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Changes in the properties of a solution using pulsed electric field treatment as pretreatment of membrane filtration

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ABSTRACT

The objective of this study is to investigate the changes in the physicochemical properties of humic acid, surfactants, and water after pulsed electric field treatment of the surrounding membrane. The critical micelle concentration (CMC) of the surfactants and the physicochemical properties of the water were determined by measuring conductivity, using Fourier transform infrared (FT-IR), and nuclear magnetic resonance (NMR). After the electric field processing, structural changes in the C–N complex and the C=O were found through FT-IR analysis. The increase in the frequency was from 2.3 to 9.9 Hz in the NMR analysis. The CMC of the cation and anion surfactants decreased to 1.3 and 9.2%, respectively, while the value of the UV–vis increased. The UV–vis of the humic acid decreased in the pulsed electric field. Therefore, the application of the pulsed electric field system was directly shown to have influenced the physicochemical properties of the water and the organic compounds.

Keywords: Pulsed electric field; Critical micelle concentration; NMR; FT-IR; Surfactant

1. Introduction

Recent environmental issues are closely related to the population growth, urbanization, and industrialization. A population growth increases production and consumption, which may increase the amount of discharged contaminants and destroy the environment. Biological and chemical techniques have been used to remove the hazardous chemicals and organic pollutants in the industrial wastewater. However, these techniques produced a large amount of wastes and harmful compounds such as trihalomethane (THM) and halogenated organics, which results in secondary contamination [1]. High operating costs are also an obstacle to the wide usage of application of such techniques.

For another approach for solving this drawback, pulsed electric field (PEF) treatment technique has been highlighted. This technique has many advantages, such as no production of harmful compounds, produced as a by-product, and it also saves operating costs. Studies on the use of the pulsed electric field have been conducted to kill bacteria, help in coagulation, and control fouling [2]. Ever since the PEF was first suggested by Gossling in 1960 [3], the following studies have been conducted [4–6].

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Wastewater treatment using pulse electric field (PEF) coagulation requires no oxidizer or reductant, and therefore, no post-treatment is required. Since its treatment capacity is relatively larger than that of biological treatment system, operating costs will decrease. It is also applicable to wastewater that is not easily biologically treated, such as heavy metal cyanide ions and works at normal temperature and pressure without seasonal effects. Finally, simple operation method and stable treatment efficiency are its strong points [7–10]. In the fouling control, the PEF coagulation induced the change in the surface potential of the colloidal particles, which are the main components of membrane fouling, suppressed the colloid fouling, improved the permeability of membrane, and contributed to the improvement of the filter replacement cycle [11–13].

Although many researches are conducted on the PEF-applied treatment, no research has been conducted yet on the structural change in water, which is the medium for the PEF treatment system. The effects of the PEF treatment system on water as the medium are shown below.

2. Material and methods

2.1. Pulsed electric field system

Fig. 1 shows the schematics of the PEF test system. The system transformed the AC voltage supplied to the control panel to 24 V DC. The transformed voltage was converted to 30 kV DC and applied to the inner high-strength polyethylene-charged electrode that was double-insulated. The current on the charged electrode generated the electric field between that electrode and the counter-electrode installed on the outer surface of the tube. The PEF test system was 130 mm long, 120 mm wide, and 1,700 mm high and its effective capacity was 2 L. The inflow rate was approximately 1.32 L/min, and the duration of one reaction of the sample in the electric field treatment system was considered as one cycle.

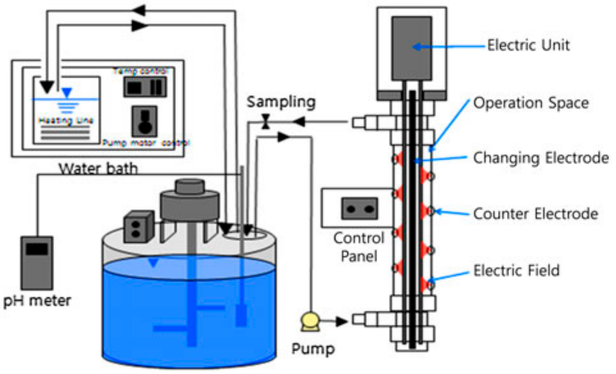

Fig. 1. Schematic of PEF test system.

2.2. Experimental conditions

A standard solution was prepared using benzalkonium chloride (Dae-Jung, Korea), anionic surfactant sodium lauryl sulfate (Sohwa Chemical, Japan), tap water from K City, ion exchange of water (Barnstead, Easy Pure—RoDi, USA), and humic acid (Aldrich, Germany).

The volume of the specimen was 4 L, and a magnetic stirrer was used for sufficient stirring at a fixed temperature of 25±1℃. The maximum contact time was determined as 640 cycles (1,920 min and 180 s/cycle). The sample was contacted for 0, 10, 20, 40, 80, 160, 320, and 640 cycles and then the samples were taken.

A critical micelle concentration (CMC) was determined using Force tensiometer (Sigma 701, Biolin Scientific, Sweden). A FT-IR (Bruker, Tensor27, Germany) analysis was performed to analyze the structure of water, which is the simplest three-atom molecule compound with special properties. The measurement range was 400–4,000 cm^{-1}, and the structure change in the solution was examined with a cm^{-1} resolution. The measurement kit for the analysis was ZnSe and KBr window for liquid cells, which is a kit for liquids. NMR (Jeol Lambda 300, Japan) was used to measure the movement speed of water. The magnetic flux density and temperature were fixed at 7.05 T (T = Wb/m) and 25℃, respectively. Finally, the wavelength using UV–vis spectrophotometer (Analytikjena, SPECORD 50, Germany) was measured within the range of 190–1,100 nm in the scan mode, and then it was qualitatively analyzed. The quantitative analysis was conducted at 280 nm. The standard 1 cm path was used as the measurement cell, the resolution was 1 nm, and the speed was 5 nm/s.

3. Results and discussion

3.1. Change in CMC

The surfactant has hydrophilic and hydrophobic radicals. When it is dissolved in a solution, its hydrophobic portion moves to the center to avoid contact with water, and its hydrophilic portion moves outward and forms a micelle. The micelle is first formed at the CMC. Only a small amount of the surfactant can change the properties of the solution interface or surface, and a higher surfactant concentration in a solution significantly changes the detergency, viscosity, refractive index, osmotic pressure, electric conductivity, and interfacial and surface tensions. Because these properties no longer significantly change at the CMC or a higher concentration, the CMC is an important property of the surfactant [14,15].

The measured conductivity of the surfactant increased rapidly with the increase in the concentration below the CMC and produced a steep slope of the curve, but it increased slowly when the concentration was above the CMC even with an increase in the concentration. Therefore, the slope of the amount increased with respect to the concentration can be calculated using the least square method to determine the CMC.

Fig. 2(a) shows the measured CMC of benzalkonium chloride as an anion surfactant. Before the PEF treatment, the calculated CMC at 25℃ was 2,068 ppm, but it became 2,042 ppm after the treatment, which is approximately 1.3% lower in comparison. On the other hand, Fig. 2(b) shows the measured CMC of sodium laurylsulfate as a cationic surfactant. Before the PEF treatment, the calculated CMC at 25℃ was 1,365 ppm, but after the treatment, it became 1,240 ppm, approximately 9.2% lower.

3.2. Change in FT-IR

Based on the vibration of atoms, the FT-IR shows a spectrum related to the chemical functional groups of

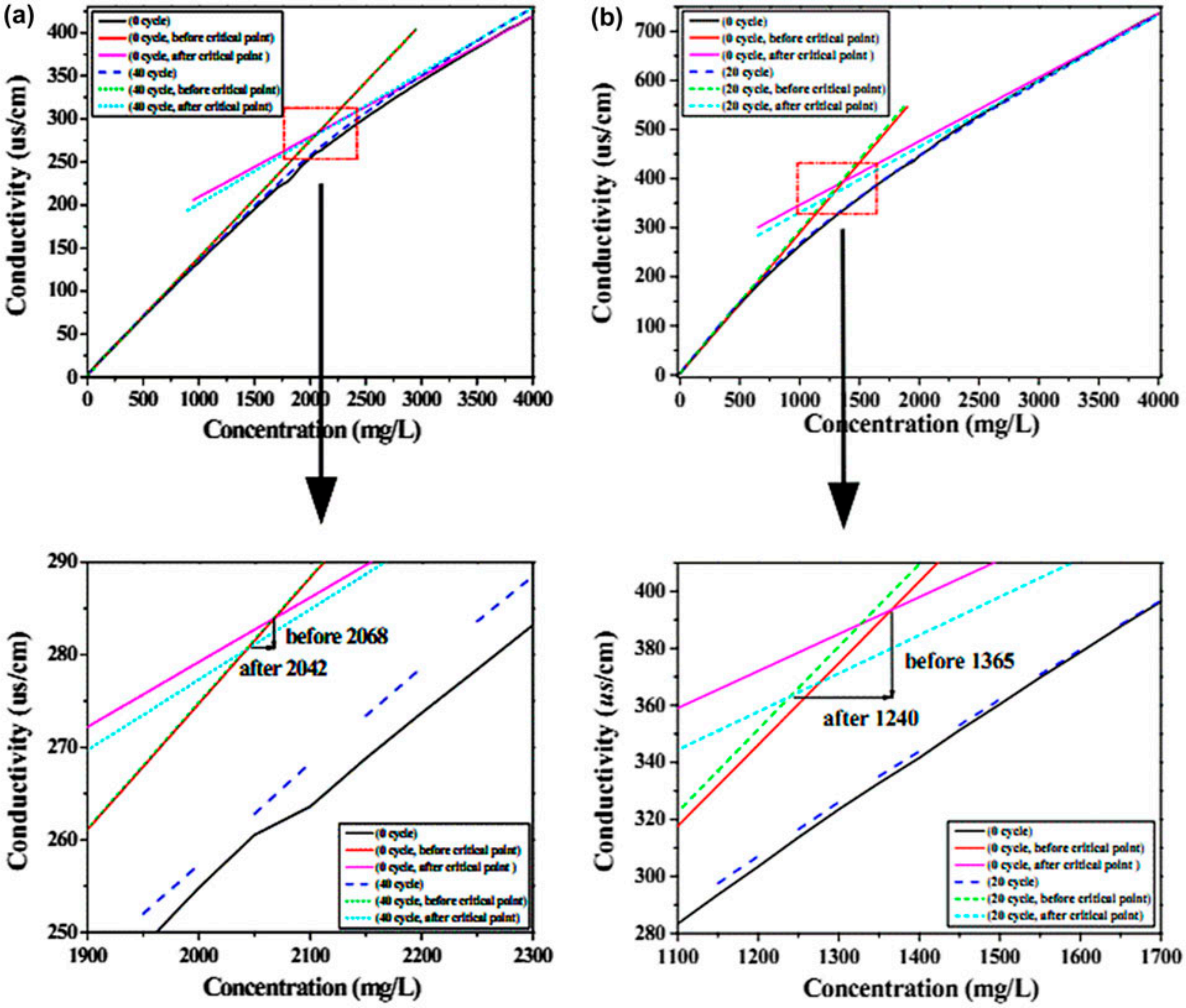

Fig. 2. Change in the CMC of (a) anion surfactant (contact time: 40 cycles) and (b) cation surfactant (contact time: 20 cycles).

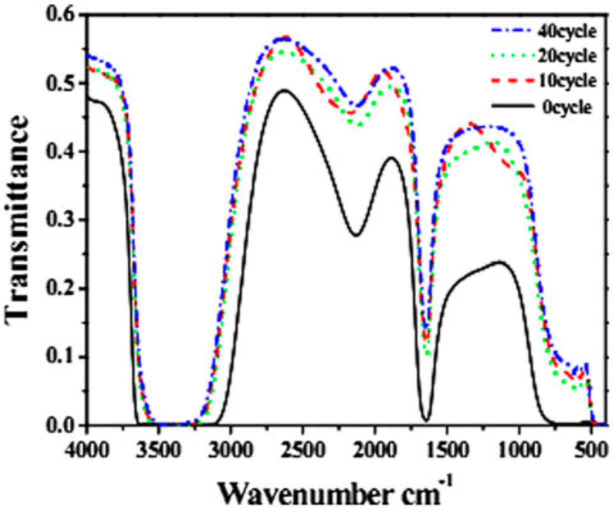

Fig. 3. Structural change in the water after the PEF treatment.

all atoms in the molecule. For the structural analysis before and after the PEF treatment was performed, tap water was used as the most general form of water.

Fig. 3 shows the spectrum of the FT-IR relative to the PEF treatment time. The transmittance before the PEF treatment significantly changed after the treatment. The C–N composite structure around a 2,200 wave number and the C=O structure at around a 1,700 wave number showed a difference in transmittance, and the pulsed electric field treatment seemingly influenced the carbon–hydrogen bond and the carbon–nitrogen bond.

3.3. Change in NMR-17O

The NMR device can measure the speed of the water molecule movement in terms of Hertz. Lower frequencies (Hz) signify fasterwater molecule movement, and higher water temperature represents lower frequencies (Hz). Considering that the hexagonal structure of water is the most stable structure, it is clearer at a lower temperature, a higher frequency (Hz) represents that the hexagonal structure of water is the most stable.

Table 1 and Fig. 4 show the results of the half width according to the PEF treatment and by cycle to measure the movement speed. With the temperature fixed at 25℃, the frequency was 52.38 Hz in the ion-exchange water before the pulse electric field treatment, and 55.71 Hz after the treatment, which resulted in a change of 4.2 Hz. The frequency was 62.27 Hz, with the largest change of 9.9 Hz, when the contact time with the pulsed electric field treatment system was 20 cycles (60 min).

3.4. Change in UV–vis

The UV–vis spectrophotometer enables qualitative and quantitative analysis of specimens by applying different wavelengths of lights to the specimens and measuring the degree of their absorbance and transmittance, given that each material has different degrees of absorbance and transmittance of UV rays and visible lights. The analyzed wavelength was measured to be 190–1,100 nm in the scan mode. With the increase in the PEF treatment time, no batho-chromic shift or hypsochromic shift appeared, but the hyperchromic effect, in which the absorbance strength increased, appeared.

Fig. 5(a) shows the results of the change in the UV–vis of tap water according to the PEF treatment time. As the pulsed electric field treatment continued,

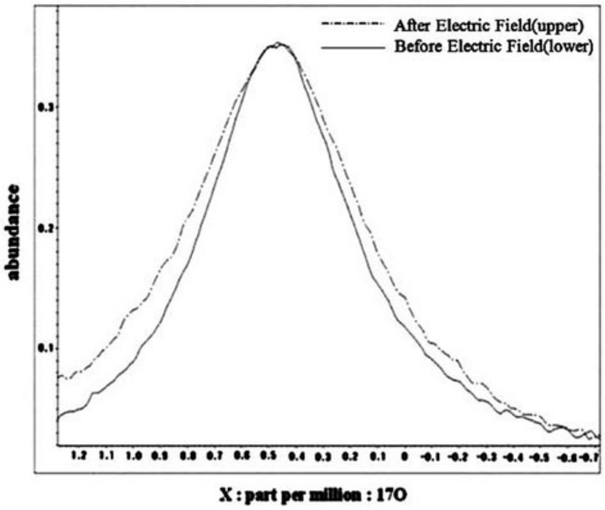

Fig. 4. Change in the half-bandwidth using the NMR device (contact time: 20 cycles).

Table 1
Change in the half width according to the pulsed electric field treatment time

Treatment time (cycle)	0	10	20	40	80	160	320	640
Half-width (Hz)	52.38	55.71	62.27	56.32	56.06	54.89	56.10	54.65

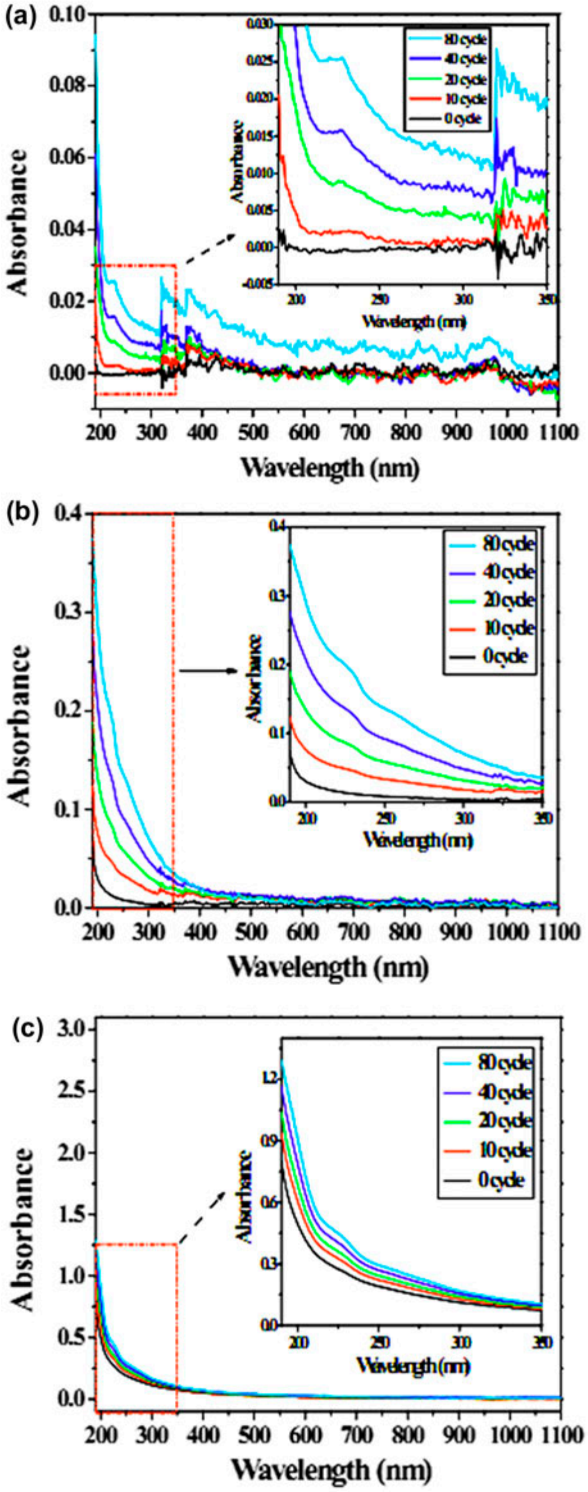

Fig. 5. Change in the UV–vis of (a) tap water, (b) anion surfactant (100 mg/L), and (c) anion surfactant (1,000 mg/L) according to PEF treatment time (contact time: 0–80 cycles).

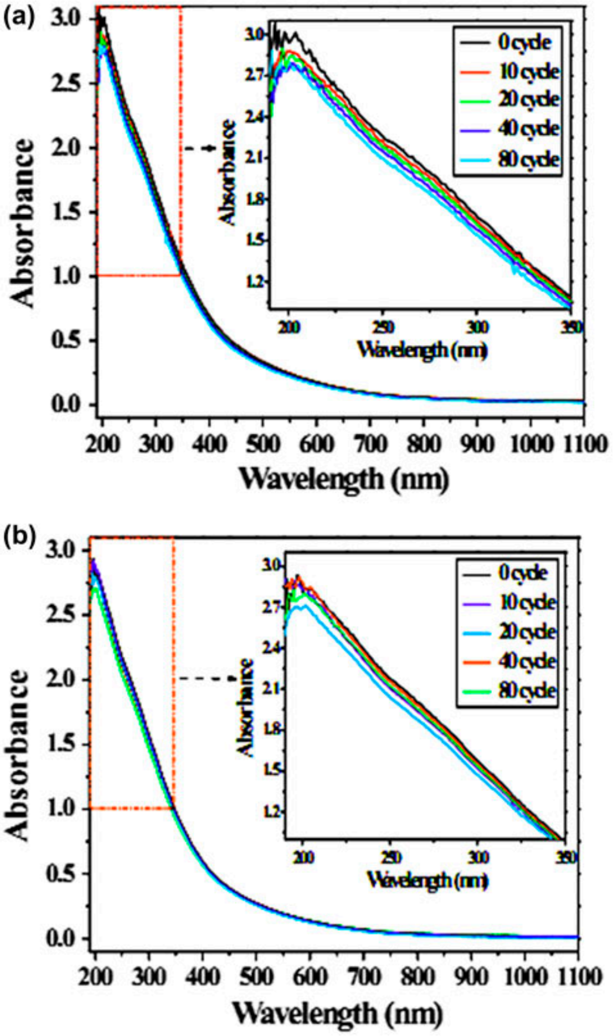

Fig. 6. Change in the UV–vis of humic acid (a) within 1 h and (b) within 7 d after PEF treatment (contact time: 0–80 cycles, concentration: 100 mg/L).

the hyperchromic effect with increased absorbance strength appeared. The hyperchromic effect was not very significant but was noticeable within the UV range. As the PEF treatment continued, the hyperchromic effect with increased absorbance strength also appeared in the surfactant. The trend was similar even when the concentration increased to 100 and 1,000 mg/L (see Fig. 5(b) and (c)).

On the other hand, Fig. 6 and Table 2 show the measured change in the UV–vis of humic acid, which produced a hypochromic effect with the $\lambda_{\max}$ at 198 nm. In addition, the $\pi \rightarrow \pi^*$ transition appeared without a blue shift which indicated that there was no hydrogen bond. Based on the results, the absorption

Table 2
Change in the humic acid concentration according to PEF treatment time

Treatment time (cycle)	No. of measurements	Measured concentration (mg/L)	Average concentration (mg/L)	Removal rate (%)
0	1	96.6	96.5	0
	2	96.3		
	3	96.7		
10	1	94.7	94.9	1.72
	2	95.0		
	3	94.9		
20	1	93.7	93.9	2.73
	2	93.7		
	3	94.2		
40	1	92.8	92.6	4.06
	2	92.6		
	3	92.3		
80	1	90.5	90.6	6.11
	2	90.8		
	3	90.6		
160	1	87.1	87.1	9.75
	2	87.2		
	3	87.1		

coefficient, which quantitatively represented the property of the chromaticity-inducing substance in the humic acid molecule, was measured at 280 nm (see Table 2). After the PEF treatment, the concentration of the humic acid decreased by 9.7% from 96.5 to 87.1 mg/L at 160 cycles. The removal rate was not high, but the PEF treatment has affected the removal efficiency of humic acid.

To examine the duration of the memory phenomenon, the sample was re-tested in the same manner and left at the normal temperature for seven days (Fig. 6(b)). The UV–vis measurement results showed that an increase in the contact time reduced the absorbance and influenced the removal efficiency of the humic acid, although the results were not quantitatively analyzed. In addition, the water that underwent PEF treatment showed a memory phenomenon even after it was left in a normal condition for seven days, which indicated that the PEF treatment caused a permanent change instead of only the reduction of the solution.

4. Conclusions

In this study, the physiochemical effects of PEF treatment system on water, a surfactant, and humic acid were tested.

(1) The increase in PEF treatment time reduced the CMC of the anion surfactant by 1.3%, and the CMC of the cation surfactant by 9.2%.
(2) Based on the results from FT-IR and NMR measurement, PEF treatment produced changes in the C–N composite structure at a 2,200 wavenumber and in the C=O structure at a 1,700 wave number, and the increase in the half-width slowed the water molecule movement speed, which helped the water to maintain the most stable hexagonal structure.
(3) The UV–vis measurement results showed that the tap water and the surfactant had hyperchromic effects, and the humic acid had a hypochromic effect. In addition, the pulsed electric field treatment influenced the humic acid removal rate (9.7%), and the memory phenomenon was maintained even when seven days were passed.

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