiment}}$  could be greater than  $VFA_{\text{theoretical}}$  if the C/N ratio value of PS was higher.

From the results, it was efficient to produce VFAs by co-fermentation compared with separately-fermentation. So it was not necessary to build two reactors for acid production by fermenting PS and WAS, one reactor was enough.

## 4 Conclusions

The amount of SCOD and acid produced by co-fermentation was equivalent, and sometimes could be a little higher than those produced by separately-fermentation. As a result, one reactor is enough for VFAs production by fermenting PS and WAS at alkaline condition. Acetic acid was the prevalent acid under any mixture ratio investigated. Acetic acid percentage decreased, whereas the *n*-butyric and *iso*-valeric acids percentages both increased with the ratio of WAS increasing. While the propionic, *iso*-butyric and *iso*-valeric acids percentages were insignificantly influenced by mixture ratio

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