



The characteristic of passive adsorption using the submerged hydrophilic membrane in biological treatment process

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ABSTRACT

This study investigated the calibration curves for the analysis of the protein and carbohydrate as foulants and the specific profiles of resistance and extracellular polymeric substances (EPS) through passive adsorption (at flux = 0) of hydrophilic polyethylene membrane in an activated sludge bioreactor. It is to recognize fouling and cleaning mechanisms of hydrophilic polyethylene material. Passive adsorption and cake formation continuously proceeded for six weeks even though flux was zero. sEPS more affected membrane fouling than eEPS because sEPS remained constant in the reactor when permeability resistance of membrane increased whereas eEPS continuously decreased. The result showed that 0.05% NaOCl was appropriate for accurately measuring the protein and carbohydrate. Resistance (R_f) of contaminated membrane was high as membrane submergence was proceeded by 43th day, then critical fouling presented. Recovery rate by physical and chemical cleaning decreased as membrane permeation kept doing and biofilm growth occurred. The majority of protein was removed by chemical cleaning, and most carbohydrate was broken by rinsing. Thus, we found that protein is the main substance featuring a serious fouling on a membrane surface.

Keywords: Membrane fouling; Adsorption; Protein; Carbohydrate; Microfiltration; Membrane bioreactors

1. Introduction

The MBR system is increasingly adopted to treat the domestic wastewater because of complete solid–

liquid separation, production of high-quality effluent, capability of handling wide fluctuations in influent quality, and small footprint [1,2]. In addition, due to more stringent discharge regulations, decrease in the membrane cost and water reuse needs, MBR applications have been widely adopted. However, the

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decrease in permeation flux during operation due to the membrane fouling is one of the major barriers to more installations of the MBR process for wastewater treatment [3].

In MBRs, the object of filtration is to separate the effluent from sludge mixed liquor, and the foulants of the membrane surfaces is originated from mixed liquor [2,4]. Properties of the mixed liquor affect membrane fouling significantly. According to previous reports, properties of the mixed liquor affect membrane permeability, such as viscosity, extracellular polymeric substances (EPS), floc size, colloidal, and soluble organic substances. [5]. Even though these factors have a complicated effect on membrane permeability, colloidal, and soluble organic substances are important factor to cause membrane fouling by adsorption of macromolecules and progressive pore clogging [6].

EPS is a high molecular-weight mixture of polymers excreted by micro-organism, produced from cell lysis and hydrolysis, and adsorbed organic matter from wastewater [7]. They are also heterogeneous and composed of various polymeric materials, including humic acids, uronic acids, deoxyribonucleic acids, a small fraction of DNA, proteins, carbohydrates, and complex organic compounds [8,9]. EPS is specifically composed of sEPS (soluble EPS is equal to soluble microbial products; SMP) and eEPS (extracted EPS from biomass surface). EPS and SMP have been identified as major foulants in many experimental studies. The removal of soluble foulants like SMP in the activated sludge is very important since they potentially cause internal fouling of membranes, and thus significantly decrease membrane permeability [10,11].

Membrane fouling in the MBR has an effect on interactions between membrane properties such as membrane material, pore size and hydrophobicity. These properties are important factors on membrane fouling. In particular, results of fouling experiment using polymeric and/or ceramic membranes represented that there was an intimate relationship between membrane material and fouling in MBR. Recently, Miyoshi et al. [4] revealed the effect of different polymeric membrane materials on the relationship between membrane pore size and development of membrane fouling in MBR. Three different polymeric membranes, cellulose acetate butyrate (CAB), polyvinyl butyral (PVB), and polyvinylidene fluoride (PVDF) were investigated, and it showed the difference of membrane fouling on membrane materials. However, most researches have shown membrane resistance when effluent was permeated through the tested membrane [12,13]. It cannot present the fouling index of membrane itself because the membrane shape,

configuration and MLSS concentration affect the fouling. Thus, the research of membrane materials and characteristics when permeate flux is zero is needed at constant shape, configuration and MLSS to find the fouling index depending on the membrane materials.

Therefore, this study was conducted to investigate the calibration curves for the analysis of the protein and carbohydrate as foulants, the variation of resistances and EPS concentrations through passive adsorption (at flux = 0) and the variation of resistances and EPS concentrations at cleaning stages with the hydrophilic polyethylene membrane in an activated sludge bioreactor to present the fouling index of membrane.

2. Materials and methods

2.1. Membrane characteristics and experimental set-up

A reactor (Fig. 1) was bench scale of 15 L with water volume of 10 L, and DO concentration was maintained 5–7 mg/L. Devices had about 10 cm gap between bundle and air diffuser in order to prevent microbes breakaway from the membrane surface by air bubbles. Temperature and pH were controlled at 20–23 °C and 7.5–8.5, respectively. After the operation started, there was no sludge waste except the sampling for measuring MLSS concentration. Permeate flux was zero for passive adsorption. Nine hydrophobic membrane bundles were submerged in an activated sludge reactor, and their resistance was measured every week during eight weeks from the next day of setting. Table 1 shows the specifications of the hollow fiber membranes used in this work.

2.2. Cleaning and analytical methods

Cleaning steps were achieved three; rinsing, backwashing, and chemical cleaning. Rinsing was physically cleaning the fouled membrane bundle in D.I. water of 500 mL strongly stirring it. Backwashing was conversely pumping the D.I. water of 500 mL to outlet of the fouled membrane bundle. In the chemical cleaning stage, the fouled membrane bundle was submerged and stirred in 0.05% NaOCl solution of 500 mL during 2 h.

Protein was measured as protein standard solution (1.45 mg Protein/mL) equivalents using a Bio-Rad protein assay kit following the Lowry method [14]. Carbohydrate was determined as glucose equivalents using the phenol-sulfuric acid method [15]. Protein and carbohydrate calibration curves were measured using deionized water (D.W.) as a solvent of the sample and cleaning water for rinsing and backwashing,

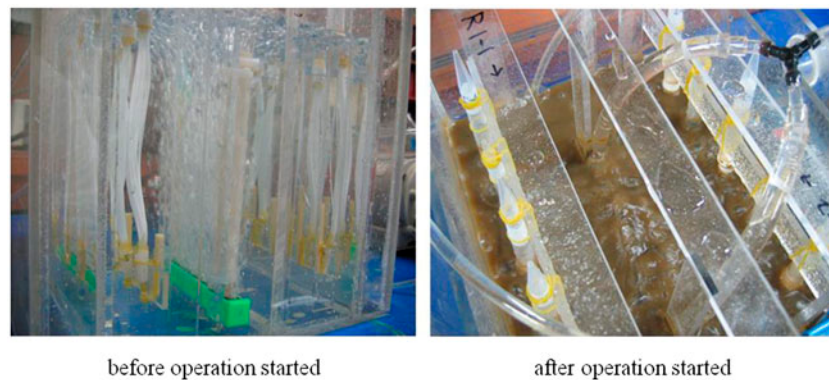


Fig. 1. The real photos of submerged membrane modules.

Table 1
Specification of membrane

Parameter	Specification
Manufacturer	Econity
Type	Hollow fiber
Material	Polyethylene
Pore size (μm)	0.4
Membrane area (m^2)	0.01
Length (cm)	10
No. of fibers/bundle	50
No. of bundles	9
No. of modules	1

and 0.85% NaCl solution for eEPS extraction, and 0.05% NaOCl solution for chemical cleaning, respectively. The standard concentrations using 0.85% NaCl and 0.05% NaOCl solution were fixed in the lower range than D.W. It was expected that extracted EPS concentration from mixed liquid and chemically cleaned solution are relatively low. sEPS was collected after 50 mL of supernatant liquid extracted from mixed liquor was filtered. Then, for getting eEPS, the remained solid was diluted to 50 mL with 0.85% NaCl solution and autoclaved for 10 min at 80°C and then centrifuged, and the filtered supernatant liquid was collected. Initial fouled resistances of each module were measured at constant flux (10 and 12.5 $\text{m}^3/\text{m}^2/\text{d}$) using a suction pump (Peristaltic pump, Cole Parmer, USA) and a pressure gauge (Vacuum Gauge, YJN, Korea). Table 2 shows the detailed method.

3. Results and discussion

3.1. The calibration curves of protein and carbohydrate

D.W., NaCl, and NaOCl were used as solvent, and the calibration curves of all solvents are shown in Fig. 2.

Above all, protein analysis is affected by chemical detergent, so it should be tested in various detergent conditions for finding the range that NaOCl, detergent for chemical cleaning, has no effect on protein measurement. Hence, NaOCl concentrations of 0.5, 0.3, 0.1, 0.07, and 0.05% were tested considering that the range of typical NaOCl concentration is 0.05–0.5% for chemical cleaning. As a result, the correlation coefficients were 0.992, 0.972, 0.959, 0.893, and 0.764 at NaOCl concentration of 0.05, 0.07, 0.1, 0.3, and 0.5%, respectively. Even though coefficients were relatively high at all conditions, low protein concentration below 100 mg/L could not be precisely detected at NaOCl concentration above 0.3%. On the other hand, high accuracy of protein concentration was expected in the range of 0.05–0.1% of NaOCl. Particularly, the correlation coefficients at 0.05% of NaOCl and carbohydrate were above 0.99, and we selected 0.05% of NaOCl as a cleaning solution.

3.2. The variation of permeation resistance during the operation

Fig. 3 shows the variation of initial resistances (R_i) measured before submerging and increased fouled resistances (R_f) through passive adsorption of membrane surface. The margin ($R_f - R_i$) was $9.45\text{E}+08 \text{ m}^{-1}$ at the 1st day after submerging, and R_f values increased as the operating period was lapsed. The (a) point presented initial fouling by simple adsorption which could be removed by physical cleaning. R_f of 43th day in the (b) point which is critical fouling steeply increased to $5.46\text{E}+09 \text{ m}^{-1}$, and then TMP (transmembrane pressure) increased to maximum. These results indicated that passive adsorption by the microbe and stagnant cake was formed continuously without physical cleaning by six weeks when flux is zero. Also, the R_f values decreased to $3.29\text{E}+09$ and $2.51\text{E}+09 \text{ m}^{-1}$ at the 50th day

Table 2

The standard concentrations for calibration curves of protein and carbohydrate

Step	Solvent	Concentration (mg/L)
Protein calibration curves	Protein + D.W.	10, 50, 100, 200, 300, 400, 500
	Protein + 0.85% NaCl	10, 30, 50, 70, 100, 200, 300
	Protein + 0.05% NaOCl	10, 30, 50, 70, 100, 200, 300
Carbohydrate calibration curves	Glucose + D.W.	10, 50, 100, 200, 300, 400, 500
	Glucose + 0.85% NaCl	10, 30, 50, 70, 100, 200, 300
	Glucose + 0.05% NaOCl	10, 30, 50, 70, 100, 200, 300

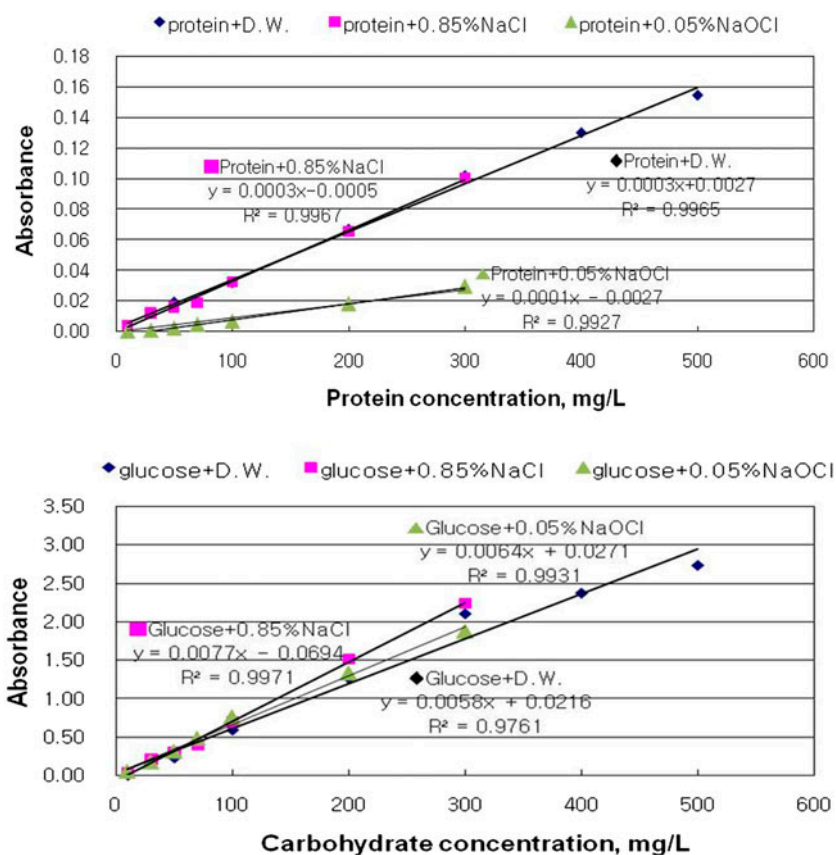


Fig. 2. Calibration curves of protein and carbohydrate.

and 57th day, respectively. As a result, membrane fouling decreased after 50th day, indicating that membrane fouling was reached at the critical state in the condition of passive adsorption.

3.3. The variation of EPS concentrations during the operation

To measure EPS concentrations in the reactor, we analyzed the protein and carbohydrate which are

main substances of EPS provoking the fouling in biological treatment. Fig. 4 shows that the almost of total eEPS (eEPS of protein + eEPS of carbohydrate) was protein of 65% as average, which suggests that protein mainly exists as adsorbed state at micro-organism. Carbohydrate of EPS existed more as soluble statement in reactor because it was detected average 23% in eEPS and average 77% in sEPS. It was observed that carbohydrate of EPS was composited mostly outside the cell whereas protein is formed by

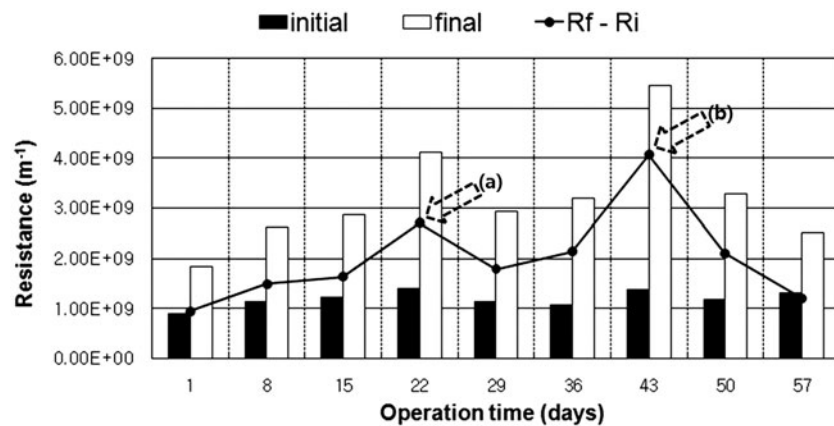


Fig. 3. Resistance profile during the operation.

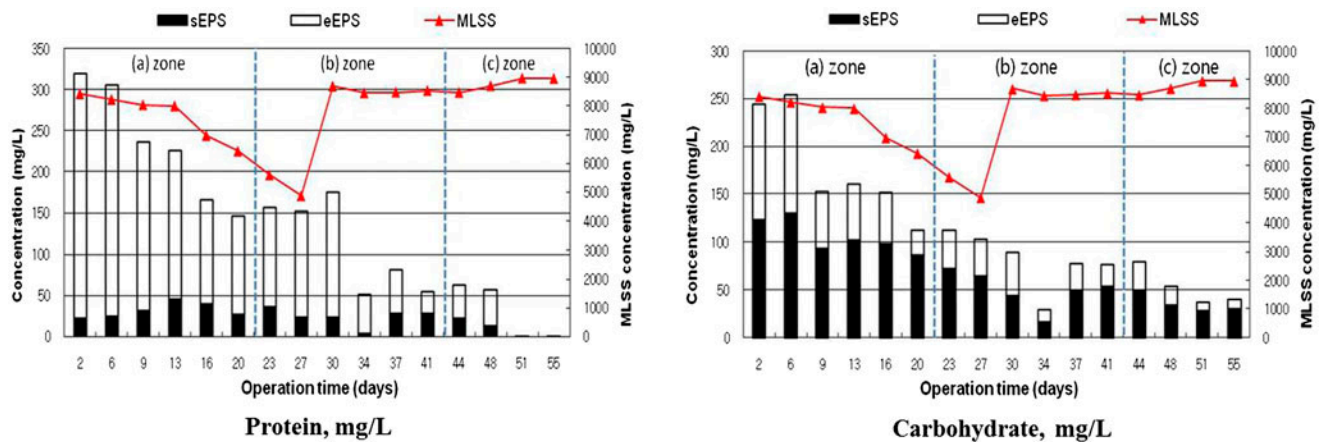


Fig. 4. EPS and MLSS concentration.

secretion of high molecular substance in cell and cell hemolysis [15]. Also, the zone (a) which is from starting to the initial fouling mainly presented the eEPS decreasing, and zone (b) which is from the initial fouling to critical fouling presented the sEPS decreasing. Hence, it caused that initial fouling was dominated by microbe's mass adsorption, and then critical fouling was dominated by soluble foulant.

MLSS concentration of the MBR remained as an average of 8.1 g MLSS/L, and the lowest concentration was 4.9 g MLSS/L after day 28. Based on the EPS and MLSS concentration results, eEPS concentration, extracted EPS of micro-organism, was diminished from 420 to 11 mg/L gradually as MLSS concentration decreased. Also, eEPS concentration unlike regular MLSS concentration continuously declined after 43 d

increased to maximum TMP. Hence, we realized that eEPS changes more sensitively to sludge state by influent rather than MLSS concentration. sEPS concentration decreased under all conditions from maximum 154 mg/L to minimum 19 mg/L, but it was maintained regularly compared to eEPS. Then, the membrane resistance increased. Hence, we found that membrane fouling might be affected by sEPS rather than eEPS. Wu et al. [16] also reported that membrane resistance and filterability were influenced by sEPS rather than eEPS.

As Fig. 4 shows, protein concentration of eEPS and sEPS approached zero after 51 d, and it was assumed that protein concentration declined because nutrients needed for metabolism could not be supplied in the long period of operating condition without influent.

Therefore, membrane resistance increased to maximum after 43 d, whereas on the 50th days, it decreased as shown in Fig. 3. Hence, membrane resistance's decline was observed as membrane foulant concentration of the MBR decreased.

3.4. The variation of permeation at the cleaning stages

Membrane pressure at the specific flux of submerged membrane bundles was measured once a week during eight weeks (57 d) to evaluate the permeability. Using these results, the resistance variation was calculated at five stages; initial resistance (R_i), fouled resistance (R_f), resistance after rinsing (R_r), resistance after backwashing (R_b) and resistance after chemical cleaning (R_c), and Fig. 5 shows these results. The R_i values of all bundles were in the range of $0.89\text{E}+09$ and $1.41\text{E}+09 \text{ m}^{-1}$, and they increased to $7.76\text{E}+07$ and $7.92\text{E}+08 \text{ m}^{-1}$ from 1st to 43rd day after chemical cleaning. It proves that irreversible fouling which is not removed by chemical cleaning is increasing as operation period proceeds.

From the start to 43rd day, resistance decreasing ($R_f - (R_r + R_b)$) by physical cleaning ranges from minimum $3.82\text{E}+08 \text{ m}^{-1}$ to maximum $2.38\text{E}+09 \text{ m}^{-1}$, which is larger than decreasing by chemical cleaning ($3.67\text{E}+08$ to $9.01\text{E}+08 \text{ m}^{-1}$). And also when operation period is shorter, simple adsorption which is able to be excluded by physical cleaning is dominantly bigger than serious membrane fouling such as pore clogging or cake formation.

Diminution range of resistance by backwashing ($R_r - R_b$) was from $7.69\text{E}+07$ to $3.72\text{E}+08 \text{ m}^{-1}$, which was not much bigger than rinsing as well. According to the range, it is certain that most reversible fouling

substance is excluded at rinsing step. However, according to resistance decreasing by backwashing, it was certain that fouling had been adsorbed inner of membrane without flux. The resistance was decreased as $5.46\text{E}+09 \text{ m}^{-1}$ at 43rd days, $3.29\text{E}+09 \text{ m}^{-1}$ at 50th days and $2.51\text{E}+09 \text{ m}^{-1}$ at 57th days, because inflow loads is zero, it had been operated, and it is expected to be deepened in the case of vigorousness by microbe's metabolism.

Also, MLSS concentration had been slightly decreased from 8,400 mg/L at the beginning of the operation to lower than 5,000 mg/L at 28 d later during the operation period of reactor, for this reason, MLSS concentration has been decreased to exhaust as foulant, eEPS with protein and carbohydrate, operating without any inflow loads to the reactor. Even if added activated sludge and kept that more than 8,000 mg/L of concentration, even MLSS concentration was changed, For this, it is certain that membrane fouling does not be effected between 5,000 and 9,000 mg/L of MLSS range.

According to permeability resistance that described before, recovery efficiency of permeate performance through each cleaning steps after final resistance is shown on Fig. 6. the recovery efficiency of membrane resistance by physical and chemical cleaning were 92, 89, 67, 73, 74, 74, 81, 72, and 92%, it generally had more than 70% of recovery efficiency except 15th day, and it tends downward after the operation starts until 43rd day, which means that when membrane fouling has been deepened, recovery efficiency was decreased, also the membrane fouling was occurred by irreversible fouling substance. After 43rd days, it is considered as explained above that fouling diminution by lower microbe's metabolism causes the second increasing of recovery efficiency.

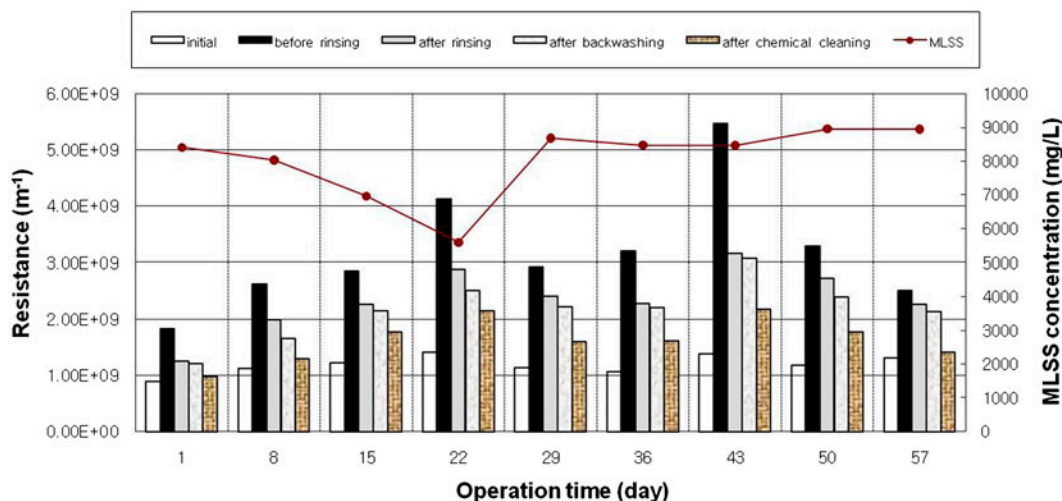


Fig. 5. Variation of membrane permeate resistance.

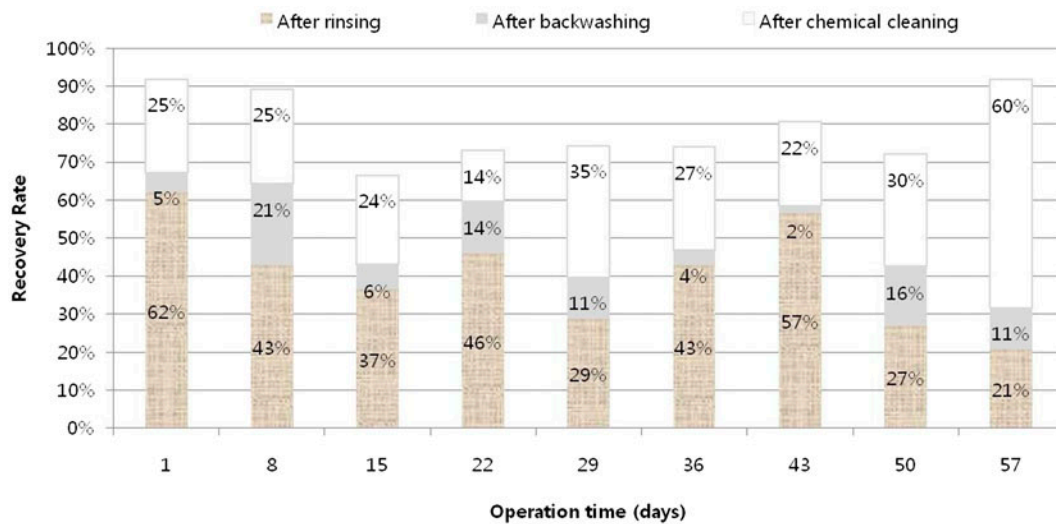


Fig. 6. Recovery rate according to different cleaning.

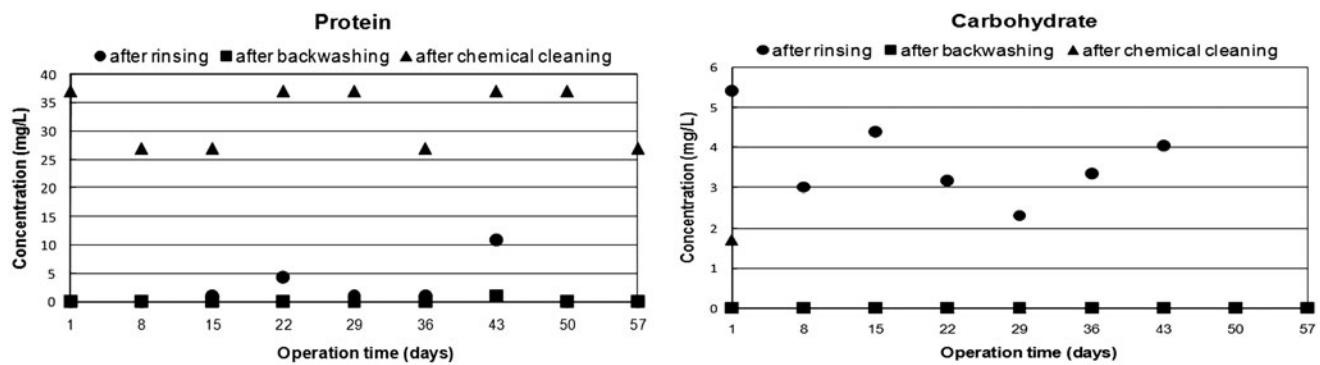


Fig. 7. Protein and carbohydrate concentration removed by cleaning.

The recovery efficiency by rinsing was minimum 21% to maximum 62%, which is important cleaning mechanism in the whole cleaning steps, cause of that shorten operation period and pressure of cake layer was weaker in a condition without flux of membrane. The recovery efficiency by backwashing was minimum 2% to maximum 21%, which shows physical cleaning could exclude 83% as maximum in the reduction of membrane fouling. Therefore, backwashing step for exclusion for fouling at inner membrane and air bubbling are essentially necessary for decreasing membrane fouling at the state of passive adsorption. The recovery efficiency by chemical cleaning was 25% at 1st day of operation, 35% at 29th day and 60% at 57th day, it is judged as formation of cake and block of pore is deepened then simple adsorption which is excluded by physical cleaning when the operation period goes by.

In addition, the reason of irregular pattern between resistance increasing and recovery efficiency is that the operation period according to adsorption is shorter to be figured. If the operation period got extended, there is expected to get obvious result.

3.5. The variation of EPS concentration at the cleaning stages

For identify the property of removed fouling from membrane after cleaning, the result of protein and carbohydrate concentration in cleaning water is as Fig. 7.

In a case of protein, only exist 0–11 mg/L in water rinsing and backwashing, but there was the concentration of 27–37 mg/L in chemical cleaning water. For this reason, protein is much better to exclude by using chemical oxidation than physical cleaning that hard to exclude such as being adsorption inner side of membrane.

On the other hand, concentration of carbohydrate was 2.31–5.41 mg/L from the operation starts to 43rd day by only physical cleaning, and there was no contained volume almost in backwashing water and chemical cleaning water. It was considered to be easily excluded by rinsing cause of it attached on the surface of membrane and it has weaker adsorption, so, it is weaker pollution substance comparing with protein.

Also, since 43rd days, carbohydrate was not detected in rinsing, it is because of that carbohydrate in EPS adsorbed on membrane is mostly compound substance from cells [17], it is used as source of carbon when the microbe's metabolism is lower and carbohydrate concentration was remarkably decreased.

4. Conclusion

This work investigated the calibration curves of the protein and carbohydrate, the main substances of EPS and passive adsorption of hydrophilic membrane in activated sludge bioreactor. The correlation coefficient of the calibration curves for the protein and carbohydrate was high above 0.97 in all conditions. When $R_f - R_i$ value continuously increased to $4.08E+09 \text{ m}^{-1}$ (after 42 d), adsorption by microbial and cake formation is made continuously without the physical cleaning and the influent (flux = 0) through the membrane resistance variation that TMP increased to maximum. Result of the protein and carbohydrate concentration of EPS showed that majority of total eEPS was protein of 65% as average, whereas carbohydrate was detected in averages 77% of sEPS. The result suggests that protein exists mainly as adsorbed state at micro-organism and carbohydrate more exists as soluble statement in reactor. Membrane resistance and filterability were influenced by sEPS rather than eEPS, which resulted that eEPS concentration was diminished from 420 to 11 mg/L gradually as MLSS concentration decreased. However, sEPS concentration was maintained regularly as an average 90 mg/L, and membrane resistance increased to $5.46E+09 \text{ m}^{-1}$ of maximum.

After submerged hydrophilic membrane module in the MBR reactor for examination of the source of membrane fouling, computed following permeability resistance by adsorption and recovery efficiency, for those all, achieved the conclusion as below.

According to the calibration curve of protein and carbohydrate, it is certain that protein calibration curve is mainly affected by the concentration of chemical cleaning water. Appropriate concentration for both protein and carbohydrate is 0.05% of NaOCl.

As a result of permeability resistance measurement, accumulation of irreversible fouling, which is

unable to exclude membrane inside and outside by chemical cleaning, increases as the period of operation is extended. Also, resistance decreasing by physical cleaning is larger than by chemical cleaning, indicating that simple absorption which is able to be excluded by physical cleaning is dominantly bigger when the period of operation is shorter.

Physical and chemical cleaning recovers more than 70% of resistance although recovery efficiency decreases with membrane fouling. In addition, rinsing is an important cleaning mechanism. Physical cleaning was able to exclude maximum 83% of membrane fouling. However, operation period was shorter, and membrane surface of cake layer compression was weaker. Recovery efficiency of chemical cleaning increased with operation time.

Based on the concentration of protein and carbohydrate within each cleaning waters, most protein was contained in chemical cleaning water. The pollution substance that was adsorbed in the inner membrane and clogged pores was comparatively hard to be excluded by physical cleaning, but potentially removed by chemical oxidation. Concentration of carbohydrate after rinsing only was 2.31–5.41 mg/L. Carbohydrate is weaker pollution substance than protein because carbohydrate is mostly attached on the surface of membrane and its' absorption is also lower.

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References

- [1] J. Sun, K. Xiao, Y. Mo, P. Liang, Y. Shen, N. Zhu, X. Huang, Seasonal characteristics of supernatant organics and its effect on membrane fouling in a full-scale membrane bioreactor, *J. Membr. Sci.* 453 (2014) 168–174.
- [2] L. Shen, Q. Lei, J. Chen, H. Hong, Y. He, H. Lin, Membrane fouling in a submerged membrane bioreactor: Impacts of floc size, *Chem. Eng. J.* 269 (2015) 328–334.
- [3] S. Mirbagheri, M. Bagheri, Z. Bagheri, A. Kamarkhani, Evaluation and prediction of membrane fouling in a submerged membrane bioreactor with simultaneous upward and downward aeration using artificial neural network-genetic algorithm, *Process Saf. Environ. Prot.* 96 (2015) 111–124.
- [4] T. Miyoshi, K. Yuasa, T. Ishigami, S. Rajabzadeh, E. Kamio, Y. Ohmukai, D. Saeki, J. Ni, H. Matsuyama, Effect of membrane polymeric materials on relationship between surface pore size and membrane fouling in membrane bioreactors, *Appl. Surf. Sci.* 330 (2015) 351–357.

- [5] Y. Liu, Z. Liu, A. Zhang, Y. Chen, X. Wang, The role of EPS concentration on membrane fouling control: Comparison analysis of hybrid membrane bioreactor and conventional membrane bioreactor, *Desalination* 305 (2012) 38–43.
- [6] J. Wu, C. He, X. Jiang, M. Zhang, Modeling of the submerged membrane bioreactor fouling by the combined pore constriction, pore blockage and cake formation mechanisms, *Desalination* 279 (2011) 127–134.
- [7] Wikipedia. Available from: <https://en.wikipedia.org/wiki/Extracellular_polymeric_substance> (accessed 15 August 2015).
- [8] J. Wingender, T. Neu, H. Flemming, *Microbial Extracellular Polymeric Substances*, Springer, Heidelberg, 2012.
- [9] A. Badireddy, S. Chellam, P. Gassman, M. Engelhard, A. Lea, K. Rosso, Role of extracellular polymeric substances in bioflocculation of activated sludge microorganisms under glucose-controlled conditions, *Water Res.* 44 (2010) 4505–4516.
- [10] Y. Tian, L. Chen, S. Zhang, S. Zhang, A systematic study of soluble microbial products and their fouling impacts in membrane bioreactors, *Chem. Eng. J.* 168 (2011) 1093–1102.
- [11] Y. Li, A. Li, J. Xu, W. Li, H. Yu, Formation of soluble microbial products (SMP) by activated sludge at various salinities, *Biodegradation* 24 (2013) 69–78.
- [12] C. Li, C. Cabassud, B. Reboul, C. Guigui, Effects of pharmaceutical micropollutants on the membrane fouling of a submerged MBR treating municipal wastewater: Case of continuous pollution by carbamazepine, *Water Res.* 69 (2015) 183–194.
- [13] T. Miyoshi, H. Yamamura, T. Morita, Y. Watanabe, Effect of intensive membrane aeration and membrane flux on membrane fouling in submerged membrane bioreactors: Reducing specific air demand per permeate (SAD_p), *Sep. Purif. Technol.* 148 (2015) 1–9.
- [14] O. Lowry, N. Rosebrough, A. Farr, R. Randall, Protein measurement with the folin phenol reagent, *J. Biol. Chem.* 193 (1951) 265–275.
- [15] M. DuBois, K. Gilles, J. Hamilton, P. Rebers, Colorimetric method for determination of sugars and related substances, *Anal. Chem.* 28 (1956) 350–356.
- [16] J. Wu, F. Chen, X. Huang, W. Geng, X. Wen, Using inorganic coagulants to control membrane fouling in a submerged membrane bioreactor, *Desalination* 197 (2006) 124–136.
- [17] R. Bura, M. Cheung, B. Liao, J. Finlayson, B. Lee, I. Droppo, G. Leppard, S. Liss, Composition of extracellular polymeric substances in the activated sludge floc matrix, *Water Sci. Technol.* 37 (1998) 325–333.