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Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor

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Abstract

This study was conducted to investigate the characteristics of membrane fouling and removal of phosphorous in a membrane bioreactor process by addition of inorganic coagulants directly into aerobic tank of a pre-anoxic nutrient removal system. In order to determine the specific cake resistance of activated sludge floc for different coagulants used, jar test and dead-end filtration experiments were performed. The permeate flow rate increased as well as phosphate removed effectively, as the dosage of alum increased, both in the jar test and dead-end filtration experiments. Considering the phosphorous removal capacity, flux variations, pH range and specific resistance, it seems that the use of alum was effective in concentration range from 200 to 500 mg/L. Ferric chloride was efficient in causing decline in specific resistance, on the other hand, it caused decrease in pH than that of alum. The bench scale MBR performance test was conducted to evaluate the effect of coagulant addition into a MBR process. It was found that addition of alum in the aeration tank had a positive effect on phosphorus removal along with minimization of membrane fouling. The MBR performance elucidated that addition of 30 mg/L of alum was effective to remove 3 mg/L phosphorous in feed for MBR process with reduction in membrane fouling factor without deterioration in nitrogen removal efficiency. The particle size analysis further confirmed that coagulation with alum could minimize membrane fouling because the relative small particles in the MBR reactor, which are considered as a cause of membrane fouling, could became bigger particles due to the addition of coagulant.

Keywords: Membrane bioreactors (MBRs); Inorganic coagulant; Phosphorus removal; Membrane fouling; Specific cake resistance

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1. Introduction

In wastewater treatment the membrane filtration is used as an alternative process for gravitational sedimentation in conventional biological process [1,2]. It is also utilized as an advanced process for secondary treated wastewater, which contains residual solids or bacteria and virus [3,4]. Most of the membrane filtration processes are generally combined with a

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biological treatment process to remove organic matter [5].

A membrane bioreactor combines the activated sludge process with a membrane separation process. This process eliminates the weakest link in the activated sludge process and makes effluent quality independent of settling characteristics of the biomass. Membrane bioreactors have several advantages over the conventional activated sludge systems, including stable and high effluent quality, easy operation and absolute removal of bacteria [6].

However, membrane bioreactor has some problems, in particular membrane fouling and concentration polarization. Operational and maintenance costs of the membrane bioreactor are high, due to membrane fouling. Membrane fouling deteriorates the permeability of the membrane and consequently increases energy consumption in a membrane bioreactor. Especially in microfiltration and ultrafiltration, the flux decline is very severe with the process flux often being less than 5% that of the pure water flux [7].

Besides, because of the nature of the membrane bioreactor system, which holds high concentration of the sludge through maintaining long SRT, the system has a problem with phosphorous removal.

The aim of this research is to investigate the characteristics of membrane fouling and removal of phosphorous in a membrane bioreactor process by the addition of inorganic coagulants.

2. Experiment

2.1. Lab-scale MBR

Continuous operation of a MBR was carried out. A schematic diagram of the MBR is shown in Fig. 1. Two flat membrane modules made from Polyethylene were submerged in a reactor. As shown in Table 1, the membranes used in this study had nominal pore size of 0.4 µm. Total surface areas of the each membrane were 0.1 m^2. Filtration was carried out with the constant flow rate and membrane permeate flux was fixed at 12 LMH. Mixed liquor suspended solids (MLSS) concentration in the reactor was maintained at 5,000 mg/L by wasting excess sludge everyday. Aeration was carried out continuously in the reactor at the flow rate of 1.5 m^3/h. When membrane fouling became significant, membrane modules were taken out and cleaned chemically by using 5,000 mg/L sodium hypochlorite (NaClO) solution.

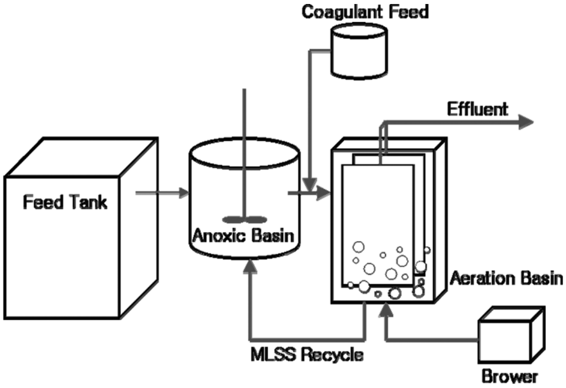

Fig. 1. Schematic diagram of membrane bioreactor.

2.2. Jar test

A jar tester was used for the coagulation of mixed liquor from an activated sludge process. The concentration of coagulants was varied from 50 to 500 mg/L and the pH for the coagulation process was changed from 5 to 7.5.

The jar test was performed using various coagulants and the mixed liquor from activated

Table 1
Specification of membrane

Pore size (µm)	0.4
Membrane material	Polyethylene
Effective surface area (m^2)	0.1 (2ea)
Object	Model wastewater
Flux (LMH)	12

sludge to determine the optimum coagulant and coagulation conditions. The procedure of the jar test was as follows: 1 L of mixed liquor was poured into a jar and predetermined amount of coagulant stock solution was added. The mixed liquor was then stirred for 5 min at a speed of 150 rpm. Stirring was further performed for another 5 min at a speed of 30 rpm. Around 200 mL of the mixed liquor was taken for dead-end filtration test. The mixed liquor was allowed to settled and clear supernatant from the upper layer of the jar was taken for further analysis.

2.3. Batch cell test for dead-end filtration

In order to determine the specific cake resistance of mixed liquor, the dead-end filtration experiment was performed. The configuration of the apparatus for dead-end filtration is depicted in Fig. 2. The volume of the vessel, called Amicon Cell (Amicon™, USA), was 200 mL. The diameter of the membrane was 6 cm, which is placed inside the vessel's bottom. The nitrogen gas was injected into the vessel to keep the constant trans-membrane pressure across the membrane. The pressure difference between inlet and outlet was equal to the trans-membrane pressure of the membrane. The applied pressure was maintained constantly using a pressure-control valve, therefore, a constant pressure across the membrane was established. It means that the permeate flux decreased as the membrane was fouled.

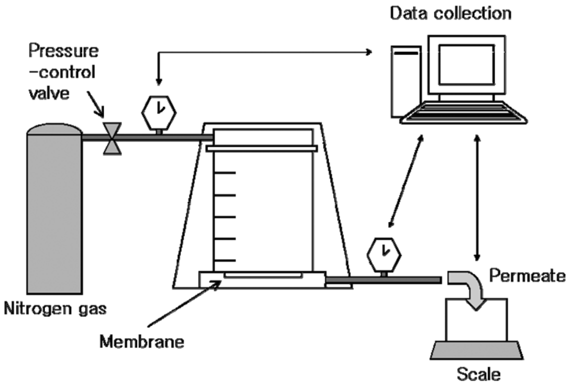

Fig. 2. Schematic of dead end filtration experiment.

The accumulated permeate mass (m_{ac}) was weighed by a digital scale. The accumulated permeate volume was calculated by converting the accumulated mass into the permeate volume. The normalized flux, at, T = 20°C and at the constant trans-membrane pressure ($\Delta p = 0.5$ psi), is represented as following:

$$\text{Flux} \approx \frac{V_{P,T} - V_{P,T-1}}{A\Delta t} \tag{1}$$

The trans-membrane pressure and the accumulated permeate volume were monitored and recorded in a personal computer using Labview 6.0 (National Instrument, Co., USA).

2.4. Sample analysis

In order to determine total phosphate (TP) and COD, samples were digested using Bychem Digestion Vials (Bychem, Co., Korea) and measured by spectrophotometer (Bechman DU520, Germany). The pH was determined using a glass electrode pH meter (Orion, Model 525A, USA) and measurement of SS and VSS followed Standard Methods. TOC/TN Analyzer (VCPN-6000, Simadzu, Japan) was used to quantify total nitrogen (TN) in the sample. The influence of coagulants on the size distribution of the activated sludge floc was also investigated. The particle size distribution of the activated sludge was measured using Mastersizer (Malvern Instruments Ltd.)

3. Results and discussion

3.1. Effect of coagulant addition on water quality

Table 2 shows the changes of quality of the supernatant of the mixed liquor treated with

Table 2
Changes of quality of supernatant after coagulation with alum

Alum (mg/L)	pH	T-P (mg/L)	COD (mg/L)	T-N (mg/L)
0	7.6	11.1	45	35.38
50	7.4	7.3	17	26.63
100	7.2	4.2	33	28.46
200	6.7	3.95	17	33.94
300	6.4	1.1	15	34.41
500	5.5	0.05	8	30.01

different dosages of alum. The phosphorous removal efficiency increased with increase in alum dosage from 0 to 500 mg/L but the pH became lower. The maximum phosphorous removal efficiency was about 99.6% at alum dosage of 500 mg/L. The increased concentration of applied coagulant also caused improvement in COD and TN removal at some extent, but trend in removal efficiencies, particularly for TN, was somewhat irregular.

Coagulation of the mixed liquor using ferric chloride as a coagulation agent was also carried out. Table 3 exhibits the changing characteristics of the mixed liquor after coagulation with ferric chloride, the results of removal of phosphorous were similar to the case of alum. The phosphorous removal efficiency increased with increase in ferric chloride dosage from 0 to 500 mg/L, but the removal efficiency was relatively low and the pH dropped dramatically comparing with the case of alum. Furthermore, less COD and TN removal tendency was observed than the case of alum.

Table 3
Changes of quality of supernatant after coagulation with ferric chloride

Ferric chloride (mg/L)	pH	T-P (mg/L)	COD (mg/L)	T-N (mg/L)
0	6	13.25	27	30.83
50	5.7	12.45	16.6	23.10
100	5.4	11.4	16	22.58
200	4.1	12.65	20.8	22.93
300	3.8	10.3	21	30.76
500	3.4	7.5	21	29.98

3.2. Effect of coagulant addition on membrane fouling

Batch filtration experiment was carried out as per the method described previously. This experiment was performed under the dead-end filtration condition, in which filtration proceeded was at a constant pressure. The permeate flux continuously decreased as filtration proceeded, because cake layer is accumulated on the membrane surface with filtration progress, in which membrane fouling was induced. In this study, the filtration process was halted when the accumulated permeate volume reached up to 100 mL. The final flux at that time is considered as the quasi-steady state flux.

Fig. 3 illustrates flux decline curves with different alum dosage. The permeate flux increased with increase in alum dosage from 0 to 500 mg/L. The permeate flux increased to 2 time when coagulant dosage was 500 mg/L as compared to the case when no alum was added.

Batch experiment was also conduced after coagulation of the mixed liquor using ferric chloride as a coagulation agent. As in the case of alum, the permeate flux increased with increase in ferric chloride dosage (Fig. 4). At coagulant dosage of 500 mg/L, the flux increased to 2.5 times that of the without ferric chloride addition.

The factors influencing on the cake layer formation inducing the hydraulic resistance increase have been investigated [8]. Among them particle size, pH, temperature of the solution, membrane material, operating pressure, membrane pore size, solute physicochemical or biological characteristic and so on are considered to be the important factors. However, the influence of these factors can be expressed and described

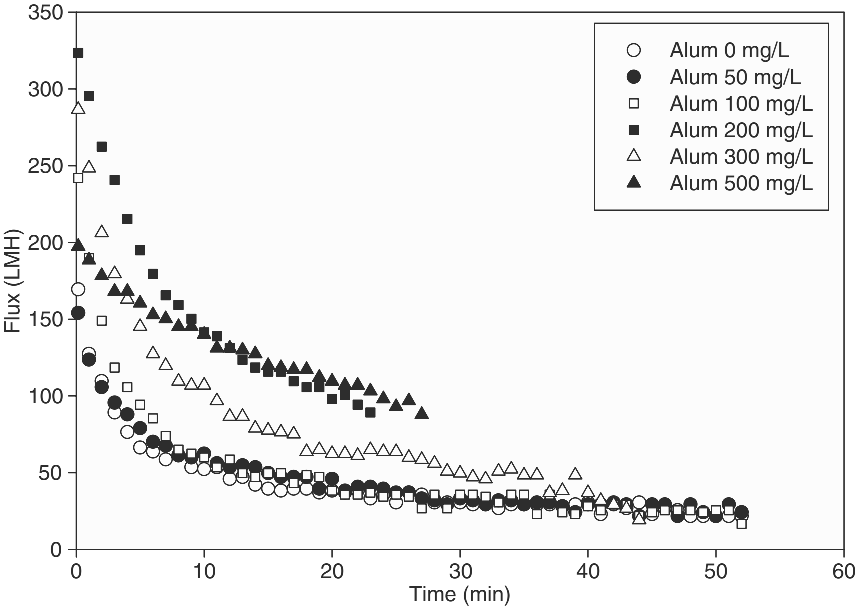

Fig. 3. Comparison of the flux decline at different alum concentrations.

simply by the one variable in the resistance-in-series model. The variable is hydraulic resistance of the cake layer, which as considered as the function of the specific cake resistance [9].

In order to calculate the specific resistance, the time per permeate volume versus the permeate volume accumulated graph was plotted and the linear regression analysis was performed. From the slope value, the specific resistance can be calculated. The specific cake resistance decreased with the increasing coagulant concentration (Table 4). The effects of coagulants dosage on specific cake resistance are shown in Fig. 5. The specific resistance decreased dramatically when dosage of both coagulants was 200 mg/L or above. Inspection of obtained results indicates that membrane fouling could be controlled by the addition of alum or ferric chloride as coagulants.

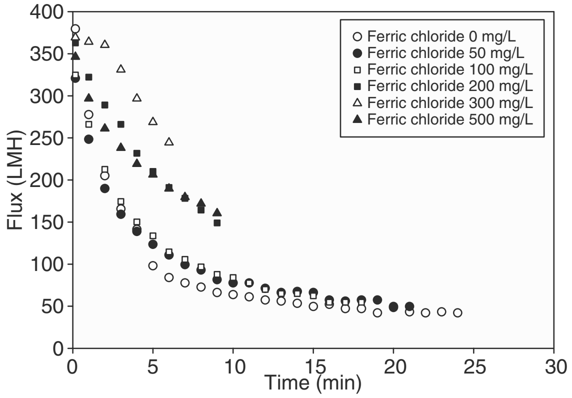

Fig. 4. Comparison of the flux decline at different ferric chloride concentrations.

Table 4
Relationship between the dose of coagulants and specific cake resistance

Dose (mg/L)	Specific resistance	
	Alum	Ferric chloride
0	2.28×10^{20}	1.11×10^{20}
50	2.25×10^{20}	1.11×10^{20}
100	2.33×10^{20}	1.00×10^{20}
200	3.15×10^{19}	2.23×10^{19}
300	7.57×10^{19}	6.68×10^{18}
500	2.07×10^{19}	2.23×10^{19}

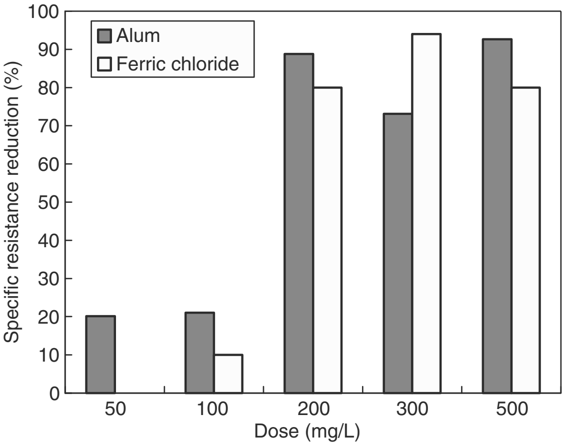

Fig. 5. Effects of coagulants dosage on specific resistance.

3.3. *Effect of coagulants on MBR system performance*

Based on above batch test results, to evaluate the effect of coagulant addition on MBR system performance in terms of phosphorus removal as well as membrane fouling, a MBR system with coagulation was operated and compared to a MBR system without coagulation.

Considering the flux, pH and specific resistance, it seems that the use of alum in concentration range from 200 to 500 mg/L (18–45 mg-Alum/mg-P) was effective. Although ferric chloride was efficient in reduction of specific resistance, its use was ruled out because it caused low pH range in jar tests than that of alum. Therefore alum was selected to apply in bench scale MBR system. Choi et al. reported that too high concentration of alum can affect the nitrification and denitrification and that the optical concentration of alum to remove 1 mg/L of phosphorus is 0.75 mg/L [10]. Therefore, 2.15 mg/L alum was added initially as phosphorus concentration in feed was 3 mg/L. Afterwards the concentration of alum increased step by step.

Table 5 shows the phosphorus removal of MBR system at various alum dosages. The removal of phosphorus increased up to 98% with increase in alum dosage to 50 mg/L of alum. The variation of extent of nitrogen removal efficiency was small at different applied alum dosage (data was not shown). However the influence of alum addition on nitrogen removal was not clear in this experiment. Choi et al. mentioned that the excess alum could have bad effect on the nitrifying bacteria [10]. However, in this study, nitrification was completely performed even though alum was added. The pH showed almost no change because the relatively small quantity of alum compare with the volume of the feed.

Table 5
Phosphorous removal at various alum dosage

Dose of alum (mg/L)	T-P		
	Inf. (mg/L)	Eff. (mg/L)	Removal (%)
0	2.48	1.46	41.0
2.25	2.40	1.44	40.0
4.5	2.34	1.42	39.3
9	2.62	1.40	46.6
18	2.88	1.50	47.9
30	2.92	0.24	91.8
50	2.64	0.05	98.1

Generally, MBR processes operate at long SRT. As a consequence, the coagulant is expected to accumulate and reside for a long time in reactor and the AlO_3 flow out from the components of insoluble phosphate. Therefore, in MBR process less coagulant are required than the activated sludge process because this AlO_3 dissolved into AlO_2 and it could reacts over again [10].

To investigate the effect of alum addition on membrane fouling, dead-end filtration test was performed using the mixed liquor taken from the membrane bioreactor and then specific resistance was calculated. As we expected, the result showed that the flux increased slightly with alum addition (Fig. 6). Therefore, the specific resistance also decreased from 2.23×10^{20} to 1.11×10^{20}, by adding alum, which was about 2 times lower than that of without alum addition.

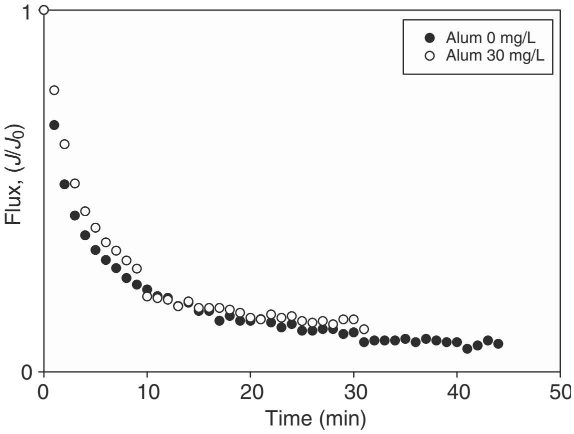

Fig. 6. Comparison of the flux decline with the different alum concentrations for activated sludge for MBR process.

In order to find out the reason for the reduction of specific cake resistance with alum addition, the particle size distribution of mixed liquor from MBR reactor was analyzed. The graph shows that the mean particle size of the mixed liquor became bigger from 45 to 57 μm after coagulant was injected (Fig. 7). It seems that the relative small particles which are the cause of membrane fouling were getting bigger due to the coagulant. Therefore, they lose the effect on the membrane fouling. Ahmed et al. [11] also pointed out that specific cake resistance increased as well as membrane bio-fouling due to colloidal particles. In sum, it is effective to remove phosphorous and reduce membrane fouling without deteriorating nitrogen removal by addition of 30 mg/L alum to remove 3 mg/L phosphorous in feed. This value corresponds to 10.3 mg-Alum/mg-P in term of phosphate and is not much different with the value obtained from batch jar test (over 18 mg-Alum/mg-P). Therefore, the MBR system with 30 mg/L alum addition could perform 90% of COD, 60% of T-N and 75% of T-P removal, and membrane fouling can be controlled effectively.

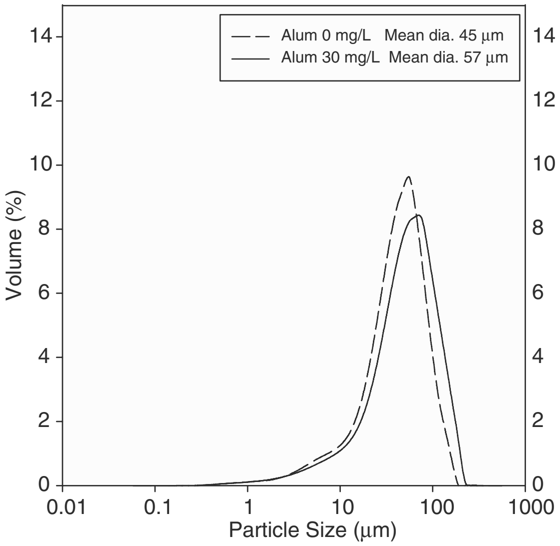

Fig. 7. Particle size distribution profile.

4. Conclusion

The permeate flow rate increased as well as phosphate removed effectively as the dosage of coagulant increased in the batch coagulation tests using alum and ferric chloride as coagulants. The flux increased more than twice at coagulant dosage over 200 mg/L than that of without coagulant addition. Considering the flux, pH and specific resistance, it seems to be effective that the use of alum in concentration range from 200 to 500 mg/L. The use of ferric chloride in bench scale MBR was ruled out, although it caused good reduction in specific resistance, because ferric chloride decrease the pH of the system comparatively more than alum.

In the MBR process, addition of alum could increase phosphorus removal but its impacts on nitrogen removal were not thoroughly investigated in present study. Furthermore, alum injection could be helpful in minimization of membrane fouling because the relative small particles, which are considered as a cause of membrane fouling, could became bigger particles having less fouling tendency due to the coagulant.

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