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Nitrogen Removal and Behavior of Soluble Microbial Products (SMP) in the MBR Process with Intermittent Aerobic Condition

Gi Cheol Cha† and Myoung Goo Hwang

Department of Environmental Engineering, Yonsei University, 234 Maeji, Wonju 220-710, Korea
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Abstract : A lab-scale submerged membrane bio-reactor (MBR) with intermittent aeration was carried out for investigating the behavior of soluble microbial products (SMP). The SMP concentration of mixed liquor at Run 1 accumulated immediately at the end of running and biodegradable SMP converted into non-biodegradable SMP, but it did not occurred at the Run 2 and 3. The SMP formation coefficient (***k***) at the anoxic phase was a little higher than oxic phase, and the lowest ***k*** was investigated at Run 3. The combination of biological denitrification with the MBR process was advantageous in the prevention of membrane bio-fouling.

Keywords : *bio-fouling, intermittent aeration, MBR process, soluble microbial products*

1. Introduction

Membrane has been demonstrated to be a useful tool in the field of biological wastewater treatment precess due to various benefits, such as high quality of permeate, safety of process, endurance at a sudden change of organic loading rate, and high density of biomass in the reactor [1]. By employing intermittent aerobic operation, simultaneous nitrification-denitrification, as well as organic removal can be accomplished in a single membrane bio-reactor (MBR) process [2,3].

However, the decrease of permeability due to the membrane bio-fouling is the most serious problem in a sumerged MBR process [4]. Many researchers suggested that the cause of bio-fouling in submerged MBR process in which used microfiltration (MF) or ultrafiltration (UF) was caused by soluble organic polymers(under 0.45 μm diameter) such as Soluble microbial products (SMP) and extracellular polymers (ECP) [5-8].

SMP is the metabolic product of microorganism result from intermediate or end products of substrate degradation and endogenous cell decomposition, and are composed of a wide range of organic compounds such as the humic acid, fulvic acid, polysaccharides, proteins, fragments of DNA, antibiotic, steroid, enzyme, etc. SMP also has various molecular weight with the range from 1K to 10^8 Dalton [9].

Origin of SMP can be categorized to three roots : the first is substrate utilization associated products (SMPs), the second is biomass associated products (non-biodegradable SMPe), and the third is SMPnd which a result of the degradation of SMPs [6,9,14]. The biodegradable SMP transfer to the non-biodegradable for time course [9] and SMP in the submerged MBR process has the following characteristics : induction of membrane bio-fouling, formation of gel layer, increase of viscosity, increase of filtration resistance [5].

†Author for all correspondences
(e-mail : gccha@dragon.yonsei.ac.kr)

Table 1. Hydrodynamic and Biological Conditions for Operating

Factor		RUN 1	RUN 2	RUN 3
HRT (hr)		12		
Reactor volume (L)		12		
MLSS & MLVSS (mg/L)		12000 & 9500		
Intermittent aeration (min)	oxic	30	30	60
	anoxic	30	60	60
Aeration amount (L/min)		13		
General temperature (℃)		25±1		
Flux (L/m^2/hr)		10		
TOC loading rate (TOCg/L/day)		0.9		

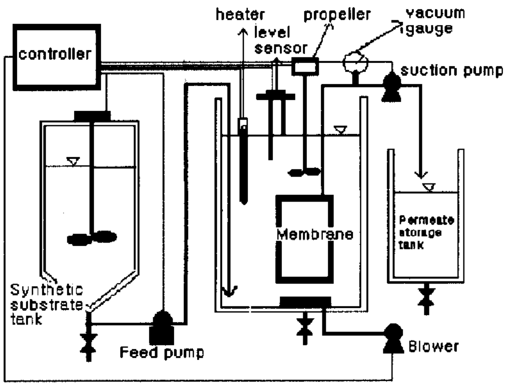


Fig. 1. Schematic diagram of lab-scale single submerged MBR process.

Finally, these performance effect to the reduction of permeate flux in the MBR process. Therefore, it is very important to decrease the membrane bio-fouling and to maintain the permeate flux.

In this study, lab-scale submerged MBR process was conducted to investigate the performance of membrane permeability and formation of SMP with variable intermittent aeration.

2. Materials and Methods

2.1. Reactor and Operating Conditions

Schematic diagram of the experimental setup was shown in Fig. 1 and overall experimental condition was described at Table 1. The membrane which used in this study was the plate & frame type (Y inc. Japan, Table 2). An air blower was set under the membrane module to provide enough shear stress which enable to remove attached matters at the membrane surface and 10 L/min of air was supplied to maintain the oxic condition. A small propeller of radius 6 cm was set at 5 cm above the top of the membrane module fot the circulation of the mixed liquor during the non-aeration period. Permeate was obtained at only aeration period.

Table 2. Description of Membrane Module

Type	Plate & frame
Material	Ployethylene
Pore size(μm)	0.4
Area (m^2)	0.1
External size(mm)	240 L×340 W×10 T

The hydraulic retention time(HRT) was 12 hours and volumetric organic loading rate was 0.9 gTOC/L/day. Initial flux was fixed at 10 L/m^2/hr (LMH) and Physical(as hand cleaning) · chemical(as NaOCl cleaning) membrane washing was done when the flux decreased to 5 LMH. At this point, the experimental conditions was also changed.

Instead of raw wastewater, synthetic substrate was used to distinguish a residual substrate with SMP, exactly. Phenol(C_6H_5OH) was used for carbon source and NH_4Cl, KH_2PO_4 were used for nitrogen · phosphate source (Table 3).

The bacterial inoculum used in this study was a mixture of cultures taken from the sewage treatment plant in W city (Korea). The mixed

Table 3. Synthetic Substrate Compositions

Composition	Concentration (mg/L)
Phenol(C_6H_5OH)	600
KH_2PO_4	80
NH_4Cl	320
$MgSO_4 \cdot 7H_2O$	100
$MnSO_4 \cdot 5H_2O$	9
$FeCl_3 \cdot 6H_2O$	1
$CaCl_3 \cdot 2H_2O$	20
$NaHCO_3$	666

culture was acclimated to the hydrodynamic and biological conditions for 30 days [10].

2.2. Analysis Methods

The contents of SMP in a mixed liquor was centrifuged at 3000 rpm for 10 minutes and filtrated through 0.45 μm membrane filter, and was identified using the total organic carbon (TOC) value. The TOC content was analyzed using a TOC auto analyzer (Shimadzu, TOC-5000A). Nitrate and nitrite analyzed using a ion-chromatography (Dionex, DX-120), E260 is looked upon as a non-biodegradable products was measured by UV spectrophotometer (λ: 260 nm, Shimadzu), and others followed standard method [11].

3. Results and Discussions

3.1. Organic Substrate and Nitrogen Removal

Cause by the high biomass density and sludge retention time, slowly grown bacteria such as the nitrifier could be cultured in MBR process successfully. By employing the intermittent aeration, denitrifier also could be cultured in MBR process.

Overall variation of TOC and phenol concentration for operating time were shown in Fig. 2. TOC removal was very stable and showed about 99% in spite of membrane fouling phenomenon or change of intermittent aeration type.

Behavior of Nitrogen at each Run was shown

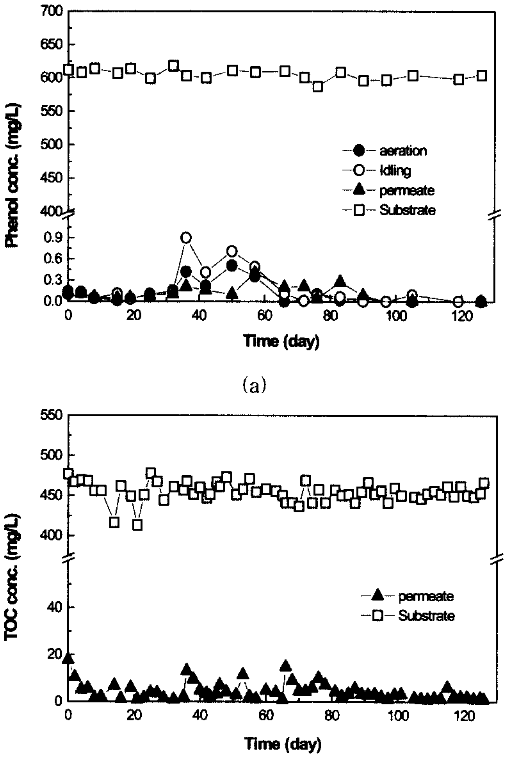


Fig. 2. Characteristics of organic (a. TOC, b. Phenol) degradation.

in Fig. 3. Several types of biological processes have been developed to remove the nitrogen. They are mainly classified into two groups. One is the two or multi stage process and the other is the single-stage process. Because of the possibility of maintenance of high microorganism density in culture medium, MBR process can removed nitrogen with simultaneous nitrification and denitrification (SND) by employing the intermittent aeration [12].

In this study, the nitrogen source of influent was only NH_4^+-N, we could investigate the characteristics of nitrification and denitrification phenomenon at each oxic/anoxic period. Ammonia-nitrogen (NH_4^+-N) removal was most stable at 60/60 min cycle (Run 3) and showed about 95.6%. Nitrification rates at each Run were 0.88, 0.69, and 0.99. Denitrification rates were 0.98, 0.99, and 0.96, respectively. Thoughout the overall

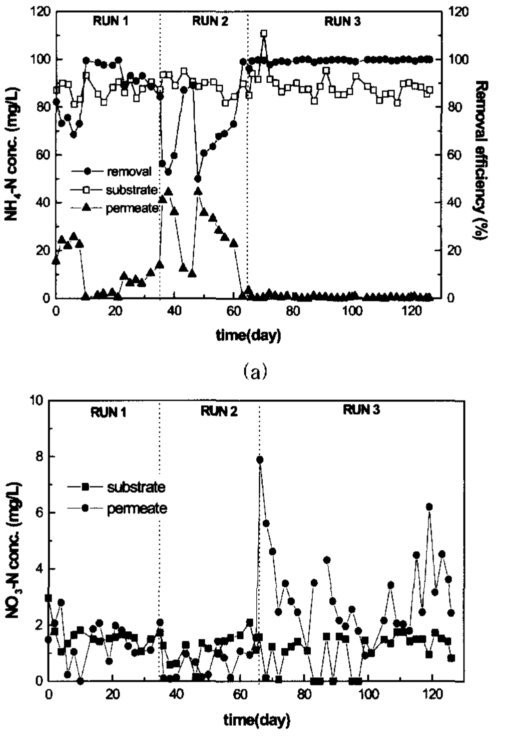


Fig. 3. Variation of (a) ammonia-nitrogen and (b) nitrate concentration at each Run.

experimental data, nitrate concentration was invastigated at low value. It was considered that the SND phenomenon was happened at micro anoxic zone in sludge floc [13].

3.2. Characteristics of Membrane Permeability

A variation of flux and suction pressure at each Run were shown in Fig. 4. A suction pressure at each Run was increased slowly till the suction pressure was 14 kPa, but it was increased immediately after 14 kPa. Tmax [14] at each run were 23 (Run 1), 17 (Run 2), and 45 days (Run 3), respectively. The stable operation time at Run 3 was maintained longer than Run 2 and Run 3. It is considered that the increase of suction pressure (till 14 kPa) was due to the formation of gel layer, and it was due to the cake layer after 14 kPa. Other hands, formation of gel layer was occurred very slowly than formation of cake layer.

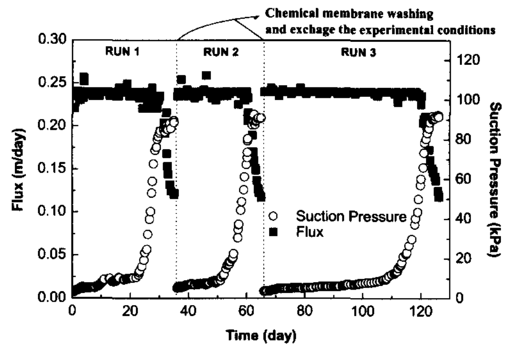


Fig. 4. Comparison of membrane permeability and suction pressure with each Run.

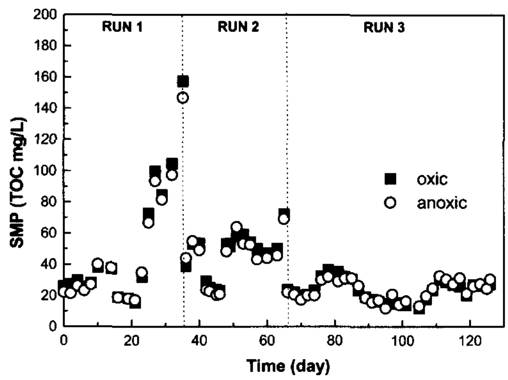


Fig. 5. SMP formation in the mixed liquor at various oxic/anoxic phase.

3.3. Influence of Intermittent Aeration on the Formation of SMP

3.3.1. Formation of SMP

A variation of SMP concentration in the mixed liquor at each run was shown in Fig. 5. SMP concentration was increased rapidly with increase of suction pressure at the end of Run 1. However, SMP concentration did not increase at Run 2 and Run 3 (with 60 min anoxic phase). It is considered that an intermittent aeration could provide a cyclic change of anoxic and oxic conditions for bacteria in the reactor, which might have accelerated biodegradation of the SMP [5].

The mass-balance for a relationship between substrate, cell growth, and products are developed by many researcher [3,5,9,13]. Boero et al.(1996) reported that the SMP formation could be divided into three steps as follows;

- SMPs formation (substrate utilization)
  Substrate, S + Cells → $Y_{X,S} \cdot X + Y_{SMPs} \cdot$ SMPs + $Y_{CO2,S} \cdot CO_2$ (1)

- SMPnd formation (degradation of SMPs)
  SMPs + Cells → $Y_{X,SMPs} \cdot X + Y_{CO2,SMPs} \cdot CO_2$ (2)

- SMPe formation (endogenous respiration)
  X → $Y_{SMPe,X} \cdot$ SMPe + $Y_{CO2,X} \cdot CO_2$ (3)

where

$Y_{CO2,S}$: CO_2 per unit mass of substrate degraded

Y_{SMPs} : SMPs per unit mass of substrate degraded

$Y_{X,S}$: biomass yield coefficient from substrate degradation

$Y_{CO2,SMPs}$: CO_2 per unit mass of SMPs degraded

$Y_{X,SMPs}$: biomass yield coefficient form SMPs degradation

$Y_{SMPe,X}$: SMPe per unit mass of cells degraded

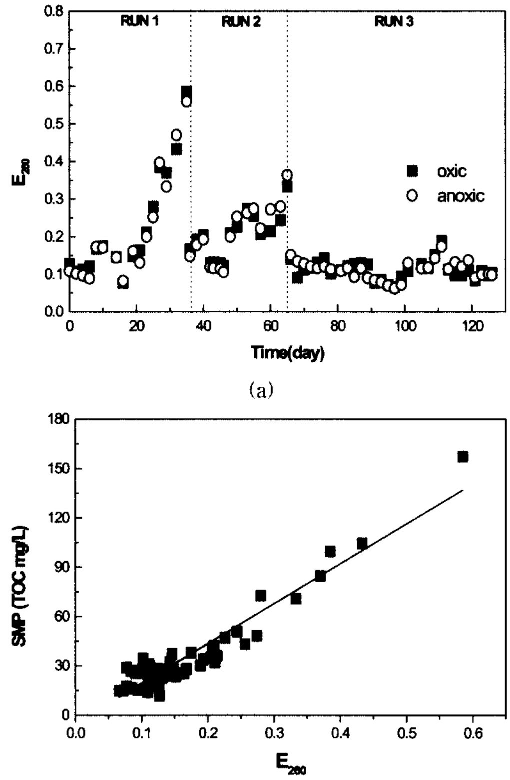
Because of the fixed biomass concentration (12,000 mgMLSS/L) by waste the exess sludge, SMPe in total SMP was constant, and SMP concentration changed only by the conversion of SMPs into SMPnd. Modeling this relation, dSMP/dt could be expressed to first order, which depended on the SMPs concentration in a mixed liquor per unit biomass (Y_{SMPs}) and the SMP formation coefficient, ***k***:

$$dSMP/dt = k \cdot Y_{SMPs} \quad (4)$$

Table 4 shows the SMP formation coefficient (***k***) at each Run. At the oxic phase, the ***k*** values in Run 1, Run 2 and Run 3 were 0.0475, 0.0208 and 0.0015 *1/day*, respectively. On the other hand, at the anoxic phase, the k values were 0.0503, 0.0224 and 0.0002 *1/day*, respectively. It could be determined that most of the SMPs in SMASP with 60/60 min cycle condition converted into SMPnd. The ***k*** value at the anoxic phase was higher than that at the oxic phase. This may have occurred due to the release of SMPe by endogenous respiration.

Table 4. The SMP Formation Coefficient (k) at Each Run

	Run 1	Run 2	Run 3
k at oxic phase (*1/day*)	0.0475	0.0208	0.0015
k at anoxic phase (*1/day*)	0.0503	0.0224	0.0002



(a)

(b)

Fig. 6. Variation of (a) E_{260} and (b) relationship between SMP with E_{260}.

3.3.2. Behavior of Nonbiodegradable Substance

Figure 6 shows the variation of UV absorbance at 260 nm (E_{260}) and relationship between SMP and E_{260}. E_{260} is a general term of non-biodegradable

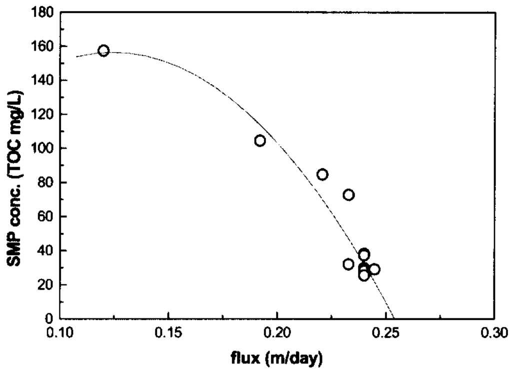


Fig. 7. Influence of SMP concentration on the membrane permeability.

matters, based on the appearance characteristics of non-biodegradable substance at the U.V wave-length (260 nm), compared with biodegradable substance [8].

The E_{260} increased with SMP accumulation in the Reactor (Figure 4) and the accumulated SMP converted into non-biodegradable matter. These results suggested that the biomass metabolic products such as SMPnd and SMPe exist as a non-biodegradable substance in MBR process. This non-biodegradable substance decreased the permeate flux.

3.3.3. Relationship between SMP formation with membrane permeability

Performance of membrane permeability according to the change of SMP concentration was shown in Figure 7. SMP did not effected to the decrease of SMP at the low SMP concentration range (20~35 mgSMP/L), but as the SMP concentration was increased, membrane permeability was decreased exponentially. It is considered that high concentration of soluble organic substance distribute to the forming of layer on the membrane surface.

3.3.4. Variation of Viscosity in the Mixed Liquor

Figure 8(a,b) shows the variation of viscosity in relation to a SMP concentration. The accumulated SMP in the reactor increased a viscosity of mixed liquor. Ueda et al.(1997) reported that

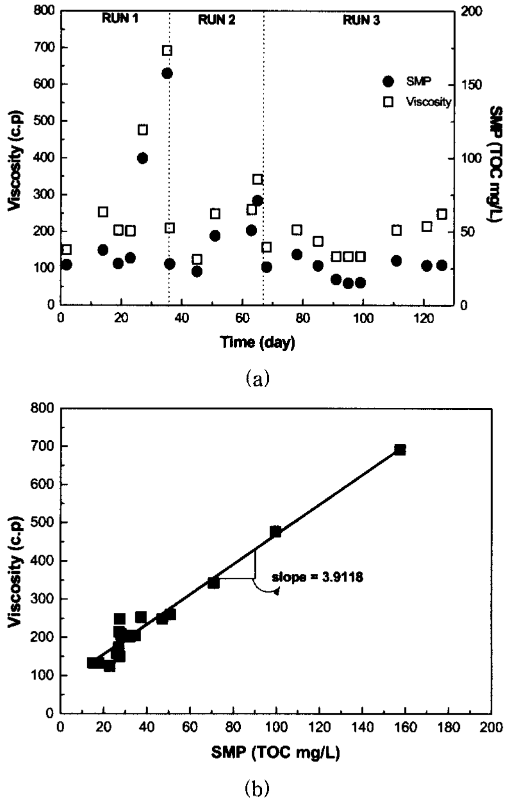


Fig. 8. Variation of (a) viscosity and (b) relationship between SMP with viscosity.

the accumulated SMP increased the filtration resistance, and the filtration resistance accelerate the membrane bio-fouling and decrease the permeate flux. Even though a viscosity in the mixed liquor changed variously, the viscosity of a permeate was generally 1 c.Pa. This means that substance bring about the increase of viscosity did not flow out throughout the permeate and accumulated in the reactor [5]. By simulating the relationship between SMP and viscosity, SMP could be regarded as substance with increased viscosity. These results lead to the conclusion that the 1 mgSMP/L increased 3.9 c.Pa viscosity.

4. Conclusion

The results of overall performance were described at Table 5.

The stable operation time at Run 3 was

Table 5. Overall Change of Concentration and Removal Efficiency

		RUN 1			RUN 2			RUN 3		
		Influent (mg/L)	effluent (mg/L)	removal (%)	Influent (mg/L)	effluent (mg/L)	removal (%)	Influent (mg/L)	effluent (mg/L)	removal (%)
phenol		610.29	< 0.2	>99.9	605.64	< 0.2	>99.9	600.64	< 0.2	>99.9
TOC		455.76	4.45	99.023	458.52	5.01	98.908	453.72	5.47	98.793
T-N		89.92	12.69	85.92	91.23	29.04	68.26	91.27	4.06	95.56
NH_4^+-N		87.86	10.61	87.86	89.20	27.65	69.04	88.34	0.43	99.52
TKN		88.31	10.95	87.62	89.93	27.95	69.05	90.08	0.65	99.28
NO_3^--N		1.61	1.41	-	1.17	0.63	-	1.07	3.32	-
NO_2^--N		N.D.	< 0.5	-	N.D.	< 0.5	-	N.D.	< 0.5	-
Nitrification rate		0.879			0.690			0.995		
Denitrification rate		0.982			0.990			0.963		
DO		0.01～7.5			0.01～7.5			0.01～8.4		
ORP(mV)	oxic	38.74			26.69			135.38		
	anoxic	-78.47			-264.85			-100.71		

N.D. : not detected

maintained longer than Run 2 and Run 3. Total organic removal efficiency at all experimental conditions was very stable (over 98.6% TOC mg/L). Compared with Run 2 and Run 3, SMP concentration in mixed liquor at Run 1 was accumulated highly at the end of the operation. The Run 3 (60/60 min oxic-anoxic cycle condition) accelerated a degradation of SMPs, and most of the SMPs in SMASP with 60/60 min cycle condition converted into SMPnd. The E_{260} increased with the accumulation of SMP. The control of SMP concentration and the oxic-anoxic time is very important factor in submerged MBR process.

From this study, we suggest that the intermittent aeration is suitable to decrease SMP and remove the nitrogen. The intermittent aeration can provide a cyclic change of anoxic and oxic conditions for bacteria in the reactor, which might have accelerated biodegradation of the SMP. The SMP formation coefficient value (k) at the anoxic phase was higher than that at the oxic phase. SMP regarded as substance with increased viscosity of mixed liquor and 1 mg/L SMP increased 3.9 c.Pa viscosity.

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