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Treatment of cheese whey by a cross-flow anaerobic membrane bioreactor: Biological and filtration performance

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ABSTRACT

Whey, produced in large quantities during cheese production, is a rapidly fermentable high strength wastewater characterized by a high biodegradability and low alkalinity. In this study, a lab-scale cross-flow anaerobic membrane bioreactor was used to address the commonly experienced difficulties such as unstable reactor performance and unexpected biomass losses when treating whey wastewater with conventional anaerobic reactors. The anaerobic membrane bioreactor provided a stable treatment performance, i.e. more than 90% chemical oxygen demand removal, and moderate membrane fluxes between 8 and 11 $L\,m^{-2}\,h^{-1}$ could be obtained, applying a low cross-flow velocity of about 0.5 $m\,s^{-1}$. Short term critical flux tests revealed that higher fluxes up to 36 $L\,m^{-2}\,h^{-1}$ are possible at elevated cross-flow velocities and/or reduced mixed liquor suspended solids concentrations. Sludge filterability indicated by capillary suction time and specific resistance to filtration deteriorated throughout the study. Chemical cleaning efficiency gradually decreased, indicating irreversible membrane fouling during long term operation.

1. Introduction

Cheese whey, a by-product remaining after the precipitation and removal of milk casein and fats during the cheese making process, is considered either a resource of interest or a concentrated wastewater requiring treatment, depending on the different points of view. Whey basically represents 85–95% of the milk volume and typically contains lactose (4.5–5% w/v), soluble proteins (0.6–0.8% w/v), lipids (0.4–0.5% w/v), lactic acid (0.05% w/v) and mineral salts (8–10% of dry matter) (Siso, 1996). Although it is possible to recover many alternative products from whey, such as i) condensed or powdered whey, ii) whey protein concentrate, iii) lactose and its derivatives, many small to medium scale industries do not have the technical know-how or economic power to apply these valorization technologies. Thus, this makes it necessary to consider an efficient way for the treatment of whey as a wastewater stream (Malaspina et al., 1996; Mockaitis et al., 2006; Escalante et al., 2017).

When no valorization is possible, cheese whey is considered a very concentrated wastewater characterized by a high chemical and biochemical oxygen demand (COD and BOD), low pH and alkalinity. The whey wastewater is highly biodegradable (~ 99%) and the main portion of the COD can be attributed to the lactose content coming from the milk (Siso, 1996; Malaspina et al., 1996). Cheese whey can be classified as acid ($pH < 5$) or sweet (pH: 6–7), depending on the procedure used for casein precipitation. Acid whey generally has higher ash and salinity content, lower protein content than the sweet whey (Kosinowski, 1979; Patel and Madamwar, 1997). More than 50% of whey salts are NaCl and KCl and the rest are calcium salts, mainly phosphate (Siso, 1996). As a wastewater, whey needs extensive treatment prior to discharge into receiving water bodies (Prazeres et al.,

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Abbreviations: AnMBR, Anaerobic dynamic membrane bioreactor; AnRBC, Anaerobic rotating biological contactor; AnSBR, Anaerobic sequencing batch reactor; BOD, Biochemical oxygen demand; CFV, Cross-flow velocity; COD, Chemical oxygen demand; CST, Capillary suction time; CSTR, Completely stirred tank reactor; CEB, Chemically enhanced backwash; EGSB, Expanded granular sludge bed; EDX, Energy dispersive X-ray; FTIR, Fourier transform infrared; HPLC, High performance liquid chromatograph; MARS, Membrane anaerobic reactor separation; MBR, Membrane bioreactor; MLSS, Mixed liquor suspended solids; NF, Nano filtration; PVDF, Polyvinylidene fluoride; RO, Reverse osmosis; SEM, Scanning electron microscope; SRF, Specific resistance to filtration; SRT, Solids retention time; TKN, Total Kjeldahl nitrogen; TMP, Trans membrane pressure; TP, Total phosphorus; TS, Total solids; TSS, Total suspended solids; UASB, Upflow anaerobic sludge blanket reactor; VFA, Volatile fatty acid; VLR, Volumetric loading rate; VSS, Volatile suspended solids

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2012; Carvalho et al., 2013).

Anaerobic digestion is considered the state-of-the-art technology for the treatment of high strength industrial wastewaters such as whey. Therefore, digestion of cheese whey was investigated by many researchers and several different reactor configurations such as anaerobic upflow fixed film reactor (Gannoun et al., 2008; Patel et al., 1994), anaerobic rotating biological contactor (AnRBC) (Patel and Madamwar, 1997), two phase system consisting of a completely stirred tank reactor (CSTR) (hydrolytic stage) and an AnRBC (methanogenic stage) (Lo and Liao, 1988), upflow anaerobic sludge blanket reactor (UASB) (Yan et al., 1990; Hwang et al., 1992), two stage system consisting CSTR and UASB reactors (Diamantis et al., 2014) and anaerobic membrane bioreactor (AnMBR) (Saddoud et al., 2007; Spagni et al., 2010) were proposed for the treatment of this concentrated wastewater. Although more than 90% COD removal efficiency could be obtained, several studies reported continuous requirement of alkalinity supplementation (Mockaitis et al., 2006), impairment of biomass granulation (McHugh et al., 2003), calcification of sludge bed (El-Mamouni et al., 1995), biomass washout (Malaspina et al., 1996), and process failures (Gavala et al., 1999). Thus, the whey wastewater, despite its high biodegradability, is considered as a quite problematic substrate for anaerobic treatment due to its high rapidly acidifiable COD, salt and calcium content, and lack of alkalinity (Malaspina et al., 1996; Patel and Madamwar, 1997). It is underlined that alkalinity supplementation was crucial for the anaerobic treatment of cheese whey, especially during the reactor start-up and high organic load periods. Alternative methods to maintain a stable reactor performance for the anaerobic treatment of whey wastewater were also proposed. Anaerobic co-digestion of cheese whey together with substrates having high buffer capacity such as dairy manure and poultry waste was recommended to achieve and sustain a stable treatment performance (Lo et al., 1988; Desai and Madamwar, 1994; Comino et al., 2009; Brown et al., 2016). In case of UASB and expanded granular sludge bed (EGSB) reactors, effluent recycling is regarded conditional for achieving stabilized reactor performance, owing to effective dilution of influent COD, efficient use of effluent alkalinity for upfront neutralization (less chemical costs), and improved hydraulic mixing.

AnMBRs offer an important potential for the treatment of industrial wastewaters such as whey, which can cause problems in high-rate anaerobic reactors that rely on the granulation of biomass (Dereli et al., 2012). They provide a stable reactor performance by retaining slow growing methanogens with the help of filtration and produce particle free and high-quality effluents, which can be further used for water recovery in industries and agriculture. In fact, one of the first commercial example of AnMBRs, referred to as membrane anaerobic reactor separation (MARS) system, was developed by Dorr-Oliver Company in the early ‘80 s for the treatment of cheese whey (Gao et al., 2014). Most recently, Saddoud et al. (2007) treated cheese whey by a two staged system consisting of an acidogenic CSTR and a methanogenic AnMBR, and reported very high COD removal efficiencies and permeate fluxes up to 98.5% and 139.5 $L\,m^{-2}\,h^{-1}$, respectively. They obtained this high flux in short term tests by using a ceramic microfiltration membrane operated at a cross-flow velocity (CFV) of 5 $m\,s^{-1}$ and trans membrane pressure of 1.75 bars. However, Spagni et al. (2010) have reported much lower fluxes (2–5 $L\,m^{-2}\,h^{-1}$) compared to Saddoud et al. (2007) on long term tests for the treatment of whey and sucrose mixture (1:1 in COD basis) in a submerged AnMBR.

Anaerobic membrane bioreactors can address some of the above-mentioned problems, i.e. poor granulation and biomass washout, for cheese whey treatment and provide a high and stable treatment efficiency. The purpose of this study is to investigate the biological and filtration performance of an AnMBR treating cheese whey. Long term filtration performance of the reactor was presented and short term critical flux tests were conducted to investigate the effect of CFV and mixed liquor suspended solids (MLSS) concentration on achievable membrane flux. Finally, post-mortem analysis of the used membrane was conducted to investigate the physical and chemical cleaning efficiency on membrane foulants.

2. Materials and methods

2.1. Experimental methods

Routine parameters such as total suspended solids (TSS), volatile suspended solids (VSS), total Kjeldahl nitogen (TKN), ammonium nitrogen was measured according to Standard Methods (APHA, 1998). COD, total phosphorus (TP) and phosphate phosphorus (PO_4^{3-}-P) were measured with Hach Lange kits. Soluble parameters were measured after filtering the sample through 0.45 µm syringe filters (Millipore). Soluble protein and carbohydrates were measured by using bicinchoninic acid (Sigma Aldrich BCA) and phenol-sulfuric acid methods (Dubois et al., 1956), respectively. Anions and cations were measured using two different high performance liquid chromatographs (HPLC) (Millipores Waters Model 430 and Metrohm 761 Compact IC).

Particle size distribution of the mixed liquor was determined with laser diffraction analysis (Beckman Coulter LS230). Critical flux was measured according to Le-Clech et al. (2003) by increasing the flux with 2 $L\,m^{-2}\,h^{-1}$ increments for 15 min. Backwash with the same flux was applied for 1 min in between each step. A slope of $dP/dt \geq 1$ $mbar{\cdot}min^{-1}$ was used as the criteria to determine if the critical flux was reached. Physical and chemical membrane cleaning was performed before each critical flux test. Supernatant samples were prepared by centrifuging sludge 17,500 g for 10 min and then decanting the sample to a separate container. Colloidal COD was calculated by subtracting soluble COD from supernatant COD. Supernatant filterability, capillary suction time (CST) and specific resistance to filtration (SRF) was measured according to Dereli et al. (2014). Viscosity of the sludge at 37 °C with different TSS concentrations was measured with a viscometer (Thermo Scientific Haake Viscotester 550).

2.2. Wastewater characterization

Concentrated whey permeate obtained from a cheese manufacturer was used in the study. The substrate was prepared by diluting the concentrated feed stock with tap water in order to achieve a total COD concentration of 29.2 ± 3.3 $g\,L^{-1}$. The average soluble protein and carbohydrate concentrations in the feed was measured as 1.4 and 14.1 $g\,L^{-1}$, respectively. The concentrations of other parameters in the feed are presented in Table 1. Since whey contains low concentrations of nitrogen due to casein harvesting in the cheese making process, COD:TKN ratio of the whey was adjusted to around 50 by adding urea in order to prevent biomass growth limitation. The feed contained high

Table 1
Feed characterization (mean ± standard deviation).

Parameters	Unit	Concentration
pH	–	5.3 ± 0.5
Total COD	$g\,L^{-1}$	29.2 ± 3.3
Soluble COD	$g\,L^{-1}$	28.9 ± 3.3
TS	$g\,L^{-1}$	27.3 ± 3.0
VS	$g\,L^{-1}$	23.0 ± 2.8
TSS	$mg\,L^{-1}$	460 ± 400
VSS	$mg\,L^{-1}$	340 ± 215
TKN	$mg\,L^{-1}$	600 ± 135
NH_4^+-N	$mg\,L^{-1}$	45 ± 14
TP	$mg\,L^{-1}$	415 ± 45
PO_4^{3-}-P	$mg\,L^{-1}$	360 ± 55
Na^+	$mg\,L^{-1}$	405 ± 160
Mg^{2+}	$mg\,L^{-1}$	107 ± 60
K^+	$mg\,L^{-1}$	560 ± 130
SO_4^{2-}	$mg\,L^{-1}$	112 ± 70
Ca^{2+}	$mg\,L^{-1}$	470 ± 120
Cl^-	$mg\,L^{-1}$	2080 ± 620

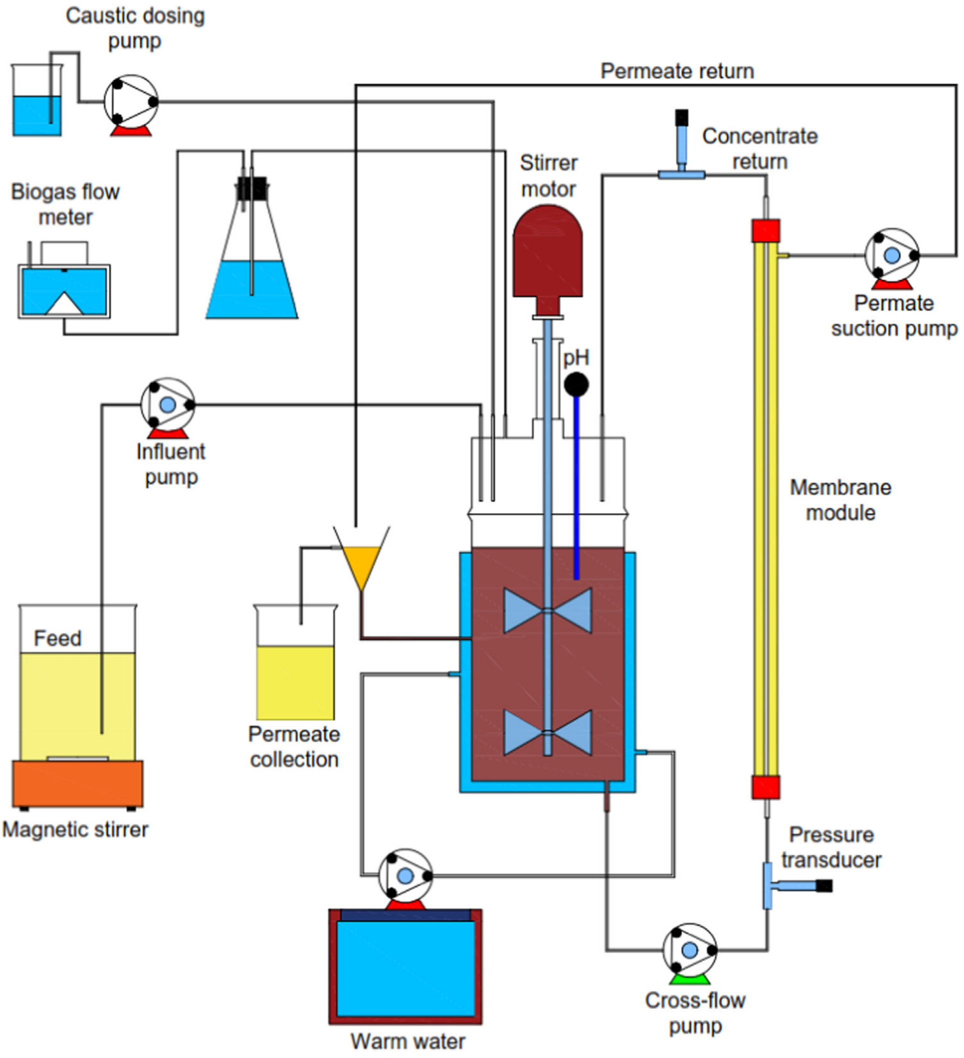


Fig. 1. Lab-scale cross-flow AnMBR setup.

concentrations of calcium and potassium.

2.3. Reactor configuration and operation

A 10 L CSTR coupled with a cross-flow tubular ultrafiltration membrane module was used as the lab-scale AnMBR (Fig. 1). The reactor was mixed with a top entry mechanical mixer (35 rpm) and membrane recirculation loop (0.92 m^{3} d^{-1}). The reactor was operated at mesophilic conditions (37 °C) for 169 days. Granular sludge obtained from a full-scale EGSB reactor treating lactose-based wastewater was crushed and used as inoculum. Trans membrane pressure (TMP), pH and daily biogas production of the reactor was logged online at different intervals. The pH was set to 6.7–7.2 and automatically controlled (Hach Lange SC-1000) by dosing 1 N caustic into the reactor. The reactor was started-up (first 4 weeks) with complete retention of the anaerobic biomass. Following this period, the solids retention time (SRT) was regulated at 50 days by discarding 200 mL of mixed liquor daily from the reactor to keep MLSS concentration at around 40 g L^{-1}.

The tubular membrane used in the study was made of polyvinylidene fluoride (PVDF) and had a pore size and effective filtration area of 0.03 µm and 0.0114 m^2, respectively. The clean water permeability of the membrane was reported as 1000 L m^{-2} h^{-1} bar^{-1} (20 °C) by the manufacturer (Pentair X-Flow). The inside-out membrane had a diameter and length of 5.2 mm and 70 cm, respectively. The membrane was operated with a CFV of 0.5 m s^{-1} supplied by a peristaltic pump (Watson Marlow 530U). The filtration was performed under variable pressure and flux method. 60 min filtration and 2 min backwash cycles were applied during operation. The backwash was automatically done by reversing the permeate suction pump (Watson Marlow 120U) direction at a double flux (16–22 L m^{-2} h^{-1}). Chemical cleaning with NaOCl (500 ppm, 2–4 h) and citric acid (1% w/v, 2–4 h) was conducted when the permeability decreased to 30 L m^{-2} h^{-1} bar^{-1}.

2.4. Membrane autopsy

An autopsy was performed on the fouled membrane at the end of the reactor operation. The membrane was cut into pieces and the samples were fixed with 3.0% glutaraldehyde in 0.1 M phosphate buffer at pH 7.2. Then the samples were dehydrated by soaking in to ethanol solutions with increasing volumetric ratios (50%, 70%, 80%, 90%, 95%). The fouling layer on the membrane was observed with a scanning electron microscope (SEM) (Jeol JSM 5600 LV). The elemental composition of fouling layer was analyzed with energy dispersive X-ray (EDX) spectroscopy (FEI Quanta FEG250). The major functional groups of foulants were characterized with a Fourier Transform Infrared (FTIR) Spectrophotometer (Perkin Elmer Spectrum 100 FT-IR).

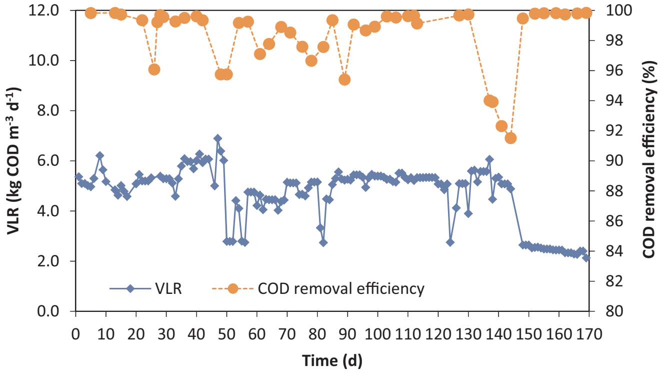


Fig. 2. VLR and COD removal efficiency of the reactor throughout the study.

3. Results and discussion

3.1. Biological performance

In general, a high COD removal efficiency over 90% was observed in the AnMBR (Fig. 2). The efficiency dropped sharply when the feed nitrogen content was decreased from 700 mg L^{-1} to 110 mg L^{-1} between 130 and 169 days. However, the reactor quickly regained its stability (> 98% COD removal efficiency), when volumetric loading rate (VLR) decreased at day 148 while maintaining the reduced nitrogen concentration. The effect of nitrogen on the performance of AnMBRs treating cheese whey was broadly discussed in Dereli et al. (2018). They reported that nitrogen limitation caused reactor instability in terms of volatile fatty acid (VFA) accumulation, especially propionic acid, and a low COD to nitrogen ratio is required for efficient treatment of rapidly degradable wastewaters. The specific methane generation of the reactor varied between 0.24 and 0.30 Nm^{3} kg^{-1} $COD_{removed}$ throughout the study.

The effluent total COD concentration at an average VLR of 5 kg COD m^{-3} d^{-1} was 365 mg L^{-1}. It was even possible to obtain a mean effluent COD concentration of 55 mg L^{-1} when the operating VLR was reduced to 2 kg COD m^{-3} d^{-1}. However, at these low VLRs, AnMBRs lose their advantage and feasibility over ordinary CSTR reactors (Liao et al., 2006).

The performance of different anaerobic reactor configurations for the treatment of cheese whey is summarized in Table 2. As it can be seen from Table 2, the studies conducted with AnMBRs reported very high COD removal efficiencies, outperforming the other types of reactors. This is mainly due to the presence of membrane separation that removes all the particulate matter from the effluent. At normal operation conditions (VLR around 5 kg COD m^{-3} d^{-1}) the COD removal efficiency of the AnMBR was always over 95% which indicates the stability of the system compared to other types of reactors with a wide range of COD removal efficiency (10–99%). This is due to the prevention of uncontrolled biomass washout which makes the AnMBRs more stable under changing operation conditions such as VLR and pH variations. Another advantage of AnMBR is the particle and pathogen free permeate production which can be directly reused in agriculture or in industries after nano filtration (NF) or reverse osmosis (RO) polishing.

The high lactose content of cheese whey is known to promote acidogenic biomass growth (Yang et al., 2003; Diamantis et al., 2014; Dereli et al., 2015, 2018). The sludge yield was calculated as 0.19 ± 0.03 g VSS g^{-1} $COD_{removed}$. This is considered very high but it agrees well with the yields reported for the anaerobic treatment of carbohydrate-based wastewaters (Fernández et al., 2011; De Kok et al., 2013). The TSS and VSS concentrations in the reactor are depicted in Fig. 3. The reactor was initially started-up without biomass discharge except sampling and the MLSS concentration increased gradually up to 40 g L^{-1} within 40 days. Hereafter, routine biomass wastage was performed, targeted at keeping the MLSS concentration at about 40 g L^{-1}; the resulting SRT was about 50 days. Similarly, Spagni et al. (2010) had to increase sludge discharge to control MLSS concentration and consequently reduce the SRT while operating an AnMBR fed with whey and sucrose mixture.

3.2. Long term filtration performance

The operating flux, TMP and membrane permeability of the lab-scale cross-flow AnMBR is given in Fig. 4. The operating flux ranged from 8 to 11 L m^{-2} h^{-1}. Considering the high sludge concentration and low CFV (0.5 m s^{-1}) applied in the study, the obtained membrane flux is promising. Saddoud et al. (2007) reported remarkably high short term fluxes in an AnMBR, equipped with a cross-flow flat sheet ceramic membrane, treating whey. However, their reactor contained 8.5 g L^{-1} MLSS concentration and they applied a CFV of 5 m s^{-1} that is significantly higher than the present study. Besides that, the reported high fluxes were obtained in short term tests (< 60 min) and it is not clear that these were sustained during long term operation. Spagni et al. (2010) obtained lower operational fluxes between 2 and 5 L m^{-2} h^{-1}, while operating a submerged AnMBR fed with a mixture of whey and sucrose. They applied a gas recirculation rate of 56 m^{3} m^{-2} h^{-1} and observed rapid membrane fouling indicated by TMP jumps at slightly higher fluxes than 5 L m^{-2} h^{-1}. They applied chemical cleaning when the TMP reached to 500 mbars. In our study, the permeability of the membrane varied between 30 and 120 L m^{-2} h^{-1} bar^{-1} and it required periodic chemical cleaning in order to keep the operational TMP below 350 mbars (Fig. 4). Saddoud et al. (2007) reported a TMP of 1.75 bars at a flux of 139.5 L m^{-2} h^{-1} which corresponds to a membrane permeability of 55 L m^{-2} h^{-1} bar^{-1} at 20 °C at short term tests.

All the sludge filterability indicators tended to worsen during operation. The normalized CST and SRF of the seed sludge was 3 s L g^{-1} TSS and 42 E^{12} m kg^{-1}, respectively. At the end of the study, they increased up to 65 s L g^{-1} TSS and 1600 E^{12} m kg^{-1}. In the current study a decreasing supernatant filterability, which correlated well with gradually increasing colloidal COD, was observed (Fig. 5). The supernatant filterability provides insight in the fouling propensity of fine particles such as colloids and solutes (Rosenberger et al., 2006; Le-Clech et al., 2006; Meng et al., 2009). We found a moderate correlation between supernatant COD and membrane permeability (Pearson correlation coefficient: -0.49). Spagni et al. (2010) reported a high correlation between supernatant COD and membrane fouling when treating whey and sucrose mixture in an AnMBR. Le-Clech et al. (2006) evaluated that the relative contribution of supernatant COD to overall membrane fouling ranges from 17% to 81% in membrane bioreactors (MBRs).

In addition to the increase of supernatant COD, the median particle size of the mixed liquor decreased to 13 μm and the particle size distribution became bimodal (Fig. 6). This may be due to accumulation of colloids and/or proliferation of acidogenic bacteria which grow dispersedly over rapidly fermentable substrate, i.e. lactose (Alphenaar, 1994; Jeison et al., 2009; Dereli et al., 2015). In parallel to these findings, two different fractions of sludge became visible, a dark and a light fraction, especially in the pellet when the sludge was centrifuged. The median particle size of the light fraction was only 4 μm, which was significantly lower than the bulk sludge.

The decrease in the membrane permeability may be due to several reasons such as increasing TSS concentration, viscosity and supernatant COD and decreasing median particle size of the sludge. These parameters are known to influence the fouling in membrane bioreactors (Le-Clech et al., 2006; Meng et al., 2009). Although there is no consensus on the effect of TSS concentration on membrane fouling and sludge filterability, it is often regarded as one of the main foulant parameters (Le-Clech et al., 2006). The interaction between the solutes, colloids and particles makes the TSS concentration a difficult parameter to evaluate. Lousada-Ferreira et al. (2015) reported for aerobic MBRs that there is an optimum MLSS concentration, which ensures both particle

Table 2
Performance summary of different types of anaerobic reactors used for the treatment of cheese whey.

Substrate type	Reactor type	Effective reactor volume (L)	Temperature (°C)	HRT (d)	VLR (kg COD m^{-3} d^{-1})	COD removal efficiency (%)	Specific methane generation (m^3 kg^{-1} $COD_{removed}$)	Reference
Diluted whey permeate	AnMBR	10	37	5–13 (6)[a]	2–6 (5)[a]	90–99 (98)[a]	0.24–0.30 (0.28)[a,b]	This study
Whey permeate	CSTR + AnSBR	3 + 25	35 + 55	1st stage: 1.5–3.0 2nd stage: 12.5–25	1st stage: 12.7–25.3 2nd stage: 1.2–2.4	–	0.25–0.35	Fernandez et al. (2015)
Whey permeate	AnSBR	25	55	8.3–25	1.5–4.6	87	0.29–0.32[b]	Fernandez et al. (2015)
Whey permeate	CSTR	2	37	31	3.1	86	–	Dereli et al. (2015)
Whey Permeate	AnSBR + CSTR	2 + 2	37	1st stage: 2.2 2nd stage: 29	1st stage: 30.8 2nd stage: 1.9	88	0.31	Dereli et al. (2015)
Diluted whey	UASB	2	30	0.5–1.2	10–23	68	0.28	Diamantis et al. (2014)
Diluted whey	CSTR + Settling tank + UASB	2 + 2	Ambient + 30	1st stage: 0.4 2nd stage: 0.5–1.2	1st stage: 22.2 2nd stage: 6.7–15	78	0.31	Diamantis et al. (2014)
Diluted whey	CSTR[c] + Settling tank + UASB	2 + 2	Ambient + 30	1st stage: 0.4 2nd stage: 0.5–0.7	1st stage: 22.2 2nd stage: 7–19	88	0.37	Diamantis et al. (2014)
Raw whey	CSTR + Upflow AF	2 + 2	32 + 35	1st stage: 0.83 2nd stage: 1–4	1–4	72–90	0.09–0.11	Gannoun et al. (2008)
Raw whey	CSTR + AnMBR	5 + 15	37 + 37	1st stage: 1 2nd stage: 4	3–19.8	99	0.3	Saddoud et al. (2007)
Raw whey	UASB	4	12–20	0.75–2	0.5–13.3	52–92	–	McHugh et al. (2006)
Reconstituted whey powder	ASBR	5	30	0.83	0.6–4.8	79–84	–	Mockaitis et al. (2006)
Diluted whey	CSTR + CSTR	1 + 5	54 + 55	1st stage: 0.4 2nd stage: 2.6–9.6	1.0–3.3[d]	64–96	0.1–0.38	Yang et al. (2003)
Diluted whey	CSTR	5	55	4.5–10	1.0–4.4[d]	10–95	0.06–0.36	Yang et al. (2003)
CW diluted with dairy wastewater	AnRBC	5	37	1–5	6–30	65–80	–	Patel and Madamwar (1997)
Raw whey	Two-stage, unmixed digester	155	25–35	10–20	–	28–36	–	Ghaly (1996)
Raw whey	Downflow-Upflow hybrid reactor	51	–	–	< 10	91–99	0.33[b]	Malaspina et al. (1996)
Whey permeate	UASB	7.2	35	0.4–5	2.1–26.7	64–99	–	Hwang et al. (1992)
Raw whey	UASB	17.5	33	5	0.9–7.6	> 90	–	Yan et al. (1990)

[a] Average of total operation time.
[b] In Nm^3 CH_4 kg^{-1} COD_{fed} unit.
[c] With biomass return to CSTR from settling tank.
[d] Calculated from the reported data.

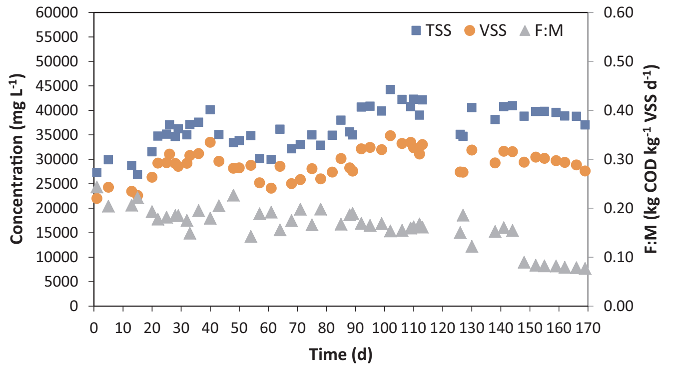


Fig. 3. Mixed liquor TSS and VSS concentrations in the reactor and F:M ratio throughout the study.

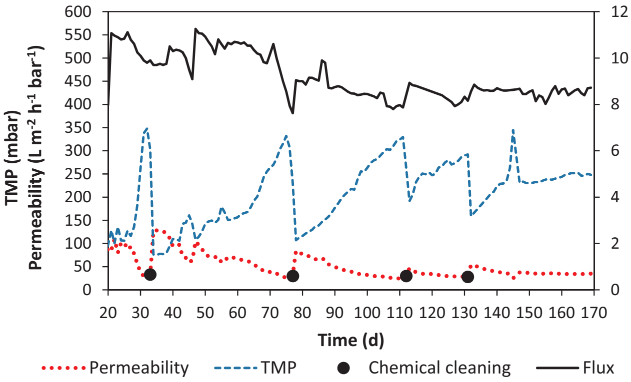


Fig. 4. Long term membrane flux, TMP and permeability (20 °C).

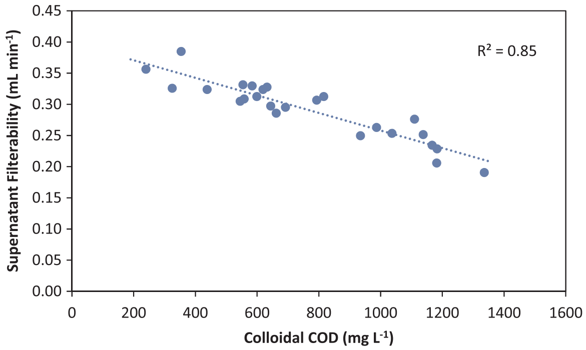


Fig. 5. Relationship between colloidal COD and supernatant filterability.

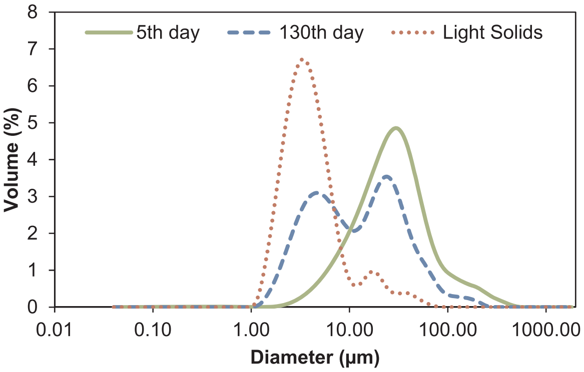


Fig. 6. Particle size distribution of mixed liquor and light solids.

flocculation and good filterability.

Cake layer formation was reported as the most important fouling mechanism in AnMBRs (Jeison and van Lier, 2007; Charfi et al., 2012). According to standard filtration theory, explained by Carman-Kozeny equation, the filtration resistance of cake layer increases as its porosity decreases. Thus, accumulation of small sized particles on the membrane results in compact and less porous structures with a high filtration resistance. It was also reported that small sized particles have a higher tendency to interact with membrane surface (Shen et al., 2015). The back transport of particles from the membrane surface is strongly dependent on their diameter (Choo and Lee, 1998) and it requires a higher shear rate to prevent the small particles depositing on the membrane. On the other hand, several researchers reported that even at high crossflow velocities and/or at very low fluxes, the fouling continues to develop due to adsorption of foulants on the membrane surface (Le-Clech et al., 2003; Zhang et al., 2007). Adhesion of solutes, colloids and small particles on the membrane generates the so called “gel layer” with a high porosity and water content but an extremely high filtration resistance (Chen et al., 2016). Recent studies shed some light on the unexpectedly high filtration resistance of gel layer and led to the development of osmotic pressure effect due to chemical pressure gap hypothesis (Chen et al., 2016). According to that, chemical potential of bound water in the gel layer is relatively lower than permeate water, thus thermodynamically it requires an extra energy to overcome this difference and drag the water molecules to permeate side. This hypothesis was further explained by using Flory-Huggins theory (Teng et al., 2018). Moreover, it was reported that divalent cations, i.e. calcium, can affect the coordination and physical structure of gel layer, further enhancing its filtration resistance through binding and cross-linking of organic polymers (Zhang et al., 2017, 2018). Therefore, high concentration of calcium in cheese whey can be an important factor on fouling development and decreasing membrane permeability in the AnMBR.

3.3. Short term critical flux tests

During operation, the critical flux decreased from 20 to 9 L m^{-2} h^{-1} within 2.5 months and remained stable until the end of experimental study (Table 3). The decrease in critical flux agrees well with decreasing supernatant filterability and median particle size, and increasing colloidal COD. In order to investigate the effect of MLSS concentration (10, 20 and 32 g L^{-1}) and CFV (0.25, 0.5, 1.0 and 1.4 m s^{-1}), a series of critical flux experiments were conducted at the end of reactor operation. It is worth noting that short term critical tests do not predict the long term permeability and fouling profile of extended membrane operation (Le-Clech et al., 2006). The results of short term critical flux tests are presented in Fig. 7. As expected, increasing CFV and decreasing MLSS concentrations significantly improved the critical flux. A critical flux as high as 36 L m^{-2} h^{-1} could be obtained at a MLSS concentration and CFV of 10 g L^{-1} and 1.4 m s^{-1}, respectively. High TSS concentrations also increase the mixed liquor viscosity, which results in retardation of back transport effect and increased deposition of small sized particles on the membrane surface (Deng et al., 2016). At a shear rate of 483 s^{-1}, the viscosity of the sludge at 10, 20 and 32 g TSS L^{-1} was measured as 4.5, 6.9 and 11.6 mPa s, respectively. Similar results were reported by Ho and Sung (2009) who observed that the apparent viscosity of the AnMBR sludge at 500 s^{-1} shear rate varied between 1.3 and 10 mPa s at total solids (TS) concentrations of 5–30 g L^{-1}, respectively. They

Table 3
Evolution of critical flux measured in the reactors.

Parameter	Unit	20th day	77th day	113th day	165th day
TSS	g L^{-1}	32	33	42	38
Critical flux	L m^{-2} h^{-1}	20	9	8	9

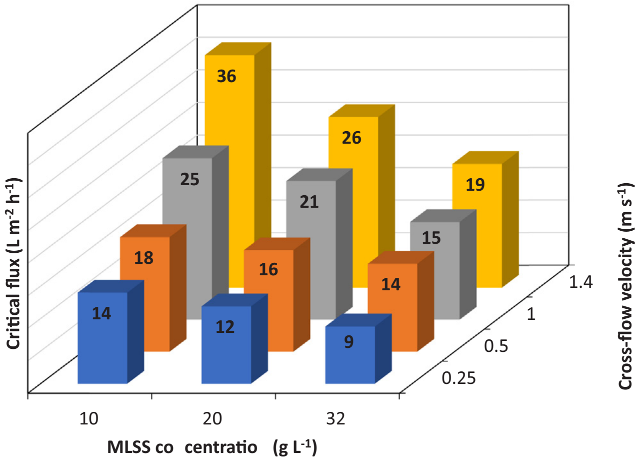


Fig. 7. Effect of CFV and MLSS concentration on critical flux.

reported that a CFV of at least 0.5–0.8 m s^{-1} is required in order to create transitional flow (Reynolds number ≥ 2100) around the membrane surface when the TS concentration is between 10 and 20 g L^{-1}, and even higher CFVs are necessary at elevated TS levels. Choo et al. (2000) showed that cake layer resistance in AnMBRs can be decreased by increasing the CFV, but at a Reynolds number of 2000 a plateau was reached and no further reduction could be obtained.

In AnMBRs, increasing CFV is a strategic decision, which has several consequences on performance and feasibility. The first is the trade-off between lower membrane area requirement due to increased flux and higher energy consumption (Dereli et al., 2012). It is also reported that more severe long term fouling may occur at elevated CFVs due to the thinning of cake layer, which may subsequently lead to increased inner pore blocking (Choo and Lee, 1998; Le-Clech et al., 2006; Zhang et al., 2007, 2011). Therefore, high CFVs may result in increased irrecoverable fouling on the long term operation (An et al., 2009). Moreover, in membrane bioreactors, an increased shear rate results in floc disruption, yielding an increased number of small sized particles (Ho and Sung, 2009). Considering the fact that the smallest particle size determines the attainable flux in membrane filtration (Jeison et al., 2009; Zhang et al., 2011), selective disposal of light solids fraction with a smaller median particle size is a promising option to increase the flux. This may help both decreasing the TSS content and increasing the median particle size of the mixed liquor. In such way, a higher operating flux can be obtained without significantly increasing the CFV which is both economically and energetically more attractive. Another option for controlling the particle size distribution in AnMBRs may be adding flocculants to the reactor (Díaz et al., 2014). Two staged reactor configurations consisting of an anaerobic dynamic membrane bioreactor (AnDMBR) as acidogenic phase may also be considered for controlling extensive accumulation of dispersed acidogenic biomass in methanogenic AnMBR.

3.4. Membrane autopsy

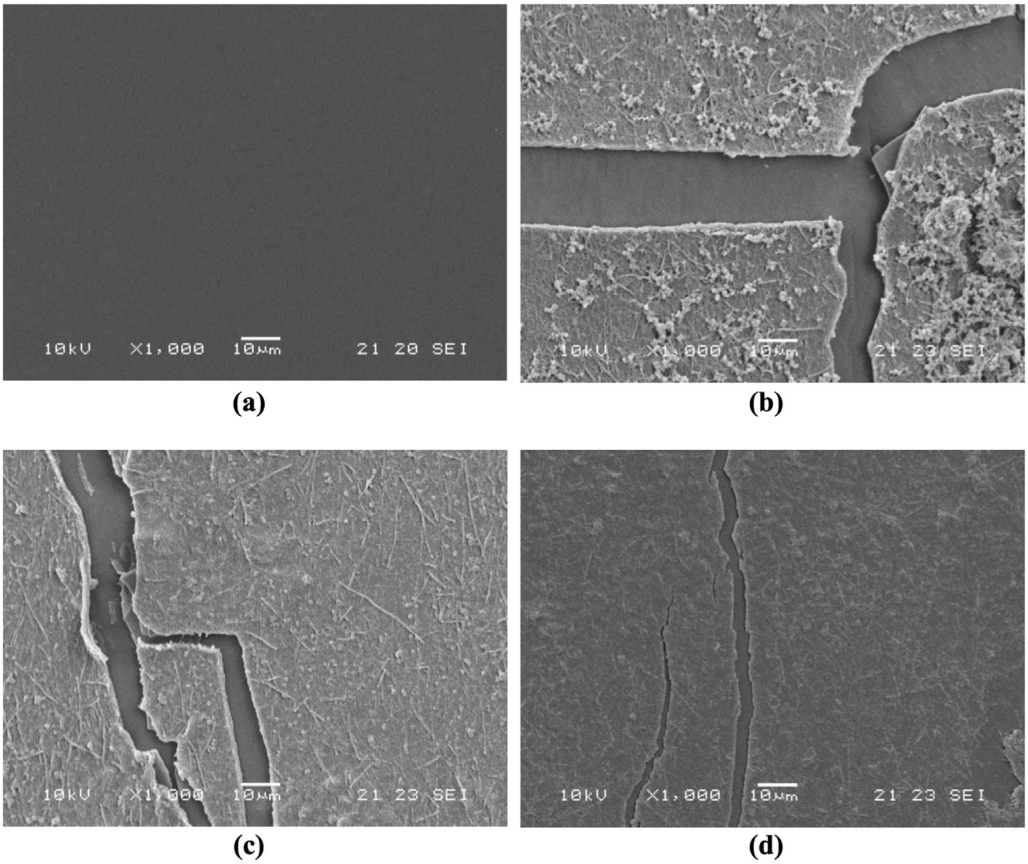
The SEM photographs of the fouled membrane showed a thin and compact cake layer on the membrane (Fig. 8b). Flushing the membrane with tap water did not seem to effectively remove the cake layer. Moreover, the chemical cleaning procedure applied in the study could not completely remove the fouling layer from the membrane surface. Although the duration of chemical cleaning was extended up to 4 h towards the end of the study, its effectiveness gradually decreased (see also Fig. 4). This indicates irreversible fouling has occurred on the membrane. The remaining thin but compact fouling layer (Fig. 8d) seems to be the reason for the deteriorating permeability recovery towards the end of the study. The EDX spectra of fouled membrane showed that the cake layer contained several inorganic foulants such as calcium, phosphorus, sulphur, silicon, iron and copper (Supplementary document). This is not unexpected since whey contains several salts, and heavy metals were dosed as micronutrients to sustain a stable biological performance in the AnMBR. It was noted that after soaking into NaOCl solution, several inorganic species still remained in the fouling layer indicating the inefficiency of NaOCl cleaning for the removal of inorganic foulants. Only after citric acid cleaning, a number of inorganic foulants, i.e. calcium, could be removed from the surface.

Fig. 9 depicts the FTIR spectra of fouled, physical and chemical cleaned membrane pieces. The peaks at 1017 and 1094 cm^{-1} are typically due to C–O bonds of polysaccharides and alcohols, respectively (Lin et al., 2009). Gao et al. (2010) reported that peak in the vicinity of 1240 cm^{-1} is due to C-N stretching of secondary protein structures, namely amides. Peak around 1450 cm^{-1} can be associated with C-H bonds of alkanes (Gao et al., 2010). The strong peak at 1713 cm^{-1} can be attributed to carboxyl groups and representing typical characteristics of humic acids (Tian et al., 2011). FTIR analysis revealed that the membrane was fouled with polysaccharides and proteins and neither physical cleaning nor NaOCl cleaning was effective on removing the foulants. However, citric acid cleaning showed a relatively better performance which suggest inorganic foulants were present in the cake layer. These result are in line with SEM and EDX observations and they validate that complexation of organic foulants with cations, i.e. calcium, were the main fouling mechanism in the AnMBR treating cheese whey.

Spagni et al. (2010) applied a much more vigorous chemical cleaning procedure (immersion to 0.5% NaOCl for 7 h, 0.1% HCl to 16 h and then 0.3% NaOCl for 5 h) which could almost completely remove fouling in an AnMBR treating whey and sucrose mixture. During operation, they applied frequent relaxation cycles (1 min in every 5 min), which may help to mitigate membrane fouling. In situ physical cleaning supplied by intermittent backwash cycles (60 min filtration and 2 min backwash) applied in our study was not very effective in preventing long term fouling, and more frequent and/or stronger backwash might reduce membrane fouling due to cake compaction. Yigit et al. (2009) compared the effect of different backwash scenarios on fouling development and concluded that frequent and extended backwash successfully mitigates fouling when the membrane is operated below critical flux. On the other hand, Wu et al. (2008) reported that strength of backwash is more important compared to its frequency in fouling control. It should be noted that increasing backwash strength and/or frequency would inevitably decrease the net flux, thus membrane operation should be optimized to obtain both effective fouling control and permeate recovery. Another option for fouling control is using chemically enhanced backwash (CEB) to address inorganic fouling observed in this study (Wang et al., 2014). Ramos et al. (2014) reported that CEB with NaOCl could efficiently remove the internal fouling resistance in an AnMBR treating wastewater with a high oil and grease content. Obviously, there is a necessity to optimize the types of chemicals used in CEB depending on the composition of membrane foulants.

4. Conclusions

Cheese whey was successfully treated in a cross-flow AnMBR at an average VLR of 5 kg COD m^{-3} d^{-1}. A stable treatment performance (over 95% COD removal) was obtained due to the prevention of any unwanted biomass loss by the membrane. Sludge filterability deteriorated due to gradual increase of fine particles and colloidal COD. Short term critical flux tests revealed that it is possible to increase the flux at higher CFVs and/or lower MLSS concentrations. Effectiveness of chemical cleaning decreased and irremovable membrane fouling occurred during long term operation. Membrane autopsy showed that the membrane was fouled with organic (proteins and polysaccharides) and inorganic foulants (i.e. calcium) Therefore, it is necessary to prolong membrane permeability by improving the chemical cleaning efficiency through



(a) (b)

(c) (d)

Fig. 8. SEM photographs of the membrane (a): virgin membrane, (b): fouled membrane, (c): after physical cleaning, (d): after chemical cleaning.

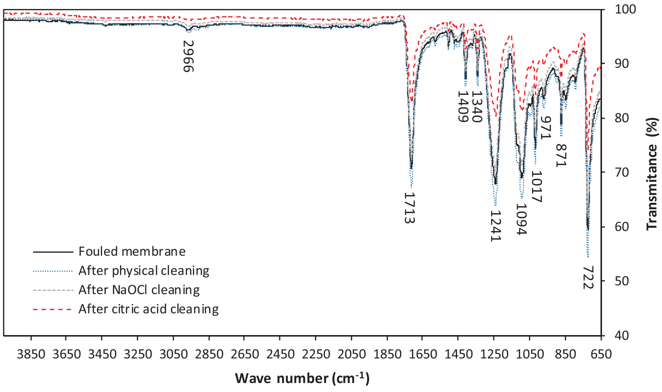


Fig. 9. FTIR spectra of the membrane.

optimization of its frequency and intensity of chemicals. Moreover, optimization of membrane operation (backwash and/or chemically enhanced backwash frequency and strength) is required for mitigating long term fouling.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envres.2018.09.021.

References

Alphenaar, A., 1994. Anaerobic Granular Sludge: Characterization, and Factors Affecting its Functioning (Ph.D. Thesis). Wageningen Agricultural University, Wageningen, the Netherlands.

An, Y.Y., Yang, F.L., Bucciali, B., Wong, F.S., 2009. Municipal wastewater treatment using a UASB coupled with cross-flow membrane filtration. J. Environ. Eng. 135, 86–91.

APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 1995, 20th ed. American Public Health Association/American Water Works Association/ Water Environment Federation, Washington DC.

Brown, N., Güttler, J., Shilton, A., 2016. Overcoming the challenges of full scale anaerobic co-digestion of casein whey. Renew. Energy 96 (Part A), 425–432.

Carvalho, F., Prazeres, A.R., Rivas, J., 2013. Cheese whey wastewater: characterization and treatment. Sci. Total Environ. 445–446, 385–396.

Charfi, A., Ben Amar, N., Harmand, J., 2012. Analysis of fouling mechanisms in anaerobic membranebioreactors. Water Res. 46 (8), 2637–2650.

Chen, J., Zhang, M., Li, F., Qian, L., Lin, H., Yang, L., Wu, X., Zhou, X., He, Y., Liao, B.Q., 2016. Membrane fouling in a membrane bioreactor: high filtration resistance of gel layer and its underlying mechanism. Water Res. 102, 82–89.

Choo, K.-H., Lee, C.-H., 1998. Hydrodynamic behavior of anaerobic biosolids during crossflow filtration in the membrane anaerobic bioreactor. Water Res. 32 (11), 3387–3397.

Choo, K.H., Kang, I.J., Yoon, S.H., Park, H., Kim, J.H., Adiya, S., Lee, C.H., 2000. Approaches to membrane fouling control in anaerobic membrane bioreactors. Water Sci. Technol. 41 (10–11), 363–371.

Comino, E., Rosso, M., Riggio, V., 2009. Development of a pilot scale anaerobic digester for biogas production from cow manure and whey mix. Bioresour. Technol. 100, 5072–5078.

De Kok, S., Meijer, J., van Loosdrecht, M.C.M., Kleerebezem, R., 2013. Impact of dissolved hydrogen partial pressure on mixed culture fermentations. Appl. Microbiol. Biotechnol. 97, 2617–2625.

Deng, L., Guo, W., Ngo, H.H., Zhang, H., Wang, J., Li, J., Xia, S., Wu, Y., 2016. Biofouling and control approaches in membrane bioreactors. Bioresour. Technol. 221, 656–665.

Dereli, R.K., Ersahin, M.E., Ozgun, H., Ozturk, I., Jeison, D., van der Zee, F., van Lier, J.B., 2012. Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters. Bioresour. Technol. 122, 160–170.

Dereli, R.K., Grelot, A., Heffernan, B., van der Zee, F.P., van Lier, J.B., 2014. Implications of changes in solids retention time on long term evolution of sludge filterability in anaerobic membrane bioreactors treating high strength industrial wastewater. Water Res. 59, 11–22.

Dereli, R.K., Loverdou, L., van der Zee, F.P., van Lier, J.B., 2015. A systematic study on the effect of substrate acidification degree and acidogenic biomass on sludge filterability. Water Res. 82, 94–103.

Dereli, R.K., Wang, X., van der Zee, F.P., van Lier, J.B., 2018. Biological performance and sludge filterability of anaerobic membrane bioreactors under nitrogen limited and supplied conditions. Water Res. 137, 164–172.

Desai, M., Madamwar, D., 1994. Anaerobic digestion of cheese whey, poultry waste and cattle dung: a study of the use of adsorbents to improve digester performance. Environ. Pollut. 86, 337–340.

Diamantis, V.I., Kapagiannidis, A.G., Ntougias, S., Tataki, V., Melidis, P., Aivasidis, A., 2014. Two-stage CSTR–UASB digestion enables superior and alkali addition-free cheese whey treatment. Biochem. Eng. J. 84, 45–52.

Díaz, H., Azócar, L., Torres, A., Lopes, S.I., Jeison, D., 2014. Use of flocculants for increasing permeate flux in anaerobic membrane bioreactors. Water Sci. Technol. 69 (11), 2237–2242.

Dubois, M., Grilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric methods for determination of sugars and related substances. Anal. Chem. 28, 350–356.

El-Mamouni, R., Guiot, S.R., Mercier, P., Safi, B., Samson, R., 1995. Liming impact on granules activity of the multiplate anaerobic reactor (MPAR) treating whey permeate. Bioprocess Eng. 12, 47–53.

Escalante, H., Castro, L., Amaya, M.P., Jaimes, L., Jaimes-Estévez, J., 2017. Anaerobic digestion of cheese whey: energetic and nutritional potential for the dairy sector in developing countries. Waste Manag. 71, 711–718.

Fernández, F.J., Villaseñor, J., Infantes, D., 2011. Kinetic and stoichiometric modelling of acidogenic fermentation of glucose and fructose. Biomass Bioenergy. 35 (9), 3877–3883.

Fernandez, C., Cuetos, M.J., Martínez, E.J., Gomez, X., 2015. Thermophilic anaerobic digestion of cheese whey: coupling H_2 and CH_4 production. Biomass Bioenerg. 81, 55–62.

Gavala, H.N., Kopsinis, H., Skiadas, I.V., Stamatelatou, K., Lyberatos, G., 1999. Treatment of dairy wastewater using an upflow anaerobic sludge blanket reactor. J. Agric. Eng. Res. 73, 59–63.

Gannoun, H., Khelifi, E., Bouallagui, H., Touhami, Y., Hamdi, M., 2008. Ecological clarification of cheese whey prior to anaerobic digestion in upflow anaerobic filter. Bioresour. Technol. 99, 6105–6111.

Gao, W.J.J., Lin, H.J., Leung, K.T., Liao, B.Q., 2010. Influence of elevated pH shocks on the performance of a submerged anaerobic membrane bioreactor. Process Biochem. 45 (8), 1279–1287.

Gao, W., Liao, B.Q., Hai, F.I., 2014. Chapter 11: anaerobic MBRs. In: Hai, F.I., Yamamoto, K., Lee, C.H. (Eds.), Membrane Biological Reactors: Theory, Modeling, Design, Management and Applications to Water Ruse. IWA Publishing, London, UK.

Ghaly, A.E., 1996. A comparative study of anaerobic digestion of acid cheese whey and dairy manure in a two-stage reactor. Bioresour. Technol. 58 (1), 61–72.

Hwang, S.H., Hansen, C.L., Stevens, D.K., 1992. Biokinetics of an upflow anaerobic sludge blanket reactor treating whey permeate. Bioresour. Technol. 41, 223–230.

Ho, J., Sung, S., 2009. Effects of solid concentrations and cross-flow hydrodynamics on microfiltration of anaerobic sludge. J. Membr. Sci. 345, 142–147.

Jeison, D., van Lier, J.B., 2007. Cake formation and consolidation: main factors governing the applicable flux in anaerobic submerged membrane bioreactors (AnSMBR) treating acidified wastewaters. Sep. Purif. Technol. 56 (1), 71–78.

Jeison, D., Plugge, C., Pereira, A., van Lier, J.B., 2009. Effects of the acidogenic biomass on the performance of an anaerobic membrane bioreactor for wastewater treatment. Bioresour. Technol. 100 (6), 1951–1956.

Kosinowski, F.V., 1979. Whey utilization and whey products. J. Dairy Sci. 62, 1149–1160.

Le-Clech, P., Jefferson, B., Chang, I.S., Judd, S.J., 2003. Critical flux determination by the flux-step method in a submerged membrane bioreactor. J. Membr. Sci. 227 (1), 81–93.

Le-Clech, P., Chen, V., Fane, T.A.G., 2006. Fouling in membrane bioreactors used in wastewater treatment. J. Membr. Sci. 284 (1–2), 17–53.

Liao, B.Q., Kraemer, J.T., Bagley, D.M., 2006. Anaerobic membrane bioreactors: applications and research directions. Crit. Rev. Environ. Sci. Technol. 36 (6), 489–530.

Lin, H.J., Xie, K., Mahendran, B., Bagley, D.M., Leung, K.T., Liss, S.N., Liao, B.Q., 2009. Sludge properties and their effects on membrane fouling in submerged anaerobic membrane bioreactors (SAnMBRs). Water Res. 43 (15), 3827–3837.

Lo, K.V., Liao, P.H., 1988. Laboratory scale studies on mesophilic anaerobic digestion of cheese whey in different digester configurations. J. Agric. Eng. Res. 39, 99–105.

Lo, K.V., Liao, P.H., Chiu, C., 1988. Mesophilic anaerobic digestion of a mixture of cheese whey and dairy manure. Biomass 15, 45–53.

Lousada-Ferreira, M., van Lier, J.B., van der Graaf, J.H.J.M., 2015. Impact of suspended solids concentration on sludge filterability in full-scale membrane bioreactors. J. Membr. Sci. 476, 68–75.

Malaspina, F., Cellamare, L., Stante, L., Tilche, A., 1996. Anaerobic treatment of cheese whey with a downflow-upflow hybrid reactor. Bioresour. Technol. 55, 131–139.

McHugh, S., Collins, G., O'Flaherty, V., 2006. Long-term, high-rate anaerobic biological treatment of whey wastewaters at psychrophilic temperatures. Bioresour. Technol. 97 (14), 1669–1678.

Meng, F., Chae, S.-R., Drews, A., Kraume, M., Shin, H.-S., Yang, F., 2009. Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. Water Res. 43 (6), 1489–1512.

Mockaitis, G., Ratusznei, S.M., Rodrigues, J.A.D., Zaiat, M., Foresti, E., 2006. Anaerobic whey treatment by a stirred sequencing batch reactor (ASBR): effects of organic loading and supplemented alkalinity. J. Environ. Manag. 79, 198–206.

Patel, C., Madamwar, D., 1997. Biomethanization of salty cheese whey using anaerobic rotating biological contact reactor. J. Ferment. Bioeng. 83 (5), 502–504.

Patel, P., Desai, M., Madamwar, D., 1994. Biomethanation of cheese whey using anaerobic upflow fixed film reactor. J. Ferment. Bioeng. 79 (4), 398–399.

Prazeres, A.R., Carvalho, F., Rivas, J., 2012. Cheese whey management: a review. J. Environ. Manag. 110, 48–68.

Ramos, C., Zecchino, F., Ezquerra, V., Diez, V., 2014. Chemical cleaning of membranes from an anaerobic membrane bioreactor treating food industry wastewater. J. Membr. Sci. 458, 179–188.

Rosenberger, S., Laabs, C., Lesjean, B., Gnirss, R., Amy, G., Jekel, M., Schrotter, J.-C., 2006. Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. Water Res. 40, 710–720.

Saddoud, A., Hassairi, I., Sayadi, S., 2007. Anaerobic membrane reactor with phase separation for the treatment of cheese whey. Bioresour. Technol. 98, 2102–2108.

Shen, S., Lei, Q., Chen, J.R., Hong, H.C., He, Y.M., Lin, H.J., 2015. Membrane fouling in a submerged membrane bioreactor: impacts of floc size. Chem. Eng. J. 269, 328–334.

Siso, M.I.G., 1996. The biotechnological utilization of cheese whey: a review. Bioresour. Technol. 57, 1–11.

Spagni, A., Casu, S., Crispino, N.A., Farina, R., Mattioli, D., 2010. Filterability in a submerged anaerobic membrane bioreactor. Desalination 250, 787–792.

Teng, J., Shen, L., Yu, G., Wang, F., Li, F., He, Y., Lin, H., Zhou, X., 2018. Mechanism analyses of high specific filtration resistance of gel and roles of gel elasticity related with membrane fouling in a membrane bioreactor. Bioresour. Technol. 257, 39–46.

Tian, Y., Chen, L., Zhang, S., Zhang, S., 2011. A systematic study of soluble microbial products and their fouling impacts in membrane bioreactors. Chem. Eng. J. 168 (3), 1093–1102.

Wang, Z., Ma, J., Tang, C.Y., Kimura, K., Wang, Q., Han, X., 2014. Membrane cleaning in membrane bioreactors: a review. J. Membr. Sci. 468, 276–307.

Wu, J., Le-Clech, P., Stuetz, R.M., Fane, A.G., Chen, V., 2008. Effects of relaxation and backwashing conditions on fouling in membrane bioreactor. J. Membr. Sci. 324 (1–2), 26–32.

Yan, J.Q., Lo, K.V., Liao, P.H., 1990. Anaerobic digestion of cheese whey using an upflow anaerobic sludge blanket reactor: iii. Sludge and substrate profiles. Biomass 21, 257–271.

Yang, K., Yu, Y., Hwang, S., 2003. Selective optimization in thermophilic acidogenesis of cheese-whey wastewater to acetic and butyric acids: partial acidification and methanation. Water Res. 37, 2467–2477.

Yigit, N.O., Civelekoglu, G., Harman, I., Koseoglu, H., Kitis, M., 2009. Effects of various backwash scenarios on membrane fouling in a membrane bioreactor. Desalination 237 (1–3), 346–356.

Zhang, J., Padmasiri, S.I., Fitch, M., Norddahl, B., Raskin, L., Morgenroth, E., 2007. Influence of cleaning frequency and membrane history on fouling in an anaerobic membrane bioreactor. Desalination 207, 153–166.

Zhang, H., Gao, J., Jiang, T., Gao, D., Zhang, S., Li, H., Yang, F., 2011. A novel approach to evaluate the permeability of cake layer during cross-flow filtration in the flocculants added membrane bioreactors. Bioresour. Technol. 102, 11121–11131.

Zhang, M., Lin, H., Shen, L., Liao, B.Q., Wu, X., Li, R., 2017. Effect of calcium ions on fouling properties of alginate solution and its mechanisms. J. Membr. Sci. 525, 320–329.

Zhang, Z., Hong, H., Lin, H., Shen, L., Ma, G., Chen, J., Liao, B.Q., Yu, H., 2018. Mechanistic insights into alginate fouling caused by calcium ions based on terahertz time-domain spectra analyses and DFT calculations. Water Res. 129, 337–346.