Carbon capture for blackwater: chemical enhanced high-rate activated sludge process

Haixin Jiang, Xianchun Tang, Yexuan Wen, Yi He and Hongbin Chen

ABSTRACT

Blackwater has more benefits for carbon recovery than conventional domestic wastewater. Carbon capture and up-concentration are crucial prerequisites for carbon recovery from blackwater, the same as domestic wastewater. Both chemical enhanced primary treatment (CEPT) and high-rate activated sludge (HRAS) processes have enormous potential to capture organics. However, single CEPT is subject to the disruption of influent sulfide, and single HRAS has insufficient flocculation capacity. As a result, their carbon capture efficiencies are low. By combining CEPT and HRAS with chemical enhanced high rate activated sludge (CEHRAS) process, the limitations of single CEPT and single HRAS offset each other. The carbon mineralization efficiency was significantly influenced by SRT rather than iron salt dosage. An iron dosage significantly decreased chemical oxygen demand (COD) lost in effluent. Both SRT and iron dosage had a significant influence on the carbon capture efficiency. However, HRT had no great impact on the organic mass balance. CEHRAS allowed up to 78.2% of carbon capture efficiency under the best conditions. The results of techno-economic analysis show that decreasing the iron salt dosage to 10 mg Fe/L could promise profiting for blackwater treatment. In conclusion, CEHRAS is a more appropriate technology to capture carbon in blackwater.

Key words | blackwater, carbon capture, carbon recovery, chemical enhanced high-rate activated sludge process, chemical enhanced primary treatment technology, high-rate activated sludge process

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INTRODUCTION

Currently, carbon recovery from domestic wastewater is a hot topic in the field of environmental science and engineering. In addition to classical anaerobic digestion, a variety of new carbon recovery technologies such as carboxylate platform (De Groof *et al.* 2019), bioplastic production (Mannina *et al.* 2019) and microbial electrosynthesis (Glaven 2019) have been investigated and developed. However, the low carbon concentration in domestic wastewater increases the specific capital and operational costs, and sometimes results in low recovery efficiency. In general, organic concentration is lower than 500 mg/L because of the conventional centralized collection and transportation system. Thereafter, up-concentration technologies are needed to capture carbon from domestic wastewater (Alloul *et al.* 2018; Guven *et al.* 2019; Orhon *et al.* 2019; Rahman *et al.* 2019).

Owing to source separation, >50% of organics is collected in blackwater with only 1/3 volume ratio to total domestic wastewater (Henze *et al.* 2008). As a result, blackwater has higher organic concentration than domestic wastewater. In this case, blackwater is more appropriate for recovering carbon. In a vacuum collection system, chemical oxygen demand (COD) concentration of blackwater can reach >10,000 mg/L (Gao *et al.* 2019), which is fitted for using anaerobic technologies directly, like anaerobic digestion and fermentation, to recover carbon as CH_4 and volatile fatty acids (VFAs). It seems that up-concentration technologies are unnecessary for blackwater. However, due to the maintenance and noise problems and higher costs, vacuum collection systems are seldom adopted in practice. Gravity collection systems are still more popular. With flush toilets, COD in faeces is diluted to ~1,000 mg/L in real blackwater (Hocaoglu & Orhon 2013; Zhang *et al.* 2017). In addition, pipe misconnection problems could decrease COD concentration further to <800 mg/L (Ren

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et al. 2018; Tolksdorf et al. 2018), which is close to the medium value of raw municipal wastewater (750 mg/L) (Henze et al. 2008). These organic concentrations are much lower than thickened primary and wasted sludge fed to anaerobic digestion tanks for CH_4 production (Tchobanoglous et al. 2014). The same as for traditional domestic wastewater, carbon capture and condensation are crucial prerequisites for organics recovery from blackwater.

It has been found that some old technologies, such as chemical enhanced primary treatment (CEPT) and high rate activated sludge (HRAS) processes, emerge as a strong prospect for carbon capture. Dosing 20 mg Fe/L of $FeCl_3$ to domestic wastewater with total COD (tCOD) = 451 mg/L, CEPT could remove 75.6% organic matter, and 27% of influent organics could be recovered as VFAs via sludge fermentation (Lin et al. 2017). Blackwater has a high percent of colloidal COD (cCOD) and particulate COD (pCOD). Theoretically, cCOD and pCOD could be completely flocculated and captured by CEPT. However, the sCOD capture efficiency of CEPT is limited by negligible adsorption function. High-rate activated sludge (HRAS) processes have gained more and more attention as pre-concentration technologies because of their capability to capture sCOD, cCOD and pCOD. Attributed to low SRT and HRT, the hydrolysis of hydrolysable COD and the endogenous respiration of biomass are limited to a large degree. As such, the mineralization of COD is minimized as far as possible, which promises a higher carbon capture efficiency (Meerburg et al. 2016; Rahman et al. 2016). Treating high-strength raw municipal wastewater (tCOD = 450–800 mg/L), at the average 0.22 d SRT condition, both the conventional high-rate activated sludge (HRCAS) process and high-rate contact stabilization process (HRCS) had similar carbon capture behavior (42–43%) and thus similar potential for energy recovery (Rahman et al. 2019). At an optimal SRT between 0.5 and 1.3 d, contact time of 15 min, and stabilization time of 40 min, the HRCS system recovered up to 55% of incoming organics in sludge with 10% influent COD mineralized (Meerburg et al. 2016). Gravity clarifiers are regularly used to separate solids and liquid for HRAS. However, collision efficiency, floc formation and floc strength are limited by low sludge concentration, immature microbial community and low EPS production and its composition (Van Winckel et al. 2019). Therefore, solids separation is dramatically hindered in HRAS, and results in the observed yields were only 9–43% (Orhon et al. 2019).

There are some remedies to avoid limitation of solids separation: (1) return excess sludge from biological nutrient removal (BNR) system to HRAS, increasing the protein/polysaccharide ratio in EPS to promote colloid efficiency (Van Winckel et al. 2019); (2) directly replace clarifier to membrane filtration, forming a superfast MBR (SFMBR) (Sözen et al. 2017; Orhon et al. 2019); and (3) dose chemical flocculant or coagulant to HRAS, combining as a chemical enhanced HRAS (CEHRAS) (Cagnetta et al. 2019). For the first one, there is no need to dose chemicals, but it predominantly overcomes the flocculation limitation caused by the lower protein/polysaccharide ratio rather than the destabilization and coagulation problems (Van Winckel et al. 2019). Meanwhile, it brings up a floc strength limitation. Additionally, enough excess sludge is required, and what is contradictory is that the sludge production will be lower in future mainstream anammox systems. SFMBR could almost retain full suspended solids, achieving an excellent solids separation. Membrane systems consistently yield much higher observed yields of 50–60% (Orhon et al. 2019). The perspectives of SFMBR will depend heavily on major breakthroughs in new membrane materials, which should work with less fouling and clogging as well as low energy consumption and operational costs. Unfortunately, no breakthroughs in these aspects have occurred in some decades (Hao et al. 2018). Generally, the aggregation of colloidal particles in wastewater is limited by insufficient destabilization and coagulation. Dosing a small amount of Fe salt to HRAS is helpful to lessen the surface charge and compress the diffuse electric layer. Subsequently, destabilization and coagulation are completed, and the floc formation problem is resolved. Dosing 20–40 mg Fe/L of iron salt and a little polymer, the HRAS-DAF system allowed up to 78% removal of influent solids, and the HRCS-DAF 67% (Cagnetta et al. 2019). Furthermore, Fe salt can enhance the removal of phosphorus to form vivianite mineral. With aeration, CEHRAS could inhibit the reduction of Fe^{3+} to Fe^{2+} to form FeS (Rebosura et al. 2018), and the effectiveness of Fe salt is improved. In a word, CEHRAS is a more appropriate technology to capture carbon in wastewater.

To the best of our knowledge, CEHRAS aimed at organic matter recovery has been seldom reported, especially in blackwater. Information about operational conditions to optimize for higher carbon capture efficiency with lower energy or chemical cost is little-known. Firstly, this paper characterized blackwater fractions from two dimensions: the particle size distribution and biodegradable property. Then, a comprehensive investigation of single CEPT, single HRAS and CEHRAS was conducted. The impact of Fe salt dosage, SRT and HRT on the CEHRAS performance for carbon capture was evaluated. Meanwhile, the advantage of CEHRAS in capturing carbon and phosphorus simultaneously was also highlighted. Lastly, operational efficiencies and costs were compared among single CEPT, single HRAS and CEHRAS.

MATERIAL AND METHODS

Reactor setup

HRAS and CEHRAS reactors were operated as SBR procedures. The SBR comprised a conical plastic reactor with a working volume of 8 L, air pump, overhead stirrer, and peristaltic pumps for influent, Fe salt dosing, excess sludge and effluent (Figure S1 in the Supplementary Data file). The volume exchange rate was 50%. SBR operational steps consisted of fill wastewater with Fe salt dose, react (aerate), sludge waste, settle, decant and idle periods. The cycle times were controlled by microcomputer time controller (Figure S1). The total cycle time was 120 min. Fill, waste, settle and decant times were fixed at 5 min, 5 min, 60 min, and 15 min, respectively, while react and idle times were changed with HRT.

CEPT tests were carried out in jars. 1 L wastewater was feed with a range of Fe salt ($FeCl_3 \cdot 6H_2O$, 0, 10, 20 and 30 mg Fe/L). This was stirred fast for 1 min, immediately, then slowly stirred for 14 min and settled for 60 min.

Wastewater characteristics and operational conditions

The feed to the reactor was collected from the grilled influent of the blackwater module in the SEMIZENTRAL Resource Recovery Centre, Tsingtao, China, a demonstration project of Sino-German cooperation (Ren *et al.* 2018; Tolksdorf *et al.* 2018). The regular wastewater characteristics are listed in Table 1; because of the occurrences of blackwater and greywater pipeline misconnections, the contaminant concentrations in blackwater were lower than regular level. The biodegradable COD estimation procedure is exhibited in section 2 of the Supplementary Data file.

Three operational parameters were investigated (Table S1 in the Supplementary Data file): Fe salt ($FeCl_3 \cdot 6H_2O$) dosage, 0, 10, 20 and 30 mg Fe/L; SRT, 0.5, 1.0, and 1.5 d; and HRT, 30, 60 and 80 min. Manual correction of the air flow was made to ensure DO levels were above 2.0 mg/L at the end of the aerate period. There were 14 operational conditions or periods in total. Each period was maintained for at least 10 days.

Analytical methods

With particle size distribution, COD is fractionated to sCOD, cCOD and pCOD. To separate pCOD from tCOD, samples were filtered with a 1.5 μm nylon filter. For separating sCOD and cCOD, samples were flocculated with $ZnSO_4$ followed by filtering with a 0.45 μm PES filter. COD was measured by HACH COD test kits. Nitrogen (TN and ammonia), phosphorus (TP and orthophosphate), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS) and sludge volume index (SVI) were measured by *Standard Methods* (APHA *et al.* 1999). Temperature and dissolved oxygen (DO) were monitored with a HACH HQ40d.

Statistical analysis and calculations

The statistical analysis was performed with Origin 2016 (OriginLab). The averages of measurable parameters were used to analyze the influences of operational parameters by one-way or two-way analysis of variance (ANOVA). Differences were considered significant at a p-value <0.05. For calculations for COD mass balance see section 4 of the Supplementary Data file.

RESULTS AND DISCUSSION

Influent organic characterization

Influent in this study was collected from the full-scale blackwater module of the SEMIZENTRAL Resource Recovery Center, Tsingtao, China, and tCOD was 789 ± 124 mg/L. Organic characterization has two dimensions: particle size distribution and biodegradable quality. With particle size distribution, COD is fractionated to sCOD, cCOD and pCOD (see 'Analytical methods'). Accordingly, the influent COD fractions value was 148 ± 31, 231 ± 45 and 411 ± 99 mg/L, respectively (Table 1); and occupied tCOD

Table 1 | Summary of ordinary influent wastewater characteristics (mean ± standard error)

pH –	SS mg/L	tCOD mg/L	sCOD mg/L	cCOD mg/L	pCOD mg/L	TN mg/L	NH_4^+-N mg/L	TP mg/L	OP mg/L
8.00 ± 0.19	562 ± 166	789 ± 124	148 ± 31	231 ± 45	411 ± 99	126 ± 11	97.9 ± 8.3	12.5 ± 1.9	10.9 ± 1.8

of 18.9 ± 3.9%, 29.5 ± 5.1% and 51.6 ± 6.1%, respectively. The cCOD and pCOD proportion were summed to 81.1%, which was higher than mid-strength municipal wastewater (60%). Given such a high proportion of suspended COD, could single CEPT achieve satisfactory carbon recovery efficiency? This question will be answered in 'Performance of single CEPT'.

Another dimension of organic characterization is the biodegradable property. Oxygen utilization rate (OUR) tests are frequently used to estimate wastewater biodegradable COD fractions. For HRAS, the OUR of raw wastewater was sufficient (Mathieu & Etienne 2000). The original ASM1, which classified biodegradable COD to readily biodegradable (S_S) and slowly biodegradable (X_S) (Henze *et al.* 2000), could not explain the respirograms of HRAS in our work (Figure S2 in the Supplementary Data file). While the dual hydrolysis model (Allı *et al.* 2018), a modified ASM1, which divided hydrolysable COD to rapidly hydrolysable (X_{SR}) and slow hydrolysable (X_{SS}), fitted respirograms perfectly (Figure S2). S_S, X_{SR} and X_{SS} accounted for 14.4%, 11.2% and 12.4%, respectively. If blackwater was treated by CAS, the corresponding proportion was 14.7%, 29.7% and 50.7%, respectively (Hocaoglu *et al.* 2010). For municipal wastewater in CAS, S_S, X_{SR} and X_{SS} was 15.0%, 25.0% and 27.5%, respectively (Henze 1992). In comparison, HRAS had a poor ability to degrade hydrolysable COD (X_{SR} and X_{SS}). Since the biomass inventory and diversity were low because of low SRT and HRT, HRAS could not use hydrolysable COD as effectively as CAS. Hence, in terms of wastewater characteristics, the mineralization efficiency was much lower than CAS.

Effluent tCOD of the full-scale blackwater treatment module, an AAO-MBR process, was ~25 mg/L, reported by our partner research group (Tolksdorf *et al.* 2018). Because 0.04 μm pore size PES plates are used in membrane tanks to separate liquid and solids, sCOD is equal to tCOD. The soluble inert COD (S_I) was identified as 25 mg/L because particulate matter and soluble biodegradable organics were removed in the effluent (Rieger *et al.* 2012). Soluble endogenous inert organics (Orhon & Çokgör 2010) are not considered in this paper. Checking values of S_S estimated by respirometry, we found the sum of S_S and S_I ($f_{SS} + f_{SI} =$ 17.6%) was very close to influent sCOD (18.9%). Hence, we consider that rapidly hydrolysable organics (X_{SR}) belong to a colloidal or particulate fraction rather than a soluble one. This is different from the works of Orhon *et al.* (2019), Allı *et al.* (2018) and Noyan *et al.* (2017), where soluble biodegradable organics were divided to soluble readily biodegradable organics (S_S) and soluble rapidly hydrolysable organics (S_H). The reason is that in this paper, sCOD was a true soluble COD (Rieger *et al.* 2012; Tchobanoglous *et al.* 2014) since cCOD was removed by a flocculation process.

Performance of single CEPT

The suspended COD ratio to tCOD reached 81.1%. In theory, it could be captured completely with single CEPT. That is to say, if the negligible coagulant adsorption of sCOD was ignored (Alloul *et al.* 2018), the maximum carbon capture efficiency was 81.1%. However, when Fe salt is dosed as coagulant, the negative influence of sulfide should not be overlooked (Haydar & Aziz 2009). The formation of FeS not only decreases COD capture efficiency but also damages performance for phosphorus precipitation (Wilfert *et al.* 2015; Wilfert *et al.* 2016; Wilfert *et al.* 2018). As Figure S3 shows, even dosing 30 mg Fe/L of coagulant, the carbon capture efficiency was as low as 63.6 ± 0.2%, and the TP removal efficiency was only 61.1 ± 0.4%. CEHRAS had an aeration period, where high ORP was maintained to prevent Fe^{3+} from reducing to Fe^{2+} and forming FeS. Compared with single CEPT, dosing 10, 20 and 30 mg Fe/L of Fe salt, the tCOD removal efficiency of CEHRAS was increased by 26.7%, 16.1% and 15.8%, respectively, and 22.3%, 8.42% and 21.1%, respectively, for the TP removal efficiency. Meanwhile, the carbon capture efficiency of CEHRAS was 22.7%, 13.7% and 12.0% more than single CEPT, respectively. It was obvious that CEHRAS had better performance for contaminants removal and carbon capture than single CEPT. CEHRAS compensated for the disadvantage of single CEPT.

Performance of single HRAS

The above section analyzed and discussed the existing problem of single CEPT to capture wastewater carbon; how about single HRAS? In the single HRAS process, cCOD and pCOD in wastewater are mainly captured by bioflocculation with activated sludge floc. However, it is bioflocculation limitation that resulted in the poor suspended solids capture capacity and COD removal efficiency of HRAS (Orhon *et al.* 2019; Van Winckel *et al.* 2019). When SRT = 1 d and 1.5 d, cCOD removal efficiency of the single HRAS (without Fe salt dosing, Figure 1) was 28.5 ± 11.9% and 29.8 ± 8.7%, respectively. Both pCOD removal efficiencies of the two SRTs were high, 83.0 ± 3.8% and 83.6 ± 4.6%, respectively, in accordance with a regular CEPT (60–85% (Tchobanoglous *et al.* 2014)). However, the cCOD removal

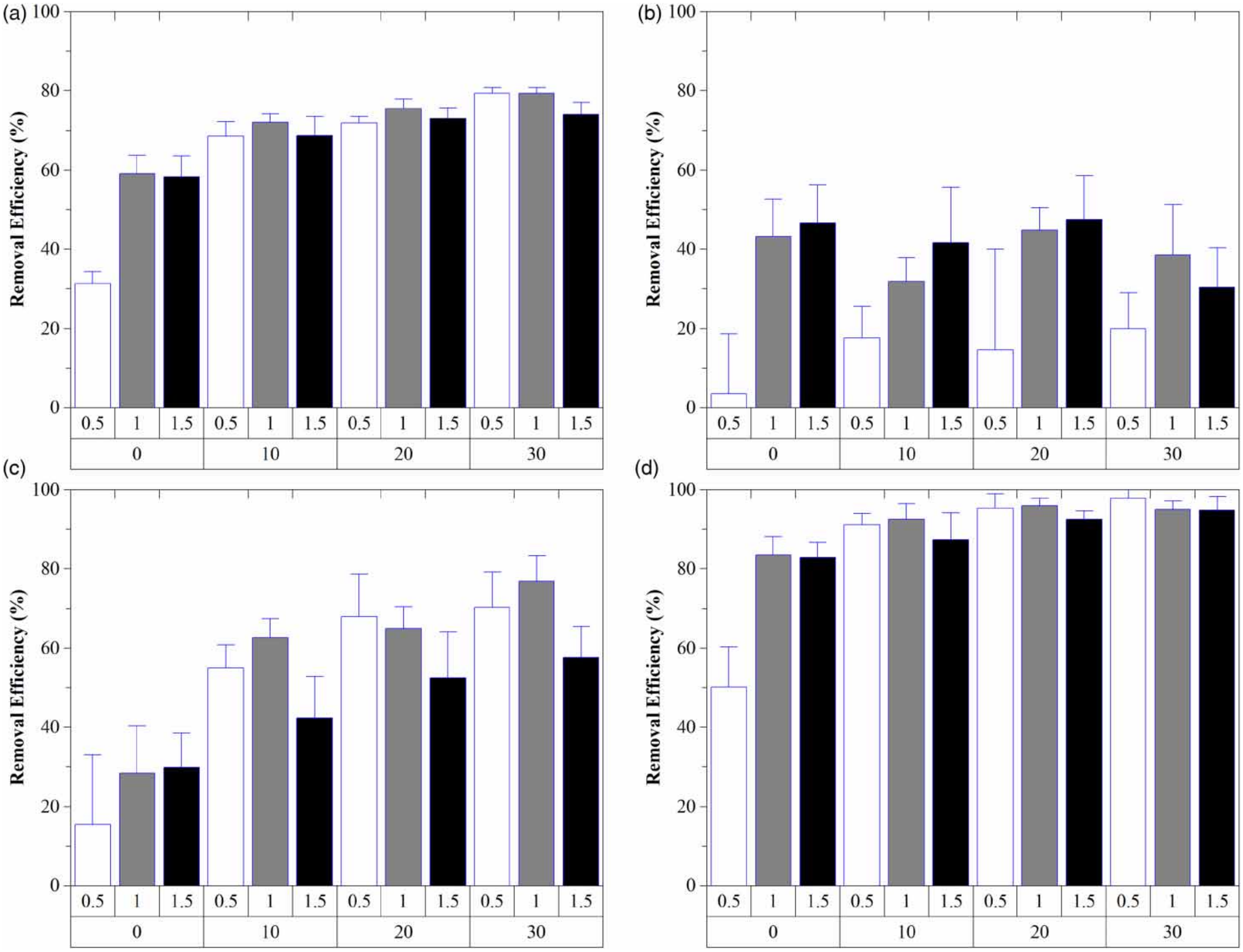

Figure 1 | Influence of Fe salt dosage and SRT on removal of tCOD (a), sCOD (b), cCOD (c) and pCOD (d). HRT = 60 min.

efficiencies were remarkably lower than the reported value 60% (Meerburg *et al.* 2016). As SRT decreased to 0.5 d, the cCOD and pCOD removal efficiency obviously declined to 15.4 ± 17.6% and 50.2 ± 10.0%, respectively. Because of the bad COD removal performance, a high proportion of COD was lost in the effluent, which resulted in the low carbon capture efficiency of the single HRAS. The COD effluent loss, under SRT = 0.5, 1.0 and 1.5 d, was as much as 53.5 ± 2.7%, 36.1 ± 4.0% and 38.4 ± 4.9%, respectively (Figure 2). If the invalid carbon source (sCOD) is considered, the effluent loss was higher. Consequently, carbon capture efficiencies were 40–50%. Other studies obtained similar results (Akanyeti *et al.* 2010; Jimenez *et al.* 2015; Meerburg *et al.* 2015; Meerburg *et al.* 2016).

Orthophosphate (OP) was the main phosphorus species, occupying 88.1% of TP (Table 1). Therefore, the dominant phosphorus removal pathway of the single HRAS was that

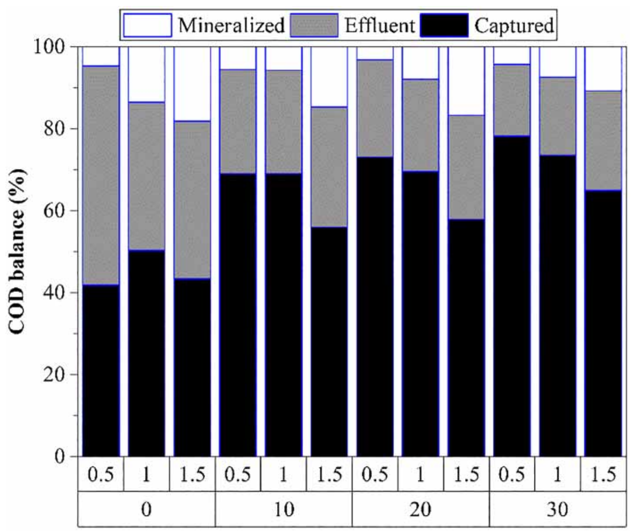

Figure 2 | Influence of Fe salt dosage and SRT on COD mass balance (HRT = 60 min).

of ordinary heterotrophic organisms uptaking OP as a nutrient for growth. Because of the low phosphorus content (~2%) in sludge (Henze *et al.* 2008), single HRAS had poor phosphorus removal efficiency. As Figure S4.a and S4.b depict, while SRT = 0.5, 1.0 and 1.5 d, TP removal efficiency was 14.0 ± 2.0%, 28.4 ± 2.7% and 28.7 ± 10.0%, respectively, and OP was 10.0 ± 4.5%, 29.7 ± 4.8% and 26.6 ± 10.7%. Treated by HRAS, most of the COD was captured, resulting in a low biodegradable COD concentration in the effluent. Hence, chemical precipitation is the best practical way to remove or recover phosphorus rather than enhanced biological phosphorus removal (EBPR), with having a high requirement for biodegradable COD. And CEHRAS might be a potential choice for capturing carbon and phosphorus simultaneously (Wilfert *et al.* 2015; de Graaff *et al.* 2016).

Performance of CEHRAS

Influence of Fe salt dosage and SRT on contaminant removal

The COD removal performance is given in Figure 1. ANOVA results suggested that Fe salt dosage had a significant impact on tCOD and cCOD ($p = 0.030$ and 0.002), while not being significant on sCOD and pCOD ($p = 0.795$ and 0.090). Only sCOD was significantly influenced by SRT ($p = 0.005$), while tCOD, cCOD and pCOD were not ($p = 0.069$, 0.137 and 0.543). The pCOD removal efficiency raised to 83.6 ± 4.6% and 83.0 ± 3.8%, respectively, with the function of bioflocculation (SRT = 1.0 and 1.5 d, Fe salt dosage = 0 mg/L). Even with increased Fe salt dosage and SRT, the strengthening effect on pCOD removal was not observable. Fe^{3+} and its hydrolyzed products can improve colloidal particle destabilization and aggregation. With Fe^{3+} dosing, cCOD removal efficiency increased significantly; as a result, tCOD removal efficiency increased, because of the high cCOD over tCOD ratio. Although chemical coagulant could adsorb sCOD, this function was negligible, so Fe salt dosage had no significant impact on sCOD. Since the total biomass in the tank increased with increased SRT, using readily biodegradable COD, it promoted sCOD removal. However, Jimenez *et al.* (2015) found that when SRT >0.5 d, the sCOD removal efficiency of HRAS reached more than 70%, and SRT had no significant influence owing to the different influent characteristics between their and our work. Theoretically, sludge concentration increases with prolonged SRT, and improving collisions between particles (Mancell-Egala *et al.* 2017). However, in our work, the cCOD removal efficiency did not increase with the increasing sludge concentration and SRT. This implied that collision number was not the limiting factor for floc formation, because MLSS was higher than the threshold of flocculation (TOF) (Mancell-Egala *et al.* 2016; Mancell-Egala *et al.* 2017). The operational condition where SRT was 0.5 d and Fe salt dosage was 0 mg/L was an exception. The MLSS (525 ± 82 mg TSS/L), lower than TOF, resulted in limitation of the number of collisions, and the removal efficiency of cCOD and pCOD was low. Increasing SRT to 1.0 d, MLSS significantly increased to 1,450 ± 157 mg TSS/L, and the number of collisions between particles was increased. Therefore, pCOD removal efficiency raised significantly ($p = 0.001$), and cCOD increased from 15.4% to 28.4%.

Figure S4 illustrates the influences of Fe salt dosage and SRT on phosphorus and nitrogen removal. Because OP occupied 88.1% of TP, the trends of OP and TP were similar (Figure S4.a and S4.b). Fe salt dosage significantly affected TP and OP removal with positive correlation. SRT had no significant impact on TP and OP. However, while Fe dosage was 20 mg Fe/L, the removal efficiencies had a significantly positive correlation with SRT ($p \ll 0.001$). For the weak biological phosphorus removal ability of HRAS, with Fe salt dosage, CEHRAS removes phosphorus by chemical or physicochemical pathways (Tchobanoglous *et al.* 2014; Wilfert *et al.* 2015) including: (1) formation of hydrous ferric oxides which serve as a substrate for phosphate adsorption; (2) incorporation of phosphate into the hydrous oxide structure; and (3) formation of ferric phosphate. Under anaerobic conditions, like an anaerobic bioreactor in the mainstream, an anaerobic digestion tank in the side stream, and a sludge layer under a clarifier, ferric phosphate in sludge can convert to vivianite by biological or chemical reactions. Vivianite is a promising recovered phosphorus species (Wilfert *et al.* 2018).

At room temperature (18–22 °C, Table S1), nitrifying bacterium could not exist in such short-SRT CEHRAS or HRAS. In addition, Fe salt had no removal effect on ammonia (Lin *et al.* 2017). As a result, at all operational conditions, TN and ammonia removal efficiencies were very low, less than 15% and 5%, respectively. Fe salt dosage and SRT had no remarkable influence on nitrogen removal, either. Since the effluent COD/TN ratio was 2.79 ± 0.34 mg COD/mg N, mainstream anammox technologies might be a better selection for nitrogen removal (Nogaj *et al.* 2014). However, 11.2% of TN (nitrite and ammonia) is converted to nitrate (Strous *et al.* 1998). As a simple calculation, if influent TN was 126 mg N/L, effluent nitrate would be 14.2 mg N/L, which can't guarantee a strict standard, like 15 mg N/L of TN in Grade A (GB 18918-2002) in China. Combine anammox and denitrification, and a lower nitrogen effluent will be realized (Ma *et al.* 2017; Ding *et al.* 2018; Xie *et al.* 2018). The carbon source required for denitrification can be supplied from VFAs produced by anaerobic fermentation (Lin *et al.* 2018) or CH_4 from anaerobic digestion (Xie *et al.* 2018).

Influence of Fe salt dosage and SRT on COD mass balance

With CEHRAS or single HRAS, transformation of influent tCOD has three final pathways: (1) capture as sludge; (2) loss in effluent; and (3) mineralization to CO_2. Colloidal and particulate COD fractions are the effective carbon captured in sludge (Orhon *et al.* 2019), while sCOD should be returned to the mainstream. The influences of Fe salt dosage and SRT on COD mass balance are shown in Figure 2. Fe salt dosage had no significant effect on mineralization efficiency ($p = 0.206$), while higher SRT resulted in a significant increase in mineralization efficiency ($p = 0.002$). The reason is that the utilization rate of readily biodegradable COD, hydrolysis rate of hydrolysable COD and endogenous respiration rate have positive correlations with SRT. The effluent COD loss, including the sCOD in sludge, was not influenced significantly by SRT ($p = 0.520$). Fe salt dosage had significantly negative impact on effluent COD loss ($p = 0.010$). The sum of effluent loss and mineralization decided the carbon capture efficiency. Both Fe salt dosage and SRT significantly influenced carbon capture efficiency, with $p < 0.001$ and $p = 0.022$, respectively. Similarly, other studies on single HRAS suggested SRT had remarkable influence on carbon capture efficiency (Jimenez *et al.* 2015; Meerburg *et al.* 2015). When Fe dosage was 30 mg Fe/L and SRT was 0.5 d, carbon capture efficiency achieved the highest value, 78.2 ± 3.6%, which was equivalent to SFMBR (Orhon *et al.* 2019).

Influence of HRT on pollutant removal and COD mass balance

As shown in Figure 3(a), HRT had no significant removal influence on tCOD, TN and TP ($p = 0.190$, 0.114, and 0.076, respectively). HRT had no significant impact on carbon capture efficiency and mineralization efficiency ($p = 0.325$ and 0.965, respectively). The effluent loss under three HRTs was 21.2 ± 1.6%, 17.5 ± 1.5% and 20.4 ± 1.4%, respectively. Although the effect of HRT on effluent loss was significant with $p = 0.014$, their values were very close. At conditions of HRT = 30 min, SRT = 0.5 d and Fe salt dosage = 30 mg Fe/L, the carbon capture efficiency was 74.0 ± 4.7%, 4.2% less than that at HRT = 60 min. But the aeration time or tank volume decreased by half, and the construct and operational capital were less.

Evaluation and interpretation of observed sludge yield

The results of the measured observed sludge yield, mX_V, and the model-based yields, Y_{NH} and Y_{NHP}, are shown in Table S5. If all COD fractions in influent were biodegradable and completely utilized by the heterotrophic

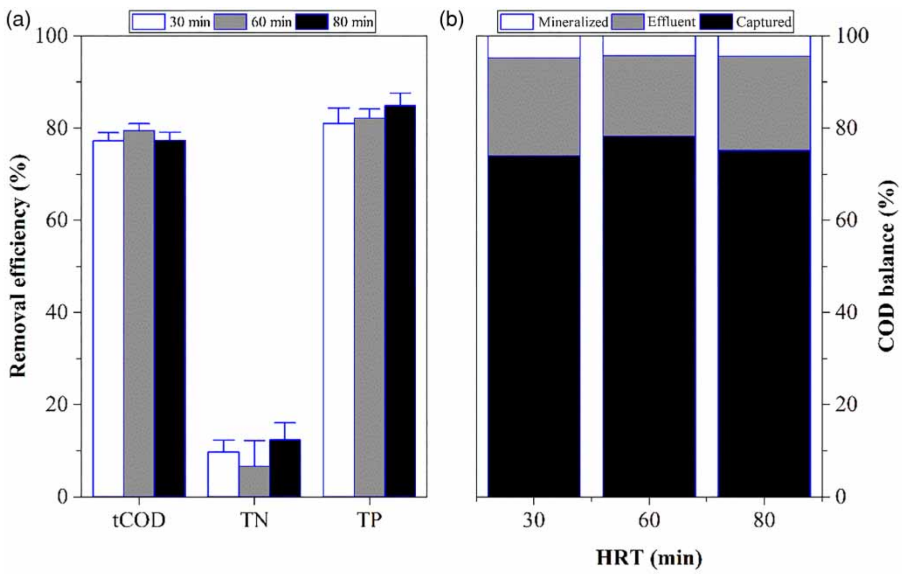

Figure 3 | Influence of HRT on pollutant removal and COD mass balance (Fe salt dosage = 30 mg Fe/L, SRT = 0.5 d).

organism, mX_V would be equal to Y_{NHP} under an ideal settling condition (Orhon et al. 2019). In most of these experimental runs, mX_V is higher than Y_{NHP}. This is because of a high percentage of particulate inert COD fraction, f_{SI}, in blackwater influent. A part of the sludge generated in the aeration phase of the SBR is lost in the effluent (mX_{Eff}), as high as 0.308 (30.8%), when the settleability is insufficient. With the coagulation and flocculation function of iron salt, settleability is improved and makes mX_{Eff} lower than 5%. Also, the remaining unutilized X_S in sludge, $mX_{S,Rm}$, is much lower than ~5% in all experimental runs. As a rule of thumb, S_S is almost completely consumed before X_S is used up. However, the unused readily biodegradable COD (soluble, S_S) is much higher than mX_{Eff} and $mX_{S,Rm}$ (see Table S5 and Figure S5). A possible way to interpret the abnormal phenomenon is that the maximum specific growth rate and specific hydrolysis rates are approximate in our study; under short HRT, there is not enough time to consume S_S. Fortunately, the equivalent of Ss in influent, f_{SS}, is remarkably lower than the sum of the particulate fractions ($f_{XSR} + f_{XSS} + f_{XH} + f_{XI}$). The loss of S_S is not so important in this paper.

A simple techno-economic analysis for different carbon capture techniques

Three carbon capture techniques, HRAS, CEPT and CEHRAS, are compared in this paper. For techno-economic comparison, we propose a benchmark process for carbon capture and recovery (Figure S6). Firstly, organics in blackwater are captured to primary sludge by single HRAS, the single CEPT or CEHRAS. The solids concentration is increased in the thickener, and then fed to the anaerobic digester. Methane produced from the anaerobic digester is transported to a co-generation device to recover chemical energy to electricity and heat. Before dewatering, digested sludge is conditioned by Fe salt with other polymers to improve dewatering characteristics. In the full-scale blackwater module in SEMICENTRAL Resource Recovery Center, the actual influent flowrate was 279 m^3/d, and we use this value as a daily treatment capacity. Influent tCOD is 789 mg/L, the average value of experimental influent (Table 1).

Four scenarios are analyzed and compared: (1) HRAS, SRT = 0.5 d, HRT = 1 h; (2) CEPT, Fe salt dosage = 30 mg Fe/L, HRT = 1 h; (3) CEHRAS1, Fe salt dosage = 30 mg Fe/L, SRT = 0.5 d, HRT = 1 h; and (4) CEHRAS2, Fe salt dosage = 30 mg Fe/L, SRT = 0.5 d, HRT = 1 h. For details and calculation notes see Table S6.

The daily methane production of HRAS, CEPT, CEHRAS1 and CEHRAS2 is 4.93, 10.0, 11.5 and 8.03 kg/d, respectively. Although the daily primary sludge of CEPT is only 1.3 times that of HRAS, the daily methane production of CEPT is 2.02 times higher than HRAS. Because iron is required for methanogenesis, an iron element in A-stage sludge could increase the biomethane production potential (Cagnetta et al. 2016). With co-generation technology, these four scenarios could recover total energy of 54.2, 110, 126 and 88.2 kWh/d, respectively. As the same time, air supply is required for HRAS, CEHRAS1 and CEHRAS2, and the aeration energy consumption is 35.2, 11.1 and 14.2 kWh/d, respectively. The electricity production from co-generation can not compensate for the aeration energy consumption of HRAS. If effluent nitrogen of the A-stage is considered, an additional 63.9 kWh/d aeration energy consumption will be required for partial nitritation. Whatever the carbon capture technology is, it is difficult to realize energy neutrality for blackwater treatment. A pre-treatment technology before anaerobic digestion is needed to raise the methane production. It is also ascribed to the low biomethane production potentials we selected: 0.178, 0.286, 0.266 and 0.211 kg COD_{CH4} per kg COD fed. In a work of Cagnetta et al. (2019), a biogas yield of up to 68% on a COD basis was demonstrated in methanation tests. Fe salt has a remarkable promotion for carbon capture and recovery. However, the price of Fe salt is high (0.588 USD per kg $FeCl_3 \cdot 6H_2O$). Both the operating cost of CEPT and CEHRAS1, dosing 30 mg Fe/L, are apparently higher than HRAS with no Fe dosing and CEHRAS2 with 10 mg Fe/L dosage. In total, the cost of energy recovery of HRAS, CEPT, CEHRAS1 and CEHRAS2 is 0.13, 0.21, 0.19 and 0.10 USD/kWh, respectively, while the price of electricity for the industry is 0.11 USD/kWh. It seems that CEHRAS2 is the unique scenario to promise profiting, and HRAS is the second best. Higher Fe dosage seems not to be economical. However, other advantages of iron dosage, like inhibiting H_2S gas production, and recovering phosphorus as vivianite (Rebosura et al. 2018), are not considered in this paper. A deep and considerate techno-economic analysis based on life cycle management should be conducted in future.

CONCLUSIONS

Both single CEPT and single HRAS had low carbon capture efficiency because of sulfide issue or insufficient flocculation capacity. Compared with single CEPT and single HRAS, CEHRAS demonstrated a superior potential for carbon capture and recovery from blackwater. SRT and Fe salt dosage had significant influence on the carbon capture efficiency. A little Fe salt dosage could promise CEHAS a great increase in energy recovery. Excessive Fe salt would increase the operational cost remarkably. Energy neutrality is a challenging work, an effective and cheap technology is required to be developed for increasing the biomethane production potential of the captured carbon in future.

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SUPPLEMENTARY MATERIAL

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