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Phosphorus removal by a combined electrocoagulation and membrane filtration process for sewage reuse

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ABSTRACT

With an increase in awareness of water scarcity, water reuse has received significant attention. The reuse of sewage has attracted attention, because sufficient amounts of sewage can be obtained even in a drought. As a large amount of algae has been generated owing to the lack of oxygen due to global warming, concerns about phosphorus have rapidly increased. This study explores the removal of phosphorous in treated sewage and shows how sewage can be reused. A combined electrocoagulation (EC) and membrane filtration process was used in order to remove turbidity, particulate matter, colloids, and total coliforms, illustrating the suitability of sewage reuse. The optimal EC conditions for phosphorus removal were determined including the electrode type and spacing, reaction time, temperature, voltage, and current. Optimal conditions for the membrane process, such as pressure and time, were also established. Analysis of zeta potential and distribution of particle size demonstrated the coagulation treatability of particles, while backwashing confirmed the recovery of the film. The purpose of this study is (i) to show how phosphorus and other contaminants can be removed by advanced processes such as a combined EC and membrane process and (ii) to investigate the quality of water obtained from this process.

Keywords: Sewage treatment; Electrocoagulation; Phosphorus removal; Aluminum; Membrane; Sewage reuse

1. Introduction

Owing to the scarcity of water, the importance of securing alternative water resources to meet the demand has increased. As sewage treatment effluent can be obtained even during drought periods, coagulation and filtration have gained significant attention as advanced processes. To facilitate sewage reuse, phosphorus should be removed from treated sewage [1]. The removal of phosphorus can be achieved by several physical, chemical, and biological methods [2]. Among the many available methods for removing phosphorus, electrocoagulation (EC), a reliable and cost-effective sewage treatment process, has a number of advantages including the simplicity of its

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equipment, a short operation time, nonexistent or negligible amount of required chemicals, and decreased production of sludge [3,4]. The flocs formed by EC are relatively large, stable, and amenable to filtration, which lead to a reduction in the number of unit process and decrease the process area [5]. In addition, in order to obtain high quality sewage amenable to reuse, all organic, inorganic, and ionic contaminants should be removed, which requires additional membrane processes [6]. Therefore, this study introduces an advanced treatment called the "combined EC and membrane filtration process" for the reuse of treated sewage.

Water treatment by EC refers to a process of pollutant removal via current and voltage through a metal electrode called the sacrificial anode. This leads to the dissolution of metals from hydroxides, which then agglomerates with colloidal materials in sewage. Also, this chemical reaction triggers oxidization on the anode and deoxidation on the cathode. Because of the negative charge on ions such as OH^-, $HCOO^-$, PO_4^{3-}, and SO_4^{2-} in water, these functional groups form various complexes that hydrolyze polynuclear metallic ions [2,5].

In the case of negatively charged phosphorus in water, PO_4^{3-} combines with +3 charged metal ions and precipitates as $MePO_4$. Moreover, Al^{3+} released from the anode reacts with phosphate and forms $Al_n(OH)_{3n}$ and $AlPO_{4(s)}$, which precipitates as a salt. These insoluble salts are deposited and physically separated from the water and discharging supernatant. As a result, phosphorus is removed by EC. Nitrogen can be separated from water through electro-oxidation. These reactions can effectively remove all phosphorus. Notably, EC can remove other pollutants as well [6,7]. Optimum operation conditions were determined including an aluminum plate-type electrode, reaction time of 60 s, temperature of 15.1 ℃, voltage of 20, electrode gap of 3 mm, and 577 µs/cm conductivity. For 577 µs/cm, the degree of phosphorus removal in the final water output was examined through the membrane filtration of the supernatant following EC. Filtration precisely removes bacteria as well as other solid matter to produce high purity water. Membranes separate or remove particles that are not removed through normal filtration. In addition, a membrane maintains the amount of flux without fouling [8]. Flux is represented in Eq. (1) [9]. Precision filtration explains permeate flux in lmh units through Darcy's law as shown below (Eq. (1)).

$$Q = k \times \frac{P_b - P_a}{PgL} \times A \tag{1}$$

In order to maintain a constant flux, optimal conditions relating to pressure, temperature, and resistance of a membrane should be utilized to minimize fouling, which is considered the most critical problem in membrane filtrations. Therefore, this study presents the optimum pressure and temperature for the membrane process, and also explores backwashing in order for resistance reduction. In addition, coagulation, treatability, and fouling are described based on the zeta potential and size distribution of particles.

2. Materials and methods

2.1. Raw water

This study utilized the secondary effluent of the A_2/O process of the *J* water reuse center in Seoul. In case where there was a low Total Phosphorus (T-P) concentration in the raw water, 0.1 N-KH_2PO_4 solution was added to the raw water prior to conducting the experiment. Analysis was carried out by the standard method [10]. The pH, conductivity, and dissolved oxygen content were measured by a PCD 6500 (Eutech Instruments). Chromaticity (Platinum Cobalt Units (PCU)) was measured by a HI96727 (Hanna Instruments). Turbidity was evaluated with a 2100P Turbidimeter (Hach). Zeta potential was measured by a Zeta plus from Brookhaven Instruments. Particle size was determined by a Phamas-SBSS. The heavy metal content was determined by a ICPE-9000 from SHIMADZU. Table 1 contains the ranges and average values of the pollutants in the secondary effluent of the *J* water reuse center.

2.2. Experiment

The EC and Microfiltration (MF) experiments were conducted through the batch process. The electrode was 8.5 cm wide, 0.3 cm thick, and 31 cm tall, provid-

Table 1
Characteristics of raw water

	Value	
Item	Range	Average
pH	6.96–7.13	7.1
Conductivity (S/cm)	499.0–666.0	512.2
BOD_5 (mg/L)	9.72–10.06	10.3
COD_{Cr} (mg/L)	27.43–34.29	31.2
SS (mg/L)	2.0–14.0	4.8
T-P (mg/L)	0.5–2.97	1.2
PO_4-P (mg/L)	0.3–2.02	0.8
T-N (mg/L)	8.85–15.7	9.79

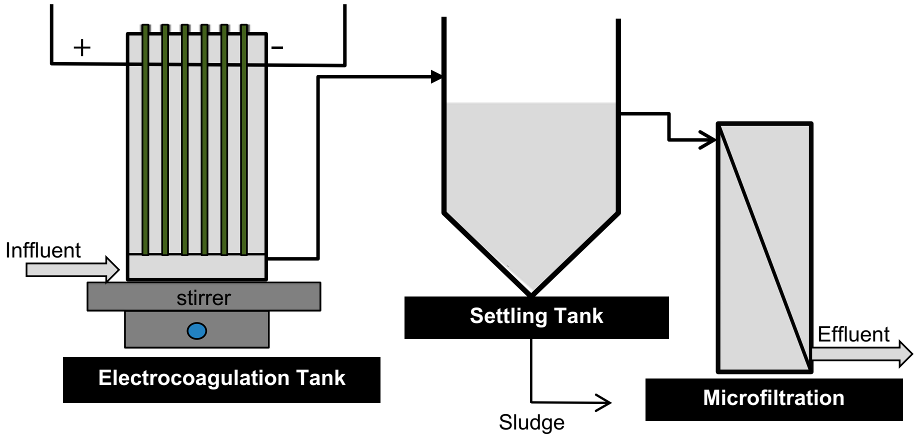

Fig. 1. Experimental equipment.

ing 263.5 cm^2 of surface area. A digital DC power supply (Kap Jin KJP-600S) was used to generate current, which was connected to the electrode in bipolar mode. The EC reactor was made by Plexiglas (9.5 cm wide, 8.0 cm long, and 31.5 cm tall). The optimum conditions for the removal of phosphorus via EC, such as the type and spacing of electrodes, time, temperature, voltage, and conductivity, were determined. Raw water was precipitated for 30 min in a settling tank following the EC. Subsequently, only the supernatant of the settling tank flowed into the membrane process.

Amicon Filtration Cell (Model 8200, USA) was used for the membrane filtration process in the dead-end method. The diameter of the membrane was 90 mm, and it was made of CA, a mixed cellulose ester manufactured by GSWP09000 Millipore, USA. The pore size of the membrane was 0.22 μm. The permeated water was produced by the membrane filtration of the influx supernatant, which was pushed through the filter by the pressure created by the addition of nitrogen gas. The filtered flux was measured with a digital scale. The experimental equipment is shown in Fig. 1.

3. Results and discussion

3.1. EC for phosphorus removal

3.1.1. The optimum factors

The most efficient electrode was determined by evaluating soluble electrodes such as iron and aluminum and insoluble electrodes like Steel Use Stainless (SUS). Iron and Al electrodes were more efficient than SUS + Iron and SUS in the removal of phosphorus, as shown in Fig. 2.

Since iron electrodes were tinged with a red which induced secondary pollution, the aluminum electrode was determined to be optimal.

In EC, the spacing of the electrodes, reaction time, temperature, and voltage should be considered [11]. As for the spacing of electrodes, the highest removal

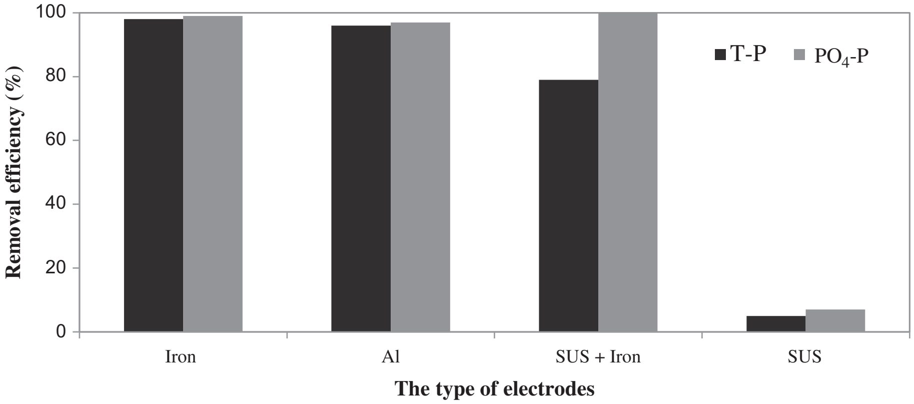

Fig. 2. Removal efficiency of T-P, PO_4-P arranged by electrode type.

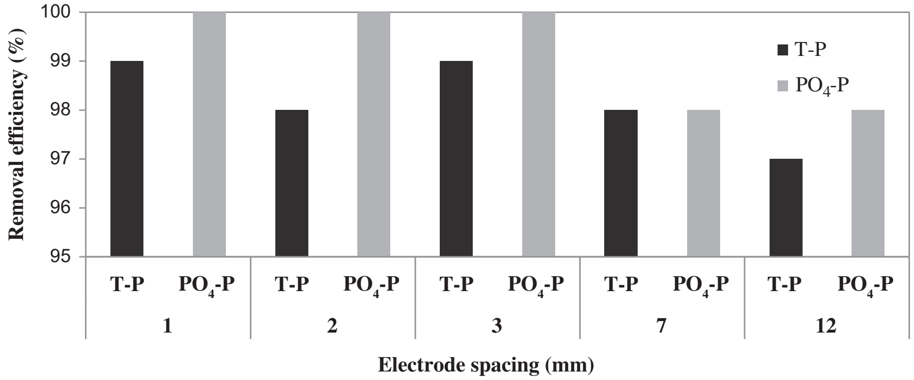

Fig. 3. Removal efficiency according to electrode spacing.

efficiency was realized when 1 and 3 mm gaps were utilized, as shown in Fig. 3.

When the space between electrodes was 1 mm, more electrodes were required, thus demanding additional current and voltage. Therefore, an electrode spacing of 3 mm was considered to be more efficient and economical than 1 mm.

The optimum reaction time for the EC process was 60 s, when phosphate was not detected According to Faraday's law, the concentration of the aluminum was highest during the first 60 s. The temperature of water affects the formation of floc during coagulation, due to the change in viscosity and the effect on the rate of the chemical reaction [11]. Therefore, 15.1℃ was selected as the optimum temperature because most of the phosphorus was removed by this point.

Experiments were conducted at different voltages, with 1 A as the standard. Since phosphorus was completely removed at 20 V, the optimum voltage was determined to be 20 V.

3.1.2. Conductivity for phosphorus removal

When resistance increases due to the formation of oxide films, electricity consumption increases and the release of aluminum is hindered, which renders the formation of metal hydroxides slow and inefficient [12]. To prevent this phenomenon, the addition of electrolytes such as NaCl reduces the formation of oxide films on the electrode surface and electricity consumption and increases the EC efficiency [12,13].

The average conductivity of raw water was between 309 and 577 µs/cm. The removal efficiency of phosphate increased at 309 µs/cm, but a high removal efficiency of both T-P and PO$_4$-P was observed at 577 µs/cm, as shown in Fig. 4. Conductivities of 600, 800, and 1,000 µs/cm are less economical than 577 µs/cm, because they require the addition of NaCl. Consequently, 577 µs/cm was selected as the optimal conductivity.

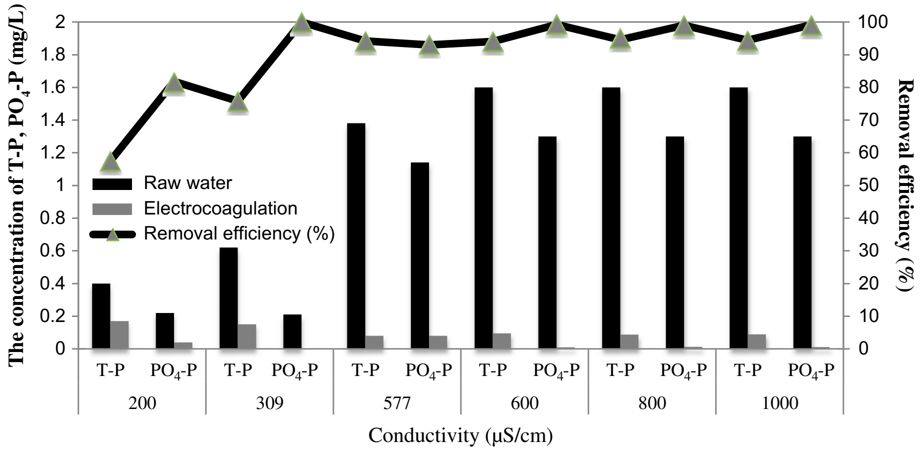

Fig. 4. T-P, PO$_4$-P concentration and removal efficiency according to conductivity.

3.1.3. Comparison between chemical coagulation and EC

pH is an important factor since it affects the efficiency and solubility of metal hydroxides in the EC reaction [14]. In this regard, a standard pH must be determined. Raw water presented a pH range of 6.96–7.13, and the mean value, 7.13, was selected for this study. EC and chemical flocculation were therefore compared using the jar test, with a pH of 7.13. An aluminum plate was used for the EC, and 17% PAC (poly aluminum chloride) [14] was used for the chemical flocculation. The experiment was implemented with a fixed pH of 7.1, and a varied coagulant dose of 50, 60, 70, 80, 90, and 100 ppm.

As a result, 60 ppm was determined to be the optimum coagulant dose. EC was conducted under the optimal conditions of 60 s reaction time, 1 A current, and 20 V voltage. Fig. 5(a) shows that a similar removal efficiency was obtained with the exception of T-N. Fig. 5(b) represents the cost difference when treatment flux is assumed to be 100 m^3/d for 1 year. This differs by 110,000 won per year; however, it is believed that this will become more economical in the future. Therefore, pollutant removal rate is higher for EC than chemical coagulation.

3.2. Membrane

3.2.1. Flux change

Pressure is an important factor in membrane filtration [15] since it affects flux volume. To determine the optimum pressure, experiments were conducted at 0.5, 1, 1.5, 2, 2.5, and 3 kgf/cm^2.

A large amount of flux is generated with high pressure, but a reduction in flux is caused by high resistance [6,14,15]. In the study, sufficient flux was gained under a pressure of 2 kgf/cm^2. Fig. 6 presents the flux. The measured pressure P refers to the pressure on the feed side which is identical to transmembrane pressure, since the permeate side pressure is equal to the atmospheric pressure.

3.2.2. Backwashing of MF

Treated water after EC contains numerous pollutants that contribute to reversible and irreversible

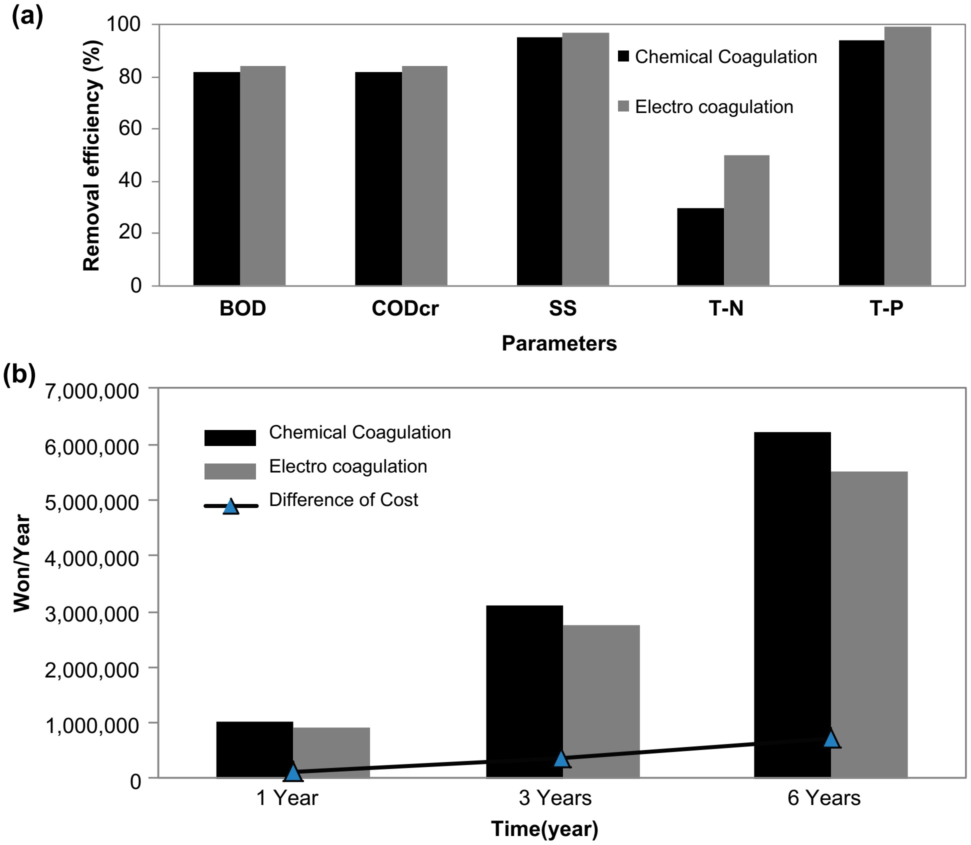

Fig. 5 (a) Pollutant removal efficiency comparison between chemical coagulation and EC and (b) Economic feasibility comparisons between EC and chemical coagulation over time.

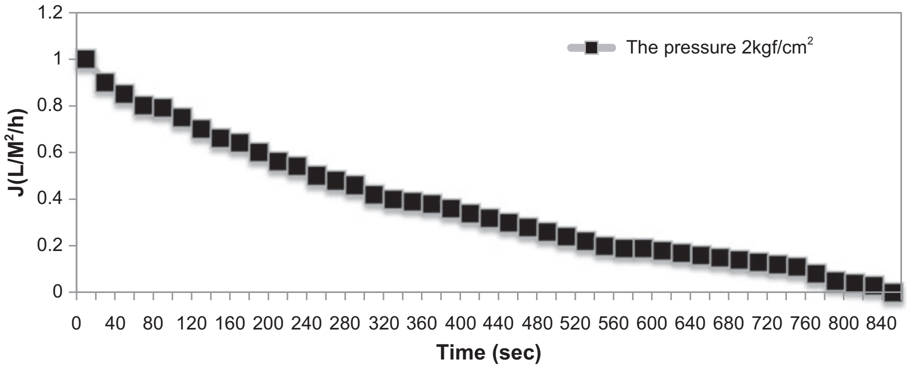

Fig. 6. Flux of MF process according to time at the pressure of 2 kgf/cm^2.

Table 2
Types and characteristics of chemical cleaning CIP

CIP conditions Concentrations	Time (h)
1 N HCl	3
0.3% NaOCL	3
1 N HCl	3

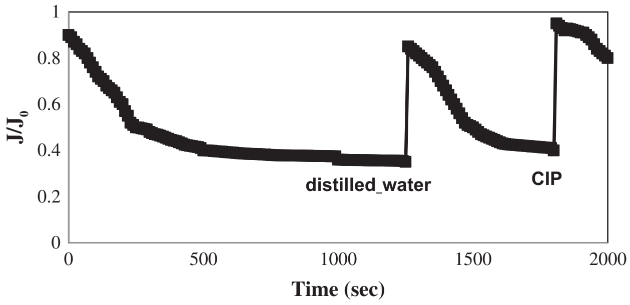

Fig. 7. Backwashing in J/J_o of MF according to time.

membrane contamination [16,17]. The backwashing with distilled water was performed to determine the reversible contamination. An irreversible experiment was implemented with Clean-In-Place (CIP) on contaminated membranes [17] and the characteristics are shown in Table 2.

Compared with the initial membrane, backwashing with distilled water and with CIP led to a recovery rate of 84 and 92%, respectively, as shown in Fig. 7. Consequently, chemical cleansing of contaminated membranes with Enhanced Flux Maintenance (EFM) or CIP may be more appropriate than backwashing using distilled water [17,18].

3.3. Zeta potential

Fig. 8 shows a linear graph of the zeta potential values of raw water, EC and MF.

The zeta potentials of raw water and EC+MF were -20 and 0 mA, respectively. The cohesiveness of raw water was changed from incipient instability to strong agglomeration [17,18], which demonstrates that EC and MF generate highly cohesive flocs, as shown in

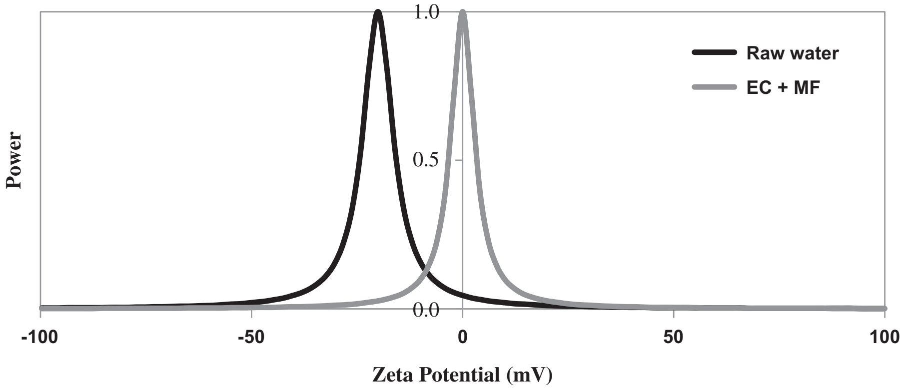

Fig. 8. Zeta potential of raw water and treated water through EC + MF.

Table 3
Stability characteristics according to zeta potential

Stability characteristics	Zeta potential (mv)
Strong agglomeration	+5 to −5
Incipient instability	−10 to −30
Moderate stability	−31 to −40
Good stability	−41 to −60
Excellent stability	−61 and up

Table 3. This refers to particle stabilization at the MF, which separates large insoluble particles that collide and have coagulation treatability. This is a result of the optimum operation of the coagulation treatability of EC and MF.

3.4. Size of particles

The size of particles is a significant factor that influences coagulation and fouling [18]. Fig. 9 shows the size distribution of the particles in the raw water and supernatant after the EC process and EC+MF. As shown in Fig. 9, particles with diameters between 3 and 50 μm were evenly distributed in each process. The diameter of the particles following EC+MF exhibited a higher distribution rate than EC, except when they were less than 1 μm. The diameter of particles less than 1 μm of EC was recorded at the highest in the distribution. The formation of flocs after EC altered the distribution rate, because most of the small particles were eliminated, thus leading to the generation of flocs. Then, the broken particles re-entered into the MF process, causing the re-aggregation of the particles on the surface of the MF [19].

As presented in Fig. 9, 90% of the particles over 3 μm precipitated, but the rate of distribution of particles between 3 and 50 μm was insignificant after EC and EC+MF, owing to the strong cohesiveness of EC and efficient filtration of MF using the filter with a pore size of 0.22 μm.

3.5. The result of the combined EC and membrane filtration processes

3.5.1. Phosphorus removal

Fig. 10 shows how much phosphorus was removed through the EC and membrane processes. EC removed more than 80% of T-P and PO_4-P, which was further eliminated (almost 100%) by the membrane process, since the MF removed remnants such as other flocs and organic compounds [20]. Consequently, the EC and membrane processes are highly efficient in the elimination of phosphorus.

3.5.2. Changes in other pollutants

Removal rates after the EC and membrane process are presented in Figs. 11(a) and (b). More than 70% of other pollutants were removed with the exception of T-N, which satisfies the water quality standard for sewage reuse.

On the other hand, the removal of T-N through the EC and membrane process was difficult when the initial T-N concentration was high. In order to achieve a higher quality of water through EC and MF, T-N should be removed to the optimum level by biological nitrification and denitrification treatment, prior to EC and MF.

The chromatility and turbidity values obtained in this study satisfy the water quality standards for sewage reuse despite the fact that their removal efficiency was less than 70%. The combined residual chlorine is also shown in Table 4. On the contrary, the removal efficiency of E-Coliform was 100% following the EC+MF process.

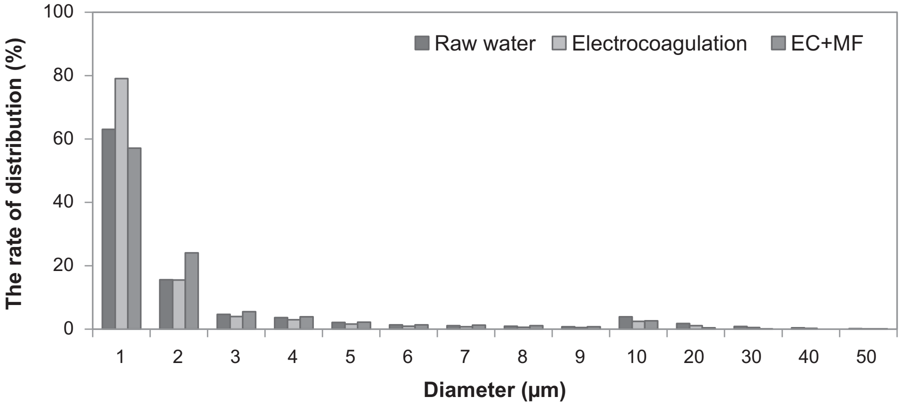

Fig. 9. Distribution of particle of raw water and EC and EC + MF-treated water.

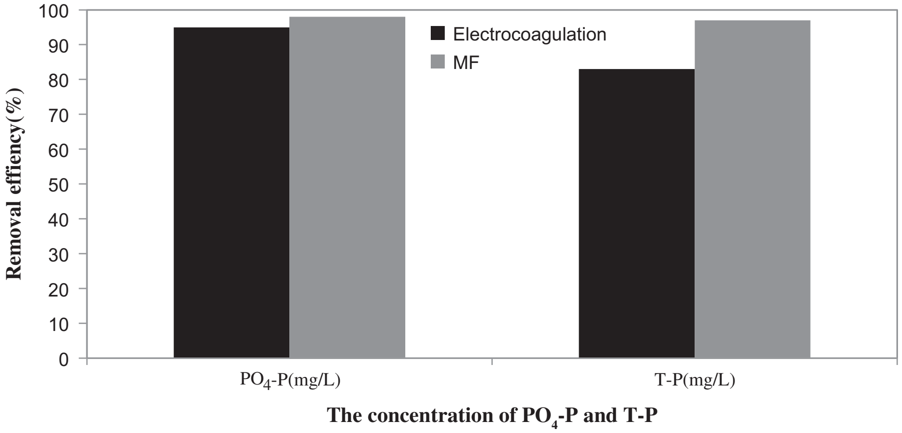

Fig. 10. PO_4-P and T-P removal efficiency according to EC + MF process.

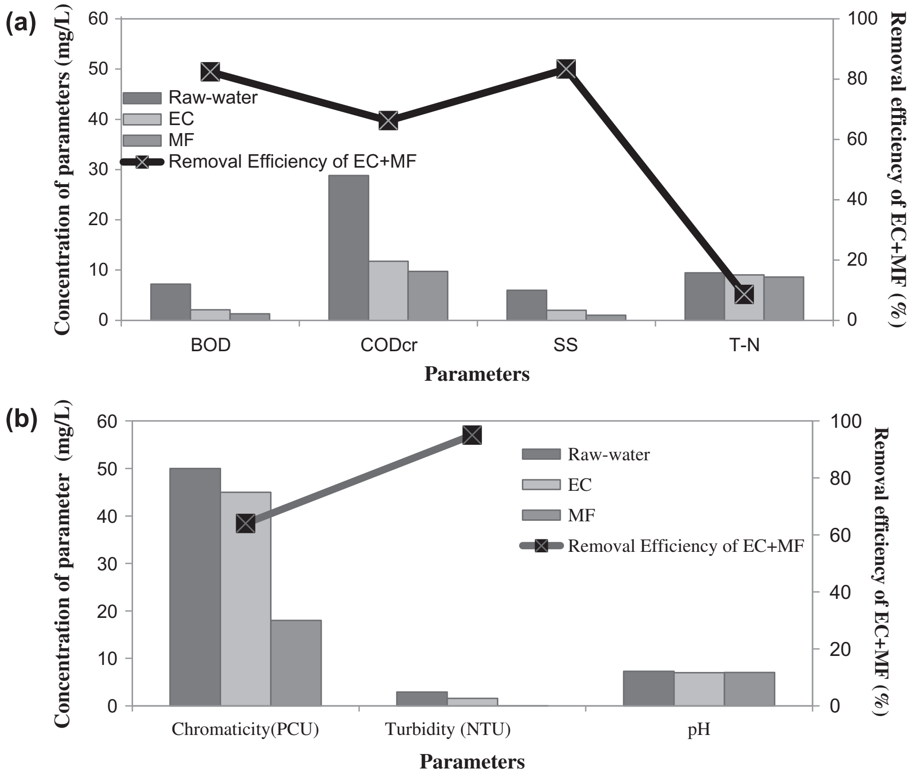

Fig. 11. (a) Removal efficiency and concentration of pollutants through EC + MF process and (b) Removal efficiency and concentration of pollutants through EC + MF process.

Table 4
Concentration of E-Coliform and combined residual chlorine through EC+MF process

Parameters	Raw water	EC	MF
E-Coliform (number/100 ml)	2,030	996	0
Combined residual chlorine (mg/L)	0.3	0.4	0.2

Table 5
EC+MF results and heavy metal water quality standard for sewage reuse

	ABS	CN	A1	Cd	Co	Cr^{6+}	Cu	Mn	Se
Raw water (mg/L)	ND	ND	0.408	ND	0.003	ND	0.190	ND	0.001
EC (mg/L)	ND	ND	2.965	ND	0.001	ND	0.180	ND	0.008
MF (mg/L)	ND	ND	0.502	ND	0.000	ND	0.180	ND	0.026
Recommended water quality for sewage reuse (mg/L)	0.500	ND	5.000	0.010	0.050	ND	0.050	0.050	2.000

The heavy metal content satisfied the water quality standard for sewage reuse, as shown in Table 5.

Because of the low-current treatment in the study, the removal rate of heavy metals was slightly lower than expected. However, the amount of current in the actual process, not in lab test, sufficiently removed heavy metals [21,22]. As a result, the resulting water met the recommended sewage reuse standard for cleaning water, landscaping water, and industrial water. Therefore, the efficiency of EC+MF in the removal and reuse of sewage was demonstrated.

4. Conclusions

The optimum factors for the inexpensive removal of phosphorous were determined, and an EC+MF process that satisfies the water quality standards for sewage reuse was identified. The optimum conditions for the removal of phosphorus by the EC process included the following: aluminum plate with 3 mm gap, 60 s reaction time, 15℃ temperature, 20 V voltage, 1 A current, and 577 μs/cm conductivity. The phosphorus removal rate under these conditions was over 95% and the removal of most of other pollutants was over 70%. The result of implementing MF for securing stable water quality is as follows: 2 kgf/cm^2 pressure and 0 mV as a zeta potential. An 84% recovery of the initial membrane was achieved by backwashing in distilled water, but chemical cleaning resulted in a 94% recovery. Therefore, chemical backwashing was considered to be appropriate for the recovery of the contaminated membrane.

The water produced after the EC and MF process satisfied the recommended water quality standard for sewage reuse for cleaning water, landscaping water, and industrial water with the exception of the heavy metal content. Although further studies are required, the EC+MF process has a strong influence on sewage reuse for enhanced treatment and is the best treatment to remove phosphorus before an MF process.

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