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Hollow fiber membrane fouling and cleaning in a membrane bioreactor for molasses wastewater treatment

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ABSTRACT

The limitation of membrane microfiltration for activated sludge wastewater treatment is membrane fouling which is indicated by the decline of the permeation flux. In this study, molasses were used to prepare a synthetic feed substrate with addition of urea $(NH_2)_2CO$ and sodium pyrophosphate Na_4PO_4 to adjust the COD:N:P ratio. A polyethersulfone hollow fiber membrane was operated under the typical range of concentrations of mixed liquor suspended solids of an activated sludge process. The membrane bioreactors (MBR) system was operated in two modes, first with increasing flux and then at constant flux. In this study, the amount of extracted extracellular polymeric substance (eEPS) was lower than in earlier reports, whereas the soluble microbial product (SMP) was quite similar. Carbohydrates were the main part for both eEPS and SMP, reflecting the composition of molasses. Since membrane fouling occurred, several maintenance and recovery cleaning procedures were tested: NaOCl, NaOCl + Memcare, and citric acid. The results showed that besides organic fouling, the inorganic fouling was also occurred.

Keywords: Molasses wastewater; Membrane performance; Membrane cleaning

1. Introduction

The activated sludge process is commonly used in municipal and industrial wastewater treatment for removal of organic compounds. There are two main variants of the activated sludge process: the conventional activated sludge process and the extended aeration process, with typical mixed liquor suspended solid concentration ranges from 2.5 to 4.5 g/L and 3.5 to 5.5 g/L, respectively [1]. Activated sludge processes usually consist of an aeration tank and a clarifier or secondary sediment tank. Membrane filtration can be used to replace the clarifier and secondary sediment tank. There is no limitation of sludge-effluent separation by the settleability of the activated sludge. Thus, a higher and more consistent effluent quality can be achieved [2,3]. Thanks to many other advantages, such as good disinfection capability, higher volumetric loading, less sludge production, small footprint and reactor requirements [4], membrane bioreactors (MBR) have been applied already in many municipal and industrial wastewater treatments applications. Membrane fouling is the major problem however. Membrane fouling and its consequences in terms of plant maintenance and operating costs is the main limitation of the MBR system. It is a complicated phenomenon and typically results from multiple causes, such as wastewater characteristics, biological properties, operating conditions and membrane characteristics [5].

Molasses are an important by-product from cane sugar factories, as it has a high commercial value due to its use as a carbon source for fermentation industries [6] and papermaking industries [7]. Molasses contain

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relatively large amounts of total sugars or carbohydrates and no significant levels of crude protein. The nitrogenous materials which are present consist mainly of non-protein nitrogen compounds which include amides, albuminoids, amino acids and other simple nitrogenous compounds. Also, molasses contain a certain amount of mineral elements, such as potassium, calcium, magnesium, sodium, chlorine, sulfur and so on [8].

The purpose of this research is to use an activated sludge process with microfiltration membrane system (MBR) to simulate a molasses wastewater treatment process to remove the organics by lowering the chemical oxygen demand (COD) of the wastewater, and to evaluate the various membrane cleaning chemicals and procedures.

2. Materials and methods

2.1. Experiment setup

The laboratory submerged MBR as shown in Fig. 1, which was built up at the lab of WATERLEAU N.V., site in Wespelaar (Belgium), consisted of an aerobic reactor (effective volume of 105 liter) and a submerged curtain hollow fiber membrane (*VITO*, Flemish institute for technological research). The membrane was made of polyethersulfone (PES) with mean pore size 0.30 µm and an effective filtration area of 0.26 m^2. The membrane module was mounted vertically between two baffle plates located above an air diffuser. The cross-flow velocity was provided by a pump with a 1 m^3/h capacity to produce an air shearing flow along the membrane surface. The aeration for activity sludge was supplied by a blower controlled by a valve. The influent pump was controlled by a water level sensor. The membrane-filtration force was provided by a dosing pump (Watson Marlow 323U/D). The effluent flow rate was controlled by a programmable logic controller. Trans-membrane pressure (TMP) was monitored by a pressure gauge.

2.2. Operating conditions

In most cases, the membrane flux was around 16 $l\ m^{-2}h^{-1}$. The operation cycle was: 300 seconds extraction followed by 35 seconds backwash with effluent. The average hydraulic retention time was about 35 hour. There were two sludge discharges at the 70^{th} and 119^{th} day, respectively. The mixed liquor suspended solids (MLSS) was then set to be at around 5.5 (by discharging sludge) and 8.0 g/L (by concentrating and adding same sludge), respectively. Dissolved oxygen in the reactor was above 3 mg/L during the entire experiment. The MBR was operated within the temperature range of 13 to 21°C.

2.3. Composition of synthetic wastewater

The synthetic wastewater was made by molasses diluted with tap water. Molasses were used to prepare the lab "wastewater" because: (1) no pre-fine screen is needed; (2) the COD concentration is easy to control; (3) a good COD:N ratio is present; (4) the pH range is acceptable; (5) as model substrate for MBR, it contains a non-biodegradable "rest-COD" which also contains

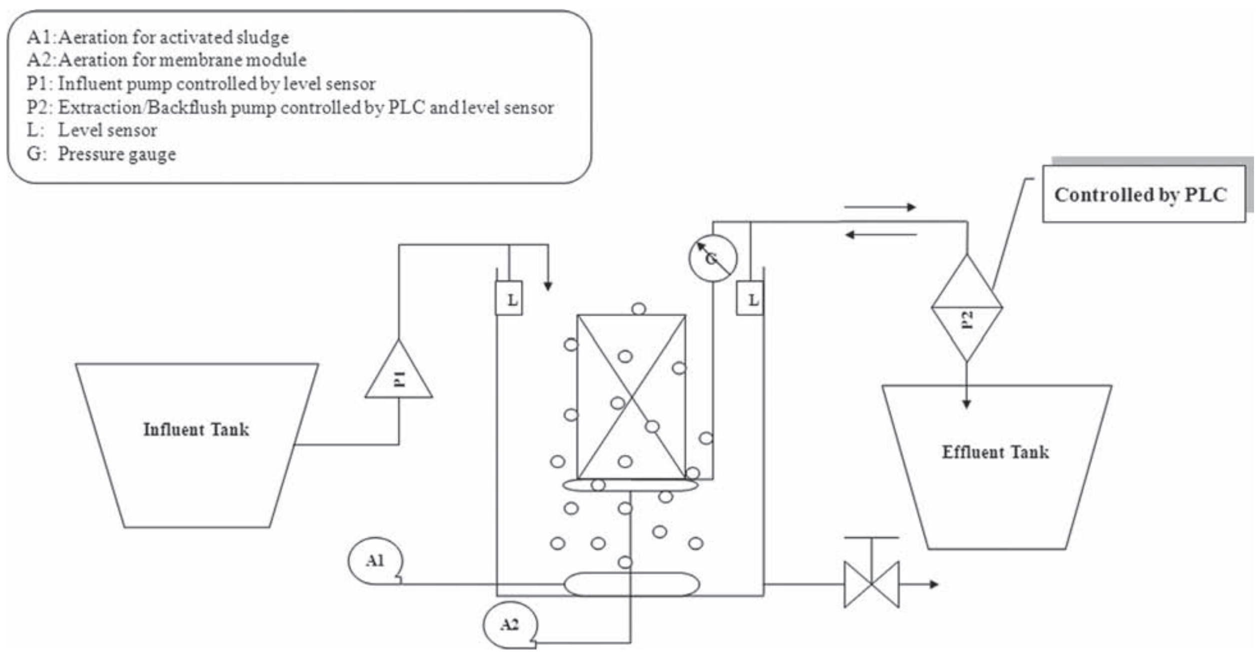

Fig. 1. Schematic diagram of MBR experimental setup.

Table 1
Synthetic molasses wastewater characteristics for the aerobic MBR.

Items	Influent mean concentration (Unit)
pH	6.97 ± 1.17[a] (---)
Chemical oxygen demand (COD)	963 ± 447[a] (mg/L)
Total nitrogen (TN)	25.0 ± 22.4[b] (mg/L)
Total phosphorous (TP)	4.11 ± 3.80[b] (mg/L)
NH_4-N	4.07 ± 3.90[c] (mg/L)
NO_3-N	3.25 ± 3.20[c] (mg/L)
PO_4-P	1.54 ± 1.30[c] (mg/L)
Calcium	0,952[d] (mg/L)
Iron	0,048[d] (mg/L)
Potassium	64,6[d] (mg/L)
Magnesium	0,0597[d] (mg/L)
Manganese	0,0275[d] (mg/L)
Sodium	7,09[d] (mg/L)
Zinc	0,0694[d] (mg/L)
Sulfur	5,79[d] (mg/L)

[a]Number of samples taken n=48.
[b]Number of samples taken n=24.
[c]Number of samples taken n=18.
[d]Measured by Lisec N.V.

color. Melanoidin, present in molasses, is the main reason for color in the effluent, because it cannot be removed completely by biological treatment [9]. Thus, some extra fouling is expected which can also provide opportunities to test different cleaning procedures. Urea $(NH_2)_2CO$ and sodium pyrophosphate Na_4PO_4 were used to adjust the COD:N:P ratio in order to suffice the requirement of microorganism. The characteristics of synthetic molasses wastewater are listed in Table 1.

2.4. Analytical methods

The influent and permeate quality as well as the condition of the activitated sludge were routinely monitored. COD, total nitrogen (TN), nitrate-N (NO_3-N), ammonium-N (NH_4-N), total phosphorous (TP), and orthophosphate-P (PO_4-P) were measured using a HACH-Lange test cuvette, and the spectrophotometer was a Dr. Lange Lasa 100 (HACH-Lange). pH was measured using WTW *MultiLine P3* pH/LF SET with a pH probe (WTW model SympHony). Dissolved oxygen and conductivity were recorded by using HACH HQ40d Digital Multi-Parameter Meter with LDO probe (HACH) and conductivity probe (HACH). The MLSS and mixed liquor volatile suspended solids (MLVSS) were analyzed according to the Chinese NEPA standard methods [10]. The performances of the system such as operation flux and TMP were also monitored regularly.

Extracellular polymeric substances (EPS) and soluble microbial products (SMP) were characterized by their relative content of protein and carbohydrate. A heating method suggested by Le-Clech et al. [5] was used for extraction of EPS and SMP in this study. The extracted samples of protein and carbohydrates were both measured by a spectrophotometer at 490 nm and 595 nm, respectively. The methods were based on the bio-rad protein assay for the proteins and the phenol-sulfuric acid method for the carbohydrates.

2.5. Cleaning chemicals and procedures

Memcare 101 and 201 were supplied by Christeyns N.V. (Gent, Belgium). Memcare 101 consisted of phosphoric acid (H_3PO_4) and nitric acid (HNO_3) with concentrations (wt%) of 5 to 15 and >30, respectively. Memcare 201 consisted of potassium hydroxide (KOH) and ethylene diamine tetra acetate with concentrations (wt%) of 15–30 and 5–15, respectively. Sodium hypochlorite solution (12% active chlorine) and citric acid were supplied by VWR international bvba (Leuven, Belgium).

Maintenance cleaning (MC) was included one acid cleaning with Memcare 101 and four times with sodium hypochlorite solution during different times (45, 13, and 6 min) and at different concentrations (500 ppm and 1000 ppm). Recovery cleaning (RC) was performed four times with different chemicals, different concentration and during different performed times.

3. Results and discussion

3.1. Degradation performance

The COD biodegradation performance was excellent. The COD removal efficiencies were all above 80%, mostly around 95%, regardless of the fluctuating influent COD concentration above 1200 mg/L. Average effluent COD concentration was 95.7 ± 84.4 mg/L (n=63) and the removal efficiency was 90 ± 9% (n=63) (Fig. 2).

Average effluent TN concentration was 15.1 ± 14.6 mg/L. Before the 66[th] day, the influent TN concentration increased linearly up to 25 mg/L, whereas the effluent TN concentrations were correspondingly

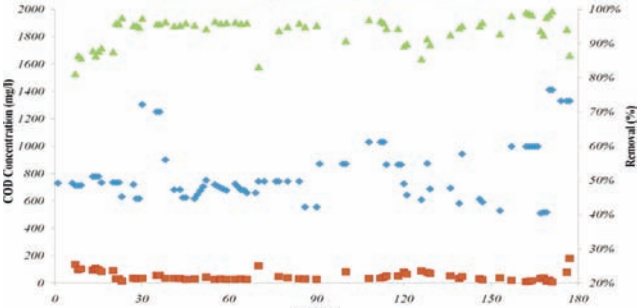

Fig. 2. COD removal in this MBR system.

stable below 10 mg/L. The influent TN concentrations remained around 30 mg/L from70st to 90th day. During this period, the relative effluent TN concentration dropped from above 30 mg/L to around 10 mg/L. This might be caused by the acclimatization of the activated sludge. From the 99th day, the influent TN concentration was increased to more than 40 mg/L; the effluent TN concentration was raised slightly, between 10–15 mg/L until the 120th day. Average effluent TP concentration was 2.4 ± 2.3 mg/L. The effluent TP concentrations were quite stable before day 120. As to adjust the COD:N:P ratio of influent, the influent TP concentration was increased, and effluent TP concentration fluctuated greatly from then onward.

As COD removal was the main target of this study, nitrogen and phosphate were only used to supply ample nutrient substances for the growth of microorganism, the removal efficiency of TN and TP were not concerned.

3.2. Microbial growth and viability

There were four different periods of microbial condition over the entire experiment (Fig. 3). During periods "a" and "b", the MLSS concentrations increased linearly. MLSS concentration was below 6 g/L ("a") and 7 g/L ("b"). Within periods "c" and "d", MLSS concentrations were kept around 5.5 g/L and 8 g/L, respectively. MLVSS/MLSS ratio during the entire experiment was around 84%, indicating that no inorganic matter accumulated in the MBR. The MLVSS/MLSS ratio achieved in this study was slightly higher than those commonly reported for municipal wastewater treatment plants (70–80%) [11]. The mean food-to-microorganism (F/M) ratios were 0.13, 0.14, 0.13, and 0.11 kgMLVSS/kgCOD/day corresponding to periods "a", "b", "c" and "d", respectively. Although the F/M ratio was quite similar in periods "a", "b" and "c", there was no increasing of MLSS concentrations growth in periods "c". The reason might be the different COD:N:P ratio. The average COD:N:P ratio of periods "c" was 100:2.8:0.5, whose TN concentrations were lower than during periods "a" (100:4:0.2) and period "b" (100:4.4:0.1). During period "d", the F/M ratio was lower than other three periods as well as COD:N:P ratio (100:2.4:0.6), hence the MLSS concentrations was not increased neither. It has been reported that the ratio of COD:N:P in wastewater to be treated should be approximately 100:5:1 for aerobic treatment [12]. In this study, as the F/M ratio was quite similar in periods "a", "b" and "c", the ratio of COD:N seems to be the dominating factor for microorganism growth besides F/M.

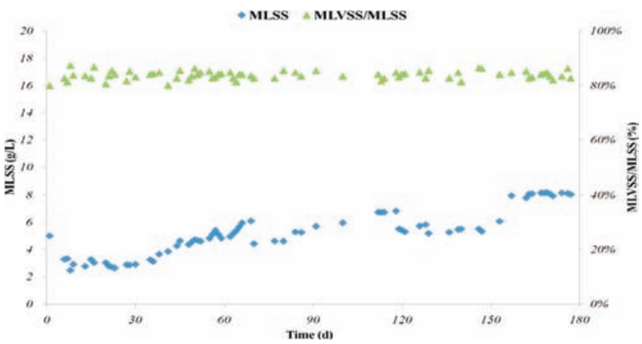

Fig. 3. Variation of MLSS concentration and MLVSS/MLSS ratio during this study.

3.3. Extracted extracellular polymeric substances and soluble microbial products

For the measurement of extracted EPS (eEPS) and SMP, the activated sludge samples were collected once per week within four continuous weeks. SMP was expressed in mg per litre sludge, eEPS was in mg per gram MLVSS.

The results are summarized in Table 2. Compared with former studies, EPS in this study was lower than Cabassud et al. (eEPSp=25–30 mg/L and eEPSc=7–8 mg/L) and SMP was similar with Cabassud et al. (SMPp=8 mg/L and SMPc=25 mg/L) [13]. Carbohydrate was the main constituent for both SMP (76% in average value) and eEPS (82.5% in average value) which can be attributed to using molasses as feed substrate. Melanoidin, which is the non-degradable part of molasses, can release carbohydrate into aqueous environment by hydrolytic reactions which may introduce a relative large number of carbohydrates into the activated sludge system [14].

3.4. Membrane performance and chemical cleaning

The variations of membrane flux and TMP with operation time are shown in Fig. 4. It can be observed that there were two operation strategies during this study, increasing flux and constant flux. Between 7 and 76 days, the membrane flux was increased step by step. The TMP variation during this period can be summarized as follows: When the flux was around 9 and 12 $lm^{-2}h^{-1}$, the TMP was quite stable (below 100 mbar).

Fouling appeared when flux around 16 $lm^{-2}h^{-1}$. When the TMP was around 300 mbar, a RC1 was performed to drop the TMP to around 100 mbar. It was kept at this level

Table 2
Constituents of EPS and SMP in activated sludge.

Week	SMP (c) [mg/L]	SMP(p) [mg/L]	SMP [mg/L]	eEPS (c) [mg/g MLVSS]	eEPS (p) [mg/g MLVSS]	eEPS [mg/g MLVSS]
1	21	8	29	10	2	12
2	27	8	35	10	2	13
3	27	8	35	9	3	12
4	17	5	22	11	2	12

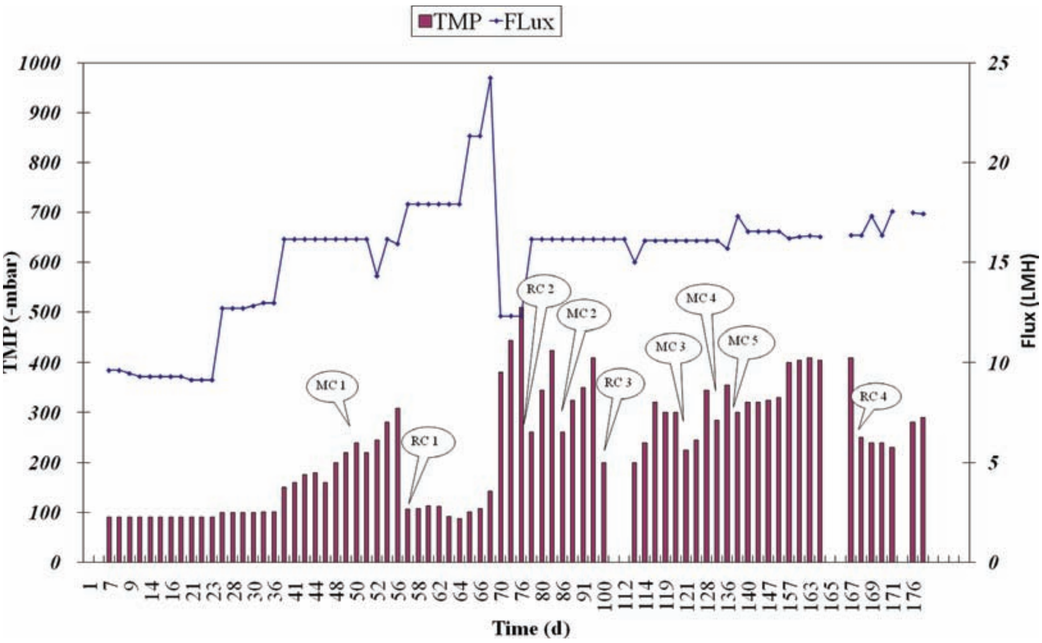

Fig. 4. Variations of membrane flux and TMP.

until the flux was raised again: from days 67 to 70, the flux were increased to 24 $lm^{-2}h^{-1}$ followed by serious fouling, lowering the flux to 12 $lm^{-2}h^{-1}$. The TMP was still above 500 mbar. Rosenberger et al. reported a more detailed fouling trend with different MLSS concentrations. At low MLSS concentrations (<6 g/L), a rise in MLSS decreased fouling. At MLSS concentrations between 8 and 12 g/L, there was no significant effect [15]. In this study, the MLSS was low at most of the time. Le-Clech et al. summarized that, when the MLSS concentrations were lower than 5 g/L, in fact hydrodynamics (more than the MLSS concentration) controlled the critical flux [5].

From day 78 onward, the operation flux was kept around 16 and 17 $lm^{-2}h^{-1}$ until the end of the experiment. The TMP was never recovered back below 100 mbar. The best result was achieved after RC3 (day 100), TMP dropped to 200 mbar. Fouling was easily occurred during this period, and both MC and RC cannot clean the membrane as good as RC1, which means some irreversible fouling existed. Even a chemical cleaning cannot remove the fouling completely. As discussed in former chapter, the high level of carbohydrate in SMP may be one of the driving forces of this irreversible fouling.

Chemical cleaning procedures and results are summarized in Table 3. For all of MCs, except for MC1, pH was adjusted to 12 with NaOH. An important impact of the right choice of chemicals can be recognized. MC1 compared to all others, NaOCl shows a much better result than Memcare 101. NaOCl can react with the surface of PES membrane to result in generating $PhSO_2^-$ and $PhSO_3^-$ groups on the membrane surface [16]. NaOCl as a good oxidant thus generates more oxygen-containing functional groups that

Table 3
Cleaning procedures and results (M 101 and 201 mean Memcare 101 and 201; MC and RC mean MC and RC, respectively).

Procedure	Day	Na0Cl [mg/L]	M 101 [%]	M 201 [%]	Citric – Acid [mg/L]	Flux [L/m2.h]	Time [min]				TMP before [-m bar]	TMP after [-m bar]	TMP decrease [m bar]
							Na0Cl	M 101	M 201	Citric Acid			
MC 1	51	------	2	----	----	17.3	----	45	----	----	240	220	20
MC 2	86	500	----	----	----	15.3	45	----	----	----	425	260	165
MC 3	121	500	----	----	----	15.3	13	----	----	----	300	225	75
MC 4	132	1000	----	----	----	15.3	13	----	----	----	345	285	60
MC 5	138	1000	----	----	----	17.3	6	----	----	----	355	300	55
RC 1	57	1000	2	2	----	16.3	45	45	45	----	300	100	200
RC 2	78	1000	2	----	----	13.8	45	45	----	----	510	260	250
RC 3	100	1000	----	2	1000	13.8	30	30	----	30	410	200	210
RC 4	168	1000	2	2	----	16.3	30	30	30	----	410	250	160

increase the membrane hydrophilicity, hence reducing the adhesion of fouling materials on membranes [17]. Second, the longer the treatment takes, the better (MC2–5).

For the RC, RC1 and RC3 give better result. RC2 can only reduce TMP to 260 mbar, even though the initial TMP was substantially high. The cleaning performance of RC4 is worse than that of RC3, which indicates 1000 mg/L citric acid provided a better efficiency than M 101, although the backwash flux of RC4 (16.3 $lm^{-2}h^{-1}$) is higher than RC3 (13.8 $lm^{-2}h^{-1}$).

4. Conclusions

The COD of molasses based influent can be removed by an activated sludge process with a submerged MBR system successfully. The synthetic molasses wastewater releases a mass of carbohydrates into the activated sludge environment which was found to introduce more fouling on the membrane. As the F/M ratio was quite similar in periods "a", "b" and "c", there was no increase of MLSS concentration in periods "c". The COD:N ratio seems to be the other dominating factor for microorganism growth. For MC, 500 mg/L NaOCl with 45 min backwash was the best chemical solution. The RC required both caustic and acid solutions as well as NaOCl, since besides organic fouling, inorganic fouling also occurred by feeding synthetic molasses wastewater.

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