

Change of foulant concentration in an anaerobic membrane bioreactor

Susumu Hasegawa, Genki Murakami, Ryosuke Takagi
and Hideto Matsuyama

ABSTRACT

Anaerobic membrane bioreactors (AnMBRs) have many advantages, such as producing methane gas for energy generation and little excess sludge. However, membrane fouling is a serious problem because the foulant, which causes the membrane to foul, may get rejected by the membrane and accumulate in the reactor, resulting in an acceleration of membrane fouling. However, there is no information related to a change in the foulant concentration in an AnMBR. Therefore, we examined the changes in the foulant concentration in the reactor, related to membrane fouling in an AnMBR. For the influent, reactor solution, and effluent, the concentration of each component of the foulant was analyzed by using a liquid chromatography-organic carbon detector (LC-OCD). It was found that fouling in the AnMBR was closely related to the components in the reactor, and the main foulant of the ultrafiltration (UF) membrane was biopolymers (BPs). BP accumulated in the reactor because of a high rejection by the UF membrane. However, once the BP accumulated in the reactor was biodegraded, the concentration of BP decreased with time even under a high organic loading rate of 1.9 kg TOC/m³/day.

Key words | anaerobic membrane bioreactor, biopolymers, foulant, membrane fouling, tubular membrane

Susumu Hasegawa
Genki Murakami
Ryosuke Takagi
Hideto Matsuyama (corresponding author)
Center for Membrane and Film Technology,
Department of Chemical Science and
Engineering, Graduate School of Engineering,
Kobe University,
1-1 Rokkodai-cho, Nada-ku, Kobe, 657-8501,
Japan
E-mail: matsuyama@kobe-u.ac.jp

HIGHLIGHTS

- Fouling in an anaerobic membrane bioreactor (AnMBR) was closely related to the components in the reactor.
- The main foulant of the ultrafiltration (UF) membrane was biopolymers (BPs).
- BP was almost completely rejected by the UF membrane.
- BP in the reactor was biodegraded, and not accumulated even at the high loading rate of 1.9 kg TOC/m³/day.

INTRODUCTION

Anaerobic biological wastewater treatment systems have many advantages, such as the production of methane gas for energy generation and small amounts of excess sludge. In addition, air bubbling is not necessary because the system is anaerobic. However, anaerobic methane fermentation is generally carried out at temperatures of 37–40 °C or 55 °C for mesophilic and thermophilic fermentation, respectively. Therefore, it is not so economical, for it becomes expensive for anaerobic systems to be applied to

wastewater with a low organic content except in areas such as East Asia, where the wastewater temperature is already high (Van Lier *et al.* 2010), because the energy required for heating the wastewater is larger than that supplied by the generated methane. Although several studies have investigated the use of anaerobic systems for municipal wastewater treatment at low temperatures, the amount of biogas production is relatively low because of the low methanogenic activity at low temperatures (Grundestam &

Hellstrom 2007; An *et al.* 2009a). In addition, the solubility of methane gas in water increases with the decrease of temperature. Smith *et al.* reported that half of the produced methane remained in the liquid phase (Smith *et al.* 2013), which indicates a significant decrease of the methane gas recovery. The minimum organic concentration for anaerobic biological systems is reported to be about 1,500 mg/L as the chemical oxygen demand (COD) (Tchobanoglous *et al.* 2003) (approximately 600 mg/L as the total organic carbon (TOC)) (see Supplementary materials Figure S1).

Recently, condensation of municipal wastewater has been studied using a forward osmosis (FO) system (Gao *et al.* 2018). We reported a 95% recovery of municipal wastewater as the permeate of an FO membrane using seawater as the draw solution. This indicates that the TOC of municipal wastewater can be concentrated up to 20 times with FO membranes (Takahashi & Matsuyama 2016). The TOC concentration of municipal wastewater in Japan is approximately 100 mg/L. Thus, if the municipal wastewater is concentrated 20-times with the FO process, the TOC concentration is sufficiently high to apply anaerobic biological wastewater treatment. Concentrated municipal wastewater, including a high concentration of particulate organic carbon (POC), requires a long retention time in the reactor to hydrolyze and dissolve. For treating wastewater including a high concentration of POC, a fixed bed anaerobic bioreactor may cause an accumulation of POC among the fixed media, and requires frequent washing of media. Upflow anaerobic sludge blanket bioreactors (UASBs) may be adopted for wastewater with such high POC concentrations. However, a long hydraulic retention time (HRT) is required to allow more time for POC hydrolysis, so that influent water flow and flow velocity are low. On the other hand, an anaerobic membrane bioreactor (AnMBR) can maintain a high POC concentration for a long time in a reactor with a short hydraulic retention time (HRT) using microfiltration (MF) or ultrafiltration (UF) membranes. In addition, AnMBRs are compact and simple to maintain and produce high-quality treated water.

Many studies on AnMBR with various membrane materials and module configurations have been reported (Saddoud *et al.* 2007; Yoo *et al.* 2012; Gouveia *et al.* 2015). However, membrane fouling is a severe problem in MBRs that cannot be avoided. Particularly, in an AnMBR there are two difficulties that do not arise with aerobic MBRs.

The first is the lack of an aeration system. In aerobic MBRs, the aeration system for the cultivation of activated sludge can also be used as a membrane cleaning system, which vibrates the membrane surface and peels off the

deposited foulants. Instead of an aeration system, a gas circulating system using methane gas produced in AnMBRs has been proposed (Martinez-Sosa *et al.* 2011). However, this requires a highly specialized system with features such as explosion protection, since a combustible gas is used. Instead of a gas circulating system, a granular activated carbon (GAC) circulating system has been examined (Kim *et al.* 2011; Ahmad *et al.* 2018). Fluidized GAC provided a scouring action on the membrane surface with low energy consumption. Different approaches to control membrane fouling by applying shear stress were examined with rotating flat sheets or tubular membrane modules (Herrera-Robledo *et al.* 2011; Jiang *et al.* 2013). In this study, we used a tubular-type AnMBR similar to that of a previous study (Herrera-Robledo *et al.* 2011), since it can be operated simply at a laboratory scale and membrane fouling might be prevented by the shear stress of the cross-flow through the tubular membrane.

The second difficulty of AnMBR usage is the prevention of fouling because foulants accumulate in the reactor. In aerobic MBRs, foulants also accumulate in the reactor, but a portion of these foulants is drawn out with a large amount of excess sludge produced by the aerobic bacteria. Therefore, in aerobic MBRs, the concentration of the foulant in the reactor reaches a steady state. In contrast, an AnMBR produces less excess sludge than an aerobic MBR. Thus, the foulant concentration in the reactor may be higher than that in an aerobic MBR in its steady state, resulting in the acceleration of membrane fouling. Recently, an analysis of membrane fouling in AnMBRs was reported (An *et al.* 2009b; Kim *et al.* 2016). However, the changes in the foulant concentration in AnMBRs have not been studied.

The purpose of this study is to clarify the changes in the concentration of foulants that cause membrane fouling under a loading rate 20 times higher than that of a normal municipal wastewater treatment system. To consider foulant accumulation, we first determined the major foulant in an AnMBR treatment. Then, we investigated the rate of change of the foulant concentration during AnMBR treatment of municipal wastewater.

METHODS

Feed water

The AnMBR tests were carried out in a municipal wastewater treatment plant (hereafter referred to as 'the field') and at a laboratory at Kobe University (hereafter referred

to as ‘the laboratory’). In the field, the feed water was continuously taken from the overflow channel of the first settling tank by a submersible pump. In the laboratory, artificial wastewater containing poly-peptone, yeast extract, and glucose was used as the feed water to perform high organic loading tests. To maintain the HRT of the AnMBR constant, the TOC concentration of the feed water was increased. As a result, the organic load was increased. The weight ratio of poly-peptone, yeast extract, and glucose in the artificial wastewater was always kept at a ratio of 10:5:4, which corresponds to a weight ratio of C, N, and P of approximately 35:7:1, which is almost similar to that of actual municipal wastewater, 30:9:1. The average TOC of the standard artificial wastewater was 93 mg/L, which is similar to the TOC of actual municipal wastewater (approximately 100 mg/L).

In this study, we use ‘TOC’ not ‘COD’ as an indicator of organic matter, because we evaluated the concentration of foulants by dissolved organic carbon (DOC) measured by using a liquid chromatography-organic carbon detector (LC-OCD) and it is easy to consider the carbon balance by DOC. For municipal and artificial wastewater, the COD value is approximately 2.5 times the value of TOC (see Supplementary materials Figure S1).

AnMBR equipment and conditions

Figure 1 shows a schematic of the AnMBR test equipment used in the field and in the laboratory. The equipment consisted of an anaerobic reactor and a membrane filtration system. A commercial 10 L jar fermenter was used as the anaerobic bioreactor, which was equipped with an agitator, pH and temperature control units, electrodes for water level control, and a redox potential (ORP) indicator. The temperature in the reactor was controlled at 37.0 ± 0.2 °C by a

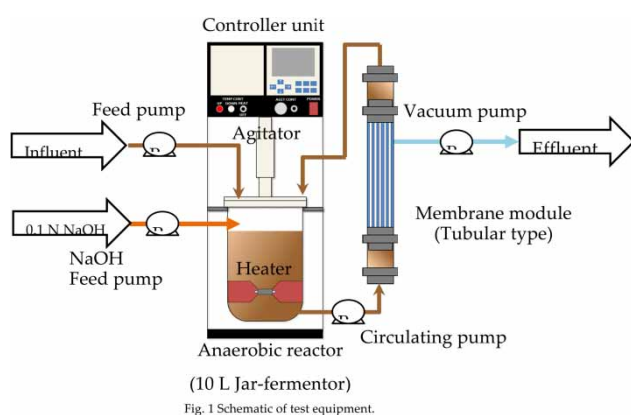


Figure 1 | Schematic of test equipment.

ribbon heater wrapped around the reactor, and the pH was adjusted to 7.0 ± 0.2 by 1 N NaOH dosing. The reactor volume was kept almost constant by the water level control electrode. The feed water was fed, and the permeated water was pulled through the membrane using a micro tube pump. The conditions were determined to be anaerobic if the ORP value was lower than -400 mV. During the operation, no sludge was discharged except for sludge sampling. This corresponded to an SRT of approximately 120 days. The HRT of the AnMBR was maintained at 1 day. Thus, the volumetric TOC load was approximately 0.1 kg-TOC/m³/day when an actual sewage wastewater of approximately 100 mg/L TOC was fed.

In this study, a tubular type UF membrane module made of polyvinyl chloride (PVC) was used. The molecular weight cutoff of the membrane was 100 kDa. The inner and outer diameters of the membrane were 4 and 6 mm, respectively, and the effective length was approximately 240 mm. Twelve membranes were set in the module. The total effective membrane area was approximately 0.04 m² based on its inside surface. The membrane module (40 mm diameter \times 700 mm length) was set externally to the anaerobic reactor and the mixed liquor was circulated from the reactor through the inside of the tubular membrane at a linear velocity of 0.4 m/s. The permeate was pulled from the inside to the outside of the tubular membrane. The operational flux of the membrane filtration was controlled at 0.2 m³/m²/day to maintain the HRT of the reactor at 1 day. The operating conditions of the AnMBR are summarized in Table 1.

To start up the AnMBR, a seed culture was taken from other anaerobic biological wastewater treatment test equipment, which had been operated for more than 1 year with seed sludge from an actual sludge digestion system. After 2 months of operation for the acclimation to the artificial wastewater under the operating conditions of a TOC volumetric load of approximately 0.5 kg-TOC/m³/day (470 mg-TOC/L, five times the standard artificial wastewater load), the feed TOC concentration was increased stepwise to

Table 1 | Operating conditions of AnMBR

Anaerobic biological treatment		Membrane filtration	
Reactor volume	10 L	Material	PVC
Temperature	37 °C	Inner/outer diameters	4/6 mm
Agitation	180 rpm	Molecular weight cut off	100 kDa
Operating pH	7	Flux	0.2 m/d
HRT	1d	Linear velocity in tube	0.4 m/s

930, 1,400, and 1,900 mg-TOC/L, which is approximately 10, 15, and 20 times higher than that of conventional municipal wastewater. In each step, the TOC concentration was increased after the mixed liquor suspended solids (MLSS) in the reactor and the biogas production rate became stable. As a result, the periods of each step were 14, 21, and 28 days for the volumetric loading rates of 0.9, 1.4, and 1.9 kg-TOC/m³/day, respectively.

The UF membrane module was changed to a new module with a stepwise increase in the loading rate to compare the membrane fouling state under each loading rate condition. We evaluated the membrane fouling state by its membrane filtration resistance, R_m (1/m), which is defined by Equation (1).

$$R_m = \Delta P / (\mu \cdot J) \quad (1)$$

where ΔP is the transmembrane pressure (TMP) (Pa), μ is the viscosity of water (Pa·s), and J is the filtration flux (m/s). Note that a larger value of R_m indicates a higher membrane fouling state.

In this study, the predetermined flux could not be kept stable when the TMP exceeded 60 kPa because of the vacuum capacity of the tubing pump. Therefore, the membrane was cleaned or replaced when the TMP reached a value of approximately 60 kPa.

Extraction of foulants on and inside the membrane

The fouling experiment was performed until the TMP increased to approximately 60 kPa using municipal wastewater (about 100 mg/L TOC, 0.1 kg-TOC/m³/day) in the field and 470 mg/L TOC using artificial wastewater (0.5 kg-TOC/m³/day) in the laboratory. Then, six samples of 10 cm in length were cut from the membrane from the middle part of the module radius and half of the membrane length. Samples were slightly washed with ultrapure water. Three of them were immersed in 100 mL of 0.1 N NaOH. Then, the foulant was extracted by shaking the vessel using a 20 mm stroke and 120 rpm for 12 h at 20 ± 0.2 °C. The amount of foulant extracted in this way was measured using LC-OCD. This measured value is referred to as the total foulant F_t . Three other samples were obtained by wiping the inner surface of the tubular membrane with a small sponge to remove the foulant accumulation on the inner surface. Then, the remaining foulant was extracted in a similar manner, as described above. The amount of foulant extracted after wiping with the sponge was referred to

as the irreversible foulant, F_{ir} . The reversible foulant is given by Equation (2).

$$F_r = F_t - F_{ir}, \quad (2)$$

ANALYSIS METHOD

Total organic carbon

Prior to the TOC measurements, the sampled water was filtered through a 0.45 μm hydrophilic polytetrafluoroethylene membrane (DISMIC 13HP045AN, Advantec, Tokyo, Japan). The TOC of the sampled water was measured with a TOC analyzer (TOC-V_{CSH}, Shimadzu Corporation, Kyoto, Japan). First, inorganic carbon was removed from the sampled water as carbon dioxide by adjusting the pH to less than 3. Then, the sampled water was burnt at 680 °C on a platinum catalyst. The burnt gas was cooled and dehumidified, and the CO₂ in the gas was detected with a non-dispersive infrared gas detector. Phthalate hydrogen potassium was used as the standard for calibration.

Liquid chromatography organic carbon detector

In our previous study, we revealed that more than 90% of DOC could be detected by using LC-OCD measurement and some components identified by LC-OCD were strongly related to membrane fouling (Hasegawa *et al.* 2017, 2019). Therefore, in this study, we used LC-OCD analysis for the evaluation of foulants. LC-OCD measurements were performed to analyze the concentration of each component of the foulant in the sampled water. Prior to the LC-OCD measurements, all samples were filtered through the same filter used in the TOC measurements. The organic carbon content was measured with a Model 8 DOC-Labor instrument (DOC-Labor, Karlsruhe, Germany). A hydrophilic weak cation exchange resin (TOYOPEARL HW-50, Tosoh, Tokyo, Japan) was used in the chromatography column. The organic carbon content separated through the column was oxidized by using UV light in a thin film reactor. Then, it was converted to CO₂ using an acidification liquid and removed from the sampled water. The concentration of the organic carbon content was determined by the concentration of CO₂ using a non-diffusion infrared detector. The mobile phase was a phosphorus acid buffer at a pH of 6.58, comprising sodium dihydrogen phosphate and disodium hydrogen phosphate (Sigma-Aldrich Japan,

Tokyo, Japan). The acidification liquid was a phosphorus acid buffer at a pH of 1.5, comprising phosphoric acid and potassium peroxodisulfate (Sigma-Aldrich Japan, Tokyo, Japan). The mobile phase was injected at a flow rate of 1.1 mL/min, and the volume of the injected sample was 1,000 μ L. The total retention time was set to 130 min. The concentration of the organic carbon content was calculated using the software chromCALC (DOC-Labor, Karlsruhe, Germany), customized to our system.

The membrane rejection of the foulant, R_f , was calculated using Equation (3).

$$R_f = 1 - C_e/C_r \quad (3)$$

where C_e (mg/L) and C_r (mg/L) are the concentrations of each component of the foulants in the effluent that permeated the membrane and the AnMBR, respectively.

Biogas production

Biogas produced by methanogenic bacteria was exhausted from the upper part of the AnMBR, and the gas production rate was measured with a wet gas meter (W-NT type for experimentation, Shinagawa, Tokyo, Japan) without any pretreatment. It can be assumed that denitrification does not occur in the reactor because the actual municipal wastewater and the artificial wastewater contain low levels of nitrate. In addition, the pH in the reactor was controlled at 7, which means that ammonia, and volatile fatty acids (VFAs) exist mostly in their ionized form. Therefore, we neglected the volumetric percentage of nitrogen, ammonia, and VFAs in biogas. Therefore, the concentration of methane in biogas C_{CH_4} (%) was estimated using Equation (4).

$$C_{CH_4} \cong 100 - C_{CO_2} \quad (4)$$

where C_{CO_2} (%) is the concentration of carbon dioxide measured by a carbon dioxide detector tube (No. 2 HH, Gastec, Kanagawa, Japan).

RESULTS AND DISCUSSION

Foulants on the fouled membrane

The fouled membranes were taken from the test equipment operated until a TMP of 60 kPa was reached with an influent of artificial wastewater in the laboratory or actual municipal wastewater taken from the effluent of the primary settling

tank in the field. We measured the amount of foulant extracted by 0.1 N NaOH from the fouled membranes with and without sponge wiping using LC-OCD. The amount of reversible foulant F_r and irreversible foulant F_{ir} was calculated from Equation (2). The results are shown in Figure 2. The amount of irreversible foulant was lower than 1% of the total foulant and much lower than that of the reversible foulant (more than 99%). In both the actual and artificial wastewater cases, the main reversible and irreversible foulants were biopolymers (BPs) that appeared after approximately 30 min in the LC-OCD measurements. This result is in agreement with some reports on membrane fouling (Miyoshi et al. 2012; Tian et al. 2013). Regarding the ratio of foulant components, BPs accounted for more than 60% in the reversible foulants, but less than 40% in the irreversible foulants. It was found that, in the irreversible foulants, the ratio of smaller molecular materials, including humic substances (HS), building blocks (BB), low molecular weight acids (LA), and low molecular weight neutrals (LN) was higher than that of BPs, as shown in Figure 2.

Figure 3 shows the rejection of the foulants detected by LC-OCD obtained from a stepwise increase in the loading rate with artificial wastewater as a function of retention time. The retention time is associated with the molecular size (Huber et al. 2011). As the molecular size decreases, the retention time generally increases. In particular, BP (retention time: 30 min) was almost completely rejected, suggesting that large molecular size materials such as BPs were rejected by the UF membrane and accumulated on the membrane surface. Therefore, BP became the main

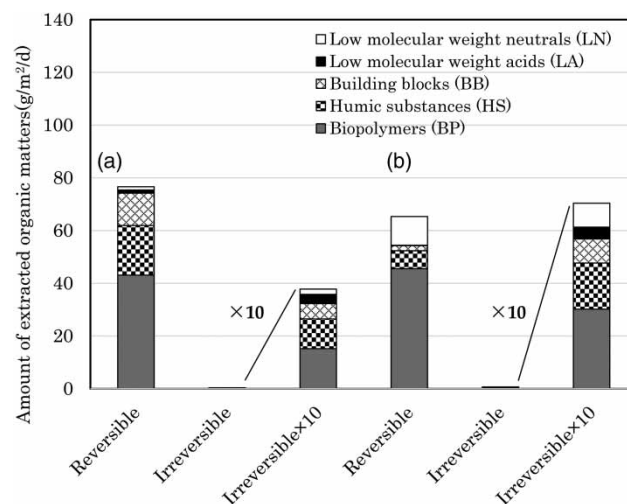


Figure 2 | Amount of dissolved organic matter extracted from the fouled membrane used for treating (a) actual municipal wastewater and (b) artificial wastewater.

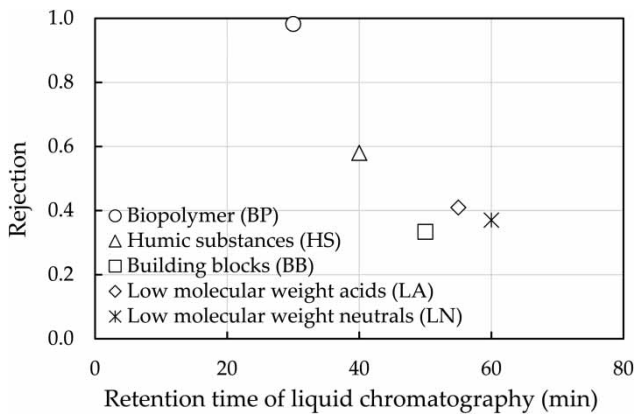


Figure 3 | Relationship between rejection of components and retention time.

foulant in reversible fouling. On the other hand, relatively small molecular components could permeate through the UF membrane. However, some were retained within the pores of the membrane. Therefore, the ratio of smaller molecular size materials increased in the irreversible fouling compared to that of the reversible fouling, as shown in Figure 2.

Furthermore, it was expected that the foulants rejected by the membrane would accumulate in the AnMBR, and this increase in foulant concentration would accelerate the membrane fouling. Therefore, we investigated the change in foulant concentration in the AnMBR under high loading conditions, in which the concentration of foulants in the feed water was so high that they could accumulate easily.

In addition, in this fouling experiment, we compared the water quality and biodegradability of actual and artificial municipal wastewaters. The components of both wastewaters analyzed by LC-OCD were almost the same, and

the removal of each component, indicating biodegradability, showed the same tendency (refer to Supplementary materials Table S1). Therefore, artificial wastewater could be used as a substitute for municipal wastewater.

Performance of anaerobic membrane bioreactor under high loading conditions

As described in the Introduction, it was reported that the TOC of municipal wastewater could be increased 20 times with the FO membrane by using seawater as the draw solution. Thus, in this study, assuming a 20 times higher concentration of municipal wastewater, the maximum TOC of the artificial wastewater was adjusted to approximately 1,900 mg-TOC/L.

Figure 4 shows the performance of the AnMBR. The vertical solid lines in Figure 4 indicate the point where the influent TOC was increased. The dotted line represents the planned TOC concentration in the influent. The influent TOC was increased when the MLSS in the reactor and the biogas production rate became stable in each step. According to the stepwise increase of the influent TOC concentration from 470 to 1,900 mg/L, corresponding to a TOC volumetric loading rate stepwise increase from 0.5 to 1.9 kg-TOC/m³/day, the biogas production rate increased immediately and became stable within a week in each step. However, it required a longer time to reach a stable MLSS concentration in each step. As a result, the periods of each step were 14, 21, and 28 days for the loading rates of 0.9, 1.4, and 1.9 kg-TOC/m³/day, respectively. Finally, MLSS increased from 3,500 to 8,000 mg/L, indicating an increase in the number of microorganisms. As shown in Figure 4(a), the effluent TOC was very low. This was due

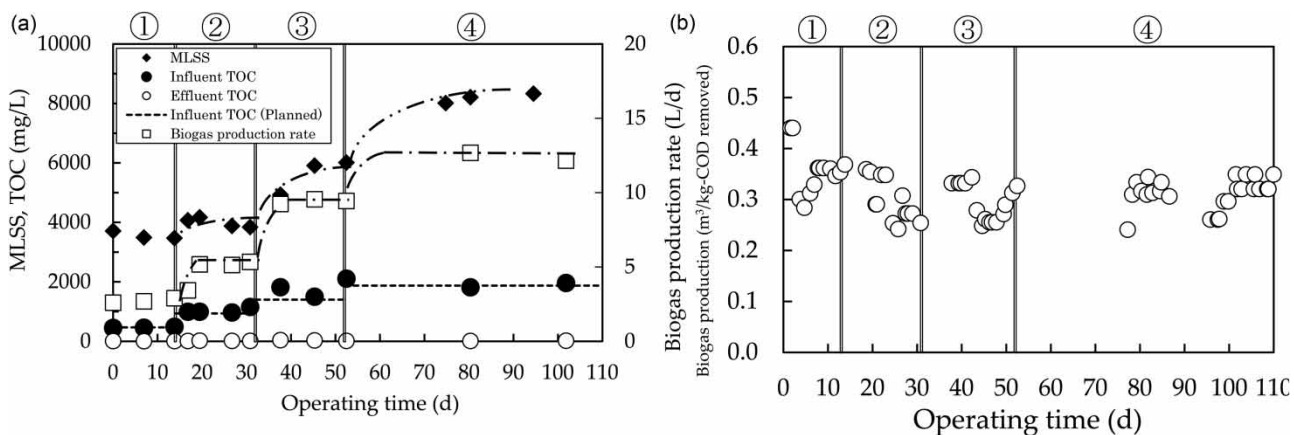


Figure 4 | Performance of an AnMBR under high loading conditions (a) MLSS in the reactor, influent TOC, effluent TOC, and biogas production rate, (b) biogas production. Volumetric loading rate: ○ 0.5, ◎ 0.9, ⊙ 1.4, and ⊕ 1.9 kg-TOC/m³/day.

to the growth of microorganisms. More than 95% of the TOC was decomposed, even under high loading conditions, such as a loading 20 times higher than that of conventional municipal wastewater. The biogas production per removed COD was almost constant at about $0.32 \text{ m}^3/\text{kg-COD}$ removal, as shown in Figure 4(b). This value is within the range of values reported in a previous study (Lin *et al.* 2013) and is almost the same as the theoretical value of $0.382 \text{ m}^3/\text{kg-COD}$ removal at 25°C .

Change in foulant concentration in the AnMBR

Membrane fouling is caused by foulants contained in the influent or produced by microorganisms in the reactor. Therefore, it is important to investigate the change in foulant concentration in the AnMBR. Under high organic load conditions, the concentrations of foulants will be high inside the reactor.

Prior to the analysis of the foulant components by LC-OCD, we confirmed whether the LC-OCD measurements detected all the components correctly, as shown in Figure S2. For the influent and the reactor solution, more than 90% of the DOC measured by TOC (TOC-DOC) was detected by LC-OCD. For example, the concentrations of each component of standard artificial wastewater measured by LC-OCD were as follows: BP, 2.7 mg/L; HS, 9.2 mg/L; BB, 5.7 mg/L; LA, 4.6 mg/L; and LN, 46.8 mg/L. The sum of components measured by LC-OCD (LC-OCD-DOC) was 69.0 mg/L, which is equivalent to 91% of a TOC-DOC of 76 mg/L. Therefore, we can discuss organic fouling by considering the components measured by LC-OCD.

Figure 5 shows the change in foulant concentration in the reactor and the influent measured by LC-OCD. Artificial

wastewater was used in this experiment. The vertical solid lines in Figure 5 indicate the point where the influent TOC was increased.

As shown in Figure 5(a), the concentration of BP in the reactor increased quickly and became higher than that in the influent when the TOC in the influent water was increased stepwise. This is likely because BP was produced by microorganisms in the AnMBR. In addition, BP seems to be biodegradable and gradually decreases with an increase in the number of microorganisms. We found that BP was decreased in the biological contact filters and was also produced in some conditions (Hasegawa *et al.* 2017). Zheng *et al.* investigated the biological degradability of biopolymers and verified that BP is biodegradable (Zheng *et al.* 2010). In a case like this study, TOC loading might influence the change of BP concentration in the reactor. At the point of increasing TOC volumetric loading, biomass in the reactor does not increase at the same time. The biomass starts to increase a little later. Thus, the TOC sludge loading increases temporary and BP might be produced. According to the increase of biomass in the reactor, the TOC sludge loading would decrease gradually and the accumulated BP in the reactor would be decreased biologically. Thus, BP did not accumulate in the reactor, even at the high loading rate of $1.9 \text{ kg TOC}/\text{m}^3/\text{day}$. The other components, HS, BB, LA, and LN, also increased in the reactor, as shown in Figure 5(b), when the TOC in the influent was increased; however, they never exceeded the influent concentration, contrarily to BP. They also decreased within two or three weeks and never accumulated in the reactor at loading rates lower than $1.4 \text{ kg-TOC}/\text{m}^3/\text{day}$. However, the concentrations of HS and LN in the reactor increased for loading rates greater than $1.9 \text{ kg-TOC}/\text{m}^3/\text{day}$. From the above results, the TOC

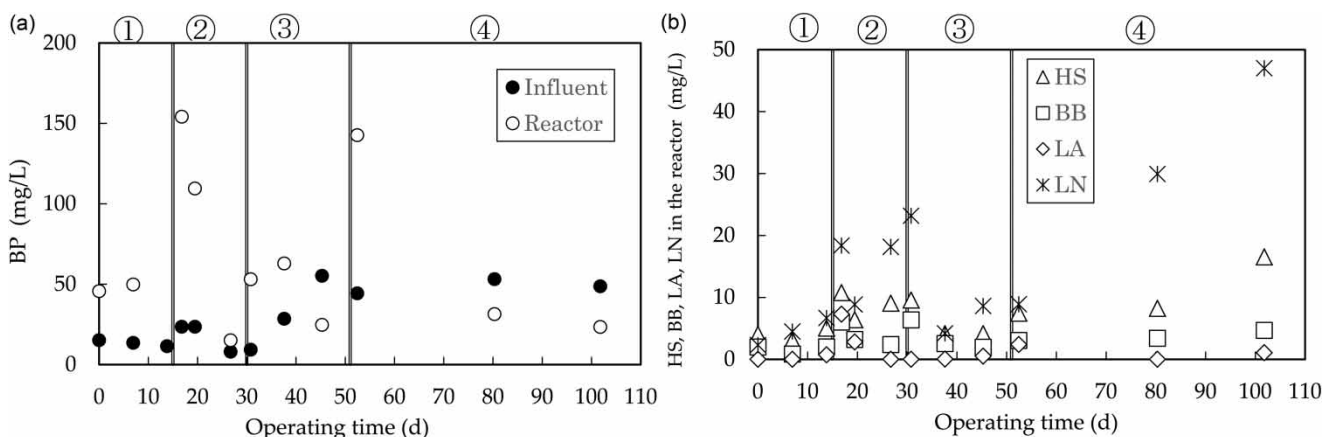


Figure 5 | Change of each component in the reactor detected by LC-OCD. (a) Biopolymers (BP), (b) humic substances (HS), building blocks (BB), low molecular weight acids (LA), low molecular weight neutrals (LN). Volumetric TOC loading rate: ① 0.5, ② 0.9, ③ 1.4, ④ 1.9 kg-TOC/m³/day.

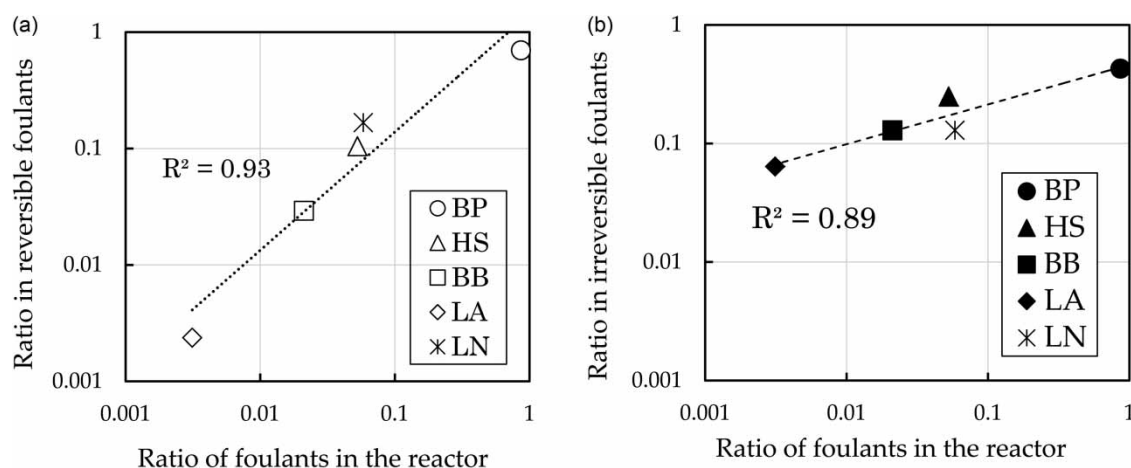


Figure 6 | Relation between the ratio of foulants in reversible or irreversible foulants and in the reactor. (a) Reversible fouling case, (b) irreversible fouling case.

loading rate at which the foulants are not accumulated in the reactor should be lower than $1.4 \text{ kg-TOC/m}^3/\text{day}$.

Figure 6(a) shows the relationship between the ratio of each foulant in the reversible foulants and in the reactor. Figure 6(b) shows the relationship between the ratio of each foulant in the irreversible foulants and in the reactor. It is clear from Figure 6(a) and 6(b) that the fouling in the AnMBR is not related to the components in the influent (refer to Supplementary materials Figure S3), but is close to the components in the reactor. In particular, the ratio of each component in the reversible foulants was almost the same as the ratio of foulants in the reactor. On the other hand, the ratios in irreversible foulants were not the same as the ratios of foulants in the reactor. The ratios of lower molecular weight foulants in the irreversible foulants, such as LA or BB, were larger than the ratios of foulants in the reactor. In contrast, the ratio of higher molecular weight foulants in the irreversible foulants, such as BP, was smaller than the ratio of foulants in the reactor. This means that the ratio in foulants must be closely related to the ratio of foulants in the solution at which the surface contacts. In drinking water treatment systems with membranes, membrane fouling is influenced by the components of the feed water (Kimura et al. 2014; Hasegawa et al. 2017). However, in an AnMBR, the components in the reactor are more important than those in the influent because the components of the influent may be changed biologically in the reactor.

Figure 7 shows the filtration resistance of the membrane over time. The increasing rate of filtration resistance is almost the same, independent of the TOC loading rate. This is because, as shown in Figure 5(a), the BP concentration in the reactor increases with the TOC loading rate. However, BP is biodegraded with time and does not

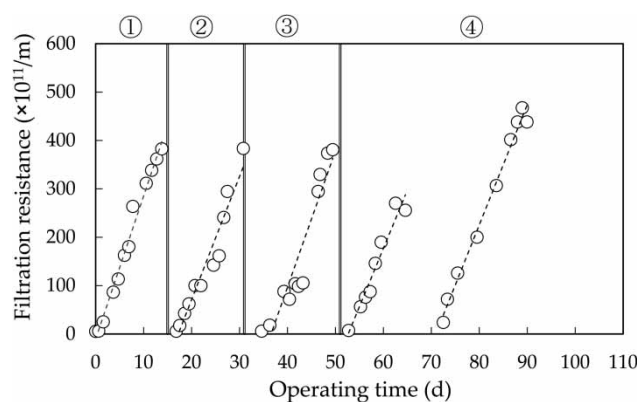


Figure 7 | Time course of filtration resistance of a UF membrane in an AnMBR. Volumetric loading rate: \circ 0.5, \otimes 0.9, \oplus 1.4, \otimes 1.9 $\text{kg-TOC/m}^3/\text{day}$. \downarrow : The UF membrane module was changed to a new module at this point.

accumulate for a long time even under the high organic loading rate of $1.9 \text{ kg TOC/m}^3/\text{day}$. Thus, the increasing rate of filtration resistance does not depend on the TOC loading rate under the conditions used in this study.

Advantage of an AnMBR with UF membrane

From Figure S4, the TOC-DOC in the reactor and in the effluent were roughly 8.1% and 1.7% of that in the influent, respectively. Therefore, the rejection of TOC-DOC by the UF membrane was estimated to be about 80% ($= (1 - 1.7/8.1) \times 100$). The rejected TOC-DOC of about 6.5% ($= 8.1 - 1.7$) of the TOC-DOC in the influent might be gasified in the reactor. This is the advantage of using a UF membrane. Thus, the AnMBR provides an increase in methane gas production and a higher quality effluent compared to other anaerobic systems without a membrane.

It should be noted that this advantage of an AnMBR will depend on the membrane used. An MF membrane can permeate large molecular weight substances, such as BP, and low molecular weight substances with low rejection (Figure S5). Therefore, it is easily expected that when an MF membrane is adopted on an AnMBR, the foulant concentration in the reactor will be decreased because of its low rejection and decreased biogas production. The ratio of BP in the irreversible foulant will increase because BP can also pass through an MF membrane.

CONCLUSIONS

AnMBR systems are attractive owing to their many advantages. However, there is a possible accumulation of foulants in the reactor, which results in membrane fouling. Thus, in this study, we examined the change in foulant concentration in an AnMBR.

It was found by LC-OCD measurements that the main foulant causing fouling on UF membranes was BP. It was also found that both reversible and irreversible fouling in the AnMBR were closely related to the components in the reactor. BP accumulated in the AnMBR because it was almost completely rejected by the UF membrane. However, once the accumulated BP in the reactor was biodegraded, it did not accumulate for a long time in the AnMBR, and did not accelerate membrane fouling, even at the high loading rate of 1.9 kg TOC/m³/day.

AUTHOR CONTRIBUTIONS

Susumu Hasegawa and Genki Murakami conceived and designed, and performed the experiments; Susumu Hasegawa, Genki Murakami, and Ryosuke Takagi analyzed the data. Susumu Hasegawa, Ryosuke Takagi, and Hideto Matsuyama contributed to writing the manuscript.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at <https://dx.doi.org/10.2166/wst.2020.296>.

REFERENCES

- Ahmad, R., Aslam, M., Park, E., Chang, S., Kwon, D. & Kim, J. 2018 Submerged low-cost pyrophyllite ceramic membrane filtration combined with GAC as fluidized particles for industrial wastewater treatment. *Chemosphere* **206**, 784–792. <https://doi.org/10.1016/j.chemosphere.2018.05.045>.
- An, Y. Y., Yang, F. L., Buccioli, B. & Wong, F. S. 2009a Municipal wastewater treatment using a UASB coupled with cross-flow membrane filtration. *Journal of Environmental Engineering* **135**, 86–91.
- An, Y., Wang, Z., Wu, Z., Yang, D. & Zhou, Q. 2009b Characterization of membrane foulants in an anaerobic non-woven fabric membrane bioreactor for municipal wastewater treatment. *Chemical Engineering Journal* **115**, 709–715.
- Gao, Y., Fang, Z., Liang, P. & Huang, X. 2018 Direct concentration of municipal sewage by forward osmosis and membrane fouling. *Bioresource Technology* **247**, 730–735. <https://doi.org/10.1016/j.biortech.2017.09.145>.
- Gouveia, J., Plaza, F., Garralon, G., Fdz-Polanco, F. & Pena, M. 2015 Long-term operation of a pilot scale anaerobic membrane bioreactor (AnMBR) for the treatment of municipal wastewater under psychrophilic conditions. *Bioresource Technology* **85**, 225–233. <https://doi.org/10.1016/j.biortech.2015.03.002>.
- Grundestam, J. & Hellstrom, D. 2007 Wastewater treatment with anaerobic membrane bioreactor and reverse osmosis. *Water Science and Technology* **56**, 211–217.
- Hasegawa, S., Iwamoto, T., Miyoshi, T., Onoda, S., Morita, K., Takagi, R. & Matsuyama, H. 2017 Effect of biological contact filters (BCFs) on membrane fouling in drinking water treatment systems. *Water* **9**, 981–990.
- Hasegawa, S., Miyoshi, T., Takagi, R. & Matsuyama, H. 2019 Fouling prediction method using TOC and EEM analysis. *Water Science and Technology – Water Supply* **19**, 610–617.
- Herrera-Robledo, M., Cid-Leon, D. M., Morgan-Sagastume, J. M. & Noyola, A. 2011 Biofouling in an anaerobic membrane bioreactor treating municipal sewage. *Separation and Purification Technology* **81**, 49–55. <https://doi.org/10.1016/j.seppur.2011.06.041>.
- Huber, S. A., Balz, A., Abert, M. & Pronk, W. 2011 Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND). *Water Research* **45**, 879–885. <https://doi.org/10.1016/j.watres.2010.09.023>.
- Jiang, T., Zhang, H., Qiang, H., Yang, F., Xu, X. & Du, H. 2013 Start-up of the anammox process and membrane fouling analysis in a novel rotating membrane bioreactor. *Desalination* **311**, 46–53. <https://doi.org/10.1016/j.desal.2012.10.031>.
- Kim, J., Kim, K., Ye, H., Lee, E., Shin, C., McCarty, P. L. & Bae, J. 2011 Anaerobic fluidized bed membrane bioreactor for wastewater treatment. *Environmental Science & Technology* **45**, 576–581.

- Kim, N., Oh, S. & Liu, W. 2016 Enrichment and characterization of microbial consortia degrading soluble microbial products discharged from anaerobic methanogenic bioreactor. *Water Research* **90**, 395–404.
- Kimura, K., Tanaka, K. & Watanabe, Y. 2014 Microfiltration of different surface waters with/without coagulation: clear correlations between membrane fouling and hydrophilic biopolymers. *Water Research* **49**, 434–443.
- Lin, H., Peng, W., Zhang, M., Chen, J., Hon, H. & Zhang, Y. 2013 A review on anaerobic membrane bioreactors: applications, membrane fouling and future perspectives. *Desalination* **314**, 169–188. <https://doi.org/10.1016/j.desal.2013.01.019>.
- Martinez-Sosa, D., Helmreich, B., Netter, T., Paris, S., Bischof, F. & Horn, H. 2011 Anaerobic submerged membrane bioreactor (AnSMBR) for municipal wastewater treatment under mesophilic and psychrophilic temperature conditions. *Bioresource Technology* **102**, 10377–10385. <https://doi.org/10.1016/j.biortech.2011.09.012>.
- Miyoshi, T., Aizawa, T., Kimura, K. & Watanabe, Y. 2012 Identification of proteins involved in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater. *International Biodeterioration & Biodegradation* **75**, 15–22. <https://doi.org/10.1016/j.ibiod.2012.08.003>.
- Saddoud, A., Ellouze, M., Dhoub, A. & Sayadi, S. 2007 Anaerobic membrane bioreactor treatment of domestic wastewater in Tunisia. *Desalination* **207**, 205–215. <https://doi.org/10.1016/j.desal.2006.08.005>.
- Smith, A. L., Skerlo, S. J. & Raskin, L. 2013 Psychrophilic anaerobic membrane bioreactor treatment of domestic wastewater. *Water Research* **47**, 1655–1665.
- Takahashi, T. & Matsuyama, H. 2016 Forward osmosis technology using seawater for filtration concentration of municipal wastewater. *Bulletin the Society of Sea Eater Science Japan* **70**, 340–346.
- Tchobanoglous, G., Burton, F. L. & Stensel, H. D. 2003 *Wastewater Engineering Treatment and Reuse*, 4th edn. McGraw-Hill, New York, NY, USA.
- Tian, J., Ernst, M., Cui, F. & Fekel, M. 2013 Correlations of relevant membrane foulants with UF membrane fouling in different waters. *Water Research* **47**, 1218–1228.
- Van Lier, J. B., Vash, A., Van der Lubbe, J. & Heffernan, B. 2010 Anaerobic sewage treatment using UASB reactors: engineering and operational aspects. In: *Environmental Anaerobic Technology, Applications and New Developments* (H. H. Fang, ed.). World Scientific, Imperial College Press, London, UK (Chapter 4).
- Yoo, R., Kim, J., McCarty, P. L. & Bae, J. 2012 Anaerobic treatment of municipal wastewater with a staged anaerobic fluidized membrane bioreactor (SAF-MBR) system. *Bioresource Technology* **120**, 133–139. <https://doi.org/10.1016/j.biortech.2012.06.028>.
- Zheng, X., Ernst, M. & Jekel, M. 2010 Pilot-scale investigation on the removal of organic foulants in secondary effluent by slow sand filtration prior to ultrafiltration. *Water Research* **44**, 3203–3213.

First received 17 December 2019; accepted in revised form 8 June 2020. Available online 18 June 2020