Optimization of In Situ Backwashing Frequency for Stable Operation of Anaerobic Ceramic Membrane Bioreactor

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Keywords: flux recovery, ambient temperature, backwashing, domestic wastewater, ceramic membrane

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The cost-effective and stable operation of an anaerobic ceramic membrane bioreactor (AnCMBR) depends on operational strategies to minimize membrane fouling. A novel strategy for backwashing, filtration and relaxation was optimized for stable operation of a side stream tubular AnCMBR treating domestic wastewater at the ambient temperature. Two in situ backwashing schemes (once a day at 60 s/day, and twice a day at 60 s × 2/day) maintaining 55 min filtration and 5 min relaxation as a constant were compared. A flux level over 70% of the initial membrane flux was stabilized by in situ permeate backwashing irrespective of its frequency. The in situ backwashing by permeate once a day was better for energy saving, stable membrane filtration and less permeate consumption. Ex situ chemical cleaning after 60 days' operation was carried out using pure water, sodium hypochlorite (NaOCl), and citric acid as the order. The dominant cake layer was effectively reduced by in situ backwashing, and the major organic foulants were fulvic acid-like substances and humic acid-like substances. Proteobacteria, Firmucutes, Epsilonbacteria and Bacteroides were the major microbes attached to the ceramic membrane fouling layer which were effectively removed by NaOCl.

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Abstract: The cost-effective and stable operation of an anaerobic ceramic membrane bioreactor (AnCMBR) depends on operational strategies to minimize membrane fouling. A novel strategy for backwashing, filtration and relaxation was optimized for stable operation of a side stream tubular AnCMBR treating domestic wastewater at the ambient temperature. Two in situ backwashing schemes (once a day at 60 s/day, and twice a day at 60 s × 2/day) maintaining 55 min filtration and 5 min relaxation as a constant were compared. A flux level over 70% of the initial membrane flux was stabilized by in situ permeate backwashing irrespective of its frequency. The in situ backwashing by permeate once a day was better for energy saving, stable membrane filtration and less permeate consumption. Ex situ chemical cleaning after 60 days' operation was carried out using pure water, sodium hypochlorite (NaOCl), and citric acid as the order. The dominant cake layer was effectively reduced by in situ backwashing, and the major organic foulants were fulvic acid-like substances and humic acid-like substances. *Proteobacteria*, *Firmucutes*, *Epsilonbacteria* and *Bacteroides* were the major microbes attached to the ceramic membrane fouling layer which were effectively removed by NaOCl.

Keywords: ceramic membrane; domestic wastewater; ambient temperature; backwashing; flux recovery

1. Introduction

Nowadays, anaerobic membrane bioreactors (AnMBR) have become an emerging and potential technology for domestic wastewater (DWW) treatment and reuse [1]. AnMBR integrates anaerobic technology with membrane technology [2] which offsets the disadvantages of conventional treatment technologies [3]. Sustainable DWW treatment scenarios highlight this technology since AnMBR distinctly reduces the overall energy demand by producing methane-rich biogas, mineralized nutrients in the form of ammonia and orthophosphate enabling direct agricultural use of the effluent for ferti-irrigation [4]. These unique advantages of AnMBR technology have attracted the interest of both the research and industrial community for its application [5]. Nonetheless AnMBR is still an immature technology with a very limited research and practical applications in developing countries [6]. For developing countries in tropical regions, the ambient temperature operation of AnMBR is profitable, which significantly reduces the energy cost for maintaining mesophilic conditions. AnMBR operation for treating DWW at ambient conditions is also very limited, and there have been only a few studies [2,7–9]. Despite the aforementioned advantages, membrane fouling poses a big hindrance to widespread application of AnMBR because it increases both capital and operating costs [10]. Reportedly, polymeric membranes which have high fouling potential over ceramic membranes have been widely employed in AnMBR [11]. Presently, ceramic membranes have gained more attention owing to their superior mechanical strength, higher chemical stability and better acid- and alkali-resistant ability and low fouling propensity [12]. However, a careful literature survey shows only a handful of research publications on anaerobic ceramic membrane bioreactor (AnCMBR) applications and fouling control for DWW treatment. This implies that research on fouling control of AnCMBR is still at the embryonic stage. Chemically enhanced backwashing (CEB) has been widely applied for fouling control of AnCMBR [10]. There are two main disadvantages of online CEB; one is excessive cost for backwashing chemicals, and another is building up of harmful effects on the biomass sometimes aggravating membrane fouling as reported by Kimura et al., 2019 and Lee et al., 2019 [13,14]. Permeate backwashing is one resort to overcome both of these issues.

Duration, frequency and flux of backwashing are important parameters for achieving sustainable fouling control. Several relaxation and backwashing combinations are usually applied in AnMBR systems for membrane fouling control [1]. Wang et al., 2014 reported that the backwashing fluxes were usually one to three times the operating fluxes and the backwashing durations were either longer for a less frequent backwash (i.e., 7–16 min filtration/30–60 s backwash) or shorter for a more frequent backwash (i.e., 5–12 min filtration/5–20 s backwash) [15]. Different backwashing, filtration and relaxation protocols have been applied for ceramic membrane fouling control in previous research. Yue et al., 2018 employed 30 s backwashing at a flux of 30 $Lm^{-2}h^{-1}$ once in every 9 min suction. Chung et al., 2014 alternated filtration for 9 min and effluent backwashing for 30 s for a flat sheet ceramic membrane [16]. Another study using a ceramic flat sheet membrane by Zhang et el, 2018 used a 540 s filtration–60 s backwash mode [17]. Filtration/relaxation ratio of 9 min/1 min was used by Ren et al., 2019 using ceramic flat sheet membrane [18]. All above previous research works have employed more frequent backwashing that might lead to frequent pump and membrane damage. If the filtration time is too long, the re might be a build-up of irreversible fouling whereas if the time is too short, an unnecessary amount of permeate will be wasted for the backwashing [19].

Backwashing of ceramic flat sheet membranes coupled with submerged AnMBR were common in previous literature [17,20]. But the operation of a ceramic tubular membrane with a side-stream AnMBR is more convenient [21]. Hence, this study focused on in situ backwashing optimization for the stable operation of a ceramic tubular AnMBR. A novel membrane with Yittria composite ceramic material was used in this study considering Yittria has a strong ability to reduce biofouling by enzyme immobilization [22]. The AnCMBR with stable operation with a minimal in situ backwashing by permeate is an approach with merit for future research and practical applications. In addition, identification of microbial fouling of ceramic membrane was given priority as related previous literature was limited [18,23]. Accordingly, the two main objectives of this study were to optimize the in situ backwashing frequency in order to achieve a sustainable membrane filtration, and to elucidate the key organic and microbial foulants of the AnCMBR in order to provide technical support for spreading AnCMBR application in DWW treatment at the ambient temperature for tropical areas. The significance of this study includes optimization of a novel filtration, relaxation and backwashing strategy alone with a novel cost-effective cleaning process in AnCMBR to introduce its application to Sri Lanka on a pilot scale in the future.

2. Materials and Methods

2.1. Lab-Scale Tubular Anaerobic Membrane Bioreactor (AnCMBR) Setup and Its Operation

A laboratory-scale completely stirred tank reactor (CSTR) of 15 L effective volume (diameter × height = 120 mm × 650 mm), coupled with a mono-tubular ceramic microfiltration unit of 50 cm (HeFei ShiJie Membrane Engineering Co.Ltd, Hefei, China) (pore size × filtration area: 100 nm × 0.011 m^2) was operated at the ambient temperature (26.68 ± 4.0 °C) as shown in Figure 1. The membrane was made of ceramic composite, Yttria and Zirconia. It was housed in a single tubular channel stainless steel housing and operated in the inside-out orientation. The feed pump (BT100-1L, Longer YZ1515x Pump, Hebei, China) was used to feed the influent into the AnCMBR. A Xin Xishan DP-35 diaphragm pump (Xin Xishan industries Co.Ltd, Shanghai, China) was used to feed the membrane and recycling retentate to the reactor. A back wash pump (25WZR-15, Xin Xishan industries Co.Ltd, Shanghai, China) was used for back washing. The anaerobic reactor was equipped with a level sensor (AF-E2A3C1D1B2), pH sensor and oxidation reduction potential (ORP) probe (ACTEON5000, PONSEL group, Aqualabo Analysis, Caudan, France). A programmable logic controller (PLC) system (LAB VIEW, PLC, Siemens AG, Frankfurt, Germany) was used for automatic control of the setup operation. A biogas flow meter (μ-Flow, Bioprocess Control AB, Stockholm, Sweden) was used for monitoring biogas. A flow meter (NRLD-20, Ruiji automation company, Nanjing, China) was used to record the membrane flux.

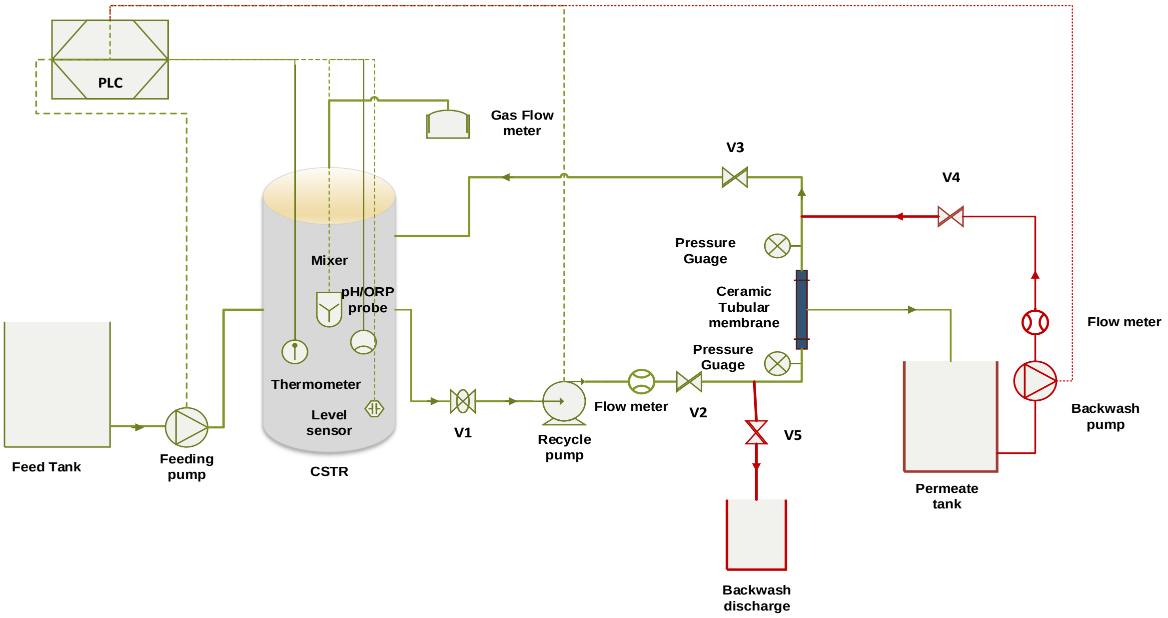

Figure 1. Schematic illustration of the anaerobic membrane bioreactor (AnCMBR) set-up.

2.1.1. Reactor Inoculation and Startup

Anaerobic sewage sludge was obtained from a full scale anaerobic digester (AD) of Gao'an'tun water reclamation plant in Beijing, China as the inoculum. Inoculum was initially filtered with 1 mm sieve mesh to remove the debris and then washed thrice in order to remove residues. The ratio of mixed liquor volatile suspended solids (MLVSS) to mixed liquor suspended solids (MLSS) in the inoculum was 67.5%. The CSTR of the AnCMBR was fed with synthetic DWW including essential micronutrients as listed in the supplementary information (S1) [24].

2.1.2. Operation of Lab-Scale Side-Stream Tubular AnCMBR

Based on the function of the recycle pump the automatic control strategy was 55 min membrane filtration and 5 min relaxation. It was counted as one cycle (Figure S1). This control strategy was applied according to the previous study undertaken in our research group using a polymeric membrane [25] and expert opinions. Valve adjustment at the feed and retentate side was used to maintain the constant flux mode. The transmembrane pressure was recorded using two pressure gauges (MIK-P300, MEACON, Hangzhou, China) at the inlet and outlet of the membrane module. Permeate was collected for backwashing. Two in situ backwashing schemes were employed for fouling control. The details of the different operational stages are listed in the Table 1.

Table 1. Operational parameters in the AnCMBR of this study.

Parameters	Startup Stage	Stage I	Stage II
Time (days)	1–10	11–50	50–60
Effective volume (L)		15	
Hydraulic retention time (HRT) (h)		24	
Organic loading rate (OLR) (kg CODm^{-3}d^{-1})	0.58 ±0.13	0.329 ± 0.073	0.23 ± 0.05
Cross Flow Velocity (CFV) (m/s)	2.49 ±0.13	2.50 ±0.10	2.60 ±0.001
* Backwashing (s d^{-1})	No backwash	60	2 × 60
Temperature (°C)	26.68 ± 4.0	26.86 ± 4.12	28.47 ± 1.57
Solid retention time (SRT) (days)		50	
MLSS (g/L)	7.95 ± 1.71	4.19 ± 2.93	1.57 ±0.61
MLVSS (g/L)	3.5 ± 0.88	1.89 ± 1.45	0.6 ±0.14
MLVSS/MLSS	0.46 ± 0.14	0.6 ± 0.07	0.41 ±0.10
Soluble Chemical Oxygen Demand(sCOD) removal %	43.42%	43.84%	43.09%
Trans membrane pressure (TMP)(kPa)	82.27 ± 6.30	79.36 ± 4.31	80.31 ± 0.34
Flux (Lm^{-2}h^{-1})	35.32 ± 19.57	38.78 ± 5.76	39.81± 1.70

* Backwashing flux/backwashing pressure = 1(150 Lm^{-2}h^{-1}/150 kPa) in stage I and stage II.

2.1.3. In Situ Backwashing and Membrane Cleaning Protocol

Backwashing protocols can be scheduled based on (i) trans-membrane pressure (TMP-based), (ii) flux (flux-based), (iii) fixed interval based (time–based) [26]. In this study time based method was used considering the durability of the pumps, cost effectiveness and energy conservation. In the first 10 days, membrane filtration was continuously carried out without backwashing. In stage I, backwashing was conducted 60 s/day (once a day) after 24 cycles (in the 24th cycle of the recycling pump operation); 3 L of permeate was used for backwashing. During backwashing, a high-pressure permeate with a maximum value of 150 kPa and flux of 150 Lm^{-2}h^{-1} was applied. As shown in Figure 1 an alternative pathway for backwashing as per [27] was used due to the inability of applying this high pressure through the permeate line of this mono-tubular membrane configuration. But this configuration was able to facilitate the outside in filtration mode during backwashing as shown in Figure S2. In stage II, backwashing was carried out 60 s × 2/d after 12 cycles for 60 s (twice a day); 6 L of permeate was used. In order to completely recover the membrane permeability after 60 days running, the membrane module was dismantled from the reactor unit and ex-situ chemical cleaning was conducted. Chemical cleaning sequence included: (1) pure water cleaning then soaked in pure water for 4 h; (2) cleaning with NaOCl at effective Cl^- concentration of 500 ppm followed by soaking in pure water for 4 h; (3) cleaning with 500 ppm citric acid solution then soaked in pure water for 4 h. Cleaning solutions were selected based on [25,28]. After each cleaning step the pure water flux (at 2.5 ms^{-1} cross flow velocity (CFV) and TMP 80 kPa) and the total fouling resistance were measured. This was carried out at 25 °C and pH of pure water was maintained around 7. All cleaning solutions were collected for membrane foulants analysis.

2.2. Sampling and Analytical Methods

The standard methods (American Public Health Association (APHA) 23rd Edition, 2017) were used for the analysis of the mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of the anaerobic sludge. The particle-size distribution of the anaerobic sludge was measured using Malvern Mastersizer 2000 (Malvern Co., Worcestershire, UK). Organic foulants were characterized and analyzed using three-dimensional fluorescence excitation-emission matrices analyzer (3D-EEM, F-7000, Hitachi, Tokyo, Japan). Details are provided in the supplementary document (S2). The molecular weight distribution of organic foulants in cleaning solutions was characterized using a high-performance liquid chromatograph (HPLC Breeze 1525, Waters Co., Milford, CT, USA) with ultraviolet absorbance detection from 200 to 300 nm. The 3D fluorescence analysis [29] and molecular weight analysis [30] are used in this study due to their high accuracy for membrane-fouling analysis. Statistical analysis was carried out using IBM SPSS Statistics 23 software produced by SPSS Incorporation (USA). DNA of the chemical cleaning solutions, inoculum and AnCMBR sludge was extracted by using a FAST DNA Spin Kit for Soil (MP Biomedicals, Solon, OH, USA) according to the manufacturer's instructions. Bacterial community was evaluated by polymerase chain reaction (PCR) amplification of 16S rRNA genes using the 515F/806R primers. Sequencing was conducted at the Sangon Co., Ltd. (Shanghai, China). This procedure and analysis were in accordance with Lu et al., 2019 [31].

2.3. Membrane Filtration Performance Analysis

Transmembrane pressure and flux were recorded daily. Typical theoretical equations commonly applied in previous research for membrane fouling behavior analysis were followed. For transmembrane pressure and flux, the Equations (1) [32] and Equation (2) [33] were used.

$$\mathrm{TMP} = \frac{(\mathrm{T1} + \mathrm{T2})}{2} \tag{1}$$

where, T1—inlet pressure (kPa) of the membrane and T2—outlet pressure (kPa) of the membrane.

$$\mathrm{J} = \frac{\mathrm{V}}{\mathrm{A}\Delta\mathrm{t}} \tag{2}$$

where J—permeate flux ($Lm^{-2}h^{-1}$), V—permeate volume (L), A—effective membrane filtration area (m^2), t—unit filtration time (s).

Normalized membrane flux (NMF) was calculated with Equation (3) [22] where J_0 is the initial flux ($Lm^{-2}h^{-1}$). Total membrane resistance (RT), flux recovery ratio(FRR) and flux decline coefficient (FDC) were calculated according to Equations (4)–(6) [34–36], respectively.

$$\mathrm{NMF} = \frac{\mathrm{J}}{\mathrm{J_0}} \tag{3}$$

$$\text{Total membrane resistance (RT)} = \frac{\Delta \mathrm{P}}{\mathrm{J}\mu} \tag{4}$$

$$\text{Flux Recovery Ratio (FRR)(100\%)} = \frac{\mathrm{J_{w1}}}{\mathrm{J_w}} \times 100 \tag{5}$$

$$\text{Flux decline coefficient (FDC)} = \frac{\mathrm{J_i} - \mathrm{J_w}}{\mathrm{J_w}} \times 100 \tag{6}$$

where R is membrane filtration resistance (m^{-1}),
J is membrane permeate flux ($Lm^{-2}h^{-1}$),
ΔP is trans-membrane pressure (TMP) (Pa),
μ is viscosity of the permeate (Pas),
J_i is the recovery flux ($Lm^{-2}h^{-1}$),
J_w is the pure water flux ($Lm^{-2}h^{-1}$),
Further permeability was calculated dividing flux by transmembrane pressure [32].

3. Results and Discussion

3.1. Effectiveness of In Situ Backwashing on Membrane-Fouling Control

3.1.1. Membrane Flux

In this study, membrane fouling was mainly investigated in accordance with the TMP evolution on a daily basis [37]. Figure S4a displays the profiles of TMP, flux versus operational time. Figure S4b illustrates the plot for permeability, CFV versus operational time. Thus the reversible fouling has been evaluated referring to the slope of the straight line of TMP against filtration time [38]. As shown in the Figure S4a, a rapid flux decline occurred during the startup without backwashing. This might be associated with the rapid formation of a cake layer on the surface of the membrane. Meanwhile the reactor was out of electricity for 8 h on the 10th day as a result of maintenance in the laboratory. This sudden pause of the filtration resulted in a great flux decline to 19 $Lm^{-2}h^{-1}$ as the initial permeate flux was fixed to 54 $Lm^{-2}h^{-1}$. It clearly indicates the requirement of continuous filtration with minimum disturbance for maintaining a sustainable flux level in membrane filtration. However in stage I with in situ backwashing at 60 s/day, the flux gradually rose to maximum of 43 $Lm^{-2}h^{-1}$ after 14 days. Furthermore, the reactor was subjected to a temporary breakdown of the recycling pump during 26–40 days. Afterwards, the membrane was capable of maintaining a stable flux level without development of TMP. This consistency in TMP demonstrates that the in situ backwashing at 60 s/day greatly helped in management of reversible fouling. Thus, in order to further optimize the effect of backwashing, its frequency was doubled on the 50th day. As shown in Table 2, accordingly, the mean flux during the in situ backwashing at twice a day with 2 × 60 s/d has yielded slightly higher flux indicating its slight effectiveness over that of once a day with 60 s/d. Table S1 compares the permeability values during pure water filtration, startup, stage I, stage II and after each cleaning process. Accordingly, during the startup permeability reduced greatly and it was 16.28% of the original pure water permeability. The permeability recovery was low in both backwashing stages. But both backwashing frequencies showed more than 70% recovery of initial membrane flux during filtration (membrane flux with backwashing (F_b)/initial flux (F_i) (54 $Lm^{-2}h^{-1}$) ratio. Therefore, the in situ backwashing once a day is more cost-effective considering the energy saving and less permeate consumption.

Table 2. The membrane filtration performance during three stages.

Scheme	Startup	60 s/d Backwashing	60 s × 2/d Backwashing
TMP (kPa)	82.27 ± 6.30	79.36 ± 4.31	80.31 ± 0.34
Flux ($Lm^{-2}h^{-1}$)	35.32 ± 19.57	38.78 ± 5.76	39.81 ± 0.34
RT (m^{-1})	$1.4 \times 10^{13} \pm 1.0 \times 10^{13}$	$8.4 \times 10^{12} \pm 1.5 \times 10^{12}$	$8.11 \times 10^{12} \pm 3.3 \times 10^{11}$
FDC (%)	62.07 ± 18.22	28.88 ± 10.56	26.99 ± 3.13
$Flux_{(b)}/Flux_{(i)}$	64.76%	71.14%	73.071%
Permeability ($Lm^{-2}h^{-1}$/kPa)	0.43 ± 0.23	0.48 ± 0.06	0.49 ± 0.02

The Pearson correlation analysis was applied to identify the relationship between general theoretical parameters derived from TMP and flux such as the flux decline coefficient (FDC) and total membrane resistance (RT). As listed in Table 3, during these two in-situ backwashing schemes, the FDC and RT showed a significant negative correlation which denotes that the permeate flux was reduced with the increased resistance. Further correlation between NMF and TMP without backwashing showed a slightly negative correlation.

Table 3. Pearson Correlation analysis for FDC versus TMP and normalized membrane flux (NMF) versus TMP.

Backwashing	FDC versus RT		NMF versus TMP	
	rp	p	rp	p
Startup	−0.984 **	0.008	0.179	0.701
60 s/d backwashing	−0.974 **	0.000	0.641 **	0.000
60 s × 2/day backwashing	−0.995 **	0.000	0.064	0.851

** Correlation is significant at the 0.01 level (1 tailed).

3.1.2. Three-Dimensional Fluorescence Excitation-Emission Matrices Analysis (3D-EEM)

The effectiveness of backwashing frequencies was further described on the basis of 3D-EEM analysis of AnMBR supernatant, permeate, and backwashing solutions. Figure 2 exhibits the EEM spectra of the selected samples and cleaning solutions. In stage 1, the anaerobic supernatant as shown in Figure 2a indicated the presence of Region II and IV substances (Ex 200–250/Em 330–380 for Region II and Ex 250–280/Em200–380 for region IV). The permeate as shown in Figure 2b,e indicated the presence of Region II and IV substances in both stages I and II, but their intensities have been reduced. The reduction of peak intensities of anaerobic supernatant obviously can be due to biodegradation of organic matter [39]. Thereby the permeate also indicated low intensity of these peaks. Strikingly the backwashing solution of stage II showed very low intensity of Region II and IV substances than that of the backwashing solution of stage I. Furthermore, Region V substances which were present during stage I were also absent in stage II. Backwashing solutions received these biopolymers from the cake layer fouling of the membrane or the permeate. Thereby, the low intensities of these biopolymers in the backwashing solutions indicated that these substances were less in the membrane fouling layer. With the continuous backwashing, the surface accumulation of these biopolymers on the tubular membrane might have been reduced ultimately, showing less fluorescence intensity. Furthermore, this implies that the reversible fouling caused by the hydrophilic acid fraction (HPIA) of protein-like (tryptophan-like: Ex 225–237 Em/340–381) substances can be easily washed out due to their weak attractions on membrane with continuous backwashing. The fluorescence index (FI) of backwashing solutions in stage I and II (Table S1) also revealed the reduction of its value from 2.19 and 1.87, respectively. FI >1.9 indicates that the dissolved organic matters are mainly dominated by microorganisms [40], and shows that these microbiologically originated substances have been reduced in the membrane fouling layer.

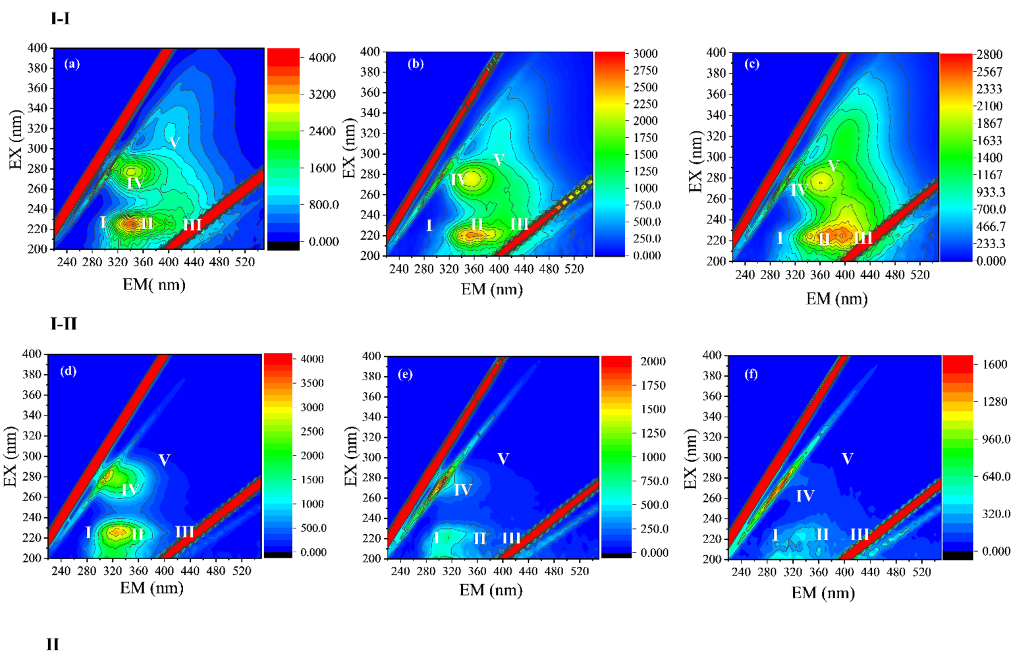

Figure 2. *Cont.*

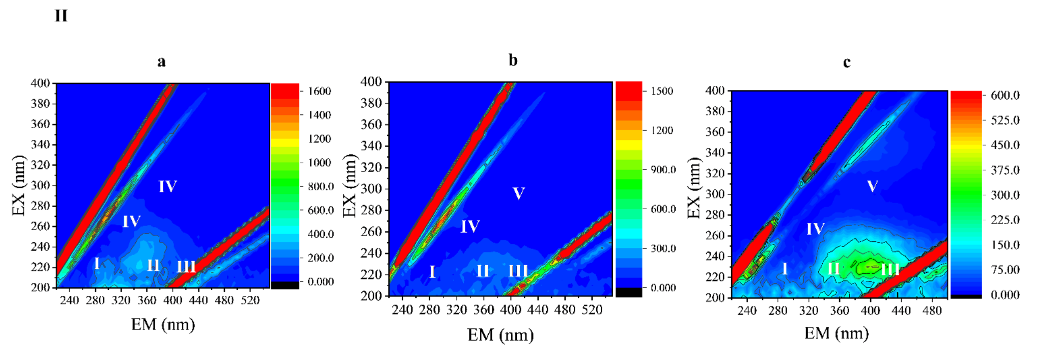

Figure 2. Fluorescence excitation–emission matrixes (EEM) of the selected samples and cleaning solutions. **I–I**: In the first backwashing (**a**) anaerobic sludge supernatant (**b**) permeate (**c**) backwashing solution. **I–II**: In the last backwashing (**d**) anaerobic sludge supernatant (**e**) permeate (**f**) backwashing solution. **II**: Chemical cleaning solutions (**a**) pure water (**b**) NaOCl (**c**) citric acid. Region I: tyrosine like proteins I; Region II: tryptophan like protein; Region III: fulvic acid-like (FA) substances; Region IV: soluble microbial by-product-like substances; Region V: humic acid-like (HA) substances [41].

3.1.3. Flux Recovery after the Membrane Cleaning

Table 4 indicates the flux recovery of the membrane after chemical cleaning. All cleaning solutions have shown considerable levels of flux recovery. Pure water, NaOCl and citric acid showed 70.54%, 92.63% and 78% of accumulated flux recovery respectively. The respective permeability recoveries are shown in Table S1. Due to over 70% recovery of the flux and permeability by the pure water cleaning in this study, this finding is very useful for more economical practical applications of pure water as a cleaning solution for ceramic membranes instead of widely applied chemicals if its flux recovery could be maximized further with more frequent cleaning. Citric acid cleaning has given only 78% flux recovery indicating less effectiveness. The pores might have been blocked during citric acid cleaning resulting in this less flux recovery. An assumption was developed based on the composition of the ceramic membrane and the chemical nature of the citric acid to elucidate this phenomena. After alkaline cleaning, citric acid has the ability to chemically react with the alkaline components and form salts such as calcium citrate because of its chemical nature. Calcium citrate can precipitate out as a solid [42,43]. This can block the membrane pores. Furthermore, as mentioned by Zeuner et al., 2019, purely ceramic membranes may be cleaned from fouling by alternately soaking in acid and alkaline solutions, but it is not viable here since the acid treatment could dissolve Y_2O_3 rich layer [22]. Less effectiveness of citric acid in recovering flux of ceramic Yttria composite membranes should be further evaluated in the future study. As proposed by Tang et al., Fenton chemical cleaning for ceramic membrane might be more successful over citric acid cleaning [44]. However, as there are concerns that repeated chemical cleaning might affect the membrane life, it should thus be limited. Considering the feasibility, tap water or permeate instead of pure water cleaning with more frequency will be a good option as it showed over 70% flux recovery in this study.

Table 4. The flux recovery of the ceramic membrane after chemical cleaning.

Parameter	Flux ($Lm^{-2}h^{-1}$)	TMP (kPa)	Flux Recovery
Virgin membrane	234.5	89.8	–
Fouled membrane	18	89.65	–
After pure water cleaning	165.45	81	70.54%
NaOCl cleaning	217.27	82.05	92.63%
Citric acid cleaning	183.63	83.95	78.29%

3.2. Major Organic Foulants of AnCMBR

3.2.1. Anaerobic Mixed Liquor

Figure 3 shows variation of MLSS, MLVSS, MLVSS/MLSS ratio, and particle size distribution (PSD) of the activated sludge. All particle sizes of anaerobic sludge are distributed in the range of 0–1000 µm. The average particle size of the initial inoculum was 16.04 µm, which showed the unimodel distribution, the n was reduced to 0.81 µm and 0.63 µm on Day 18 and Day 60, respectively. The continuous stirring and recirculation of mixed liquor in the AnCMBR can be responsible for this reduced mean particle size. When the mean particle size of anaerobic-activated sludge decreases, membrane fouling caused by anaerobic sludge can be more prone to be the pore blocking rather than the cake layer formation. But in this study, the pore size of the membrane is 0.1 µm and the mean particle size has not reduced less than this limit. Therefore, the major content of membrane fouling could be attributed to cake layer formation and for pore blocking in the lesser content. Figure S3 shows the view of the virgin ceramic membrane and the fouled membrane, and it exhibits a slight cake layer which confirms the above fact. In a study by Torres et al., 2011, the cake layer played the major role in ceramic tubular membrane fouling [45]. In this study the in situ backwashing was capable of reducing the formation of cake layer due to hydrophobicity of ceramic membrane. Cake layers on the ceramic membranes are much easier to be detached from the membrane surfaces than polymeric membranes [46].

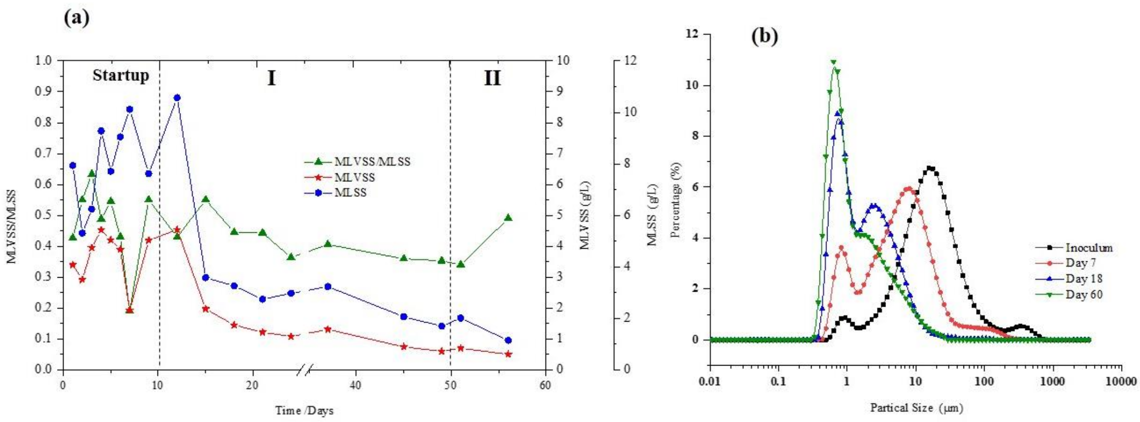

Figure 3. (**a**) Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) (**b**) and particle size distribution (PSD) during reactor operation.

During the initial days of the experiment the new inoculum adapted to the applied operational conditions, the refore rapid changes in the MLSS were observed during the initial stage (Figure 3). Initially, as backwashing was not conducted, the flux level changed very much due to the rapid formation of the fouling cake layer. However, immediately after employing backwashing at 60 s/d the flux profiles and MLSS reached stable conditions. By contrast, Hong et al. 2002 found that flux was not affected by the MLSS concentration within a moderate range of 3.5–8.5 g/L. However, some previous literature suggested that the high level of MLSS resulted in the decrease of the flux level of the membranes [47].

Table 5 indicates the correlation analysis between the variations of MLSS with TMP. It shows that there was both negative and positive correlation between the MLSS and TMP in backwashing stages I and II, respectively. The MLSS relationship to flux will be a function of reactor design [48]. Simultaneously, the high CFV at 2.5 ms^{-1} as shown in Figure S4b applied in this study might have resulted in lack of formation of biomass due to the imposed shear conditions [49]. High CFV might have a negative effect on biomass activities due to the high shear stress on the microorganisms, which destroy the sludge flocs. Throughout the in situ backwashing stages, the mean MLSS concentration was less than 3 g/L as the technical failure of the recycling pump resulted in mass washout of sludge from the system. However, Shine et al., 2018 reported that it is advisable to maintain the low MLSS which helps to reduce the energy demand of AnMBRs, but it will necessarily be accompanied by an increase in sludge production [50].

Table 5. Correlation analysis between the variations of MLSS with TMP.

Stage	MLSS vs. TMP		MLVSS/MLSS vs. TMP	
	rp	p	rp	p
60 s/d backwashing (I)	−0.526	0.145	−0.689 **	0.020
60 s × 2/d backwashing (II)	0.378	0.754	1.000 **	0.00

** Correlation is significant at the 0.01 level (1 tailed).

3.2.2. Organic Foulants

Figure 2II shows the 3D-EEM spectra for the cleaning solutions; 3D-EEM analysis of cleaning solution provides useful information on the presence of major organic foulants. In this study this cleaning process was conducted after the membrane was subjected to two backwashing stages. According to Figure 2II(a,b), the pure water cleaning solution and NaOCl cleaning solution did not indicate the presence of any clear peaks, but a slight intensity can be observed around Region II and III. This clear absence of peaks may be correlated with the continuous backwashing prior to the chemical cleaning process. As most of the biopolymers have been removed by the backwashing, the y might not appear in pure water and NaOCl solutions. Nevertheless NaOCl cleaning is very different from pure water cleaning. According to previous literature, the reason for the absence of peaks in NaOCl cleaning solutions maybe due to the destruction of biopolymers during NaOCl cleaning [51,52]. But as this study does not provide more information, the suitable concentration of NaOCl solutions and the interaction mechanism of NaOCl with ceramic membrane cleaning should be further studied. However citric acid cleaning solution indicated the presence of Region II and Region III substances (protein-like substances and fulvic acid (FA)-like substances), implying that those two components of dissolved organic carbon (DOC) have preferentially participated in irreversible fouling. Some previous works in the literature suggested that tryptophan protein-like and aromatic protein-like substances could be transformed to humic-like and fulvic-like substances gradually in the presence of NaOCl during chemical cleaning due to its oxidation process [53]. Furthermore, Sun et al., 2018 confirmed that proteins with the molecular weight greater than 20 kDa and humic acid like-substances were the principal components of dissolved organic matter (DOM) generated by NaOCl [51]. Chung et al., 2019 also showed that ceramic membrane fouling is attributed to major organic foulants such as humic acid (HA) and FA-like substances [54]. Fulvic-like substances are generated due to both soil base microbial activities and plant base microbial activities [55]. In this study, the anaerobic microbial process is their source.

The molecular weight (MW) distribution obtained from High pressure size exclusion chromatography (HPSEC) analysis is shown in Figure 4. The fractions removed by pure water cleaning are attributed to the Peaks 6, 7 and 8 at 1042 Da, 2064 Da and 3192 Da, respectively. Pure water enabled cleaning of very high MW substances (polysaccharides and HA) [56] attached to the cake layer with its rapid flush. Fractions smaller than 700 Da have been removed by citric acid while fractions between 300 Da–400 Da have been removed by NaOCl. Then these peaks are attributed to the low molecular weight substances probably irreversible fouling layer generally resulting in pore blocking, and these results imply that NaOCl and citric acid are effective in removal of irreversible fouling. On the other hand, it denotes that low molecular weight fractions of the biopolymers are the major foulants of irreversible fouling and high molecular weight fractions have resulted in the reversible fouling in this study; 3D-EEM spectra of the citric acid solution further confirms this observation by representing significant peaks in Region II and III (tryptophan like proteins and FA-like substance). Both NaOCl and citric acid are effective at removing low molecular weight substances which mostly resulted in pore blocking. This indicated that the FA-like substances and HA-like substances were the main contributors of organic fouling in this study, confirming the results obtained by 3D-EEM analysis.

Hence this part of organics might have more carboxylic groups and higher potential to adsorb on the membrane surface or inside the membrane pores. As Yttria composite ceramic membrane was used here, further analysis are suggested on membrane surface foulants interactions for fouling mechanism identification of Yttria-based ceramic tubular membranes.

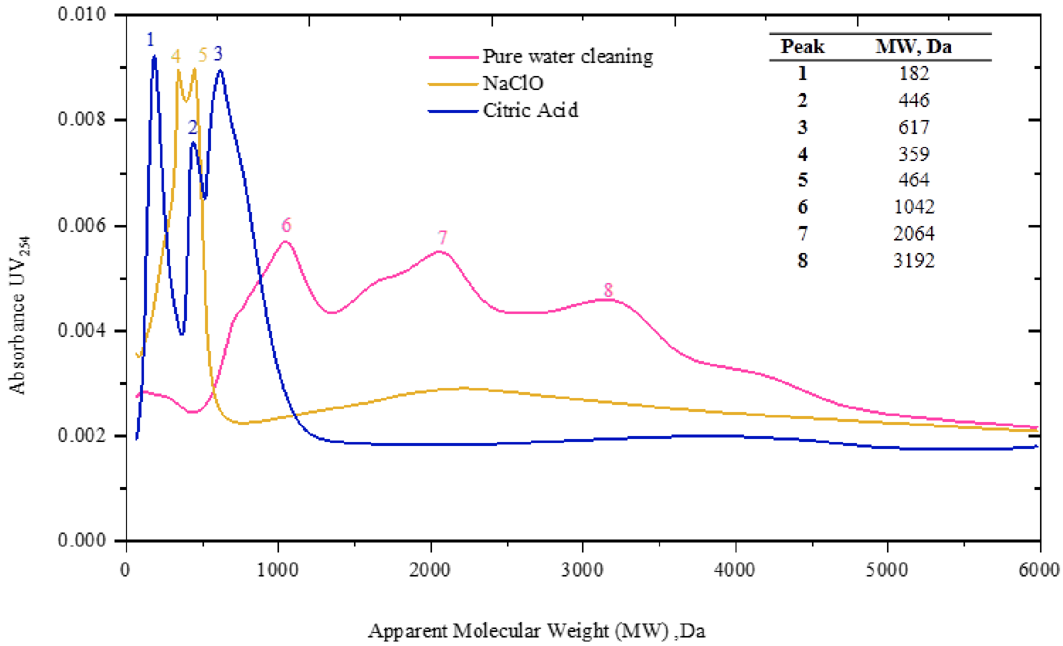

Figure 4. The apparent molecular weight distribution of cleaning solutions.

3.3. Biofouling of AnCMBR

The growth of microbes on the membrane surface termed as biofouling is an Achilles heel of membrane processes which reduces the permeability and durability of the membrane while increasing the energy consumption [57]. Biofouling is inherently more complicated than other membrane fouling phenomena and its formation mechanism includes adhesion of bacterial cells on the membrane, and their growth, multiplication and relocation on the membrane surface [58]. This study applied 16 s rRNA identification of microbial foulants for a tubular ceramic membrane, which is rarely applied for biofouling investigation of AnCMBR. Herein a destructive membrane autopsy was not obtained, enabling the use of the membrane after chemical cleaning. Instead, the cleaning solutions were subjected to DNA extraction and further analysis. Figure 5 exhibits the community bar plot analysis at phylum level for cleaning solution and anaerobic sludge. In order to describe the microbial fouling mechanism in this study, the conceptual diagram by Dong, 2015 [59] on fouling was used as shown in Figure S5. Accordingly, the membrane fouling layer is divided into three parts as loosely attached cake layer, strongly attached cake layer and pore blocking. Pure water cleaning represents the dominant bacteria in the loosely attached cake layer, while NaOCl and citric acid represents the bacteria in the strongly attached cake layer and pore blocking.

In the perspective of phylum level, pure water was numerically dominant with *Proteobacteria* (85%) meanwhile *Epsilonbacteraeota* (9.7%), *Bacteroidetes* (3.59%) and *Firmicutes* (0.7%) were subsequently dominant. NaOCl cleaning solution consisted of *Firmicutes* (35.5%), *Proteobacteria* (33.3%), *Bacteriodetes* (10.07%), *Actinobacteria* (6.67%), *Epsilonbacteria* (3.29%), *Synergistetes* (0.5%), *Chloroflexi* (1.07%), *Cyanobacteria* (4.7%), *Thermotogae* (0.7%), *Cloacimonetes* (0.57%) which were present in the strongly attached cake layer and pore blocking. Similarly, citric acid solution contained *Proteobacteria* (31.12%), *Firmicutes* (21.34%), *Epsilonbacteria* (19.01%), *Bacteriodetes* (16.6%), *Fusobacteria* (2.91%), *Actinobacteria* (7.68%). Accordingly the major bacteria involved in ceramic membrane fouling in this study can be shown in descending order in abundance as follows: *Proteobacteria* > *Firmucutes* > *Epsilonbacteria* >

Bacteroides > *Actinobacter*. Furthermore, it can be assumed that the pioneer phylum in loosely attached cake layer is *Proteobacteria*, and *Firmucutes* in strongly attached cake layer and *Epsilonbacteraeota* in pore blocking, respectively. A few studies have suggested the participation of members of the *Proteobacteria* in membrane fouling [60]. According to Watanabe et al., 2016, *Proteobacteria* is believed to cause membrane fouling and form biofilm on membrane surfaces [61]. Ziegler et al. (2016) revealed that α-,β-,δ-,γ-*Proteobacteria* were responsible for biofilm formation [62]. *Bacteroidetes* are considered to specialize in degrading complex organic matters, including those substances in the forms of polysaccharides and proteins. Members within *Bacteroidetes* are thus assumed to play a role in degradation of polysaccharides and proteins produced through bacterial secretion and cell lysis. By contrast, Xue et al., 2016 reported that *Bacteroidetes* in the membrane bioreactor (MBR) might play an important role in excellent anti-fouling performance of ceramic membrane [63]. *Firmicutes* are the key bacteria involved in anaerobic digestion process [64]. Previous studies suggest that *Proterobacteria* has largely contributed to biofouling in membranes. *Chloroflexi* recorded from NaOCl solution prefers consuming biomass associated with soluble microbial products in the biofilm, the reby minimizing accumulation of organic waste which contributes to the control of membrane fouling. In the present literature, two hypothesis consist that the microbial community in the bulk sludge is similar to that of the fouling layer [62] and not similar due to differences in the membrane environment [65]. This study examined these two controversies by comparing the bacterial community present in the bulk sludge after 60 days and the inoculum with that of the cleaning solutions. This study showed more or less similar microbial community composition of the biofouling layer with that of the bulk sludge and inoculum. Furthermore, Table S3 shows the effectiveness of the cleaning solutions on microbial fouling control on the basis of alpha diversity indices. NaOCl solution indicated highest ranks in Sobs and Shannon indices indicating its ability to remove more biofouling. Ceramic tubular membrane biofouling is a new area for research leading to development of new anti-fouling ceramic membranes. Based on the biofouling investigation of the chemical cleaning process and flux recovery values of this study, NaOCl was the most effective cleaning solution. However, the economic viability, low chemical applications and environmental friendliness of the cleaning solution should also be considered for applications in tropical developing countries.

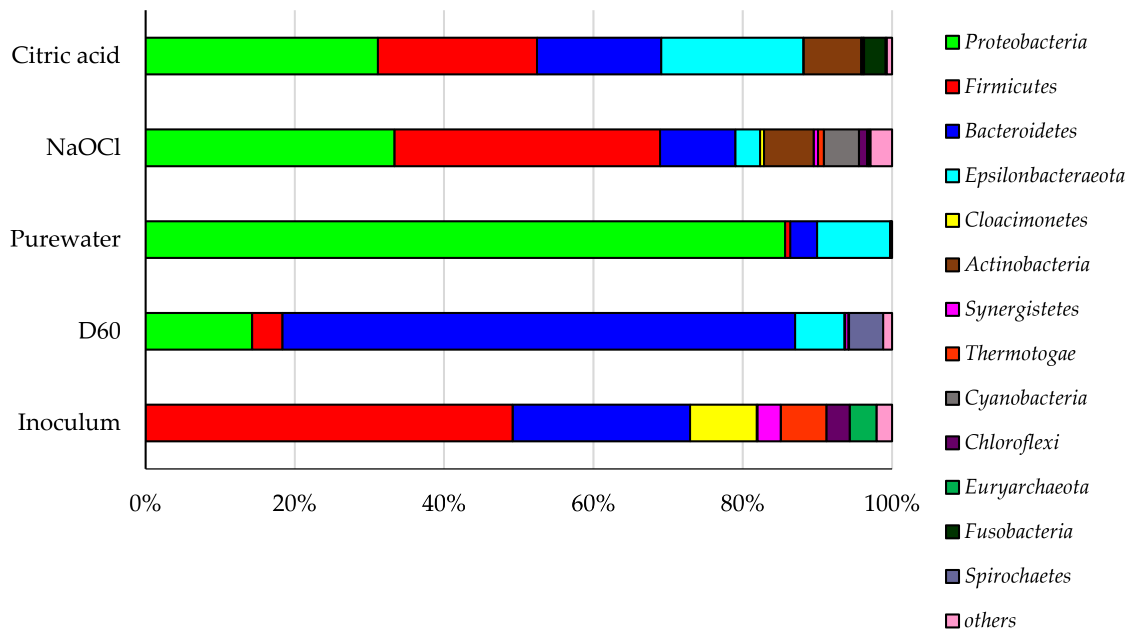

Figure 5. Community bar plot analysis at phylum level for cleaning solution and anaerobic sludge.

4. Conclusions

A novel strategy for filtration, relaxation and backwashing with minimal in situ backwashing frequency and short duration was employed for a tubular side stream membrane in an AnCMBR. This in situ backwashing with permeate at once a day significantly maintained stable flux over 70% of original flux for energy saving, because the cake layer formation was effectively reduced by in situ backwashing. Pure water cleaning resulted in over 70% flux recovery, and subsequent NaOCl and citric acid cleanings have further enhanced the flux recovery, and NaOCl was shown to be effective in controlling biofouling. This study provides implications for reducing the cost of widely applied chemical reagents for backwashing and chemical cleaning of ceramic membranes. Thus, a more environmentally and membrane-friendly form of fouling control was given by in situ permeate backwashing. Results of investigations of organic and bio-foulants of ceramic membranes showed that major organic foulants were fulvic acid-like substances and humic acid-like substances, and *Proteobacteria*, *Firmucutes*, *Epsilonbacteria* and *Bacteroidetes* contributed to biofouling of the ceramic membrane. Further long-term experiments are suggested to better evaluate these findings at a pilot scale.

Supplementary Materials: The following are available online at http://www.mdpi.com/2227-9717/8/5/545/s1: S1: Composition of synthetic wastewater; Figure S1: The novel control strategy; Figure S2: The outside in filtration mode during backwashing, S2: 3D-EEM analysis of anaerobic supernatant, permeate, backwashing solutions and cleaning solutions; Figure S3: The images of virgin and fouled membranes; Figure S4 (a) Transmembrane pressure and flux evolution; (b) permeability and cross flow velocity evolution; Table S1: The permeability values at different scenarios; Table S2: Fluorescence spectral parameters of samples of initial backwashing, final backwashing and the cleaning solutions; Figure S5: Conceptual diagram for ceramic membrane microbial fouling by Dong et al., 2015; Table S3: The effectiveness of the cleaning solutions on microbial fouling control.

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References

1. Ruigómez, I.; González, E.; Guerra, S.; Rodríguez-Gómez, L.E.; Vera, L. Evaluation of a novel physical cleaning strategy based on HF membrane rotation during the backwashing/relaxation phases for anaerobic submerged MBR. *J. Membr. Sci.* **2017**, *526*, 181–190. [CrossRef]
2. Lim, K.; Evans, P.J.; Parameswaran, P. Long-Term Performance of a Pilot-Scale Gas-Sparged Anaerobic Membrane Bioreactor under Ambient Temperatures for Holistic Wastewater Treatment. *Environ. Sci. Technol.* **2019**, *53*, 7347–7354. [CrossRef]
3. Maaz, M.; Yasin, M.; Aslam, M.; Kumar, G.; Atabani, A.E.; Idrees, M.; Anjum, F.; Jamil, F.; Ahmad, R.; Khan, A.L.; et al. Anaerobic membrane bioreactors for wastewater treatment: Novel configurations, fouling control and energy considerations. *Bioresour. Technol.* **2019**, *283*, 358–372. [CrossRef]
4. Ozgun, H.; Dereli, R.K.; Ersahin, M.E.; Kinaci, C.; Spanjers, H.; van Lier, J.B. A review of anaerobic membrane bioreactors for municipal wastewater treatment: Integration options, limitations and expectations. *Sep. Purif. Technol.* **2013**, *118*, 89–104. [CrossRef]
5. Abuabdou, S.M.A.; Bashir, M.J.K.; Choon Aun, N.; Sethupathi, S. Applicability of anaerobic membrane bioreactors for landfill leachate treatment: Review and opportunity. *IOP Conf. Ser. Earth Environ.Sci.* **2018**, *140*. [CrossRef]
6. Li, W.-W.; Yu, H.-Q. Advances in Energy-Producing Anaerobic Biotechnologies for Municipal Wastewater Treatment. *Engineering* **2016**, *2*, 438–446. [CrossRef]

7. Seib, M.D.; Berg, K.J.; Zitomer, D.H. Influent wastewater microbiota and temperature influence anaerobic membrane bioreactor microbial community. *Bioresour. Technol.* **2016**, *216*, 446–452. [CrossRef] [PubMed]
8. Chen, W.-H.; Tsai, C.-Y.; Chen, S.-Y.; Sung, S.; Lin, J.-G. Treatment of campus domestic wastewater using ambient-temperature anaerobic fluidized membrane bioreactors with zeolites as carriers. *Int. Biodeterior. Biodegrad.* **2019**, *136*, 49–54. [CrossRef]
9. Pena, M.; do Nascimento, T.; Gouveia, J.; Escudero, J.; Gomez, A.; Letona, A.; Arrieta, J.; Fdz-Polanco, F. Anaerobic submerged membrane bioreactor (AnSMBR) treating municipal wastewater at ambient temperature: Operation and potential use for agricultural irrigation. *Bioresour. Technol.* **2019**, *282*, 285–293. [CrossRef] [PubMed]
10. Yue, X.; Koh, Y.K.K.; Ng, H.Y. Membrane fouling mitigation by NaClO-assisted backwash in anaerobic ceramic membrane bioreactors for the treatment of domestic wastewater. *Bioresour. Technol.* **2018**, *268*, 622–632. [CrossRef] [PubMed]
11. Liu, Z.; Zhu, X.; Liang, P.; Zhang, X.; Kimura, K.; Huang, X. Distinction between polymeric and ceramic membrane in AnMBR treating municipal wastewater: In terms of irremovable fouling. *J. Membr.Sci.* **2019**, *588*. [CrossRef]
12. Dong, Z.; Shang, W.; Dong, W.; Zhao, L.; Li, M.; Wang, R.; Sun, F. Suppression of membrane fouling in the ceramic membrane bioreactor (CMBR) by minute electric field. *Bioresour. Technol.* **2018**, *270*, 113–119. [CrossRef] [PubMed]
13. Kimura, K.; Uchida, H. Intensive membrane cleaning for MBRs equipped with flat-sheet ceramic membranes: Controlling negative effects of chemical reagents used for membrane cleaning. *Water Res.* **2019**, *150*, 21–28. [CrossRef] [PubMed]
14. Lee, E.; Rout, P.R.; Shin, C.; Bae, J. Effects of sodium hypochlorite concentration on the methanogenic activity in an anaerobic fluidized membrane bioreactor. *Sci. Total Environ.* **2019**, *678*, 85–93. [CrossRef]
15. Wang, Z.; Meng, F.; He, X.; Zhou, Z.; Huang, L.N.; Liang, S. Optimisation and performance of NaClO-assisted maintenance cleaning for fouling control in membrane bioreactors. *Water Res.* **2014**, *53*, 1–11. [CrossRef] [PubMed]
16. Chung, J.; Kim, G.; Seo, K.W.; Jin, J.; Choi, Y.S. Effects of step-feeding and internal recycling on nitrogen removal in ceramic membrane bioreactors, and their hydraulic backwashing characteristics. *Sep. Purif. Technol.* **2014**, *138*, 219–226. [CrossRef]
17. Zhang, W.; Liu, F.; Wang, D.; Jin, Y. Impact of reactor configuration on treatment performance and microbial diversity in treating high-strength dyeing wastewater: Anaerobic flat-sheet ceramic membrane bioreactor versus upflow anaerobic sludge blanket reactor. *Bioresour. Technol.* **2018**, *269*, 269–275. [CrossRef]
18. Ren, B.; Li, C.; Zhang, X.; Zhang, Z. Fe(II)-dosed ceramic membrane bioreactor for wastewater treatment: Nutrient removal, microbial community and membrane fouling analysis. *Sci. Total Environ.* **2019**, *664*, 116–126. [CrossRef]
19. Smith, P.J.; Vigneswaran, S.; Ngo, H.H.; Ben-Aim, R.; Nguyen, H. A new approach to backwash initiation in membrane systems. *J. Membr. Sci.* **2006**, *278*, 381–389. [CrossRef]
20. Niwa, T.; Hatamoto, M.; Yamashita, T.; Noguchi, H.; Takase, O.; Kekre, K.A.; Ang, W.S.; Tao, G.; Seah, H.; Yamaguchi, T. Demonstration of a full-scale plant using an UASB followed by a ceramic MBR for the reclamation of industrial wastewater. *Bioresour. Technol.* **2016**, *218*, 1–8. [CrossRef]
21. Lin, H.; Peng, W.; Zhang, M.; Chen, J.; Hong, H.; Zhang, Y. A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. *Desalination* **2013**, *314*, 169–188. [CrossRef]
22. Zeuner, B.; Ovtar, S.; Persson, Å.H.; Foghmoes, S.; Berendt, K.; Ma, N.; Kaiser, A.; Negra, M.D.; Pinelo, M. Surface treatments and functionalization of metal-ceramic membranes for improved enzyme immobilization performance. *J. Chem. Technol. Biotechnol.* **2019**. [CrossRef]
23. Tang, S.; Li, J.; Zhang, Z.; Ren, B.; Zhang, X. Comparison of long-term ceramic membrane bioreactors without and with in-situ ozonation in wastewater treatment: Membrane fouling, effluent quality and microbial community. *Sci. Total Environ.* **2019**, *652*, 788–799. [CrossRef] [PubMed]
24. Zhang, C.; Qian, Y.; Yuan, L.; He, S.; Wang, Y.; Wang, L. Nutrients removal performance of a denitrifying phosphorus removal process in alternate anaerobic/anoxic-aerobic double membrane bioreactors (A2N-DMBR). *Water Sci. Technol.* **2018**, *78*, 1741–1752. [CrossRef]

25. Martin Vincent, N.; Tong, J.; Yu, D.; Zhang, J.; Wei, Y. Membrane Fouling Characteristics of a Side-Stream Tubular Anaerobic Membrane Bioreactor (AnMBR) Treating Domestic Wastewater. *Processes* **2018**, *6*, 50. [CrossRef]
26. Jepsen, K.L.; Bram, M.V.; Hansen, L.; Yang, Z.; Lauridsen, S.M.O. Online Backwash Optimization of Membrane Filtration for Produced Water Treatment. *Membranes (Basel)* **2019**, *9*, 68. [CrossRef]
27. Wu, R.-M.; Lin, Y.-J. Tubular Membrane Filtration with A Side Stream and its Intermittent Backwash Operation. *Sep. Sci.Technol.* **2012**, *47*, 1689–1697. [CrossRef]
28. Wang, X.; Ma, J.; Wang, Z.; Chen, H.; Liu, M.; Wu, Z. Reinvestigation of membrane cleaning mechanisms using NaOCl: Role of reagent diffusion. *J. Membr. Sci.* **2018**, *550*, 278–285. [CrossRef]
29. Yu, H.; Wu, Z.; Zhang, X.; Qu, F.; Wang, P.; Liang, H. Characterization of fluorescence foulants on ultrafiltration membrane using front-face excitation-emission matrix (FF-EEM) spectroscopy: Fouling evolution and mechanism analysis. *Water Res.* **2019**, *148*, 546–555. [CrossRef]
30. Lai, C.-H.; Chou, Y.-C.; Yeh, H.-H. Assessing the interaction effects of coagulation pretreatment and membrane material on UF fouling control using HPSEC combined with peak-fitting. *J. Membr. Sci.* **2015**, *474*, 207–214. [CrossRef]
31. Lu, T.; Zhang, J.; Wei, Y.; Shen, P. Effects of ferric oxide on the microbial community and functioning during anaerobic digestion of swine manure. *Bioresour. Technol.* **2019**, *287*. [CrossRef] [PubMed]
32. Yigit, N.O.; Civelekoglu, G.; Harman, I.; Koseoglu, H.; Kitis, M. Effects of various backwash scenarios on membrane fouling in a membrane bioreactor. *Desalination* **2009**, *237*, 346–356. [CrossRef]
33. Fan, R.; Ebrahimi, M.; Czermak, P. Anaerobic Membrane Bioreactor for Continuous Lactic Acid Fermentation. *Membranes (Basel)* **2017**, *7*, 26. [CrossRef] [PubMed]
34. Yang, T.; Xiong, H.; Liu, F.; Yang, Q.; Xu, B.; Zhan, C. Effect of UV/TiO2 pretreatment on fouling alleviation and mechanisms of fouling development in a cross-flow filtration process using a ceramic UF membrane. *Chem. Eng. J.* **2019**, *358*, 1583–1593. [CrossRef]
35. Ai, J.; Yang, L.; Liao, G.; Xia, H.; Xiao, F. Applications of graphene oxide blended poly(vinylidene fluoride) membranes for the treatment of organic matters and its membrane fouling investigation. *Appl. Surf. Sci.* **2018**, *455*, 502–512. [CrossRef]
36. Li, W.; Ling, G.; Lei, F.; Li, N.; Peng, W.; Li, K.; Lu, H.; Hang, F.; Zhang, Y. Ceramic membrane fouling and cleaning during ultrafiltration of limed sugarcane juice. *Sep. Purif. Technol.* **2018**, *190*, 9–24. [CrossRef]
37. Vera, L.; González, E.; Díaz, O.; Delgado, S. Application of a backwashing strategy based on transmembrane pressure set-point in a tertiary submerged membrane bioreactor. *J. Membr. Sci.* **2014**, *470*, 504–512. [CrossRef]
38. González, E.; Díaz, O.; Segredo-Morales, E.; Rodríguez-Gómez, L.E.; Vera, L. Enhancement of Peak Flux Capacity in Membrane Bioreactors for Wastewater Reuse by Controlling the Backwashing Strategy. *Ind. Eng. Chem. Res.* **2018**, *58*, 1373–1381. [CrossRef]
39. Hudson, N.; Baker, A.; Reynolds, D. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—A review. *River Res. Appl.* **2007**, *23*, 631–649. [CrossRef]
40. Yang, Y.; Qin, J.; Qi, T.; Zhou, X.; Chen, R.; Tan, J.; Xiao, K.; Ji, D.; He, K.; Chen, X. Fluorescence characteristics of particulate water-soluble organic compounds emitted from coal-fired boilers. *Atmos. Environ.* **2020**, *223*, 117297. [CrossRef]
41. Chen, W.W.; Leenheer, J.A.; Booksh, K. Fluorescence Excitation-Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter. *Environ. Sci. Technol.* **2003**, *37*, 5701–5710. [CrossRef] [PubMed]
42. Fultz, B.S. Using Citric Acid to Clean Concrete. *J. Prot. Coat. Linings* **2001**, *18*, 11.
43. Tanguy, G.; Tuler-Perrone, I.; Dolivet, A.; Santellani, A.C.; Leduc, A.; Jeantet, R.; Schuck, P.; Gaucheron, F. Calcium citrate insolubilization drives the fouling of falling film evaporators during the concentration of hydrochloric acid whey. *Food Res. Int.* **2019**, *116*, 175–183. [CrossRef] [PubMed]
44. Tang, S.; Zhang, L.; Peng, Y.; Liu, J.; Zhang, X.; Zhang, Z. Fenton cleaning strategy for ceramic membrane fouling in wastewater treatment. *J. Environ. Sci. (China)* **2019**, *85*, 189–199. [CrossRef]
45. Torres, A.; Hemmelmann, A.; Vergara, C.; Jeison, D. Application of two-phase slug-flow regime to control flux reduction on anaerobic membrane bioreactors treating wastewaters with high suspended solids concentration. *Sep. Purif. Technol.* **2011**, *79*, 20–25. [CrossRef]
46. Tolkou, A.; Zouboulis, A.; Samaras, P. The Incorporation of Ceramic Membranes in MBR Systems for Wastewater Treatment: Advantages and Patented New Developments. *Recent Pat. Eng.* **2014**, *8*, 24–32. [CrossRef]

47. Hong, S.P.; Bae, T.H.; Tak, T.M.; Hong, S.; Randall, A. Fouling control in activated sludge submerged hollow fiber membrane bioreactors. *Desalination* **2002**, *143*, 219–228. [CrossRef]
48. Liao, B.-Q.; Kraemer, J.T.; Bagley, D.M. Anaerobic Membrane Bioreactors: Applications and Research Directions. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 489–530. [CrossRef]
49. Gkotsis, P.K.; Zouboulis, A.I. Biomass Characteristics and Their Effect on Membrane Bioreactor Fouling. *Molecules* **2019**, *24*, 2867. [CrossRef]
50. Shin, C.; Bae, J. Current status of the pilot-scale anaerobic membrane bioreactor treatments of domestic wastewaters: A critical review. *Bioresour. Technol.* **2018**, *247*, 1038–1046. [CrossRef]
51. Sun, H.; Liu, H.; Han, J.; Zhang, X.; Cheng, F.; Liu, Y. Chemical cleaning-associated generation of dissolved organic matter and halogenated byproducts in ceramic MBR: Ozone versus hypochlorite. *Water Res.* **2018**, *140*, 243–250. [CrossRef] [PubMed]
52. Cai, W.; Hand, J.; Zhang, X.; Liu, Y. Formation mechanisms of emerging organic contaminants during on-line membrane cleaning with NaOCl in MBR. *J. Hazard. Mater.* **2019**, *386*, 121966. [CrossRef] [PubMed]
53. Zhai, S.; Zhang, W.; Li, T.; Zhang, W.; Lv, L.; Pan, B. Sodium hypochlorite assisted membrane cleaning: Alterations in the characteristics of organic foulants and membrane permeability. *Chemosphere* **2018**, *211*, 139–148. [CrossRef] [PubMed]
54. Chung, Y.; Kim, H.; Kim, T.-S.; Kim, Y.M.; Kang, S. Mitigation of organic fouling on ceramic membranes by selective removal of microbial-oriented organic matters in wastewater effluents. *Sep. Purif. Technol.* **2019**, *219*, 216–221. [CrossRef]
55. Jouraiphy, A.; Amir, S.; Winterton, P.; El Gharous, M.; Revel, J.-C.; Hafidi, M. Structural study of the fulvic fraction during composting of activated sludge–plant matter: Elemental analysis, FTIR and 13C NMR. *Bioresour. Technol.* **2008**, *99*, 1066–1072. [CrossRef]
56. Lee, N.; Amy, G.; Croue, J.P.; Buisson, H. Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Res.* **2004**, *38*, 4511–4523. [CrossRef] [PubMed]
57. Wu, Y.; Xia, Y.; Jing, X.; Cai, P.; Igalavithana, A.D.; Tang, C.; Tsang, D.C.W.; Ok, Y.S. Recent advances in mitigating membrane biofouling using carbon-based materials. *J. Hazard. Mater.* **2019**, *382*, 120976. [CrossRef] [PubMed]
58. Aslam, M.; Ahmad, R.; Kim, J. Recent developments in biofouling control in membrane bioreactors for domestic wastewater treatment. *Sep. Purif. Technol.* **2018**, *206*, 297–315. [CrossRef]
59. Dong, Q. Characterization of Anaerobic Membrane Bioreactors (AnMBR) Treating Municipal Wastewater. Ph.D. Thesis, University of Waterloo, Waterloo, ON, Canada, 2015. Available online: http://hdl.handle.net/10012/9179 (accessed on 31 March 2020).
60. Zheng, L.; Yu, D.; Wang, G.; Yue, Z.; Zhang, C.; Wang, Y.; Zhang, J.; Wang, J.; Liang, G.; Wei, Y. Characteristics and formation mechanism of membrane fouling in a full-scale RO wastewater reclamation process: Membrane autopsy and fouling characterization. *J. Membr. Sci.* **2018**, *563*, 843–856. [CrossRef]
61. Watanabe, R.; Nie, Y.; Takahashi, S.; Wakahara, S.; Li, Y.Y. Efficient performance and the microbial community changes of submerged anaerobic membrane bioreactor in treatment of sewage containing cellulose suspended solid at 25 degrees C. *Bioresour. Technol.* **2016**, *216*, 128–134. [CrossRef]
62. Ziegler, A.S.; McIlroy, S.J.; Larsen, P.; Albertsen, M.; Hansen, A.A.; Heinen, N.; Nielsen, P.H. Dynamics of the Fouling Layer Microbial Community in a Membrane Bioreactor. *PLoS ONE* **2016**, *11*, e0158811. [CrossRef]
63. Xue, J.; Zhang, Y.; Liu, Y.; Gamal El-Din, M. Treatment of oil sands process-affected water (OSPW) using a membrane bioreactor with a submerged flat-sheet ceramic microfiltration membrane. *Water Res.* **2016**, *88*, 1–11. [CrossRef] [PubMed]
64. Gao, D.-W.; Zhang, T.; Tang, C.-Y.Y.; Wu, W.-M.; Wong, C.-Y.; Lee, Y.H.; Yeh, D.H.; Criddle, C.S. Membrane fouling in an anaerobic membrane bioreactor: Differences in relative abundance of bacterial species in the membrane foulant layer and in suspension. *J. Membr. Sci.* **2010**, *364*, 331–338. [CrossRef]
65. Weerasekara, N.A.; Woo, S.-G.; Criddle, C.; Iqbal, T.; Lee, K.; Park, Y.-J.; Shin, J.-H.; Choo, K.-H. Clues to membrane fouling hidden within the microbial communities of membrane bioreactors. *Environ. Sci. Water Res. Technol.* **2019**, *5*, 1389–1399. [CrossRef]