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High-Rate Contact Stabilization Process-Coupled Membrane Bioreactor for Maximal Recovery of Organics from Municipal Wastewater

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Abstract: The high-rate activated sludge (HRAS) process is being studied for the removal and recovery of organics with short solids retention time (SRT) from wastewater, facilitating energy recovery by the subsequent anaerobic digestion process. In the present study, the feasibility of a novel high-rate contact stabilization (HRCS) process coupled with a membrane bioreactor (MBR) was investigated as a HRAS technique to harvest organics compared to a high-loaded MBR (HL-MBR) process treating the same sewage. Results showed that higher chemical oxygen demand (COD) removal efficiency and better bioflocculation performance were obtained using HRCS-MBR compared with HL-MBR with SRTs from 0.5 to 1.8 days. The increased bound extracellular polymeric substances content in the contactor was responsible for the improved biosorption and bioflocculation performance in the HRCS-MBR configuration. At an optimal SRT of 1.2 days, incoming organics of 47.5% and 40.5% were harvested in concentrate for HRCS-MBR and HL-MBR. These harvested organics from the concentrate per liter from HRCS-MBR and HL-MBR produced 4.28×10^{-3} and 3.72×10^{-3} kWh of electricity, respectively. The clear advantage of fouling control for HRCS-MBR was determined because of significantly lower concentrations of colloidal materials and soluble microbial products in the concentrate compared with HL-MBR. Therefore, HRCS-MBR holds promise for organics recovery and sustainable wastewater treatment.

Keywords: bioflocculation; membrane bioreactor (MBR); high-rate contact stabilization process; organics recovery; energy recovery

1. Introduction

Municipal wastewater is typically treated with the conventional activated sludge (CAS) process. This biological process consumes a considerable amount of energy for aeration, at 0.3–0.6 kWh/m^3 of wastewater [1], and produces a significant amount of carbon dioxide (CO_2). However, municipal wastewater should no longer be considered a waste, but a valuable resource. The organic carbon in each cubic meter of municipal wastewater typically contains a chemical energy of approximately 1.9 kW [2,3]. This energy can be partially recovered via the anaerobic digestion of surplus sludge to produce biogas for onsite heat and electric energy generation. Through this method, the organic carbon in wastewater is harvested and recovered instead of being oxidized and thus energy self-sufficiency or energy-neutral wastewater treatment can be fully realized in practice. Therefore, the first step is to maximize organic carbon harvesting and minimize respiration losses to CO_2 from municipal wastewater, enabling maximum energy recovery.

The high-rate activated sludge (HRAS) process has received attention as a wastewater preconcentration technology because of its ability to recover particulate, colloidal, and dissolved organic matters by producing high amounts of sludge. The HRAS configuration, first examined by Buswell and Long [4], involves two parts: a contact tank in which return activated sludge (RAS) is mixed with influent under aerobic conditions, and a settling tank to separate sludge from the effluent. This process combines high food-to-microorganism ratios and low solids retention times (SRT), typically one to four days, with relatively short hydraulic retention times (HRT), typically one to four hours, to remove organic matter from wastewater [5]. Under these conditions, a high sludge-specific organic loading rate (SLR) can be obtained, which favors the retention of fast-growing microorganisms. Thus, particulate and colloidal substrates of the influent can be effectively removed by biological flocculation and subsequent solid–liquid separation [6,7], whereas the soluble substrates can be removed by oxidation, intracellular storage, or biosynthesis [7]. Consequently, these incoming organics are finally redirected into the sludge stream, which has better anaerobic digestion characteristics compared with CAS sludge [8]. Therefore, achieving energy-neutral wastewater treatment should be possible. However, a contradiction exists during the operation of the HRAS system. At lower SRTs, the respiration loss of organic carbon is minimized so maximal energy recovery can be achieved, whereas the washing rate had to be increased, resulting in more wash-out of dispersed and non-flocculating microorganisms from the sludge stream as settleability deteriorated. Therefore, a high organic harvesting efficiency was difficult to obtain. To balance organics harvesting and effluent quality, high-rate MBR or high-loaded (HL) MBR (HL-MBR) was used. Akanyeti et al. [8] evaluated the feasibility of HL-MBR for organics recovery and found that 35% of chemical oxygen demand (COD) in the wastewater at an SRT of one day was recovered as methane, which was considerably higher than the typical values of around 25% in CAS systems [9,10]. Hernández et al. [11] applied HL-MBR to concentrate the COD of grey water and indicated a strong bioflocculation performance at short SRTs, suggesting that bioflocculation of HL-MBR is a promising grey water pretreatment step for energy recovery within decentralized sanitation processes. Moreover, Faust et al. [12] found that bound extracellular polymeric substances (EPSs) played a vital role in the bioflocculation process and an SRT of 0.5–1 day was the best combination of bioflocculation and organic matter recovery in HL-MBR.

Alternatively, contact-stabilization (CS) technology has been suggested as an HRAS process to enhance bioflocculation and intracellular storage of organic matters at short SRT for energy neutrality. Different from conventional HRAS, the high-rate CS (HRCS) process includes two reactors, where the contactor reactor mixes influent wastewater with stabilized sludge under aerated conditions. Later, sludge-mixed liquid from the contactor flows into a clarifier and the sludge is settled and partly discharged, while the remainder is sent to a stabilizer reactor where oxidation of biosorbed carbon from sludge matrix occurs. As such, a feast–famine regime is suggested as a strategy to enhance bioflocculation and the production of storage polymers [13]. Huang and Li [14] found that a HRCS system achieved rapid adsorption of substrates in the contactor. Meerburg et al. [15] systematically compared the HRCS and HRAS systems, and revealed that HRCS was able to recover more chemical energy from wastewater organics than HRAS at low SRTs of less than 1.2 days. However, poor solid–liquid separation performance at low SRTs remains a challenge for HRCS, which significantly limits further improvements in the harvesting efficiency of organic matters and effluent quality. The membrane is able to retain all dispersed and nonflocculating organics, enhance the COD removal efficiency, and improve organics recovery efficiency. Based on the membrane, HRCS configuration has not yet been studied.

Therefore, the overall aim of this study was to propose a HRCS configuration coupled with MBR (HRCS-MBR) for organics recovery from municipal wastewater. A comparative approach was adopted involving a HL-MBR and a HRCS-MBR system at the laboratory scale operated in parallel. The COD removal efficiency and bioflocculation performance were investigated in both MBR systems at different SRTs to identify optimum parameters to maximize effluent quality and the recovery of organic matter in municipal wastewater. Also, the energy recoveries of both concentrates of MBRs were estimated using batch experiments. The membrane fouling of two MBRs was further compared to identify the effect of varying colloidal substrates and soluble microbial products (SMP) concentrations on membrane performance under different SRTs.

2. Materials and Methods

2.1. Experimental Setup and Operation

Two different MBRs were used for the laboratory experiment on wastewater concentration increase in a full-scale municipal wastewater treatment plant (Figure 1). These two reactors were operated in parallel at identical HRTs of 1.2 h and identical SRTs. HL-MBR included a single reactor with an effective volume of 5 L, whereas HRCS-MBR included two parts (Figure 1): the contactor and the stabilizer with an effective volume of 1.25 L and 3.75 L, respectively. An identical cylindrical polysulfone (PFS) (Zhiyuanweiye, Dalian, China) hollow fiber membrane module was submerged in each reactor (the contactor for HRCS-MBR). The nominal pore size of the membranes used was 0.01 μm, and the area of the membrane surface immersed was 0.34 m^2. Two peristaltic pumps were used to maintain an identical influent flow rate of 100 L/day for the two reactors, and the effluents were obtained continuously from the membrane modules with two suction pumps equipped with vacuum gauges.

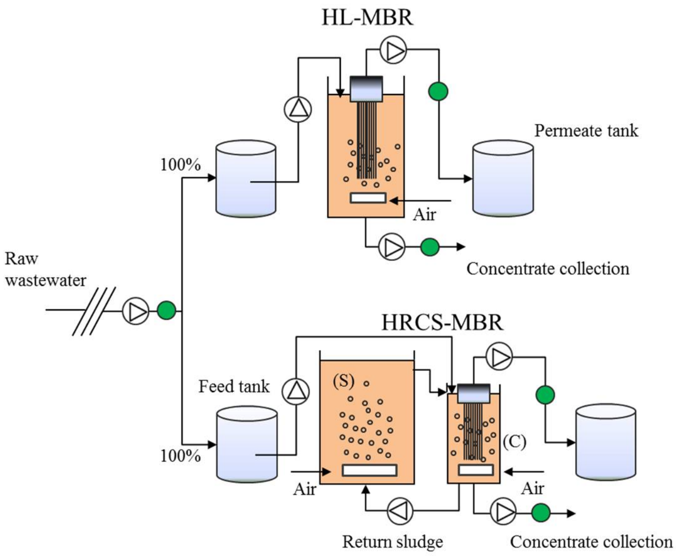

Figure 1. Schematic diagram of the experimental setup for municipal wastewater up-concentration. High-loaded MBR (HL-MBR); High-rate contact stabilization MBR (HRCS-MBR). (C) and (S) indicate contact tank and stabilization tank respectively. ● indicates sampling points.

In each reactor, the aerations and mixing were performed using coarse bubble diffusers and a blower. The required amount of aeration in each reactor was controlled by a glass rotor flow meter. In the HL-MBR, dissolved oxygen (DO) concentration was controlled between 1.0 and 1.5 mg/L. For HRCS-MBR, the influent wastewater was fed to the contactor, where biosorption of organics of wastewater occurred, and then the carbon-rich sludge was returned continuously to the stabilizer by a recycled pump to oxidize the biosorbed carbon attached to the sludge. The recycle ratio of sludge was maintained at 60%, and the DO concentrations of contactor and stabilizer were controlled at 0.3–0.8 and 1.5–2.0 mg/L, respectively. The lower DO level in the contactor of the HRCS-MBR was maintained to minimize carbon mineralization and enhance the biosorption of organic matter to sludge flocs, whereas the higher DO concentration of the stabilizer ensured that no oxygen limitation occurred [16].

Both MBRs were inoculated with activated sludge from the municipal wastewater treatment plant (Xiajiahe, Dalian, China), and the initial mixed liquid suspended solids (MLSS) concentration was 1.0 g/L. The SRT of each MBR varied from 0.5, 0.8, 1.2, and 1.8 days by continuously wasting mixed liquor from the membrane reactor. The total SRTs were calculated based on the total biomass inventory in the reactors and the solids wasted through the waste activated sludge (WAS) stream. The waste flow rate was adjusted manually at least three times per week to maintain the desired SRT. Moreover, each SRT phase was operated for no less than 20 days to ensure that the operational conditions reached the steady state. Both MBRs were directly fed to the screen (5 mm) and degritted (aerated grit removal) with the municipal wastewater treatment plant (Xiajiahe, Dalian, China). The influent wastewater characteristics are described in Table 1. Filtration performance was evaluated according to the transmembrane pressure (TMP) profile of the membrane. To investigate the membrane fouling of MBRs simultaneously, both membranes were removed from the reactors for physical cleaning in the middle of each SRT operation process or when the TMP of one of the MBRs reached 0.7 bar. Also, chemical cleaning was performed at the end of each SRT operation for both MBRs. The physical cleaning was conducted with water flushing and sponge cleaning. The chemical cleaning was carried out by soaking the fouled membrane in 0.2% (*v*/*v*) sodium hypochlorite solution for a minimum of 10 h and soaking in 0.2% (*v*/*v*) sulfuric acid for 1 h.

Table 1. Summary of influent wastewater characteristics over the sampling period. COD indicates chemical oxygen demand

Characteristic	Unit	Value	COD Fraction (%)
Total COD	mg/L	441 ± 33	100
Particulate COD	mg/L	244 ± 16	55.1
Colloidal COD	mg/L	90 ± 16	20.4
Dissolved COD	mg/L	108 ± 2	24.5
Total suspended solids	mg/L	187 ± 54	
Volatile suspended solids	mg/L	164 ± 46	
NH_4^+-N	mg/L	41.3 ± 7.2	
Total phosphorus	mg/L	3.7 ± 1.2	

2.2. COD Mass Balance and Oxygen Uptake Rate

COD mass balance was calculated for each MBR to determine the carbon redirection and organic matter recovery rate from the municipal wastewater. The amount of COD input to the reactor should be equal to the amount of COD that leaves the reactor. We assumed that any COD loss due to volatilization of organics was negligible. As a result, the influent total COD should be transformed into four categories of output fractions: concentrate COD (waste activated sludge), membrane effluent COD (dissolved COD), oxidized COD (mineralization), and COD contributing to the membrane cake layer (cake COD). The recovery rate of the wastewater organics was determined by the concentrate COD at steady-state conditions at each targeted SRT. The cake COD losses were difficult to directly estimate due to the COD losses incurred by the removal of the fouling layers on the membrane surface [12]. Thus, the cake COD was estimated by closing the mass balance to 100%, whereas oxidized COD was calculated by the oxygen use rate because nitrification was absent with such short SRTs conditions and oxygen consumption was caused only by COD oxidation [12,17].

Oxygen uptake rates (OUR) were determined according to standard methods [18]. Firstly, a 200 mL sludge sample was withdrawn from the reactor to completely fill a flask placed in a 20 °C thermostatic water bath and aerated to a DO concentration of 5 mg/L. Immediately, a 300 mL biochemical oxygen demand (BOD) bottle was filled with the aerated sludge and a DO membrane probe (WTW 556 MPS) was inserted to close the bottle and sealed so that no air intrusion occurred. Finally, the sludge in the BOD bottle was mixed with a magnetic stirring apparatus and the DO was recorded every second until reaching close to 1 mg/L. The slope was calculated between a DO of 2 and 4 mg/L with corresponding time and considered as the OUR in mg O_2/L/h. For HRCS-MBR, the OUR of the contactor and stabilizer sludge were both measured, and the sum of the product of OUR and the corresponding tank volume was divided by the total volume of the reactor to calculate this MBR OUR value.

2.3. Biochemical Methane Potential

Biochemical methane potential (BMP) tests were conducted to determine the amount of methane production from the concentrate COD through anaerobic digestion (AD) of the sludge based on methods described by Angelidaki et al. [19]. The tests were conducted in triplicate for the undiluted 150 mL samples of concentrates generated from the two MBRs (obtained from the contactor for HRCS-MBR) at different SRTs. Erlenmeyer flasks with a volume of 280 mL (250 mL working volume) were inoculated with the anaerobic digested sludge (10 g volatile suspended solids (VSS)/L) from the sludge digester of a local sludge treatment plant (Xiajiahe, Dalian, China). A substrate loading ratio of approximately 0.4 (volatile solids (VS) basis) were maintained in all the tests. The headspace of the flasks was flushed with nitrogen gas and closed with rubber stoppers and crimp caps. The flasks were then placed on a shaker (100 rpm) at a temperature of 35 °C for 20 days. At the end of the experiment, the gas composition of the biogas was analyzed using a gas chromatograph (GC-14C, Shimadzu, Japan) equipped with a thermal conductivity detector and a column packed with molecular sieve 5A 80/100 mesh. Blanks containing only inoculum and deionized (DI) water were used to measure the background methane produced from the inoculum.

2.4. Analytical Methods

Volumetric flux was measured with an electronic balance during the experiments. DO, pH, temperature, and conductivity were measured with a 556 MPS hand-held multi-parameter instrument (WTW Incorporated, Yellow Spring, OH, USA). Influent, permeate, and concentrate samples were analyzed to estimate COD, total suspended solids (TSS), volatile suspended solids (VSS), and nutrient removal. All analyses were conducted according to standard methods [18]. The COD content was measured into four different fractions: the total, particulate, colloidal, and dissolved COD (COD_{tot}, COD_{part}, COD_{coll}, and COD_{diss}, respectively). The total COD was measured on the unfiltered sample. Then, this sample was first paper filtered (12 μm) and subsequently membrane filtered using the flocculation filtration (0.45 μm) method to determine COD_{diss}. The difference between the COD_{tot} and the paper-filtered COD is referred to here as COD_{part}, and the difference between the paper and membrane filtrate as COD_{coll}.

A physical extraction method was used to measure bound EPS concentrations. Sludge samples for EPS measurement were collected from two MBRs (contactor and stabilizer for HRCS-MBR) at different operation conditions. The total EPS of the sludge sample was considered as the sum of loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS). Both LB-EPS and TB-EPS from the sludge samples were extracted using a heating and extraction method [20]. Protein content was determined using the Lowry method. Bovine serum albumin (BSA) was used for the standard [21]. The phenolsulfuric acid method introduced by Dubois was used to determine the polysaccharide with glucose as the standard [22]. The soluble microbial products (SMP) were considered to be same as soluble EPSs. In this experiment, SMP was characterized as the dissolved COD of the concentrate and effluent because the protein and carbohydrate concentrations of SMP were small and the trial error would be very large if we quantified SMP with protein and carbohydrate measurements [23].

2.5. Membrane Permeability Analysis

Membrane permeability was estimated in terms of membrane fouling rates. This value is largely temperature dependent because the permeate flux is a function of temperature due to the effects of water viscosity [24]. For two MBR membrane modules, membrane permeability normalized at 20 °C was calculated with the simple filtration model shown in Equation (1) that considers increasing TMP with continuous membrane permeate production [25].

$$K_{20} = \left(\frac{J}{TMP}\right) \cdot \exp(-0.032 \cdot (20 - \mathrm{T})) \quad (1)$$

where K_{20} is the membrane permeability at 20 °C (L/m^2/bar/h, i.e., LMH/bar), J is the permeate flux (L/m^2/h, i.e., LMH), and T is the temperature of water (°C).

3. Results and Discussion

3.1. Permeate Quality

As shown in Figure 2, high COD removal rates at different SRTs for each MBR were obtained with real municipal wastewater with high organic load variation under short HRT conditions. These permeate qualities were better than those of conventional HRAS systems without membranes [7,15], indicating that membrane modules can improve organic matter recovery and effluent quality. Furthermore, with increasing SRT from 0.5 to 1.8 days, the total COD removal rates of HL-MBR and HRCS-MBR increased from 78.1% and 79.4% at SRT of 0.5 days to 85.9% and 88.0% at SRT of 1.8 days, respectively. This may be due to the combined effects of improved biosorption and biodegradation with increasing SRT [26]. For MBRs, the differences in COD_{tot} removal efficiency for similar influent was determined via COD_{diss} removal efficiencies because particulate and colloidal organic matter that contributed most to the COD_{tot} could be completely retained by the membrane. Higher COD_{diss} removal efficiency was achieved at high SRT because a higher VSS concentration was maintained in the reactor compared with the short SRT (Table 2), in which higher numbers of fast-growing microorganisms used more soluble and easily biodegradable COD supplied with the wastewater.

Table 2. Sludge characteristics in both MBRs at different solids retention times (SRTs).

	SRT (Day)	Reactor	MLVSS (mg/L)	VSS/SS
HL-MBR	0.5		612 ± 122	0.94
	0.8		764 ± 84	0.88
	1.2		1391 ± 163	0.83
	1.8		1622 ± 186	0.82
HRCS-MBR	0.5	C	652 ± 79	0.96
		S	818 ± 126	0.92
	0.8	C	862 ± 110	0.93
		S	1037 ± 84	0.88
	1.2	C	1382 ± 142	0.91
		S	1696 ± 122	0.86
	1.8	C	1526 ± 153	0.87
		S	1985 ± 136	0.84

Note: C—Contactor, S—Stabilizer.

Also, we observed that HRCS-MBR achieved higher average COD_{total} removal efficiency compared with HL-MBR, probably caused by higher numbers of microorganisms in HRCS-MBR than in HL-MBR. A feast–famine regime applied to HRCS-MBR was demonstrated to be an effective strategy to selectively favor bioflocculation [13,27]. Under the starvation condition of the HRCS-MBR system, microbial growth on the adsorbed and stored substrate occurred and thus free surface area of flocs was created for subsequent biosorption in the contactor [28]. Furthermore, the strong substrate concentration gradient in the contactor might allow more readily biodegradable dissolved COD to be placed in storage. This was considered as an auxiliary substrate removal mechanism along with direct use for microbial growth, thus reducing the concentration of effluent COD_{diss} [29,30]. This also might be the reason for the higher COD efficiency of the membrane effluent in HRCS-MBR compared with HL-MBR (Figure 2).

On the other hand, significant removal of ammonia and total phosphate was not achieved by bothMBRs (Table S1). The poor ammonia removal of MBR is mainly attributed to the absence of nitrification at those short SRTs, whereas the absence of an alternate anaerobic/aerobic mode may inhibit phosphorus release and uptake, although short SRT generally favors phosphorus removal. This result aligned with the values of the conventional HRAS system, which showed that removal efficiencies of inorganic nitrogen and phosphorus were low to negligible, and their optimization should be considered through the compatibility between the HRAS system and downstream secondary treatments for nutrient management [7].

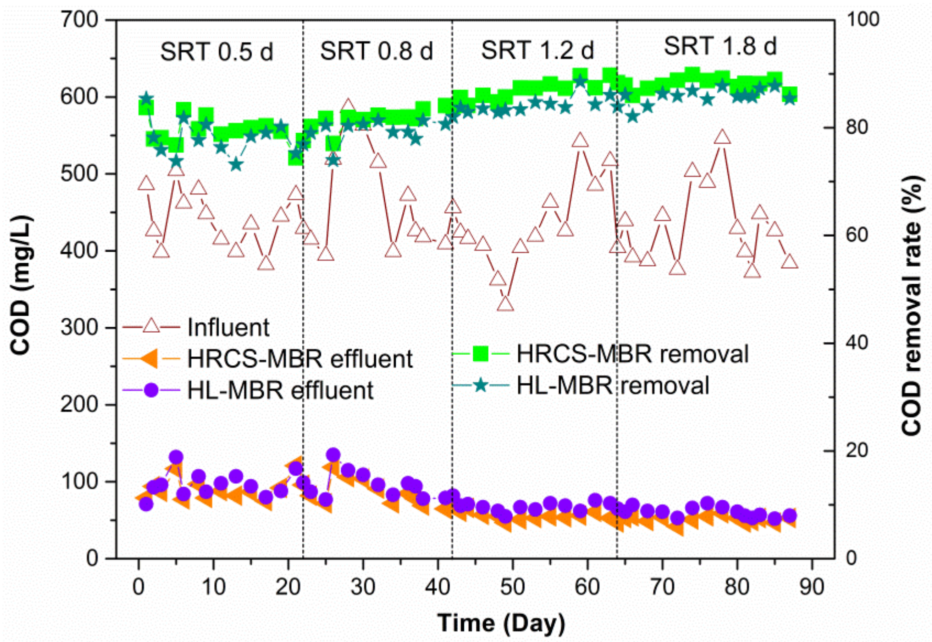

Figure 2. Evolutions of total chemical oxygen demand (COD) removal effect for two MBRs during different SRT conditions.

3.2. Bioflocculation Performance and EPS Composition

The bioflocculation ability of microbial aggregates is key to achieving low turbidity and a high-quality effluent [31]. Bioflocculation performance of sludge in the reactor is reflected by the changes in particulate COD and colloidal and dissolved COD in mixed liquid [7,16]. In this study, the average COD concentrations of concentrates in the two MBRs at different SRTs are shown in Table S2. Accordingly, fraction changes of COD_{part}, COD_{coll}, and COD_{diss} in the concentrate of the two MBRs operated at different SRTs occurred, as presented in Figure 3. The results show that the COD_{part} fractions in the concentrates of the two MBRs increased significantly with the lengthening of SRT. This suggests that the bioflocculation performance of the two reactors can be improved at longer SRTs. These results are confirmed by changes in the biomass in the reactor (Table 2), showing that the VSS concentrations of both MBRs increased as SRT increased from 0.5 to 1.8 days. Additionally, at longer SRTs, the fractions of COD_{coll} and COD_{diss} for both MBR concentrates decreased, indicating that better biosorption and bioflocculation performance can be achieved by increasing SRTs for MBRs. However, as shown in Tables 1 and S2, the COD_{coll} concentrations of the two reactors were higher than that of the influent. In the activated sludge reactor, operation at short SRTs means high food-to-microorganisms (F/M) ratios, which contribute to an increase in nonflocculating microorganisms, which are the main part of COD_{coll}. Additionally, these dispersed and nonflocculating microorganisms can be retained by the membrane instead of being settled or washed out with the effluent. This suggests that the COD_{coll}

concentration of MBR would be significantly higher than those of other HRAS systems, which would facilitate the conversion of more organics in the subsequent anaerobic digestion process.

We observed that the COD_{part} fractions of HRCS-MBR were always significantly higher than those of HL-MBR, whereas the COD_{coll} fractions of HRCS-MBR were remarkably lower than those of HL-MBR at the same SRT. The differences in biomass concentrations in both MBRs are shown in Table 2, indicating that better bioflocculation performance was obtained with HRCS-MBR compared to HL-MBR. Notably, the most significant difference between the two MBR configurations was the separate stabilizer and feast–famine regime of the CS system. The stabilizer of the CS system was regarded as a flocculent generator that can partially retain lytic products in the system to bridge particles and colloids of activated sludge instead of being lost in the effluent as in a conventional system [32]. Tsang et al. [33] demonstrated that longer stabilization times should favor sludge bioflocculation based on the kinetic selection theory [33]. Meerburg et al. found that an optimal stabilization time for the high-rate CS SBR system should be above 35 to 40 min, which was sufficient for the activated sludge to eliminate its adsorbed COD and regenerate [26]. Therefore, compared with HL-MBR, HRCS-MBR, with the separate stabilizer, facilitated microbial growth on adsorbed substrate and created free surface area on the flocs of the return activated sludge for subsequent biosorption in the contactor [28], thus enhancing the bioflocculation ability of the activated sludge.

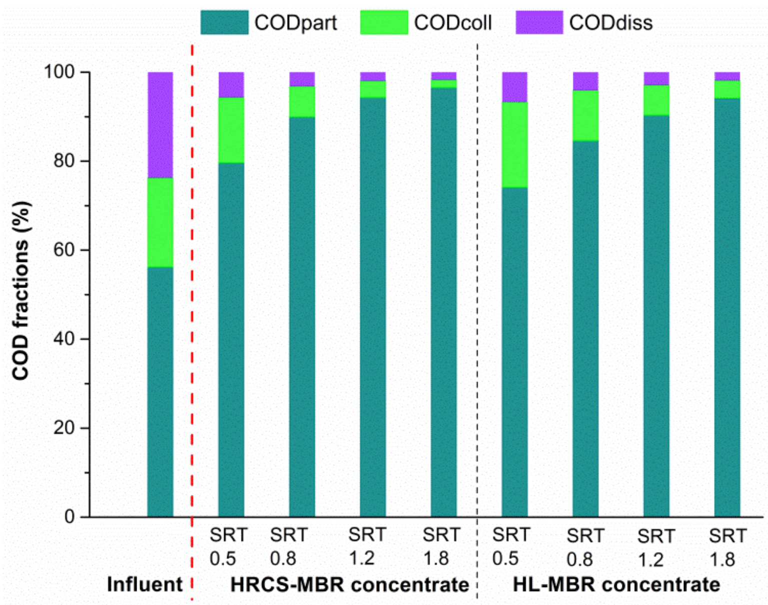

Figure 3. COD fractions in the wastewater and in both MBRs' concentrate under different SRT conditions. The total COD consists three fractions: the particulate, colloidal, and dissolved COD (COD_{part}, COD_{coll}, and COD_{diss}).

On the other hand, the bioflocculation performance of the two MBRs may be linked with bound EPS content and composition. Higher EPSs content was reported to correspond to higher floc stability [34,35]. Jimenez and Miller found that bioflocculation of COD_{coll} and COD_{part} could be enhanced by the increase in EPS content of the mixed liquid in the HRAS system [7]. These studies indicated the importance of both the quantity and characteristics of EPSs in the stability of sludge flocs. In the present study, the concentrations of total EPSs (sum of LB-EPS and TB-EPS) for the two MBRs increased with increasing SRT from 0.5 to 1.2 days (Figure 4), suggesting that EPS always displays a positive effect on the sludge bioflocculation at short SRTs. At an SRT of 1.8 days, the total EPSs of HRCS-MBR slightly decreased compared with an SRT of 1.2 days. This is probably related to the biodegradation of protein-EPS [12]. The small molecular substances produced by EPS degradation can be used as carbon and energy sources for cell growth in nutrient shortage conditions [31]. This result also suggested that the microorganisms of the stabilizer in HRCS-MBR might enter into the endogenous respiration phase, whereas HL-MBR might not enter into endogenous respiration at a 1.8-day SRT. Moreover, proteins in all EPS fractions of the two MBRs were significantly higher than polysaccharides (Figure 4), which aligns with the results of previous studies [36,37], indicating that the bioflocculation ability of sludge is closely related to protein-EPS concentrations. Correlations with the protein concentration of the two MBRs were generally positive for the COD_{part} fractions and negative for the COD_{coll} fractions in the concentrates (Figure S1), which indicates a good correlation between the protein concentration and the flocculation ability of activated sludge. This was supported by Liu and Fang [37], who found that sludge hydrophobicity increased with protein content of bound EPSs. This increased hydrophobicity generally leads to better flocculation during activated sludge processes. Thus, protein contents of all fractions play a vital role in achieving good sludge bioflocculation in the two MBRs at prolonged SRTs.

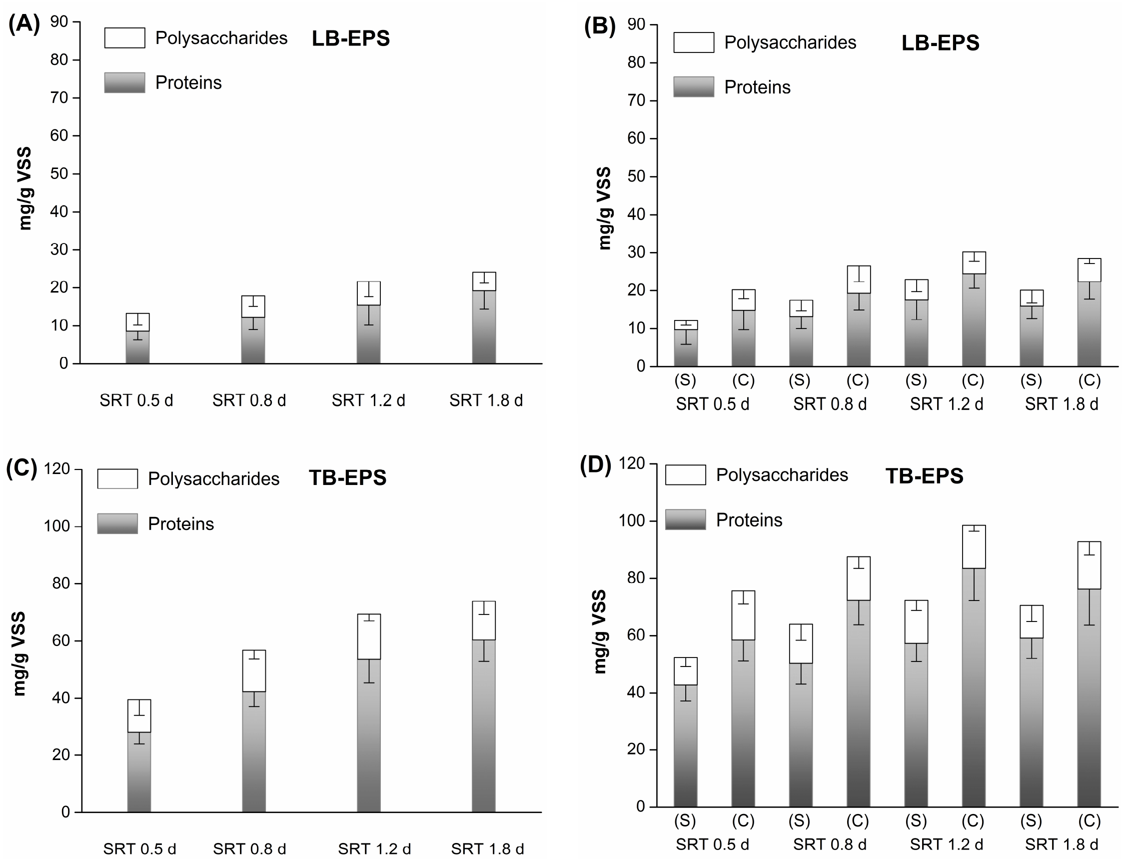

Figure 4. Specific proteins and polysaccharides concentrations of the (top) loosely bound (LB) and (bottom) tightly bound (TB) extracellular polymeric substances (EPS) fractions at different SRTs for (**A**,**C**) HL-MBR and (**B**,**D**) HRCS-MBR. Error bars show standard errors.

Both the LB-EPS and TB-EPS of HRCS-MBR increased from the stabilizer to contactor (Figure 4). The relative increases of LB-EPS and TB-EPS in the contactor were 66.94% and 44.55%, 51.43% and 36.93%, 31.88% and 36.38%, and 41.79% and 31.82% at an SRT of 0.5, 0.8, 1.2, and 1.8 days, respectively. Obviously, these relative increases also resulted in higher average EPS concentrations in the stabilizer and contactor in HRCS-MBR compared with HL-MBR at the same SRT, which led to the significant differences of all COD fractions in the concentrate between the two MBRs at the same SRT. The increased EPS content in the contactor could be a potential reason for the improved effluent quality and bioflocculation ability in HRCS-MBR. From the stabilizer to contactor, a significant increase in the organic loading rate will lead to the relative increase in EPS. Microbes shift quickly from a slow rate in the stabilizer to a maximum rate in the contactor, in which heterotrophs could use a major fraction of the overloading organic carbon through oxidation to the EPS response pathway rather than the maximum growth pathway [16].

3.3. COD Mass-Balance and Energy Recovery

COD mass balances, based on oxygen uptake rate (OUR) measurements, were performed for each MBR at different SRT conditions. The fractions of COD that entered and exited the reactor systems via concentrate, effluent, and losses to mineralization and cake layers of the membrane are shown in Figure 5. The results indicate that more influent COD was oxidized, whereas less COD was diverted to the concentrate and membrane effluent at longer SRTs in both MBRs. The best organics recovery performance was achieved at an SRT of 0.5 days, with average concentrate COD distributions of 56.9% and 47.9%, with mineralization distributions of 12.2% and 9.5% for HRCS-MBR and HL-MBR, respectively. Contrarily, at an SRT of 1.8 days, the average concentrate COD decreased to 35.0% and 31.7%, whereas mineralization rapidly increased to 37.6% and 42.5% for HRCS-MBR and HL-MBR, respectively. This suggests that a longer SRT is beneficial to promote effluent quality, whereas a shorter SRT is advantageous for organics recovery and energy savings. At an SRT of 1.2 days, 26.3% and 28.3% of influent COD_{tot} was oxidized, while 47.5% and 40.5% of incoming organics were harvested for HRCS-MBR and HL-MBR, respectively. These organics recovery percentages were slightly lower than those at a 0.8-day SRT, but were significantly higher than for conventional HRAS configurations at a similar SRT, which recovered 27% of influent COD [7].

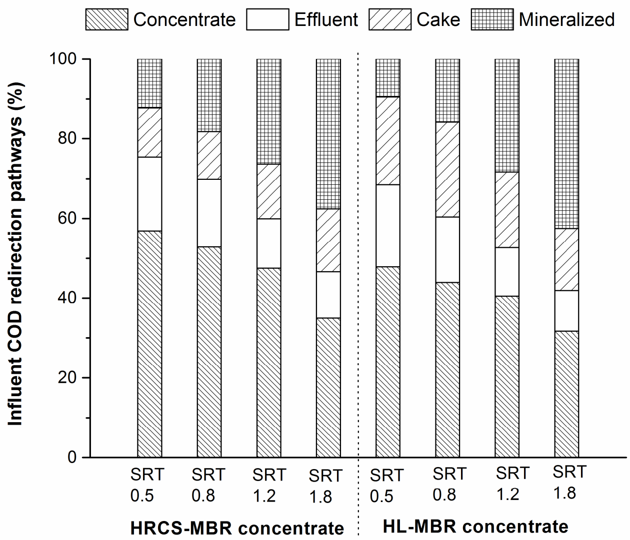

Figure 5. Total COD mass balances over the entire steady-state period of the experiment at different SRTs for both MBRs.

We observed that concentrate COD distributions of HRCS-MBR were higher than those of HL-MBR at the same SRT, which implies that more energy might be recovered with HRCS-MBR. This result was confirmed with the biochemical methane potential test that quantifies the specific methane productions of concentrate for both MBRs at different SRTs. As shown in Figure 6, the methane production of concentrate for HRCS-MBR was significantly higher than of HL-MBR at the same SRT conditions. These differences in energy recovery between the two concentrates were partly due to the higher concentrations of concentrate COD in HRCS-MBR. On the other hand, the specific methane production of concentrate COD in HRCS-MBR was relatively higher compared to HL-MBR (Figure 6). This was probably due to the higher value of the VSS/TSS ratio of the concentrate in HRCS-MBR (Table 2), suggesting that the endogenous residue fraction of the wasted concentrate was lower than that of HL-MBR concentrate, which may cause a higher methane component in biogas. Based on the theoretical electricity conversion calculation method [38], the methane yields of 1073 and 933 mL of CH_4 per liter of concentrate for HRCS-MBR and HL-MBR at 1.2 days SRT would result in energy recovery of 4.28 × 10^{-3} and 3.72 × 10^{-3} kWh, respectively, with the a 40% electrical conversion assumption. Thus, a full-scale HRCS-MBR system could potentially achieve more energy recovery compared with the HL-MBR system. The overall energy recovery is affected, as methane can be derived by the combination of the COD removal efficiency, the concentrate yield, organics concentration of the concentrate, and the anaerobic methane yield. Therefore, the conditions that affect the changes in these parameters should be further optimized to estimate the energy recovery potential of both MBR systems during long-term anaerobic digesting experiments. In addition, the residual biodegradable COD in the membrane effluent will affect the performance of secondary treatment processes, such as the nitrogen removal process with anammox. However, this residual biodegradable COD is readily converted into energy. Therefore, the COD of the membrane effluent should not be mineralized, but be further harvested to maximize the final energy recovery.

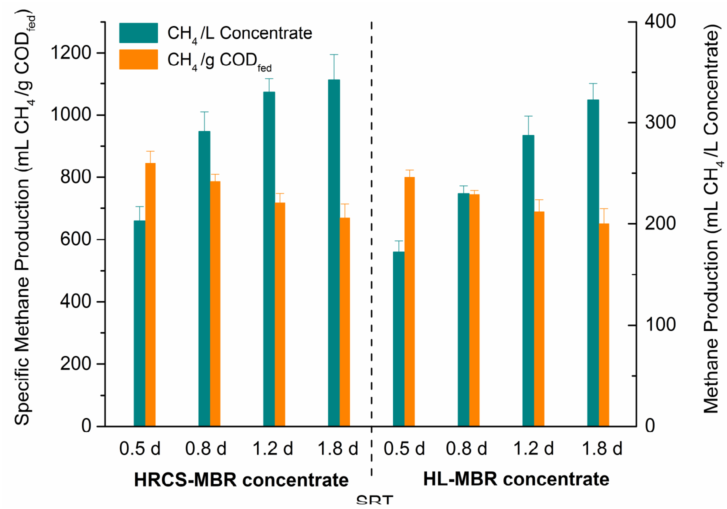

Figure 6. Cumulative methane productions of each MBR concentrate at different SRTs.

3.4. Membrane Fouling

Figure 7 shows the membrane permeability for both MBRs as a function of permeated water volume during a long-term operation process. The highest membrane fouling rates were observed under a 0.5-day SRT for both MBRs. The permeability rates declined with increasing SRT from 0.5 to 1.8 days, although initial permeability for each SRT after each cleaning slightly decreased because of the irreversible membrane fouling during continuous operation. This result indicates that the membrane fouling could be minimized as SRT increased, which is consistent with the findings of Faust et al. [12], who found that sludge samples from HL-MBRs operated at longer SRTs gave decreasing membrane resistances. With increasing SRT, the bound EPS concentrations increased in both MBRs (Figure 4), resulting in improved bioflocculation performance, which could thus mitigate membrane fouling. From Figure 7, higher membrane permeability was obtained in HRCS-MBR at each SRT condition. This was probably related to the higher concentrations of LB-EPS and TB-EPS in the contactor of HRCS-MBR compared to HL-MBR (Figure 4). However, this result was contrary to some previous studies that showed that the higher the content of bound EPSs in the activated sludge, the more rapidly the membrane fouling proceeded [39,40]. This significant difference in the impact of bound EPSs on membrane fouling may be attributed to obvious differences in the SRT range between the present and previous studies.

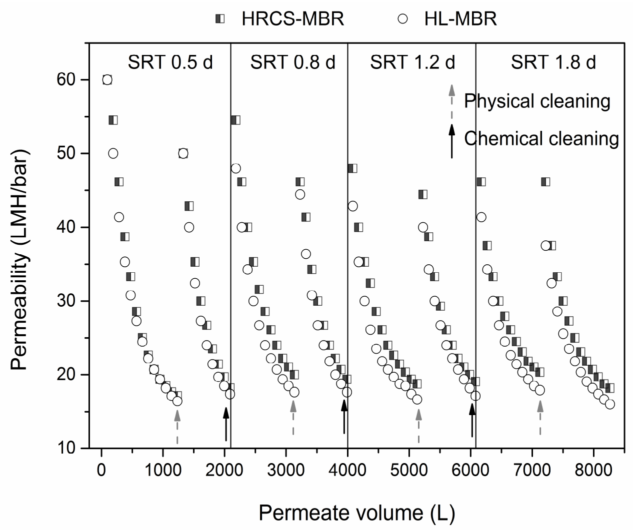

Figure 7. Evolutions of permeability as a function of permeate volume in two MBRs at different SRTs.

Conversely, colloids and SMP were reported to also be primary membrane foulants in MBRs [41]. Thus, we examined COD_{coll} and SMP concentrations of concentrate to investigate the correlation between these properties and membrane fouling. The averaged COD_{coll} concentrations of concentrates at each SRT for both MBRs showed a significant positive effect on the increase in TMP rates per day (Figure 8 and Table 3). At the same time, good correlations between the averaged SMP concentrations of concentrates and the TMP increase rates were obtained (Figure 8 and Table 3). These results indicate that both COD_{coll} and SMP in the concentrate played vital roles in membrane fouling. Most of colloidal materials were smaller than 1 μm, which could easily penetrate and block membrane pores [41,42]. In this study, however, the nominal pore size of the membranes used was only 0.01 μm and thus colloids had a stronger tendency to deposit on the membrane surface instead of pore blocking. Compared to the colloid, SMP had a lower molecular weight from 1000 to 10,000 Da, which is considered the soluble EPS produced by EPS release, cell lysis, and hydrolysis products [23,43]. Thus, SMP not only reduced the cake porosity by filling the interspaces between the particles or colloids in the cake layer, but also entered into membrane pores, and then partially accumulated in these pores or adsorbed on the pore wall due to their sticky properties [23,41]. Figure 8 also shows that the lower TMP increase rate was observed with HRCS-MBR at each SRT compared with HL-MBR. This result is similar to Figure 7, which can be partly attributed to the lower colloidal material and SMP in concentrate contents in HRCS-MBR, in which COD_{coll} and SMP could be entrapped more by the microbial flocs during the course of the bioflocculation [44].

Overall, at shorter SRTs, the bioflocculation performance of sludge was poor, whereas accumulations of colloidal materials and SMP became more pronounced, which all caused serious membrane fouling in the MBRs. Operation at longer SRTs appears to be a suitable option for MBRs. However, this would result in lower COD concentrations of the concentrate, which decreases the organics recovery. Therefore, balancing organics recovery, effluent quality, and membrane fouling in high-rate MBRs is important. For HRCS-MBR, TMP increase rates of 32.5 and 36.0 mbar/d in physical cleaning and chemical cleaning were obtained at a 1.2-day SRT, respectively, which was close to those at a 1.8-day SRT, indicating no significant difference in membrane fouling between the two SRTs. Therefore, combining the membrane fouling, organics recovery, and effluent quality, the optimum SRT might be 1.2 days for the HRCS-MBR in this study.

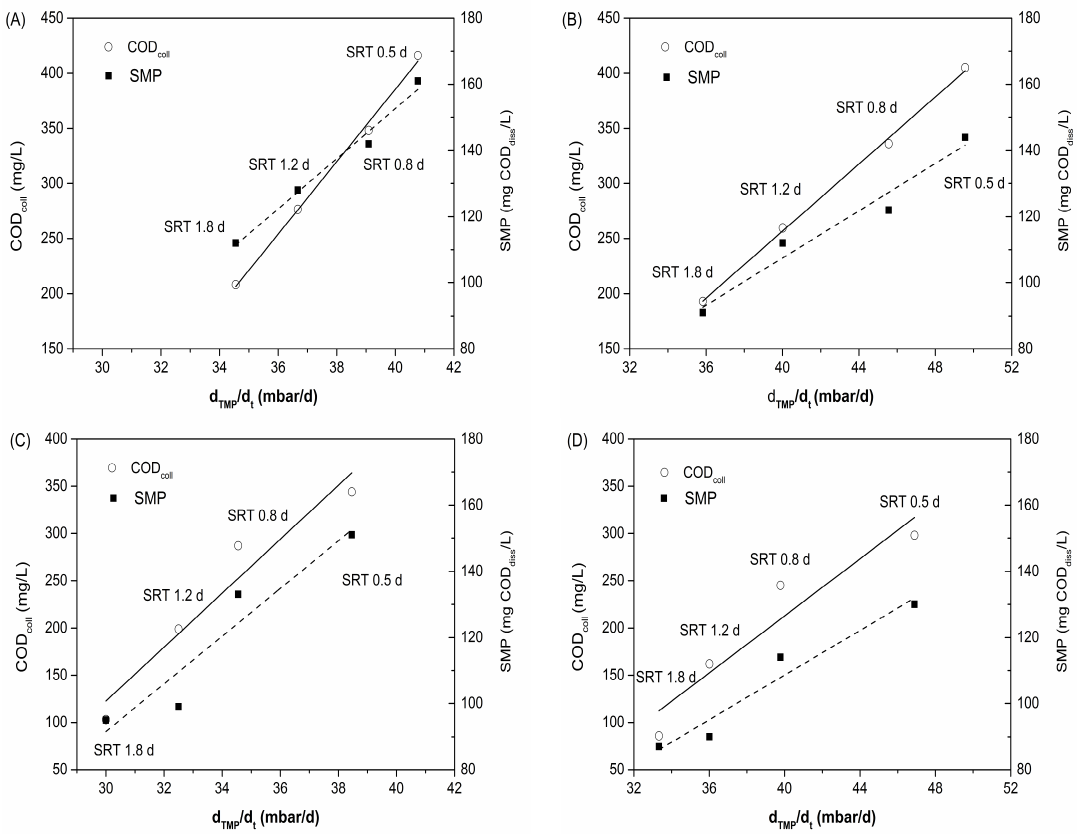

Figure 8. Effects of averaged concentrations for the COD_{coll} and soluble microbial products (SMP) at different SRTs on transmembrane pressure (TMP) increase rates of (**A**,**B**) HL-MBR and (**C**,**D**) HRCS-MBR. (**A**,**C**) demonstrate the TMP increase rates of the physical cleaning cycle for both MBRs, whereas (**B**,**D**) are the TMP increase rates during the chemical cleaning cycle in each SRT.

Table 3. Pearson's correlation coefficient (r_p) and p-values for linear correlations between transmembrane pressure (TMP) increase rate and concentrations of the colloidal fraction (COD_{coll}) and soluble microbial products (SMP).

			d_{TMP}/d_t	
			r_p	p
HL-MBR	Physical cleaning	COD_{coll}	0.998	0.002
		SMP	0.992	0.008
	Chemical cleaning	COD_{coll}	0.999	0.001
		SMP	0.980	0.020
HRCS-MBR	Physical cleaning	COD_{coll}	0.969	0.031
		SMP	0.953	0.047
	Chemical cleaning	COD_{coll}	0.953	0.047
		SMP	0.972	0.028

4. Conclusions

As a new configuration of a MBR, the HRCS-MBR combines the advantages of the complete retention of suspended organics with those of the feast–famine regime in the contact stabilization process to select for rapid sorption and storage of substrates at shorter SRTs. Compared with HL-MBR configurations, the HRCS-MBR demonstrated superior potential for organics harvesting, energy recovery, and effluent quality. At an optimal SRT of 1.2 days, the average total COD removal rate of 87.1% was obtained and incoming organics of 47.5% was harvested in concentrate for the HRCS-MBR.

These harvested organics from the concentrate, per liter, produced 4.28 × 10^{-3} kWh of electricity. Furthermore, long-term filtration experiments proved the clear advantage of fouling control compared to the HL-MBR system because of good bioflocculation performance and lower concentrations of colloidal materials and SMP in concentrate. Therefore, the HRCS-MBR can be considered a promising process to achieve organics recovery and sustainable wastewater treatment.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/10/7/878/s1, Figure S1: Impacts of proteins increase in LB-EPS and TB-EPS fraction of two MBRs (A, C for HL-MBR; B, D for HRCS-MBR) on changes of COD fractions (%) at different SRTs. Table S1: $NH4^+$-N and TP concentrations of concentrates in both MBRs at different SRTs; Table S2: COD concentrations of concentrates in both MBRs at different SRTs.

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