Reactive Extraction of Short-Chain Fatty Acids from Synthetic Acidic Fermentation Broth of Organic Solid Wastes and Their Stripping

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ABSTRACT: The effective separation of short-chain fatty acids (SCFAs) from acidic fermentation broth of organic solid wastes is difficult because of its complicated composition. The combination of tributyl phosphate (TBP) reactive extraction with vacuum evaporation stripping was investigated and its performance evaluated in this manuscript. The selection of vacuum evaporation as the stripping of SCFAs was mainly based on the "temperature swing effect" of reactive extraction. Under 15 min of extraction, room temperature, and a 1:1 extraction phase ratio (v/v), the extraction efficiency (E) of SCFAs by TBP amounted to 98.47 % after the third extraction. In view of SCFAs' stripping, the stripping efficiency (E') of 100 °C vacuum evaporation was up to 94.74 % under 0.095 MPa vacuum, a 1:1 stripping phase ratio (v/v), and 30 min of stripping. Finally, 93.29 % SCFAs and 98.21 % acetic acid could be separated and recovered from synthetic acidic fermentation broth of municipal sewage sludge. TBP could be regenerated after SCFAs were stripped from it three times.

INTRODUCTION

Through a mixed culture of anaerobic fermentation, the regeneration or recovery of useful chemicals from organic solid wastes has attracted more attention nowadays.[1,2] The anaerobic fermentation of organic wastes could not only alleviate environmental pollution caused by the waste but also produce useful biological products. A lot of research about acidic anaerobic fermentation of organic solid wastes or wastewater has been completed, including the production mechanism of short-chain fatty acids (SCFAs, such as acetic acid, propionic acid, butyric acid and valeric acid, etc.),[3,4] hydrolysis pretreatment of municipal sludge,[5,6] improvement of SCFAs' productivity, and optimization of process parameters,[7-10] which greatly increased the production intensity of SCFAs. However, in comparison with the pure culture of microorganisms, a mixed culture was frequently used during the fermentation of organic solid wastes. The composition of fermentation broth of mixed microorganisms, with a lower concentration of SCFAs, was quite complicated and instable. Hence, the separation of SCFAs from anaerobic fermentation broth of organic wastes has become a bottleneck of full-scale production.

There are five main methods, such as ion exchange,[11,12] liquid membrane separation,[13,14] esterification,[15,16] distillation,[17] and reactive extraction,[18,19] to separate SCFAs from acidic fermentation broth. Among those processes, a reactive extraction still was the mainstream one and was frequently used to extract SCFAs or other chemicals due to its lower cost. Recently, most researchers have focused on the extractant selection,[20] the extraction equilibrium mechanism,[21] the salt effect on the extraction rate,[22] and stripping processes.[23,24] Cai et al. investigated the extraction mechanisms of trialkylphosphine oxide (TRPO) and tributyl phosphate (TBP) for SCFAs (formic acid, acetic acid, etc.).[25] When the concentration of SCFAs was very low, TRPO and TBP existed in the form of their molecules. Taking TBP as the extractant and octanol and toluene as diluents, propionic acid

was successfully extracted from fermentation broth of Vitamin B$_{12}$ by Wang et al.[26] Under 0.5 mol·L^{-1} TBP and 1:2 extraction phase ratio, its extraction efficiency was 56 % and up to 98 % after four-stage cross-flow extraction.

However, few investigations investigated how to avoid the secondary pollution caused by various diluents' addition during extraction. Aimed at the separation of SCFAs from acidic fermentation broth of municipal sewage sludge, the reactive extraction without any diluents and vacuum evaporation stripping were developed, and their operating parameters were optimized according to the extractive and stripping efficiency (E and E') as well as SCFAs' distribution coefficient (D and D') in the oil and aqueous phases. Without secondary environmental pollution, this separation method could be easily used in other kinds of fermentation broth containing SCFAs.

EXPERIMENTAL SECTION

Materials. TBP (99 % mass fraction, Wuxi Donghu Chemical Factory, Jiangsu, China), a kind of phosphorus-bonded oxygen donor, was colorless with a molar mass of 266.32 g·mol^{-1} and a density of 0.975 g·cm^{-3}. Acetic acid, propionic acid, butyric acid, and valeric acid (99 % mass fraction), as well as other extractants (in analytical pure), were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). In our previous investigation,[7] a novel anaerobic fermentation process, named multistage countercurrent fermentation, was developed to improve the productivity of SCFAs from excess municipal sludge. The total SCFAs' concentration in fermentation broth reached 10.5 g·L^{-1}. Compared with the conventional anaerobic fermentation, it increased by 31 %. After its operating parameters were optimized,

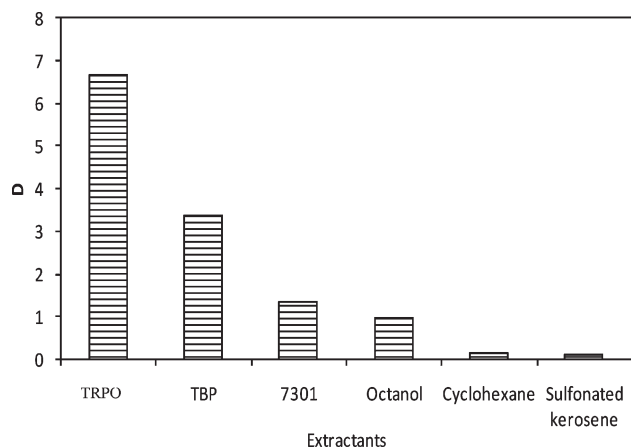**Figure 1.** Extractive distribution coefficient of SCFAs with a 1:1 extraction phase ratio (v/v), 3.6 mol·L^{-1} TBP, and 15 min of extraction. D is the extractive distribution coefficient, that is, SCFAs' concentration ratio in the oil and aqueous phases. SCFAs stand for short-chain fatty acids. TRPO stands for trialkylphosphine oxide and TBP for tributyl phosphate.
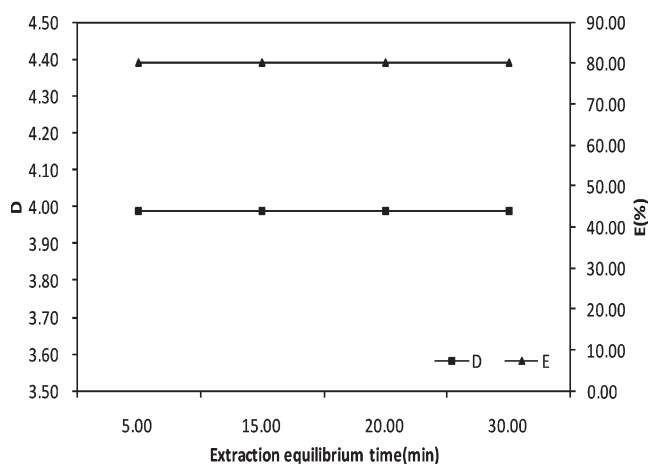

Figure 3. Effect of extraction temperature on D and E values with a 1:1 extraction phase ratio (v/v), 3.6 mol·L^{-1} TBP, and 5 min extraction. D is the extractive distribution coefficient, that is, SCFAs' concentration ratio of the oil and aqueous phases. E is the extraction efficiency of total SCFAs. SCFAs stand for short-chain fatty acids.

Figure 2. Determination of extraction equilibrium time by D and E values with a 1:1 extraction phase ratio (v/v) and 3.6 mol·L^{-1} TBP. D is the extractive distribution coefficient, that is, SCFAs' concentration ratio in the oil and aqueous phases. E is the extraction efficiency of total SCFAs. SCFAs stand for short-chain fatty acids.

Figure 4. Effect of the extraction phase ratio on D and E values with 3.6 mol·L^{-1} TBP and 5 min of extraction. D is the extractive distribution coefficient, that is, SCFAs' concentration ratio of the oil and aqueous phases. E is the extraction efficiency of total SCFAs. SCFAs stand for short-chain fatty acids.

SCFAs' concentration would be further increased. Therefore, synthetic acidic fermentation broth with 20 g·L^{-1} of SCFAs was prepared by deionized water in this manuscript.

Operation Methods. Except for experiments testing the effect of extraction temperature, the extraction of SCFAs was performed at a constant temperature (25 ± 0.5 °C) by a temperature-controlled water bath shaker (SHA-C, Jintan Ronghua Instrument Manufacture Co. Ltd., Jiangsu, China). Certain volumes of aqueous and oil phases were put into a 125 mL conical flask in turn and shaken at 120 r·min^{-1} for a certain time. Then, the mixture was moved to a separating funnel and allowed to be layered for at least 10 min under atmospheric pressure. Various SCFAs' concentrations in aqueous phase after reactive extraction were determined by the GC system (GC-2010, Shimadzu, Kyoto, Japan). Their sum was the total concentration of SCFAs.
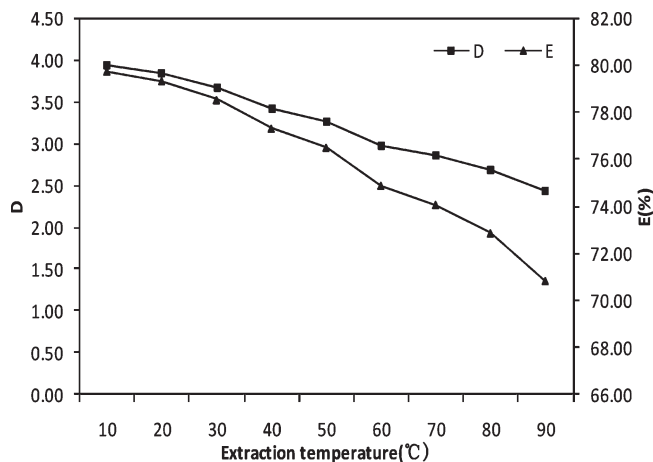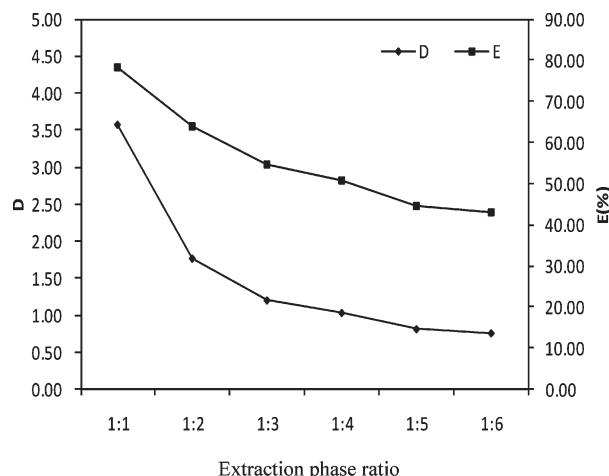
The oil phase left in the separating funnel was shifted into another 125 mL conical flask. After a certain volume of fresh deionized water was added, the conical flask was shaken at 120 r·min^{-1} for 15 min. Then, the mixture obtained was moved to a rotary evaporator (R20, Wuxi Xinghaiwang Biochemical Co. Ltd., Wuxi, China) with 0.095 MPa vacuum and 70 r·m^{-1} rotary rate to strip SCFAs from oil phase. After vacuum evaporation stripping, various SCFAs' concentrations in the distillate were determined by the GC system.

The rest of the oil phase (used TBP) in the rotary evaporator was taken away into a new 125 mL conical flask and, as described above, mixed with a certain volume of fresh synthetic acidic fermentation. Another SCFAs' extraction was completed to test the regenerative ability of TBP according to its extraction efficiency. It was assumed that there was no change in phase volumes after extraction and stripping in all

our experiments. The extraction phase ratio generally stands for the ratio of oil to aqueous phase (v/v), but the stripping phase ratio stands for the ratio of aqueous to oil phase (v/v) in this manuscript.

Analysis Methods. A GC system equipped with an auto injector (AOC-20i, Shimadzu, Kyoto, Japan) was used to determine various SCFAs' concentrations in the aqueous phase. The detector was a flame ionization type, and its column was a fused-silica capillary (PEG-20M, 30 m × 0.32 mm × 0.5 μm). Samples of 0.5 mL of aqueous phase containing SCFAs, 0.5 mL of 4-methylvaleric acid, and 0.5 mL of 3 mol·L^{-1} phosphoric acid
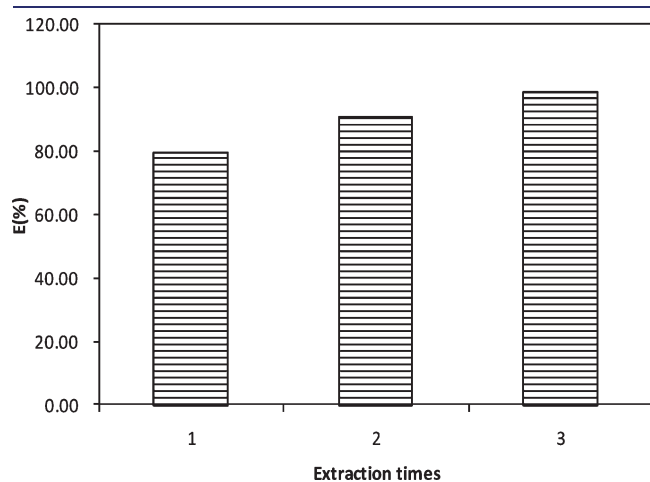

Figure 5. Effect of extraction times on E values with a 1:1 of extraction phase ratio (v/v), 3.6 mol·L^{-1} TBP, and 5 min of extraction. E is the extraction efficiency of total SCFAs. SCFAs stand for short-chain fatty acids.

were added. 4-Methylvaleric acid served as an internal standard, and phosphoric acid was used to acidify the sample to allow SCFAs to be vaporized in the GC injection port. The initial temperature of GC column was 80 °C and held for 3 min. Then, it was gradually increased by 15 °C·min^{-1} to a final temperature of 210 °C and held for 2 min. The temperatures of injection port and detector were both set at 250 °C. The concentrations of SCFAs in oil phase were determined according to the mass balance.

In the extraction experiments, the extraction distribution coefficient (D) was calculated as a ratio of the total SCFAs' mass in the oil phase to that in aqueous one. The extraction efficiency (E) of SCFAs was expressed as eq 1.

$$E = \frac{D}{1 + D} \cdot 100 \% \tag{1}$$

In the stripping experiments, the stripping distribution coefficient (D') was calculated as a ratio of the total SCFAs' mass in aqueous phase to that in oil one. The stripping efficiency (E') of SCFAs was expressed as eq 2.

$$E' = \frac{D'}{1 + D'} \cdot 100 \% \tag{2}$$

■ RESULTS AND DISCUSSION

Extractant Selection. There were three categories of extractants used in reactive extraction of SCFAs,[27] including carbon-bonded oxygen-bearing extractants, phosphorus-bonded oxygen-bearing extractants, and proton transfer or ion-pairing formation with high molecular weight aliphatic amines and their salts. D values of various extractants are shown in Figure 1.

Table 1. Effects of Stripping Temperature on Efficiency^a

temperature	stripping times	D'^b	E'^c (%)	D^d	E^e (%)
stripping with 80 °C water	first stripping	0.327	24.64		
	second stripping	0.301	42.09		
	third stripping	0.256	53.90		
	fourth stripping	0.215	62.63		
	regeneration of TBP^f			2.926	74.48
stripping with 90 °C water	first stripping	0.370	27.03		
	second stripping	0.304	44.04		
	third stripping	0.246	55.06		
	fourth stripping	0.217	63.56		
	regeneration of TBP			3.113	75.69
stripping with 100 °C water	first stripping	0.369	26.93		
	second stripping	0.322	44.72		
	third stripping	0.314	57.93		
	fourth stripping	0.259	66.57		
	regeneration of TBP			3.047	75.29
stripping with vacuum evaporation at 100 °C	first stripping	2.065	67.37		
	second stripping	1.818	88.42		
	third stripping	1.200	94.74		
	fourth stripping	4.000	98.95		
	regeneration of TBP			3.731	78.86

^{a} The stripping experiments were conducted under a 1:1 stripping phase ratio (v/v) for 30 min. ^{b} The distribution coefficient of stripping of SCFAs. ^{c} The stripping efficiency of SCFAs. ^{d} The distribution coefficient of reactive extraction using regenerative TBP. ^{e} The extraction efficiency of SCFAs using regenerative TBP. ^{f} TBP stands for tributyl phosphate.

Table 2. Effect of Vacuum Evaporation Temperature on Stripping Efficiency[a]

evaporation temperature (°C)	E'^b of acetic acid (%)	E' of propionic acid (%)	E' of butyrate acid (%)	E' of valeric acid (%)	E' of total SCFAs[c] (%)
70	46.48	25.19	13.24	12.02	32.77
80	46.91	29.30	16.55	12.40	34.66
90	78.76	50.41	22.48	12.98	57.25
100	89.62	67.08	31.40	14.16	68.79

[a] The stripping experiments were conducted under a 1:1 stripping phase ratio (v/v) for 30 min. [b] The stripping efficiency of various SCFAs. [c] SCFAs stand for short-chain fatty acids.
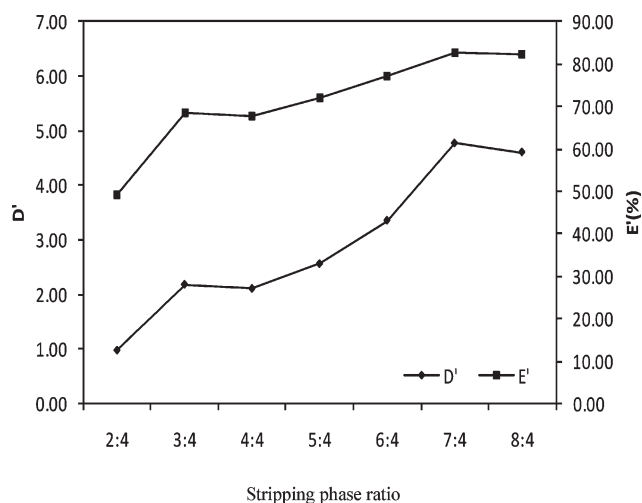

Figure 6. Effect of the stripping phase ratio on D' and E' values under 100 °C for 30 min. D' is the stripping distribution coefficient, that is, SCFAs' concentration ratio of aqueous to oil phases. E' is the stripping efficiency of total SCFAs. SCFAs stand for short-chain fatty acids.
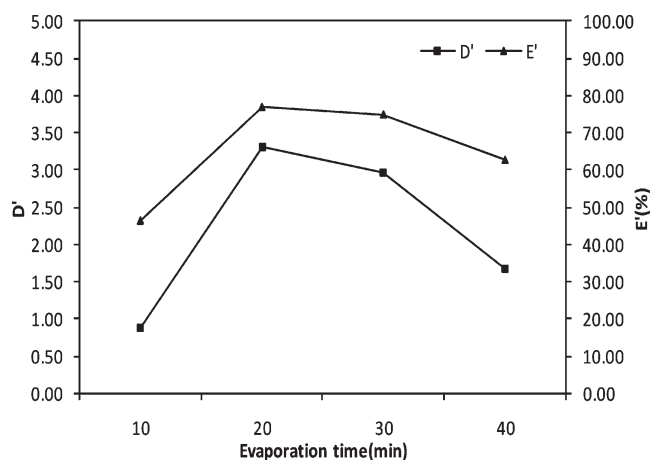

Figure 7. Effect of vacuum evaporation time on D' and E' values under a 1:1 stripping phase ratio (v/v) and 100 °C. D' is the stripping distribution coefficient, that is, SCFAs' concentration ratio of aqueous to oil phases. E' is the stripping efficiency of total SCFAs. SCFAs stand for short-chain fatty acids.

TRPO had the highest extraction efficiency ($D = 6.801$ and $E = 86.99$ %) followed by TBP. The D value of TBP was 3.332 with 62.00 % of E. In contrast, cyclohexane and sulfonated kerosene almost could not extract SCFAs from synthetic fermentation broth according to the results revealed in Figure 1. TRPO revealed the strongest combining ability with an H atom than other extractants. However, during TRPO extraction, emulsification happened easily, and the third phase formed because no dilution agent was added in our experiments. Therefore, TBP was determined as the extractant of SCFAs in the following experiments.

Extractive Equilibrium Time. The total concentration of SCFAs (presented in C_{SCFAs}) was 20 g·L^{-1} in our experiments with acetic acid/propionic acid/butyrate acid/valeric acid ratio of 5:3:1:1 (v/v).[7] Their concentrations were 0.167 mol·L^{-1}, 0.081 mol·L^{-1}, 0.023 mol·L^{-1}, and 0.02 mol·L^{-1}, respectively. The TBP concentration (presented in C_{TBP}) was 3.6 mol·L^{-1} during extraction, so there was $C_{TBP}/C_{SCFAs} = 12.37$. In theory, TBP supplied was enough to extract all SCFAs from synthetic broth, and SCFAs' extraction could be finished within a short time. The influence of extractive time on the values of D and E was manifested in Figure 2.

As predicted, the reactive extraction of SCFAs finished within 5 min and reached chemical equilibrium (Figure 2). The reaction with respect to $HA + \overline{TBP} \leftrightarrow \overline{HA \cdot TBP}$ (A stood for CH$_3$COO$^-$, CH$_3$CH$_2$COO$^-$, CH$_3$CH$_2$CH$_2$COO$^-$, or CH$_3$CH$_2$CH$_2$CH$_2$-COO$^-$) could be finished within a short period under conditions examined.[28]

Extractive Temperature. The values of D and E as a function of extractive temperature are shown in Figure 3. With increasing the extractive temperature to 90 °C from 10 °C, the values of D and E decreased to 2.414 and 70.70 %. Baniel et al. reported the effect of temperature on the extraction of citric acid using tridecylamine contained in petroleum fractions with an alcohol modifier. The distribution of citric acid into oil phase also decreased sharply with the increasing extraction temperature.[29]

Extraction Phase Ratio. The variations in the extractive distribution coefficient D and efficiency E were revealed in Figure 4 as a function of the extraction phase ratio. As shown in Figure 4, with decreasing the extraction phase ratio from 1:1 to 1:6, the values of D and E decreased. For example, E value dropped to 42.99 % of 1:6 from 78.09 % of 1:1. Although increasing the volume of aqueous phase could take up more broth within a certain time and save extractant, the extraction efficiency decreased. Considering regeneration of extractant (TBP), a 1:1 extraction phase ratio was taken in the following study.

Extractive Times. Generally speaking, the extractive efficiency of the single stage was lower, and therefore multistage extraction should be taken. The influence of extractive times on the values of E was shown in Figure 5. With increasing extractive times, the values of E gradually increased from 78.98 % of the first extraction to 98.47 % of the third one.

Stripping Temperature. According to the results by Baniel et al., citric acid back-extraction (stripping) from oil phase was allowed by the fresh aqueous phase.[29] Tamada and King called it the "Temperature Swing Regeneration".[30] From this point of view, SCFAs in our experiments were stripped by increasing the

Table 3. Effect of the Stripping Phase Ratio on Stripping Efficiency[a]

stripping phase ratio	E'^{b} of acetic acid (%)	E' of propionic acid (%)	E' of butyrate acid (%)	E' of valeric acid (%)	E' of total SCFAs[c] (%)
2:4	81.51	41.00	17.46	13.19	53.29
3:4	81.27	45.31	20.58	14.36	55.09
4:4	96.67	63.63	32.45	20.78	70.05

[a] The stripping experiments were conducted under 100 °C for 30 min. [b] The stripping efficiency of various SCFAs. [c] SCFAs stand for short-chain fatty acids.

Table 4. Effect of Evaporation Time on Stripping Efficiency[a]

evaporation time (min)	E'^{b} of acetic acid (%)	E' of propionic acid (%)	E' of butyrate acid (%)	E' of valeric acid (%)	E' of total SCFAs[c] (%)
10	33.38	27.76	16.66	14.00	27.96
20	70.14	55.12	29.77	17.14	55.96
30	78.70	72.03	48.13	29.88	68.58
40	45.61	41.02	25.55	15.92	39.13

[a] The stripping experiments were conducted under a 1:1 of stripping phase ratio (v/v) and 100 °C. [b] The stripping efficiency of various SCFAs. [c] SCFAs stand for short-chain fatty acids.

extraction temperature. Stripping the SCFAs from the oil phase was conducted by both hot water and vacuum evaporation (shown in Table 1). It was found both D' and E' values increased with increasing water temperature. The stripping efficiency of vacuum evaporation was better than hot water. For example, under 100 °C, it amounted to 98.95 % after the fourth stripping, but only 66.57 % for 100 °C with water. Additionally, D' decreased and E' increased with increasing stripping times. Taking vacuum evaporation stripping at 100 °C as an example, the E' value went up to 98.95 % on the fourth stripping from 67.37 % on the first one. To our best knowledge, this is the first report of stripping by vacuum evaporation.

In addition, the extraction efficiency of regenerated TBP under different stripping temperatures is listed in Table 1. It could be seen that those for 80 °C, 90 °C, and 100 °C water were 74.48 %, 75.69 %, and 75.29 %, respectively. The stripping temperature had little effect on the extraction efficiency of regenerated TBP. For regenerated TBP under 100 °C vacuum evaporation, the extraction efficiency was higher with 78.86 %.

The influence of vacuum evaporation temperature on E' value of the first stripping for various SCFAs was elucidated in Table 2. With increasing vacuum evaporation temperature, all values of E' for various SCFAs as well as total SCFAs increased. It amounted to 68.79 % of 100 °C from 32.77 % of 70 °C for total SCFAs. To achieve a greater E', it was inevitable to increase the evaporation temperature. Gu et al. found a similar phenomenon during vacuum distillation.[31] Furthermore, among various SCFAs, acetic acid achieved the highest stripping efficiency with 89.62 % at 100 °C. Acetic acid, with one C atom and the shortest chain length, tended to be easily stripped from TBP.

Stripping Phase Ratio. As demonstrated in Figure 6, with increasing the stripping phase ratio (contained SCFAs), the values of D' and E' increased to 4.598 and 82.14 % of 8:4, respectively. In the meantime, the concentration of SCFAs would decrease in the stripping aqueous phase. To balance the difference between E' and SCFAs' concentration in stripping aqueous phase, a 1:1 (or 4:4) stripping phase ratio was appropriate with a D' of 2.103 and E' of 69.85 %.

In addition, the variations in E' values of various SCFAs under different stripping phase ratios were listed in Table 3. E' values of acetic acid, propionic acid, butyrate acid, valeric acid, and total

SCFAs amounted to 96.67 %, 63.63 %, 32.45 %, 20.78 %, and 70.05 %, respectively, when the stripping phase ratio increased to 4:4 (1:1) from 2:4. The stripping efficiency of acetic acid was highest among various SCFAs.

Stripping Time. As clarified in Figure 7, with increasing evaporation time in the range of (10 to 40) min, the values of D' and E' first increased, and then quickly dropped. The highest D' and E' were 3.304 and 76.77 % at 20 min, respectively. In the range of (20 to 30) min there was a relative stable period for D' and E' values, and the gas—liquid phase in rotary evaporator might reach equilibrium. It was appropriate to determine 30 min as evaporation time for SCFAs' stripping.

The influence of vacuum evaporation time on the stripping efficiency of various SCFAs was revealed in Table 4. With increasing evaporation time, E' values of various SCFAs first increased within 30 min and then markedly decreased. All E' values of acetic acid, propionic acid, butyric acid, and valeric acid as well as total SCFAs achieved their maxima at 30 min with 78.78 %, 72.03 %, 48.13 %, 29.88 %, and 68.58 %, respectively. Once more, acetic acid had the highest stripping efficiency than the other kinds of SCFAs.

It should be noted that the recoveries of various SCFAs and acetic acid after TBP reactive extraction and 100 °C vacuum evaporation stripping (both for three times) went up to 93.29 % and 98.21 %, respectively. SCFAs could be effectively separated from synthetic acidic fermentation broth of municipal sewage sludge by the combination of TBP reactive extraction with vacuum evaporation stripping.

■ CONCLUSIONS

Combined the reactive extraction of TBP with vacuum evaporation striping, SCFAs could be successfully separated from synthetic acidic fermentation broth of municipal sewage sludge. When the extraction equilibrium time, temperature, extraction phase ratio, and times were 15 min, room temperature, 1:1, and 3 times, the extraction efficiency (E) of SCFAs by 3.6 mol·L^{-1} TBP amounted to 98.47 %. On the basis of the "temperature swing effect", 100 °C vacuum evaporation was taken to strip SCFAs from the oil phase. Under 0.095 MPa vacuum and a 70 r·m^{-1} rotary rate, a 1:1 stripping phase ratio

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dx.doi.org/10.1021/je2006456 | J. Chem. Eng. Data 2012, 57, 46–51

and 30 min of stripping were determined for the SCFAs' stripping process. After three stripping times under the conditions above, the E' of SCFAs was up to 94.74 %. For acetic acid, propionic acid, butyrate acid, and valeric acid, it was 99.74 %, 91.42 %, 66.63 %, and 40.52 %, respectively. Totals of 93.29 % SCFAs and 98.21 % acetic acid could be separated and recovered from synthetic acidic fermentation broth in this manuscript. In the meantime, for regenerated TBP from stripping by 100 °C vacuum evaporation, a 78.86 % extractive efficiency was achieved.

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dx.doi.org/10.1021/je2006456 |*J. Chem. Eng. Data* 2012, 57, 46–51