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A Study on Coagulation and MF Membrane Process for the Reuse of Sewage Effluent

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Abstract

Prior to the study of the sewage treatment methods, water quality for Gwangju sewage effluent was investigated from January to December, 2004 for sewage water reuse. Monthly mean values of BOD, SS, turbidity, total phosphorus and color were 4.1 mg/L, 2.9 mg/L, 0.8 NTU, 1.3 mg/L, and 27 unit, respectively. Jar-test was performed to investigate the removal efficiency of pollutants under the coagulation conditions of fast mixing for 5 min, slow mixing for 15 min and precipitation for 1 hr. Here, alum and polyaluminium chloride (PAC) were used as coagulants to reduce color, turbidity, total phosphorus (TP) and total organic carbon (TOC) in sewage effluents. The results showed that PAC gave better efficiency in removing turbidity and dissolved phosphorus than alum. It was also found from the relative molecular weight (RMW) distribution analysis that organic matter over 1,000 Dalton (Da) was easily removed by coagulation and subsequently MF treatment, while it was not effective for less than 500 Da. Based on this result, Natural organic matter (NOM) with lower molecular weight (< 500 Da) may cause harmful disinfectant by-product (DBP) after chlorine treatment. Thus, activated carbon adsorption seems to be required for the complete removal of DBP in the hybrid system.

Keywords : Coagulation, MF (microfiltration) membrane, Alum, PAC (poly aluminum chloride), RMW (relative molecular weight) distribution

I. INTRODUCTION

Industrialization, urbanization, and gravitation of population have accelerated pollution in the water system and brought about deficiency in water resources. To solve the water deficit problem in the future, some methods like constructing dams, sometimes protested by environmentalist, saving drinking water in user's side, and recycling used water with proper treatments have been considered. Among main resources as wastewater, sewage water, and rainwater, possible to reuse, sewage water has some merits that the amount is affluent and it can be supplied continuously without any contamination of heavy metals and harmful materials to human health. However, sewage effluent contains many different contaminants from housing and industrial water. Categories of these contaminants are suspended solids (SS), odor causing materials, color, nutrient and cancer causing natural organic materials. For the purpose of reusing sewage effluent as gardening and toilet water, membrane separation is an emerging process and it showed great attention recently compare to conventional treatment processes because of its ability to produce high quality treated water consistently. Laboratory scale tests were performed to treat hardness and COD in wastewater and TOC and manganese were revealed as fouling materials in microfiltration (MF) by X-ray micro analyzer.[1,2] It is nowadays necessary to recycle sewage effluent as secondary treated reuse water by introducing some advanced technical processes. Membrane process is one of the most effective techniques in removing several harmful materials as suspended solids and microbial, furthermore, detrimental heavy metal compounds, when nanofiltration (NF) membrane is used. If, however, NF is applied to the sewage water reuse treatment process, the cost will be too higher than conventional pure water treatment system to apply to water reuse plant. Microfiltration or ultrafiltration (UF) combined with coagulation and adsorption will be more effective and economical than NF in recycling sewage effluent as gardening/toilet/washing water.[3-5] Coagulation can make suspended solids, colloid materials and natural organic carbon (NOMC) be removed by van der Waals' force after neutralization of ionic materials by cationic coagulant. Chemical coagulation is conventional process in treating drinking water and also tannery wastewater, especially COD and SS.[6,7] Colloid materials in the range of 0.1 to 1㎛size can affect to MF membrane with micro pore blockage. One of several methods to avoid the blockage by removing colloid materials and make the lifetime of membrane longer is introducing coagulation before membrane process. Many researcher showed that the technique of membrane combined with coagulation could be effective in improving the removal rate of DOC and turbidity in drinking water.[8-10)

In this study, the hybrid system of coagulation and membrane was investigated to define the phenomena of removing color, turbidity, TOC and total phosphorous (TP)^in sewage effluent by checking the removal efficiency and the molecular weight distributions according to processes. The optimal condition investigated in coagulation by jar test was applied to the hybrid system of MF membrane. The performance of coagulation and MF membrane was studied by checking their ability to remove NOM of specific MW in secondary sewage effluent.

II. Materials and Methods

1. Investigation of Water Quality

To investigate water quality of influent and effluent in sewage plant, sampling was monthly executed at 4 sites by plastic bottle and 22 items were analyzed by analytical instruments of ICP-MS, UV-VIS spectrophotometer, IC and TN-TP automatic analyzer, etc. The period of investigation was during Jan to Dec 2004 for the effluent of Gwangju sewage treatment, in which domestic sewage water was biologically treated. To reuse the effluent as usable water, some elements as BOD (biologically oxygen demand), color, turbidity, phosphorus, nitrogen and bad smell must be treated in the processing of these treatments. Analytical instruments for heavy metals, phosphorous, color, turbidity, TOC, and others are inductively coupled plasma (Agilent-7500A), phosphorous-nitrogen analyzer (AACS-III/BRAN-LUEBBE), colorimeter(TC-205/ Central KAGAKU), turbidimeter (2100N/HACH), TOC-analyzer (Phoenix 8000, Tekmar Dohrmann) and spectrophotometer(UV-1201/ Shimadzu), respectively.[11]

Table 1. Characteristics of the MF hollow fiber membrane

Properties	Unit	Description/Value
Material	-	Polyethylene
Type	-	Hydrophilic
Total surface area (10 modules 0.2 m length each)	m^2	0.0034
Pore size	㎛	0.4
Internal diameter	mm	0.36
External diameter	mm	0.54

2. Materials

The membrane used in this study is a hollow fiber microfiltration membrane obtained from the Korean Express co., Korea. The characteristics of the membrane are given in Table 1. The treated water by coagulant passed the membrane for several hours and the MWD of organic matter was analyzed during the processes. MF used in this study is hydrophilic type, polyethylene hollow fiber membrane with the mean pore size of 0.4㎛.

3. Methods

The coagulation and flocculation was achieved in a jar test with the condition that fast mixing 120 rpm for 5 min, slow agitation 50rpm for 15 min, and settling for 60 min. Hydrogen chloride and sodium hydroxide solution was used to set pH 3~12 in sewage effluent by injecting at the slow agitation. Alum, 8% Al_2O_3 content, and poly aluminum chloride, 10 % Al_2O_3 content, as coagulant and MF membrane were used in this system. The coagulant dosage was changed from 10 to 350mg/L and checked concentrations of several items in coagulation. Optimal conditions of coagulation selected by Jar-test were introduced to coagulation/membrane hybrid system. Conventional coagulation process followed by membrane was automatically controlled in the lab-scale pilot plant. The pilot unit is equipped with an automated membrane backwashing system and also capable of semi-automated system. The flux in membrane system was 0.0144-0.1872 m^3/d(pressure 1090 kpa). Molecular weight distributions in raw water and treated water after coagulation and MF membrane were analyzed by HPLC(Agilent 1100) and compared in arithmetic mean RMW to evaluate treatment efficiency during each processes. PSS(polystyrene sulfonates, Polysciences, Inc.) was used as HPLC standard reagent for the calibration with the concentration of 210, 1,800, 4,600, 8,000 and 18,000 Dalton. Using the calibration data of retention time(RT) and relative molecular weight (RMW), molecular weight distributions for samples were comparatively calculated according to processes.

Ⅲ. Results and Discussion

1. Water Quality of Secondary Treated Sewage Effluent

Water quality monthly investigated during Jan to Dec 2004 in the effluent of Gwangju sewage treatment is presented in Table 2. It showed that organic matter as BOD and COD (chemical oxygen demand), color, turbidity, phosphorus, nitrogen and odor must be removed in secondary treatment process for water reuse. Especially, organic matter, color, phosphorus, nitrogen and odor were major resources to be removed during the secondary processes. Harmful heavy metals as Pb, Cd, Hg and Cr were nearly not detected in 2004, with Fe and Mn metals very low. That is why it is not necessary to introduce advanced high technique processes as ionic exchange and reverse osmosis. In this viewpoint, coagulation and microfiltration would be the best technique in just treating these kinds of materials for sewage water reuse [12].

Table 2. Characteristics of secondary treated sewage effluent

Parameters	Average values	Parameters	Average values
BOD (mg/L)	3.8	ABS (mg/L)	0.10
COD (mg/L)	9.4	Hardness (mg/L)	77.5
SS (mg/L)	2.8	Fe (mg/L)	0.03
Color (degree)	26	Mn (mg/L)	0.04
Turbidity (NTU)	0.83	Hg (mg/L)	0.000
Odor (-)	A little	As (mg/L)	0.000
Appearance (-)	Good	Pb (mg/L)	0.000
E. coli (No./mL)	0	Cd (mg/L)	0.000
Chlorine ion (mg/L)	83.2	Cr (mg/L)	0.000
Total phosphorus (mg/L)	1.78	pH (-)	7.08
Total nitrogen (mg/L)	19.58	Conductivity (μs/cm)	595

2. Coagulation

The effect of coagulant (alum and polyaluminium chloride) dosages was observed on several contaminants' reduction. For coagulation process, Jar test was executed and resulted in that polyaluminium chloride (PAC) as coagulant was more effective in removing color, turbidity and TP than alum. The removal rate of turbidity was gradually increased up to 65 % with 100mg/L alum dose, which is the optimal condition of alum in the range of 10 to 350mg/L. On the other hand, it showed the turbidity was an average of 0.15NTU in the coagulant dosage of PAC 80 to 220 mg/L as seen in Fig. 1. The removal rate of total phosphorus(TP) was 96.7 % with alum dose of 100 mg/L and 87.4% with PAC dose of 80 mg/L as seen in Fig. 2. In color, the rates were 34.6% and 38.6% with the dosage of 100mg/L alum and 80 mg/L PAC, respectively. The tendency of removing DOC was same as color in proportion to the coagulant dose as seen in Fig. 3. The optimum concentrations were 100 mg/L and 80 mg/L, respectively, for alum and PAC. According to the experimental results, the optimal pH was in the range of 6~10 for turbidity, 5~8 for DP and 5~6 for DC as seen in Fig. 4~5. The best pH range of applying to the lab-scale hybrid system was 6~7. PAC showed more effective in removing color and TOC materials than alum. Because of the low price of alum, it was selected as a coagulant to join with next process, membrane in this study.

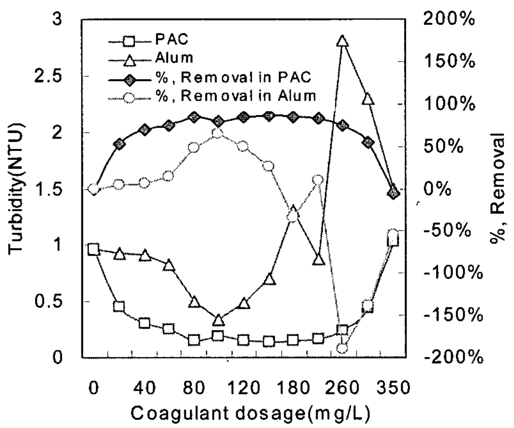

Fig. 1. Effect of coagulant on the removal of turbidity

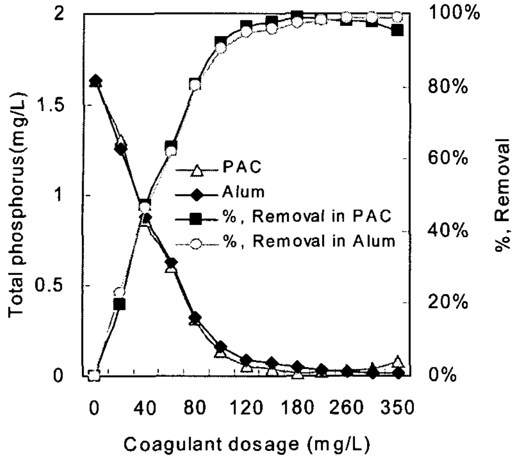

Fig. 2. Effect of coagulant on the removal of TP

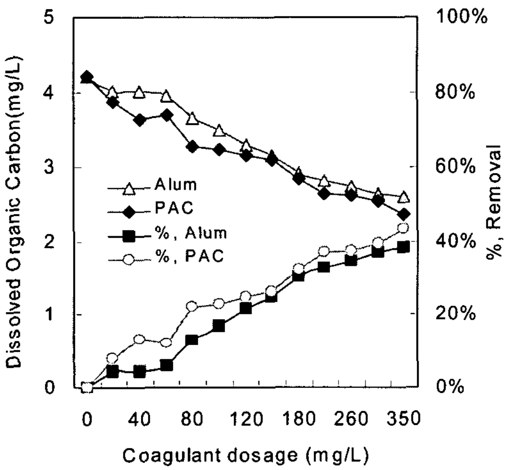

Fig. 3. Effect of coagulant on the removal of DOC

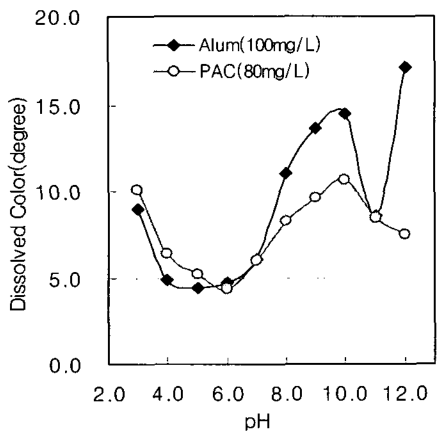

Fig. 4. Effect of pH on the removal of dissolved color

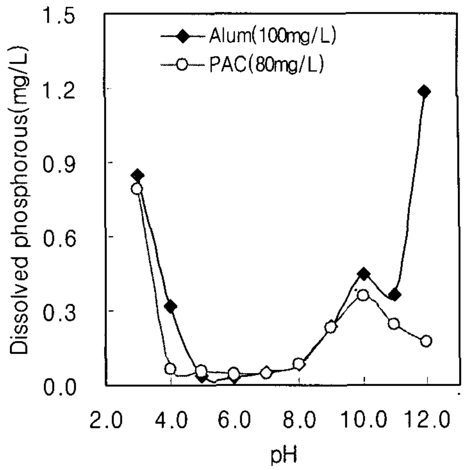

Fig. 5. Effect of pH on the removal of dissolved phosphorus

3. Coagulation / Membrane

To find the pollutants' impact on membrane, fluxes extruding from the membrane were investigated according to pH and coagulant species. At low pH as acid solution, the flux was decreased compare to raw water (pH 7.0), that means the relative pressure reached very fast up to the limit of operating pressure. Oth-

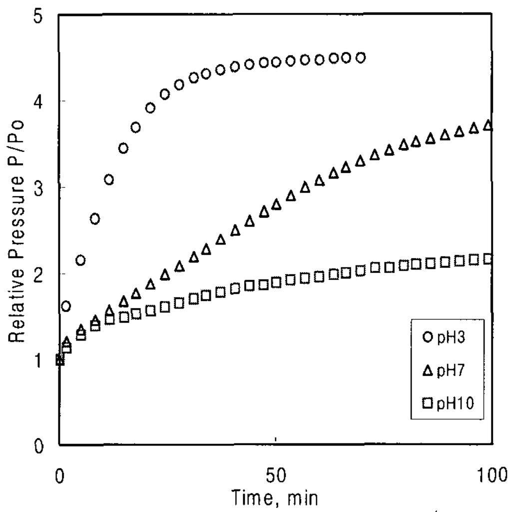

Fig. 6. Effect of pH on the relative pressure in the hybrid system of coagulation and membrane

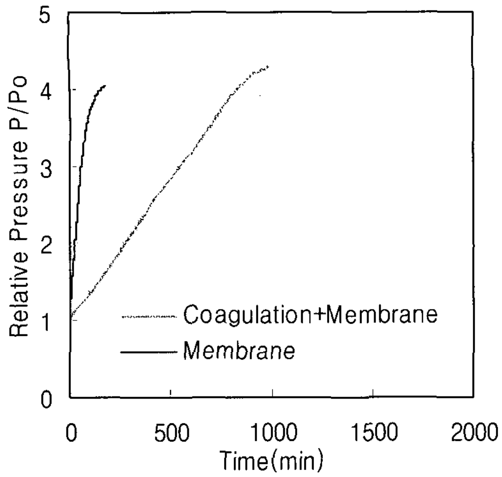

Fig. 7. Treatment efficiencies for two processes

erwise at high pH as alkali solution, the relative pressure was very slowly increased to the limit. The filtration delayed time of membrane was increased 5 times after coagulation/membrane compare to membrane only used as seen in Fig. 7. When coagulation was combined with membrane in hybrid system, almost all of materials as color, turbidity, TOC and TP were removed except odor. Treated water quality was under the limit of Korean standard for reuse water.

4. Molecular Weight Distribution

Molecular weight as Mn(number average molecular weight) and Mw(weight average molecular weight) can be calculated by equations below. Polydispersity, which can be classified with monodisperse(when Mw/Mn=1) or multidisperse (when Mw/Mn ≠1), of NOM (natural organic matter) can also be obtained by Mw/Mn using MWD (molecular weight distribution) curve analyzed by HPLC.

$$Mn = (\Sigma_i n_i M_i) / (\Sigma_i n_i) \quad (1)$$

$$Mw = (\Sigma_i n_i M_i^2) / (\Sigma_i n_i M_i) \quad (2)$$

Here, n_i : number of molecular, M_i : molecular weight of i species

Relative molecular weight (RMW) distributions were analyzed in raw water, coagulation treated water and MF membrane treated water combined with coagulation. In coagulation, the material was removed 49% in the range of 500~1,000 Dalton and removed 94% in over 1,000 Dalton, and removed only 2% in less than 500 Dalton, that means NOM can affect to the formation of harmful materials after Cl_2 treatment. In the hybrid system of MF membrane and coagulation, the material was removed 12% in less than 500 Dalton (Fig. 8). To reduce NOM at the secondary treated sewage water, another treatment must be considered for applying suitably to the hybrid system. Number average and weight average of RMW were shifted from high to low at the molecular weight data after coagulation and membrane as shown in Table 3. That means high molecular weight materials were easily removed by coagulation and membrane in all of two samples after coagulation and MF membrane treatment (Fig. 8). Otherwise low molecular weight (<500 Da) materials were nearly not removed during these processes. So other treatment methods must be introduced to remove low molecular materials of less than 500 Dalton in this system.

Table 3. Variation of molecular weight according to treatment processes

Treatmentprocess	Number average RMW	Weight average RMW	Degree of polydispersity
Raw water	526 Da	950 Da	1.808
Coagulation	318 Da	465 Da	1.465
Coagulation +Membrane	292 Da	396 Da	1.356

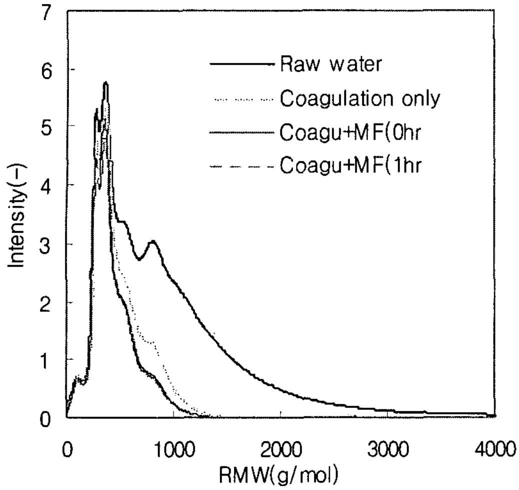

Fig. 8. Relative molecular weight distributions according to treatment processes

IV. Conclusion

Water quality for Gwangju sewage effluent showed that BOD, SS, turbidity, total phosphorus and color were 4.1 mg/L, 2.9 mg/L, 0.8 NTU, 1.3 mg/L, and 27 unit, respectively, during January to December in 2004. Jar-test showed that PAC gavebetter efficiency in removing turbidity and dissolved phosphorus than alum. It was also found from the relative molecular weight (RMW) distribution analysis that organic matter over 1,000 (Da) was easily removed by coagulation and subsequently MF treatment, while it was not effective for materials less than 500 Da. The hybrid system of coagulation and MF membrane was verified the possibility of applying to the water reuse process of sewage effluent for the lack of water resources in the future.

Acknowledgements

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<국문초록>

하수처리장 방류수의 응집 및 정밀여과 처리공정에 관한 연구

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Abstract

하수처리장 방류수의 재이용을 위해 2004년 1월~12월까지 수질상태를 조사하였다. BOD, SS, 탁도, 총인과 색도의 월별로 조사한 연평균은 각각 4.1 mg/L, 2.9 mg/L, 0.8 NTU, 1.3 mg/L, 27 unit이었다. 쟈테스트는 급속혼화 5분, 완속교반 15분, 침전 1시간의 조건 하에서 오염물질의 제거율을 조사하였다. 사용된 응집제는 Alum과 폴리염화알루미늄이고, 방류수 중의 색도, 탁도, 총인, 총유기탄소 등을 제거하는데 효과가 있었다. 특히 폴리염화알루미늄을 사용시 탁도와 용존성인의 제거 효과가 좋았다. 응집공정과 연속한 정밀여과 공정에 의한 유기물의 제거효과를 조사한 결과, 분자량 1,000 Dalton 이상의 범위에 있는 물질의 제거가 잘 이루어진 반면, 소독부산물의 생성에 영향을 주는 분자량 500 Dalton 이하 물질의 제거율은 낮은 것으로 조사되었다. 따라서 복합공정에서 이 범위 분자량의 물질을 제거하기 위해 흡착공정 등의 추가공정이 필요할 것으로 본다.