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A novel application of a submerged nanofiltration membrane bioreactor (NF MBR) for wastewater treatment

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Abstract

Nanofiltration (NF) membrane technology has made rapid progress and then extended its application fields. It has obtained in particular the good results in the removal of organic and inorganic matters or microbes in the water and wastewater. To investigate the applicability and characteristics of NF membrane, the membrane bioreactor (MBR) using the cellulose acetate NF membrane was performed to treat synthetic wastewater. A hollow-fiber-type cellulose acetate membrane was chosen to get enough water productivity regardless of its biodegradability. As a result of the experiments, enough water productivity was obtained for 60 days without fatal fouling and membrane cleaning. This raised the applicability of cellulose acetate membrane to the MBR system. Electrolytes were not accumulated in the bioreactor, as its rejection was also low. This enabled the NF MBR to be operated under a low suction pressure and prevented from inhibition against microorganisms, whose activity might be deteriorated by high salt concentration. Nitrification and denitrification happened simultaneously and this might be achieved by the module configuration. The phosphorus was not removed with the loose NF membrane. According to AFM investigation, the cellulose acetate membrane after 71 days has larger voids because of the biodegradation.

Keywords: Wastewater treatment; Nanofiltration; Membrane bioreactor; Hollow-fiber membrane; Activated sludge

1. Introduction

Membrane technology has been applied in various fields. Microfiltration (MF) and ultrafiltration (UF) membrane systems have already proved their merits concerning the cost as well as water quality. Nanofiltration (NF) membranes are also used in a wide range of drinking water treatment and wastewater reclamation. NF membranes can reject smaller size molecule that

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cannot be removed by MF and UF membranes. It, however, needs lots of energy consumption during the operation. Fortunately, a low-pressure driven type of NF membrane has been developed recently. Separation by NF membrane occurs primarily due to size exclusion and charge effect on electrostatic interactions [1]. Namely, the rejection of uncharged molecules is dominated by size exclusion, while that of ionic species is influenced by both size exclusion and electrostatic interactions. And, electrostatic characteristics of NF membranes have been known as playing an important role in rejection anions, i.e., negative zeta potential on the membrane surface varies with different pH and concentration of an electrolyte solution [2].

The membrane separation process in combination with biological treatment system has been developed for the treatment of municipal wastewater, industrial wastewater and night soil. In municipal wastewater treatment demands on effluent quality are still increasing. Not only carbon and nutrients but also bacteria and viruses have to be eliminated to a great extent. Interest in the membrane bioreactor (MBR) technology for wastewater treatment has increased due to the strict regulation on water quality, need for water reuse/recycling, and increase of cost efficiency with the improvement of membrane technology. The use of submerged membranes has reduced the energy consumption of membrane bioreactors significantly and hence increased the potential for the application of membranes in wastewater treatment [3].

In this study, a submerged membrane bioreactor system with NF membrane is introduced to wastewater treatment. NF membranes have been usually used as pressure-driven type of cross flow system in drinking water treatment until now. However, we try to use this system and investigate its applicability in the domestic wastewater treatment. Both its stability and effluent qualities are evaluated during an experimental period.

2. Materials and methods

2.1. Membrane characteristics

In this experiment, a hollow-fiber NF membrane (Toyobo Co.) was used with the effective surface area of a module at 11.7 m^2. The specifications of the NF membrane module used in this study are shown in Table 1. In the membrane performance test, the water permeability of pure water is about 0.13 m/d·MPa at 25°C and the salt rejection is 55% when a solution of 500 mg/L NaCl is treated under the conditions of 5 kg/cm^2 pressure and 25°C.

Table 1
Membrane characteristics

Items	Specifications
Materials	Cellulose acetate
Type of NF module	U-typed hollow-fiber
Fiber no. of membrane	85,000
Surface of a module, m^2	11.7
Outside diameter of a fiber, μm	175
Inside diameter of a fiber, μm	86

2.2. Reactor configuration

A schematic diagram of the bioreactor is shown in Fig. 1. The bioreactor that is filled with activated sludge has a working volume of about 12 L, in which the NF membrane module is directly submerged. It can be expected that high permeate flux will lead immediately to membrane fouling. Therefore, its flux would be set at the low value of 0.001 m/d for operation. The hydraulic retention time (HRT) was about 1 day and initial concentration of MLSS was about 3600 mg/L. Sludge in the reactor has not been wasted out. Synthetic wastewater was used in this study and diluted with tap water. Its composition is shown in Table 2. The water qualities of influent are also represented in Table 3. The suction was intermittently done by pumping on and off every 15 min.

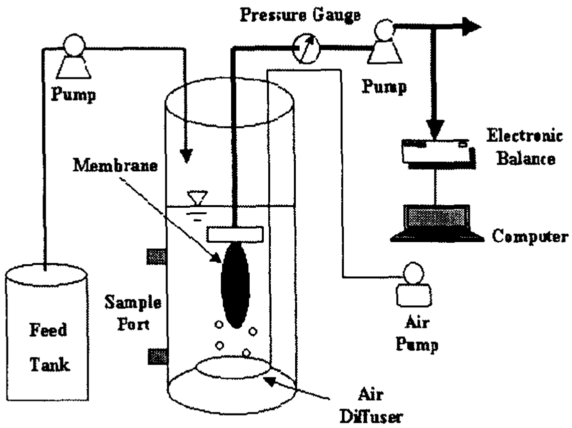


Fig. 1. Schematic of the experimental set-up.

Table 2
Composition of diluted synthetic wastewater

Substances	Amount, mg/L
Peptone	4.1
Yeast extract	3.8
$CH_3COONa{\cdot}3H_2O$	8.5
NH_4Cl	1.2
K_2HPO_4	0.6
$MgCl_2{\cdot}6H_2O$	2.1
$MnSO_4{\cdot}5H_2O$	0.35
$CaCl_2{\cdot}2H_2O$	0.25
$FeSO_4{\cdot}7H_2O$	0.1

Table 3
Average water qualities of influent

Items	Concentration, mg/L
COD	202.3
TOC	91.2
NH_4-N	7.7
T-N	24.6
T-P	4.1
pH	7.2
Conductivity, s/m	47.9
Temperature, °C	16.4

2.3. Analytical methods

Organic compounds were measured with a TOC analyzer (TOC 500 and 5000A, Shimadzu) and anions (NO_2^-, NO_3^-, PO_4^{3-}, Cl^-, SO_4^{2-}) were determined with an ion chromatographic analyzer (IC7000, Yokogawa). LASA- Kit reagent set was used to analyze T-N and NH_4-N. Atomic force microscopy (SPI 3800N, Seico Instruments Inc.) was used to characterize the surface of a membrane. Other water qualities including T-P were measured according to the Standard Methods [4]. Supernatant was filtered with a 0.45 μm filter after centrifuging the activated sludge in the reactor.

3. Results and discussion

3.1. Changes of relative productivity and transmembrane pressure

Fig. 2 represents the changes of relative productivity of permeate and transmembrane pressure (TMP). This system was operated for 71 days after acclimation for 10 days. Until about the 20th day, TMP and relative productivity were 36 kPa and 1.0–1.2, respectively. However, relative productivity increased suddenly after that time, so suction velocity was reduced to adjust for HRT 1 day. Fig. 3 shows that the difference of conductivity between supernatant and effluent is diminished at the end of operation. The increase of water productivity after 20 days operation may be explained as follows.

The water productivity of a charged membrane like the NF membrane may be caused by several mechanisms including (a) increased pore size due to conformational changes, (b) increased apparent water permeability due to decreased electroviscous effect, and (c) increased net driving pressure due to decreased osmotic pressure at the membrane surface [5]. Water productivity would be at a maximum at the pore surface point of zero charge (isoelectric point), as

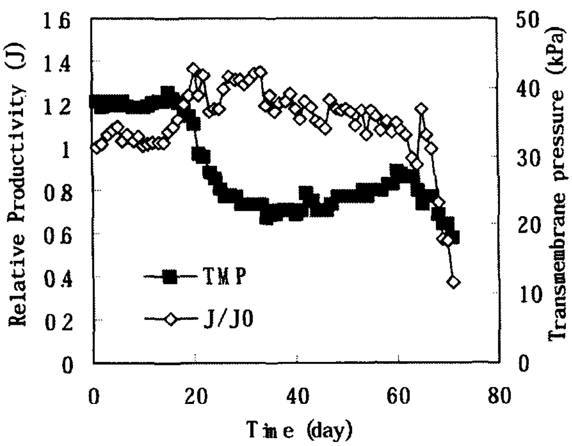


Fig. 2. Changes of transmembrane pressure and relative productivity. J, water flux; J_0, initial water flux.

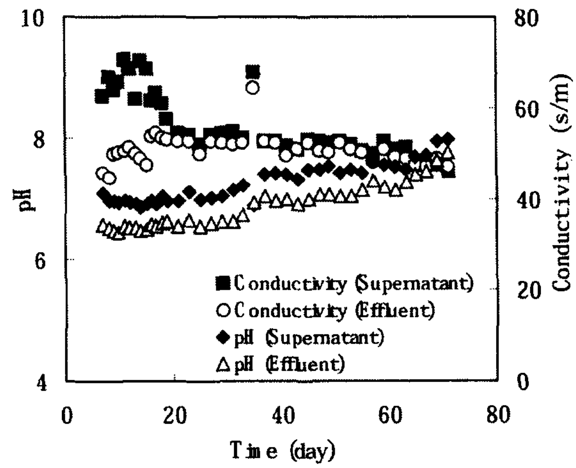


Fig. 3. Changes of pH and conductivity.

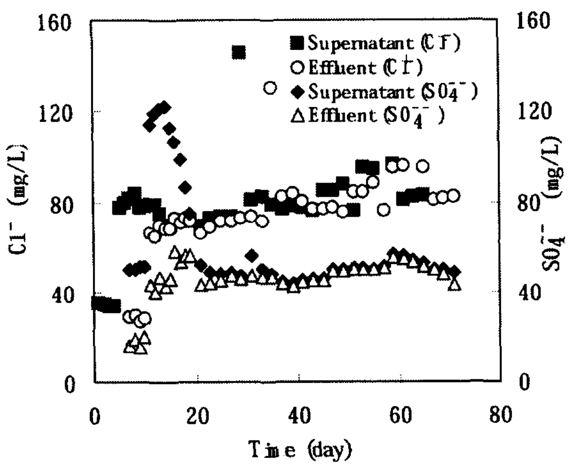


Fig. 4. Changes of anion concentration (Cl^- and SO_4^{2-}).

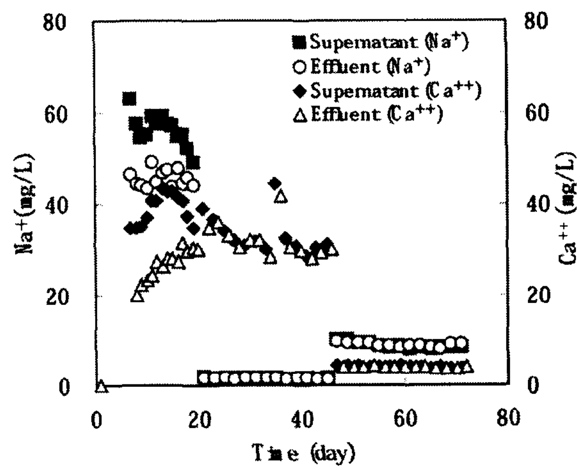


Fig. 5. Changes of cation concentration (Na^+ and Ca^{2+}).

electroviscous effect disappears at the point [6]. And, changes of osmotic pressure at the membrane surface may also be used to explain increase of water productivity. Accordingly, the decrease in conductivity difference between in supernatant and effluent may results in a decreased in osmotic pressure.

3.2. Membrane performance on ionic matters

Fig. 4 represents the concentration of anions such as Cl^- and SO_4^{2-}. As the concentration difference between supernatant and effluent is insignificant, there is little possibility of their accumulation in the bioreactor. In case of SO_4^{2-}, the concentration difference for the initial 20 days is significant due to charged property of the NF membrane. The change of SO_4^{2-} concentration is similar to that of conductivity (Fig. 2). The concentration of cations such as Na^+ and Ca^{2+} are shown in Fig. 5. The trend of the rejection is same to that of SO_4^{2-}. According to the results, electrolytes, which are mainly rejected by the charge effect of NF membrane, were mostly passed. It clearly shows that electrolytes were not accumulated in the bioreactor. It means that NF membrane bioreactor system can be operated under low suction pressure condition because osmotic pressure effect is negligible in the bioreactor, while high rejection of organic matters was obtained for wastewater treatment as presented below.

As an accumulation of electrolytes might inhibit microorganisms growth and activity in the bioreactor, no salt accumulation obtained in this type of NF membrane bioreactor is advantageous.

3.3. Removal of TOC and nutrients in the NF membrane bioreactor

Preliminary experiments, which had been performed with a spiral-wound type of NF membrane (LES 90, Nitto Denko), showed that the effluent TOC was about 1–4 mg/L. However, the LES 90 membrane was tight and led easily to an increase in transmembrane pressure and a decrease in flux, i.e., membrane fouling. A looser one like the cellulose acetate membrane was expected to keep a high enough productivity.

Fig. 6 represents the changes of TOC in supernatant and effluent. The concentration of TOC was at the range of 2–3 mg/L and was nearly the same level in comparison with TOC concentration of the LES 90 membrane. In addition, there was no significant fouling observed, and cleaning of the membrane was not required. The cellulose acetate membrane is, of course, typically biodegradable, which may cause a serious problem. However, the membrane used in this experiment lasted for 60 days without any specific care. Although it was finally degraded after 60 days, there must be a large space of improvement to control the biodegradable nature of the module. With these points, a cellulose acetate membrane will be positively introduced in a membrane bioreactor system if its biodegradation is well controlled, for example, with periodical backwashing with chlorination.

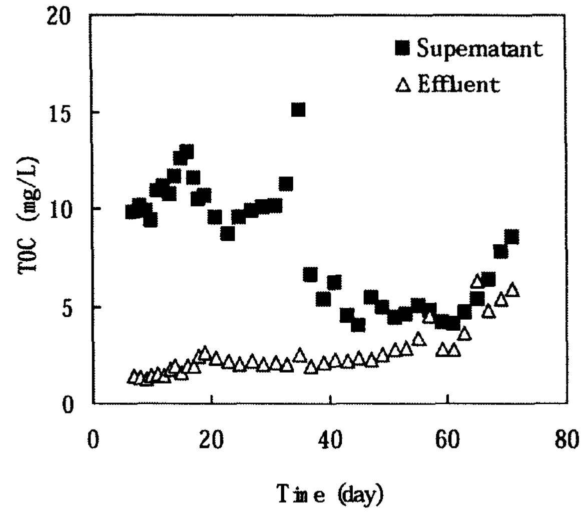


Fig. 6. TOC concentration in the NF membrane bioreactor.

Figs. 7 and 8 represent the changes of nitrate and total nitrogen, respectively. It is rather difficult to achieve denitrification in an aerobic membrane bioreactor. However, nitrification and denitrification happened simultaneously in this experiment. Judging from the results, nitrification mainly occurred outside the membrane module and denitrification might happen inside core of the module where the sludge was accumulated and anoxic condition might easily prevailed.

Figs. 9 and 10 represent the variation of phosphate ion and total phosphorus in the supernatant and effluent, respectively. It was primarily expected that phosphorus would be removed by the effect of size exclusion to some extent. However, the PO_4^{3-} and T-P were not removed except for the initial 20 days where the rejection might occur due to the effect of the surface charge. A tighter membrane can be chosen to remove phosphorus by the size effect.

3.4. Membrane surface image with time variation

Fig. 11 represents atomic force microscopy (AFM) surface images of the membrane with

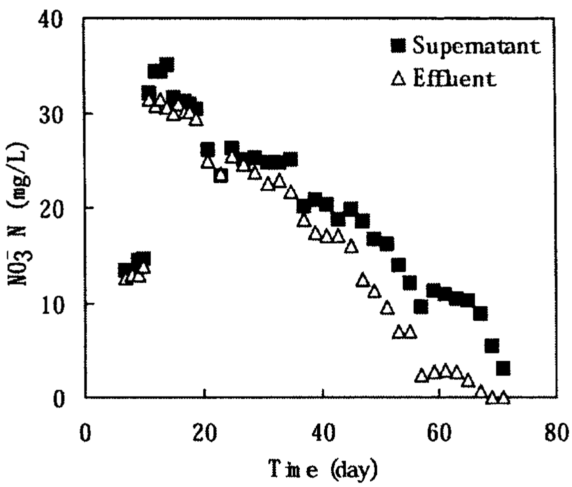


Fig. 7. Concentration of NO_3^--N in the NF membrane bioreactor.

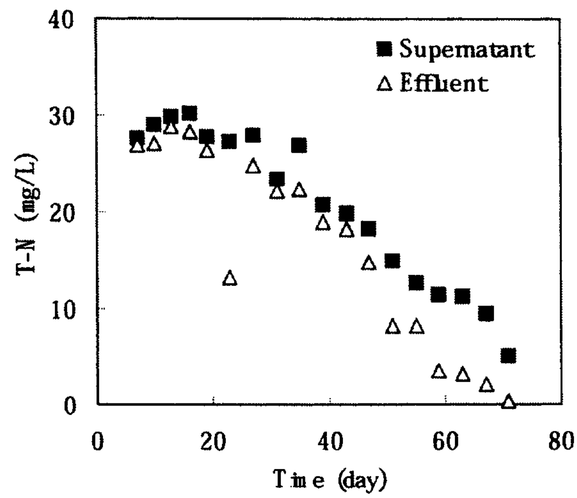


Fig. 8. Concentration of T-N in the NF membrane bioreactor.

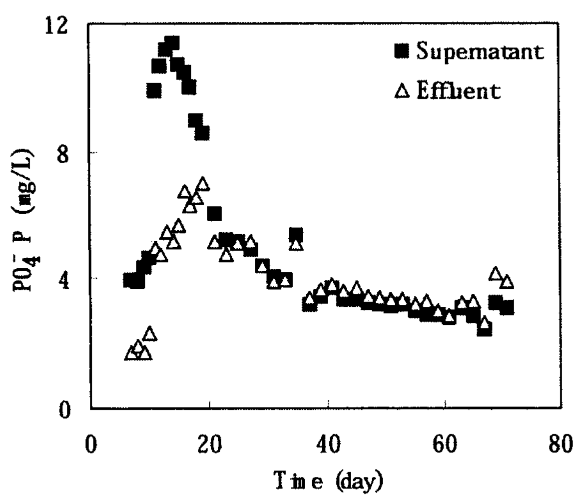


Fig. 9. Concentration of PO_4^{3-}-P in the NF membrane bioreactor.

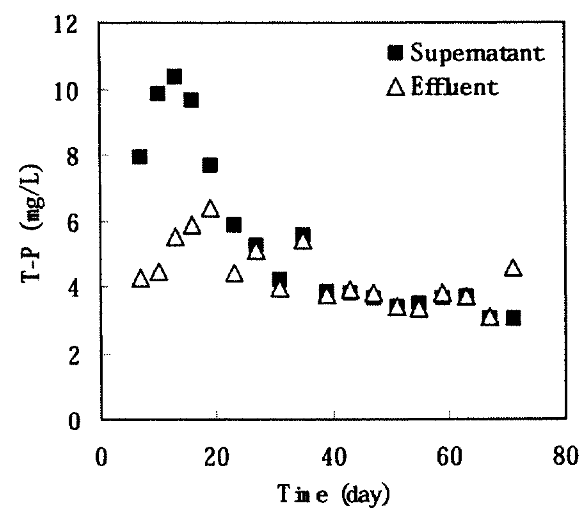
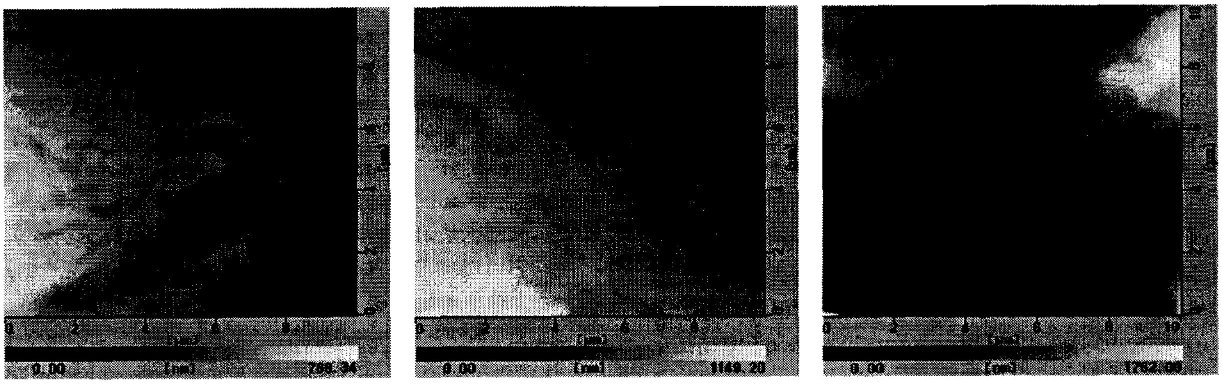


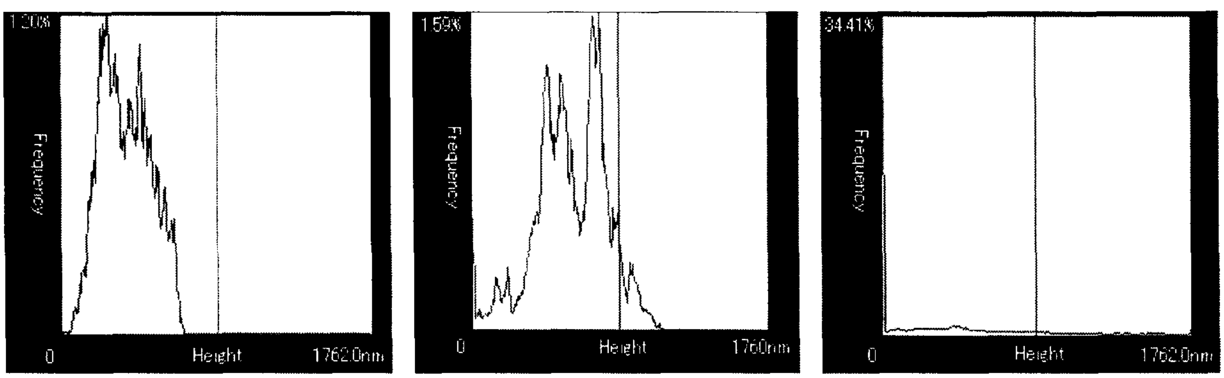
Fig. 10. Concentration of T-P in the NF membrane bioreactor.

variation of time with a projection area of 10 μm×10 μm, in which the unique and characteristic rigid-and-valley structure of the cellulose acetate membrane is shown. The bar at the bottom of each image indicates the vertical deviations in the membranes surface where the white region is the highest and the black is the lowest. Fig. 12 compares vertical height profiles along the horizontal line of 10 μm for all membranes. After 40 days of operation, the height distribution shifted to deeper peaks, indicating that the surface roughness became larger. The surface was finally occupied by large voids at the end of operation for 71 days. It is clear that these phenomena were caused by biodegradation of the cellulose acetate membrane.



(a) (b) (c)

Fig. 11. AFM surface image of cellulose membrane. (a) Fresh membrane. (b) After 40 days. (c) After 71 days.



(a) (b) (c)

Fig. 12. Vertical height profiles taken from the traversing individual AFM images. (a) Fresh membrane. (b) After 40 days. (c) After 71 days.

4. Conclusions

To investigate the applicability and characteristics of NF membranes, a membrane bioreactor using a cellulose acetate NF membrane was used to treat synthetic wastewater. A hollow-fiber-type cellulose acetate membrane was chosen because of its large surface area, which can get enough water productivity regardless of its biodegradability. As a result of the experiments, enough water productivity was obtained for 60 days without fouling and membrane cleaning. This raised the applicability of cellulose acetate membrane to the MBR system. The water productivity increased after 20 days operation. It might be caused by the decrease of electroviscous effect and decreased osmotic pressure, etc. Electrolytes are not accumulated in the bioreactor, as the rejection of it is also low. This enabled the NF MBR to be operated under low-suction pressure and prevented inhibitions to microorganisms growth and activity due to high salt concentration. The TOC of effluent is about 2.5 mg/L. Nitrification and denitrification occurred simultaneously and might be caused by the module configuration. The phosphorus was not removed with the loose NF membrane. As a result of AFM investigation, the cellulose acetate membrane after 71 days had large voids due to the biodegradation.

On the basis of this study, we will use cellulose acetate membranes for domestic wastewater treatment by developing a proper module configuration and/or by intermittently dosing chlorine to the membrane module to control the membrane biodegradation.

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