Valorization of citric acid production wastewater as alternative carbon source for biological nutrients removal: A pilot-scale case study

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A B S T R A C T

A pilot-scale process for valorization of citric acid production wastewater as alternative carbon source was developed. Calcium oxide and polyaluminum chloride were used to precipitate phosphate and suspended solids. Concentrated liquor with high concentration organic matter was obtained through filtration and concentration processes, and could be used as an alternative carbon source for biological nutrients removal. The performance of alternative carbon source for biological nutrients removal was close to traditional external carbon source (e.g., sodium acetate). The carbon source utilization efficiency was observed as 5.41 and 4.92 mg chemical oxygen demand equivalent of alternative carbon source and sodium acetate, respectively, to remove per mg total nitrogen. The process for valorization of citric acid production wastewater as alternative carbon source was profitable (4.6 USD/m^3) based on economic analysis. In summary, the process could relieve wastewater pollution issue while the product served as an efficient carbon source in biological treatment process of wastewater.

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1. Introduction

Citric acid as a tricarboxylic acid is commonly produced by *Aspergillus niger*, and it is extensively used in the food, beverage, chemical, metallurgical and other relevant industries (Angumeenal and Venkappayya, 2013). The global demand for citric acid has exceeded 2 million tons in 2015 (Ning et al., 2018). Approximately 40 tons of citric acid production wastewater (CAPW), with high chemical oxygen demand (COD), nitrogen and phosphorus content and low pH, are produced per ton of citric acid product (Wu et al., 2009). A large amount of wastewater discharge brings serious pollution issue.

To address the wastewater pollution issue, a series of measures were proposed including electrochemical oxidation (Li et al., 2013b), membrane filtration (Leyva-Díaz et al., 2013), macrophyte absorption (Valderrama et al., 2002; Li et al., 2013a) and wastewater recycling (Zhang et al., 2014). However, the large-scale application of these processes has been limited owing to their expensive operating costs. Thus, CAPW was still treated extensively by the process of anaerobic-aerobic biological treatment. Biogas and anaerobic granular sludge can be produced in anaerobic process to obtain certain economic benefits. However, it cannot offset the operations costs of subsequent aerobic treatment. Additionally, with an increasingly strict wastewater discharge standard in China, many citric acid enterprises are suffering with profit decline or even profit loss (Zhi et al., 2010).

Recently, the annually increasing municipal wastewater is required for biological nutrients removal (BNR) in wastewater treatment plants (WWTPs). However, the organic matter contained in wastewater itself is typically insufficient for satisfactory nitrogen and phosphorus removal (Berks et al., 1995; Xiong et al., 2018). To improve the performance of BNR, carbon sources (such as sodium acetate, acetate, glucose, methanol and waste organic matter) have been extensively applied in WWTPs, which leads the demand of

Abbreviation

ACS	Alternative carbon source
AGS	Anaerobic granular sludge
ASCP	Acidic soil conditioner contains trace phosphorus
BNR	Biological nutrients removal
BOD_5	Biochemical oxygen demand
CAPW	Citric acid production wastewater
COD	Chemical oxygen demand
SCOD	Soluble chemical oxygen demand
HRT	Hydraulic retention time
MLSS	Mixed liquor suspended solids
SRT	Sludge retention time
SS	Suspended solids
TN	Total nitrogen
TP	Total phosphorus
TS	Total solids
VS	Volatile solids
WWTPs	Wastewater treatment plants

carbon source gradually increasing (Puig et al., 2008; Poutiainen et al., 2010; Gao et al., 2011; Dong et al., 2012; Kim et al., 2017; Xiong et al., 2018). CAPW has considerable easily biodegradable and non-toxic organic matter (Li et al., 2013b), but it is hard to be directly as alternative carbon source (ACS) for BNR given the low ratios of COD/total nitrogen (TN) and COD/total phosphorus (TP). Furthermore, considering the background in China, almost all citric acid production plants have their own thermal power plants to decrease the energy cost of fermentation process. However, thermal power plants could generate numerous waste heat sources which cannot be effectively utilized causing heat waste. Thus, it is a meaningful study by coupling CAPW treatment and waste heat utilization to relieve the wastewater pollution issue.

The present work aimed to develop a pilot-scale process for valorization of CAPW as ACS. Firstly, the optimal conditions for the removal of nitrogen and phosphorus were determined in lab-scale. Secondly, the pilot-scale process would be established and evaluated. Thirdly, the performance of ACS for BNR in pilot-scale was determined while the sodium acetate was used as the control. Finally, the economic benefit for the process was calculated.

2. Materials and methods

2.1. Wastewater, chemicals and heat

CAPW was obtained from a citric acid plant in Wuxi City, China. The samples were stored in a 4 °C refrigerator for less than 1 week prior to use. The main characteristics of CAPW were as follows: pH (4.7 ± 0.3), total nitrogen (TN) 338 ± 29 mg/L, total phosphorus (TP) 187 ± 17 mg/L, ammonia nitrogen (NH_4^+-N) 66 ± 5.4 mg/L, phosphate (PO_4^{3-}-P) 163 ± 11.5 mg/L, suspended solids (SS) 426 ± 31 mg/L, chemical oxygen demand (COD) $21,700 \pm 298$ mg/L and biochemical oxygen demand (BOD_5) $11,501 \pm 90$ mg/L. The concentrations of polyaluminum chloride (PAC) and CaO suspension were 100 and 300 g/L. PAC and CaO were analytical reagent grade in lab-scale and industrial grade on the pilot-scale, respectively. The particle size of perlite was 100−150 mesh, and the perlite was only used in pilot-scale process to improve solid-liquid separation efficiency. High-temperature condensate water (80−90 °C) from the thermal power plant belonging to citric acid plant can be supplied free and adequately.

2.2. Optimization of pH and PAC dosage

The experiment procedures for exploring the optimal pH were as follows. First, five 500 mL beaker were separately added 400 mL CAPW, and then CaO suspension (300 g/L) was separately added to adjust the pH to 8.0, 8.5, 9.0, 9.5 and 10.0. Second, 100 mL of supernatant was separately sampled to analyze the removal rates of TN, TP, PO_4^{3-}-P, COD, suspended solids (SS), organic phosphorus and carbohydrate after sedimentation for 30 min.

The subsequent experiment procedures for the optimal PAC dosage were as follows. First, five 500 mL beaker were separately added 400 mL CAPW, and then calcium oxide suspension was used to adjust the pH to the optimal condition as determined previously. Second, 10%, 20%, 40% and 80% (calculated as the weight percentage of SS content; 100 g/L) PAC were separately added to beakers and stirred gently for 30 min. Third, 100 mL of supernatant was separately sampled after 30 min settlement to further analyze the removal rates of TN, TP, PO_4^{3-}-P, organic phosphorus, COD, SS and carbohydrates.

2.3. Pilot-scale process for ACS production

The pilot-scale process for valorization of CAPW as ACS was illustrated as shown in Fig. 1. The CAPW (20 m^3) was pumped into the flocculation tank (volume: 30 m^3) and then PAC (dosage: 20%), perlite (dosage: 0.2 kg/m^3) were added in turn after adjusting the pH to 9.5 by calcium oxide suspension. Stirring slowly 30 min for the above reaction process, the solid-liquid mixture was separated via the plate and frame filter press (filtration pressure: 0.2−0.3 MPa, average flow rate: 2.02 m^3/h, volume: 0.2 m^3, filtration ratio: 97%). And then the filtrate was pumped into the buffer tank 1 (volume: 25 m^3) while the filter cake (yield: 6.1 kg/m^3, water content: 56%) was transformed into the mud bucket via belt conveyor.

Subsequently, the filtrate in buffer tank 1 was further concentrated 20 times based on the COD concentration by an evaporator (Nanjing Delei Environmental Protection Equipment Co., Ltd, volume: 1.5 m^3) and then was pumped in the buffer tank 2 (volume: 2 m^3). During concentration process, the filtrate was heated by high-temperature condensate water (80−90 °C, COD < 50 mg/L) from the thermal power plant via a heat exchanger (volume: 0.5 m^3). Furthermore, the heated filtrate (flow rate: 32 m^3/h) was circularly pumped into the upper edge of the evaporator and then flowed naturally downward while the air blower (wind pressure: 200 Pa) at the bottom of the evaporator was producing continuous aeration (evaporation capacity: 0.3 m^3/h, average power consumption: 51.3 (kw·h)/m^3). The inlet dry air, which was comprehensively in contact with the heated filtrate, evaporated and removed moisture in the form of warm and humid air.

Ultimately, the insoluble matter in buffer tank 2 produced in a concentration process was separated by a horizontal screw centrifuge (volume: 0.05 m^3, centrifugal force: $5,800 \times g$). The supernatant was pumped into the ACS tank (2 m^3) while the centrifugal residue (yield: 52.63 kg/m^3, water content: 81%) was transformed into mud bucket mixed with filter cake as mixture (water content: 60%). After concentration process, the low-temperature condensate water (40−45 °C), satisfying emission standard, was discharged from heat exchanger.

2.4. Performance of ACS for BNR in pilot-scale

The performance of ACS for BNR was evaluated by an anaerobic-anoxic-oxic (A^2/O) process in WWTPs (Wuxi Shuofang Wastewater Treatment Plant, Jiangsu, China). The A^2/O process comprised of anaerobic, anoxic and aerobic sections with the load volume of 900,
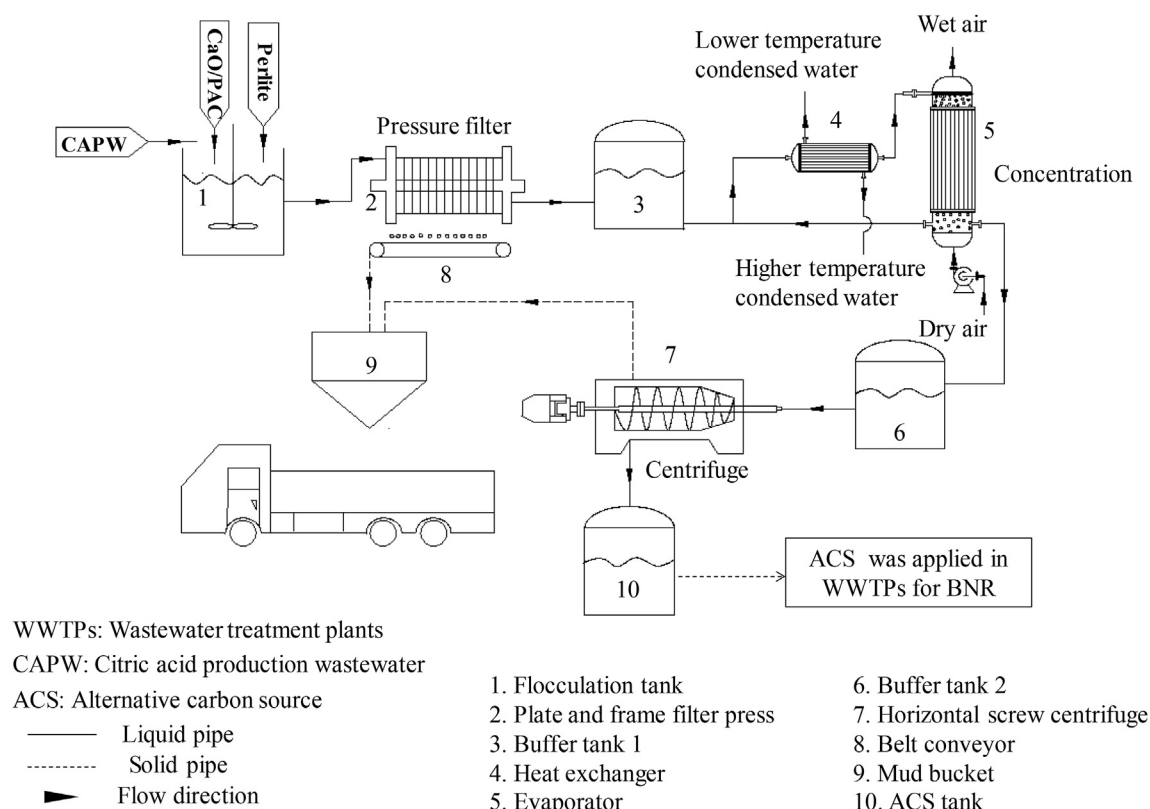
Fig. 1. Pilot-scale process for valorization of citric acid production wastewater as alternative carbon source.

900, and 2,800 L, respectively (Liu et al., 2018). The experiment procedures were divided into three periods: in which, without addition carbon source in period I, sodium acetate added in period II and ACS added in period III, correspondingly. The concentrations of TN, TP, COD and NH_4^+-N of A^2/O process in the influent and effluent, anaerobic, anoxic, aerobic and sedimentation tanks, were analyzed daily. The performance differences for BNR between sodium acetate and ACS were compared. Detailed operating parameters in different operational periods are listed in Table 1.

2.5. Analytical methods

The concentrations of total solids (TS), volatile solids (VS), mixed

Table 1
Operating parameters of anaerobic-anoxic-oxic (A^2O) process in different operational periods.

Parameters	Period I	Period II	Period III
Influent flow (L/d)	10,000	10,000	10,000
MLSS (g/L)	4.5 ± 0.26	4.6 ± 0.52	4.2 ± 0.39
Sludge recycle ratio (%, v/v)	100	100	100
Nitrification liquid reflux ratio (%, v/v)	200	200	200
Hydraulic retention time (h)	11.2	11.2	11.2
Sludge residence time (d)	25	25	25
DO aerobic section (mg/L)	2.5−3.5	2.5−3.5	2.5−3.5
Temperature (°C)	13−19	12−21	11−18
Carbon source[a] (mg/L)	0	25	25
TN increment[b] (mg/L)	0	0	0.3
TP increment[c] (mg/L)	0	0	0.02
Operation time (d)	7	14	14

[a] Additional amount of carbon source was calculated using COD as the reference. Period II: sodium acetate added (25 mg/L); Period III: ACS added (25 mg/L).
[b] and [c]: Increments of TN and TP in period III were due to the alternative carbon source (ACS) containing a small amount of nitrogen and phosphorus.

liquor suspended solids (MLSS), NH_4^+-N, PO_4^{3-}-P, TP, TN, COD, BOD_5 and pH were conducted following standard methods (APHA, 1998). The concentrations of protein, carbohydrate, reducing sugar and calcium ion (Ca^{2+}) were measured separately using Coomassie Brilliant Blue G250 (Le et al., 2016), phenol-sulfuric (Dubois et al., 1956), dinitrosalicylic acid (Miller, 1959) and EDTA titration (Kim and Vipulanandan, 2003), respectively. The element components were analyzed by energy dispersive spectrometer (SU1510, Hitachi, Japan). To measure SCOD, soluble protein and soluble polysaccharides, the samples were first centrifuged at 8,000 rpm for 15 min (centrifuge 5804 R, Eppendorf, Germany) and then were filtered with 0.45 μm membrane. The visible SS in the CAPW was observed by ordinary light microscope (Olympus, CX31RTSF, Japan).

The organic acid concentration was determined by high-performance liquid chromatography (UltiMate-3000, Dionex, USA), which equipped with a UV detector (206 nm) and AQ chromatographic column (250 × 4.6 mm, 5 μm). The mobile phase was a mixed solution (pH = 2.45) of methanol and potassium dihydrogen phosphate (10 mM) (v:v = 95:5). The flow rate was 1.0 mL/min and the column was operated at 25 °C. The approach was an external standard method and the standard samples were citric, maleic, malic, oxalic, α-ketoglutaric, lactic, fumaric, succinic, acetic and propionic acid, respectively.

All measurements were carried out in triplicate, and the results presented as mean ± standard deviation.

3. Results and discussion

3.1. Influence of pH and PAC dosage on nitrogen and phosphorus removal

The pH can directly affect the performance of calcium phosphate

formation and calcium oxide flocculation (Tran et al., 2014). Thus, an optimal pH for the removal of nitrogen and phosphorus in CAPW should be determined. As shown in Fig. 2a, the optimal removal rates of TP, PO_4^{3-}-P, organic phosphorus, SS, TN and COD (84.2%, 99.7%, 37.1%, 85.0%, 14.3% and 14.2%, respectively) were all observed at pH 9.5. Additionally, the removal rates of COD and SS were positively correlated under different pH conditions and the SS was consisted of residual tiny *Aspergillus niger* mycelium fragment based on the microscopic analysis as shown in Fig. S1. Thus, the more SS (insoluble COD) removed at pH 9.5 could further improve the biodegradability and quality of ACS. Eventually, the optimal pH condition of nitrogen and phosphorus removal was determined at 9.5.

PAC as a flocculants was introduced to deeply remove the SS which contains organic phosphorus and organic nitrogen. The optimal dosage of PAC should be determined because the flocculation performance of PAC is related to water quality conditions and the dosage (Edzwald, 1993). For the sake of the efficient SS removal performance and less carbon source loss with minimum PAC dosage, the influence of various PAC dosages on the removal of TP, COD, TN, carbohydrate and SS was investigated as shown in Fig. 2b. Results illustrated that the 40% and 80% of PAC dosages could significantly improve the removal performance of SS compared with that of 0% of PAC dosage, but the carbohydrate was also excessive removed. Excessive dosage of PAC would cause a large amount of organic matter loss to reduce the quality of carbon source and increase the cost of raw material. Nevertheless, the 10% PAC dosage was not obvious for SS removal. Balancing the performance and cost, 20% of PAC was determined as the optimal dosage. In such case, the removal rates of TP, COD, TN, carbohydrate and SS were 90.4%, 17.0%, 15.2%, 19.3% and 92.1%, respectively. The CAPW treated by calcium oxide and PAC could almost completely remove TP and further increase the ratio of COD/TN.

3.2. Process evaluation in pilot-scale

Pilot-scale production for ACS was carried out according to process established in section 2.3. The detailed components of CAPW, filtrate and ACS were analyzed as summarized in Table 2. It displays that the organic components of BOD of ACS were mainly organic acids and carbohydrates. Additionally, 92.6% of TP, 22.2% of TN and 13% of COD were separately removed during pressure filtration, which was better than that of lab-scale (Fig. 2). The result implied that the process was feasible in pilot-scale. The stability of the process was also evaluated through 10 production batches. The average removal rates of TP, SS, TN, COD and carbohydrates were 92.1 ± 1.02%, 96.1 ± 0.94%, 16.1 ± 1.08%, 11.0 ± 1.07% and 13.2 ± 1.06%, respectively.

High-concentration filtrate could reduce transportation costs and improve the organic matter concentration of ACS, which would improve the storage capacity (reduction storage area and extension shelf life) to promote ACS into a commercial product. A balanced consideration of transportation and concentration costs, 20 times could be used as the reference of concentration multiple. At the end of concentration process, the ratios of COD/TN, COD/TP and BOD_5/COD in ACS were up to 83.4, 1,304 and 0.78, respectively.

The changes related to concentrations of nitrogen, phosphorus and COD during concentration were described as shown in Table 2. In terms of the change of nitrogen, partial NH_4^+ was converted to free ammonia given the initial pH of 9.5. Numerous dry air bubbles were introduced from the bottom of the evaporator. Thus partial NH_4^+-N was stripped (Wang et al., 2010; Zhu et al., 2017) resulting in the concentration multiple of 10.1. Furthermore, 0.03% (v) of CO_2 in the dry air can be partially dissolved in the liquid phase to produce a small amount of calcium carbonate precipitate and to gradually change the pH to 5.7 at the end of the concentration operation. During the concentration process with continuous heating and gradually decreasing pH value, partial proteins underwent thermal irreversibly denaturation and/or isoelectric precipitation, which lead to the protein removal after concentration (Yang and Langer, 1985; Jablonka and Munro, 1985). The reaction loss of NH_4^+-N and soluble proteins would elucidate the concentration multiple (17.1) of TN.

In terms of the changes of COD and phosphorus, the concentration multiple of TP, PO_4^{3-}-P and carbohydrate was close to 20 because these indexes were difficult for phase transfer to cause reaction loss. Water reduction in the concentration process led to the partial salt precipitation produced by combining organic acids with calcium ions causing small amount of COD loss. The concentration multiple (14.7) of reducing sugar lower than 20 can be explained as follow. High temperature (80–90 °C) can cause Maillard reaction between partial amino acids and reducing sugars thereby decreasing the amount of reductive aldehyde and ketone groups (Ajandouz et al., 2010; Cho et al., 2010), and may also cause part of the polysaccharide hydrolyzed into oligosaccharides and
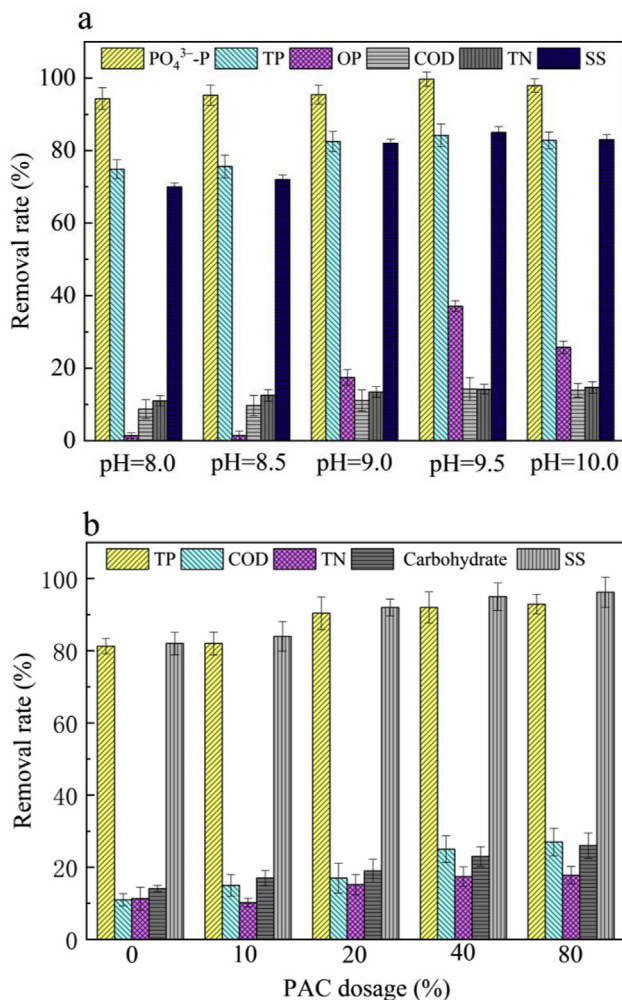

Fig. 2. (a) Removal rates of PO_4^{3-}-P, TP, organic phosphorus (OP), COD, TN and SS at different alkaline pH adjusted by calcium oxide suspension; (b) Removal rates of TP, COD, TN, carbohydrate and SS at different PAC dosages after adjusting the pH to 9.5 by the calcium oxide suspension. The concentrations of CaO and PAC were 100 and 300 g/L. The PAC dosage was calculated as the weight percentage of suspended solids in citric acid production wastewater.

Table 2
Components analysis of citric acid production wastewater (CAPW), filtrate and alternative carbon source (ACS) during the process for valorization of CAPW.

Parameters	CAPW	Filtrate	ACS	Concentration multiples
pH	4.7 ± 0.3	9.57 ± 0.6	5.71 ± 0.41	/
TN (mg/L)	338 ± 29	263 ± 17	$4,500 \pm 321$	17.1
TP (mg/L)	187 ± 17	13.9 ± 0.11	289 ± 22	20.8
NH_4^+-N (mg/L)	66 ± 5.4	77.8 ± 3.2	786 ± 15	10.1
PO_4^{3-}-P (mg/L)	163 ± 11.5	1.03 ± 0.02	19.6 ± 2.1	19.0
Calcium ion (mg/L)	670 ± 87	940 ± 45	$16,536 \pm 211$	14.2
Carbohydrate (mg/L)	$7,200 \pm 800$	$6,500 \pm 247$	$131,000 \pm 734$	20.2
Reducing sugar (mg/L)	$3,500 \pm 286$	$2,537 \pm 96$	$37,320 \pm 167$	14.7
Soluble protein (mg/L)	71 ± 6.1	49.1 ± 2.7	785 ± 69.8	16.0
Total organic acid[a] (mg/L)	$10,232 \pm 366$	$8,065 \pm 373$	$122,600 \pm 1,832$	15.2
Propionic acid (mg/L)	$2,406 \pm 16$	$2,405 \pm 31$	$36,440 \pm 234$	15.1
Citric acid (mg/L)	$2,350 \pm 24$	$1,787 \pm 41$	$31,000 \pm 261$	17.3
Lactic acid (mg/L)	$1,842 \pm 20$	$1,904 \pm 27$	$23,600 \pm 234$	12.4
Malic acid (mg/L)	916 ± 25	788 ± 25	$12,900 \pm 134$	16.3
Succinic acid (mg/L)	$2,320 \pm 11$	802 ± 29	$11,800 \pm 321$	14.7
Acetic acid (mg/L)	360 ± 10	344 ± 28	$6,414 \pm 26$	18.6
Maleic acid (mg/L)	21.0 ± 1.8	20.9 ± 1.2	270 ± 32	12.9
Oxalic acid (mg/L)	8.7 ± 1.1	6.9 ± 0.8	95 ± 11	13.8
Fumaric acid (mg/L)	8.7 ± 0.8	7.5 ± 0.6	93.0 ± 12	12.4
COD (mg/L)	$21,700 \pm 298$	$18,879 \pm 220$	$377,000 \pm 5,510$	20.0
BOD_5 (mg/L)	$11,501 \pm 90$	$12,271 \pm 162$	$294,000 \pm 4,966$	24.0
BOD_5/COD	0.53 ± 0.03	0.65 ± 0.01	0.78 ± 0.02	/

[a] Total organic acid was equivalent to the sum of the measured organic acids.

monosaccharides to promote the utilization efficiency of microorganisms (Miyazawa and Funazukuri, 2005), which can be an explanation for the ratio of BOD_5/COD of ACS increased from 0.65 to 0.78 during concentration process.

The feasibility of solid matter, which was produced in two-step solid-liquid separation during ACS production, as acidic soil conditioner contains trace phosphorus (ASCP) was evaluated. Calcium oxide, calcium carbonate and perlite as soil conditioner and calcium phosphate as a fertilizer have been extensively proved (Rajan, 1981; Su et al., 1994; Chassapis et al., 2010; Ahmad et al., 2014; Szögi et al., 2006). The main components of perlite are silica, aluminum oxide, potassium oxide, sodium oxide, iron oxide, calcium oxide and magnesium oxide (Irani et al., 2011; Rodríguezsalgado et al., 2016).

The relative amounts of water content, TS, VS/TS and ash/TS in the solid matter were 60%, 40%, 5.9% and 94.1%, respectively. It was indicated that the solid matter had great capacity of transportation and storage. Table 3 listed the relative ratios of the known elements in ash of solid matter. Ca (35.94%), O (32.36%), P (8.79%), Si (7.32%) and C (6.91%) were the top five abundant elements and the total percentage exceeded 90%. According to the supplementary material and reaction involved during ACS production, the main components of solid matter can be inferred as calcium phosphate, calcium oxide, perlite and a minimal amount of organic matter. Therefore, the solid matter had the potential to act as an ASCP.

Table 3
Relative proportions of the known elements in ash of solid matter.

Elements	Ratios (%, w/w)	Elements	Ratios (%, w/w)
Ca	35.94	Cu	0.89
O	32.36	Zn	0.76
P	8.79	K	0.71
Si	7.32	Mn	0.70
C	6.91	S	0.66
Al	1.58	Cl	0.52
Mg	1.27	Ti	0.47
N	1.16	Na	0.18
Fe	0.94		

Note: Solid matter was obtained via two-step solid-liquid separation during the process for valorization of citric acid production wastewater.

3.3. Performance evaluation of ACS for BNR

To evaluate the performance of ACS for BNR, the ACS was added into the anoxic tank of A^2/O process while the sodium acetate was used as the control. Fig. 3 showed the concentrations of COD, TN, TP and NH_4^+-N and their removal rates in different periods. Before adding carbon source, the average concentrations of COD, TN, NH_4^+-N and TP in A^2O effluent were 35.9, 16.9, 2.73 and 0.48 mg/L, in which the concentration of TN was only slightly exceeded the emission standard of China (COD $\leq$ 50 mg/L, TN $\leq$ 15 mg/L, NH_4^+-N $\leq$ 5 mg/L, TP $\leq$ 0.5 mg/L). Theoretically, the removal of 1 mg NO_3^--N requires 2.86 mg of COD to provide the electron donor for denitrification process (Bernat et al., 2012). However, the growth of microorganisms itself consumes part of COD, thus 6–8 mg COD is required for 1 mg NO_3^--N removal (Zhang et al., 2013; Chen et al., 2017). In the subsequent work, sodium acetate or ACS (25 mg/L, calculated as COD) was continuously fed into the anoxic tank to enhance the performance of nitrogen removal.

The data depicted in Fig. 3b and c indicated that sodium acetate as carbon source can quickly enhance the removal performance of TN and TP, which was in agreement with the results of Liu et al. (2018). The average concentrations of TN and TP in effluent were decreased to 11.76 and 0.26 mg/L, and the average removal rates of TN and TP were increased by 15.9% and 5.5% in comparison with that of period of without carbon source. Notably, the microorganisms had a short adaptation period (approximately 4 days) after adding the ACS in 21 days resulting in the TN in effluent did not satisfy the discharge standard (Fig. 3b). After 25 days, the microorganisms gradually adapted to the ACS, thus the performance of TN removal was gradually stabilized while meeting the discharge standard. Meantime, the removal rate (64.1%) and concentration (12.22 mg/L) of TN were slightly lower than that of sodium acetate addition. Nitrogen removal efficiency with the different carbon sources could be calculated given the data in Fig. 3b. Removing 1.0 mg TN required a 5.41 mg COD-equivalent of ACS or 4.92 mg COD-equivalent of sodium acetate. Part of polysaccharide in ACS should be hydrolyzed initially into monosaccharides before it could be used as an electron donor of denitrifying bacteria. Therefore, the electronic utilization efficiency was slightly lower than that of sodium acetate.
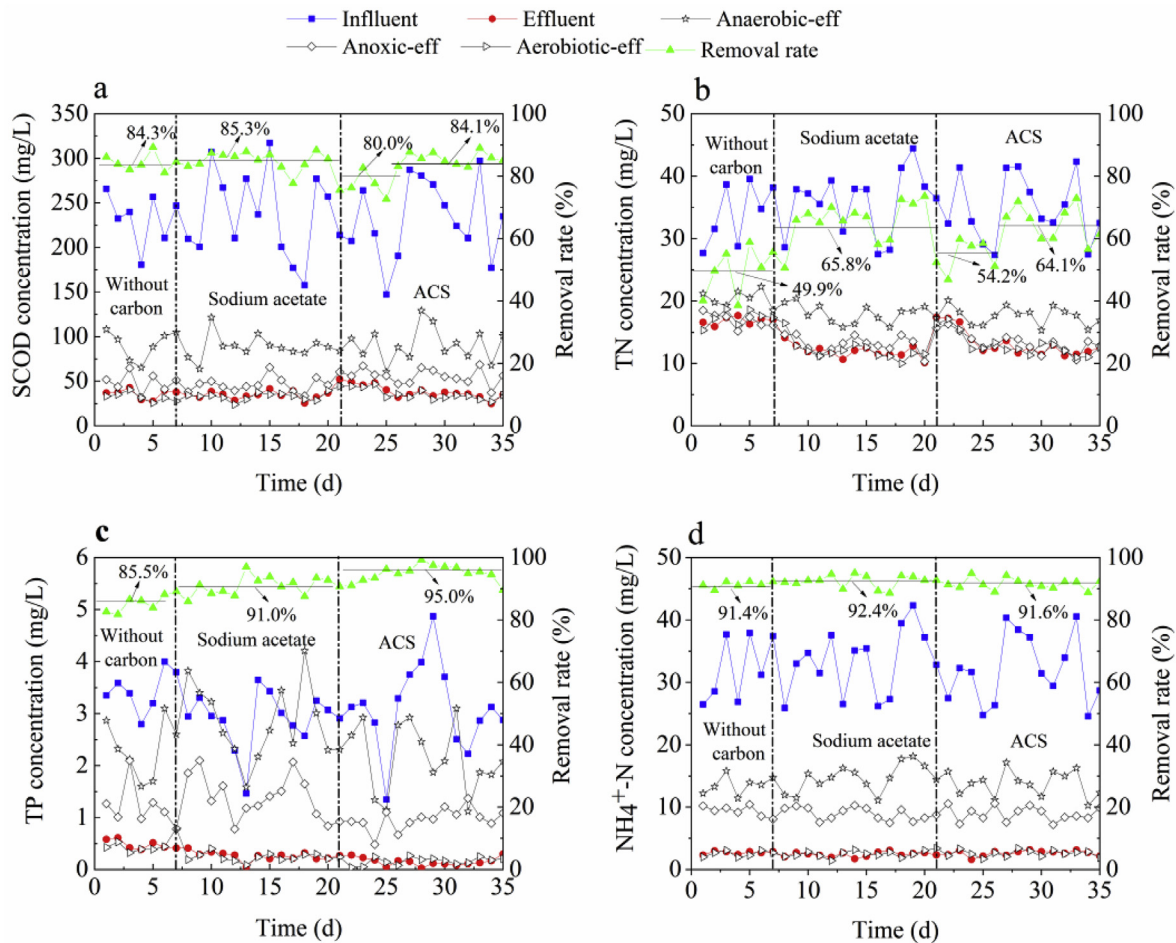
Fig. 3. Concentrations of SCOD (a), TN (b), TP (c) and NH_4^+-N (d) at different sections and their removal rates. The dosages of sodium acetate and ACS were all 25 mg/L (calculated as COD).

Fig. 3c illustrated that the removal performance of TP after ACS added became more efficient than that of sodium acetate added. Some residual ions (Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}) in the ACS enhanced the removal performance of phosphorus via precipitation reaction. Fig. 3a and d displayed NH_4^+-N and COD were insignificantly affected by ACS or sodium acetate because the nitrobacteria are autotrophic bacteria (Prosser and Nicol, 2012) whereas the addition amount of carbon source was lower than the carbon source carried by wastewater itself.

3.4. Economic feasibility analysis

To investigate the economic potential of the process for valorization of CAPW as ACS, the economic feasibility of two CAPW treatment processes, proposed in this study and anaerobic-aerobic treatment, were analyzed. In this economic assessment scenario, high-temperature condensate water could be supplied free and adequately. Thus, the heat source cost of concentration process for ACS production and the temperature preservation cost of anaerobic process were all excluded. In terms of costs, some production costs including equipment depreciation, energy consumption and supplementary material were calculated. However, the non-production costs (such as labor and management cost) were related to scale and automation of equipment, thus, they were not analyzed owing to hardly to calculate in pilot-scale.

The value of ACS would be estimated based on the price of sodium acetate in the Chinese market. The price calculation process of ACS was as follows. The price of sodium acetate (purity 99.9%, w/w) is approximately 507 USD/t, and the COD concentration of sodium acetate can be calculated as 780 kg/t based on the COD equivalent (0.78 kg/kg). Thus, the price of COD for sodium acetate can be calculated as 0.65 USD/kg. Additionally, the ratio of the COD price in sodium acetate to ACS can be calculated as 1.1 owing to the result of removing per mg TN requiring 5.41 mg COD-equivalent of ACS or 4.92 mg COD-equivalent of sodium acetate (Section 3.3). The price of per cubic meter ACS (COD: 377 kg/m³) could be calculated as 223 USD/m³. Ultimately, the price of ACS was set as 178.4 USD/m³ (deduction 20% profit) considering the promotion costs.

Taking 20 m³ of CAPW treated per day as an example, the economic feasibility for the two processes were analyzed as summarized in Table 4. The net profit for ACS produced by CAPW was 4.6 USD/m³. However, the net profit for biogas and AGS production was only 0.4 USD/m³. It is indicated that the process for valorization of CAPW as ACS had more significant economic benefits. In addition, methanol as a cheaper carbon source has comparable denitrification potential compared with that of sodium acetate. Removing per gram nitrogen requiring 4.76 gCOD supplied by methanol was investigated by Li et al. (2020). The value of per cubic meter ACS was estimated as 106.8 USD/t based on the market price (purity 99.9%, w/w; 480 USD/t) and the denitrification potential of methanol. The net

Table 4
Comparison of the economic feasibility of the two processes for treatment 20 m^3 of citric acid production wastewater (CAPW) per day.

	Parameters	Process I (ACS)[a]	Process II (Biogas and AGS)[b]
Productive costs	Equipment depreciation[c] (USD/d)	−9.6	−8.0
	Biogas purification[d] (USD/d)	\	−30.6
	Supplementary materials[e] (USD/d)	−5.8	−1.2
	Electric energy[f] (USD/d)	−71.8	−0.35
	CAPW treatment after anaerobic fermentation[g] (USD/d)	0	−4.6
	Total (USD/d)	−87.2	−44.8
Incomes	AGS[h] (USD/d)	\	+8.9
	ACS or methane[i] (USD/d)	+178.4	+44.1
	Total (USD/d)	+178.4	+53
Profits[j]	Net (USD/d)	+91.2	+8.2
	Net (USD/m^3)	+4.6	+0.4
	Profit rate (%)	+51.1%	+15.5%

Note: the concentration costs during ACS production was only power consumption (pump and blower) taken into account, because the heat source was free and surplus. Process I: the process for valorization of citric acid production wastewater as alternative carbon source. Process II: the process for anaerobic-aerobic biological treatment of citric acid production wastewater.

[a] ACS: Alternative carbon source.
[b] AGS: Anaerobic granular sludge.
[c] The costs of equipment (equipment life is 10 years) for Processes I and II were approximately 35000 USD and 29000 USD.
[d] The yield of biogas was 10.2 m^3/m^3, and the cost of biogas purification was 0.15 USD/m^3 (Liu et al., 2018).
[e] Process I, the dosages of CaO, PAC, and perlite were 2.1, 0.08 and 0.2 kg/m^3, correspondingly, and the prices of CaO, PAC, and perlite were 110, 170, and 220 USD/t, respectively; Process II, the dosage and price of NaOH were 0.156 kg/m^3 and 370 USD/t, correspondingly.
[f] The average electric energy consumptions, pump and blower, in Processes I and II were 51.3 and 0.25 (kw·h)/m^3, respectively, and the price of electric energy was 0.07 USD/(kw·h).
[g] The cost of CAPW treatment after anaerobic fermentation was 0.23 USD/m^3, which included aerobic biological treatment cost (0.07 USD/m^3), effluent charge for WWTPs (0.15 USD/m^3) and the sludge disposal costs (0.01 USD/m^3). Subsequent sludge disposal can be directly incinerated in thermal power plants, thus, the cost of dewatering was only considered.
[h] The yield and price of AGS (water content was 91%) were 3.8 kg/m^3 and 117.6 USD/m^3, respectively.
[i] The price of ACS was 178.4 USD/t; The yield of biogas was 10.2 m^3/m^3. The price and ratio of methane in biogas were 0.36 USD/m^3 and 60%, correspondingly.
[j] The profit calculation value was high mainly because only the production costs was considered and the non-production costs was excluded.

profit and profit rate was calculated as 0.98 and 18.4%. Although the economic benefits would be reduced by about 63% as compared in Table 4, the economic feasibility of the process would also be optimistic. The main limitation for the widespread application of methanol is the potential safety hazard given its transportation, handling and storage. According to our survey, WWTPs in the Yangtze River Delta of China rarely use methanol, but mostly use liquid or solid sodium acetate. To satisfy the safety standards regarding the use of a non-flammable, nonhazardous product, 25−31% additional capital is required to construct the methanol storage, pumping and delivery systems (Pelaz et al., 2018).

The economic benefits of the process were also estimated on the assumption that the heat source cannot be obtained freely. Multi-effect evaporator or mechanical vapor recompression would be selected as the concentration equipment, and commercial stream would be used as the heat source. Assume that 0.25 ton steam is required for each ton of water evaporated, and the price of steam is about 29.4 USD/t in the Chinese market. The electric energy consumption of air blower can be dropped by about 80% compared with that of the process using high-condensate water as heat source. The net profit of the process would be estimated as 0.45 USD/m^3. The process would become unprofitable if the non-production costs (such as labor and management costs) were further considered.

Honestly, the process of ACS production had certain limitations, and it was applicable to the places like citric acid production plants with sufficient waste heat source. However, considering the huge energy demand in China's densely populated areas, many power plants driven by coal, natural gas or biomass waste were established in the surrounding to satisfy energy required. Meantime, various forms of waste heat sources (e.g., waste steam and hot water) would be generated. The great environmental benefits can be generated, if these waste heat sources could be effectively utilized to deal with the high concentration fermentation wastewater.

4. Conclusions

A pilot-scale process for valorization of CAPW as ACS was established to relieve the wastewater pollution issue. The performance of ACS for BNR was close to sodium acetate, which can further decrease the demand of chemical carbon source for BNR. The removal efficiencies of TN and TP with ACS and sodium acetate added were 64.1%, 95.0% and 65.8%, 91.0% under the same operating conditions, respectively. Overall, the process proposed in this study provides a profitable case that is contributed to the treatment of high-concentration fermentation wastewater.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Wenhao Liu: Validation, Software, Investigation, Methodology. **Zhiyong Zheng:** Conceptualization, Supervision, Methodology, Validation, Visualization, Writing - review & editing. **Fuxin Sun:** Resources, Investigation. **Maodong Miao:** Resources, Investigation. **Min-Hua Cui:** Writing - review & editing. **Hongbo Liu:** Writing - review & editing. **Huimin Zhang:** Writing - review & editing. **Cheng Zhang:** Resources, Investigation. **Zhijie Hu:** Resources, Investigation. **He Liu:** Conceptualization, Supervision, Methodology, Validation, Visualization, Writing - review & editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2020.120576.

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