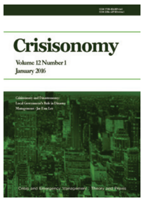

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The Effect of Surface Modified Membrane in the Oil Separation

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Abstract

In this study, the surface modified microfiltration membrane was carried out with flux and electrokinetic measurements in order to reduce the fouling of membrane in the oil separation. The polypropylene membranes were chemically modified for improving flux on the surface with formaldehyde and sodium hydroxide catalysts. The hydrophobic polypropylene membranes changed surface to hydrophillic. The modified membrane showed much higher flux than the original polypropylene membrane. The zeta potentials were varied as the function of pH, ionic strength and concentrations in the presence of surfactants. The zeta potentials of the modified membrane were shifted to more negative values. The higher the negative value of the zeta potential, the higher the membrane permeation rate. The zeta potential results were affected by the increasing SDS concentrations. The SDS may affect the attachment of oil droplets by lowering the interfacial tension.

Key words: polypropylene membrane, oil emulsion, flux, zeta potentials, surface modification

Ⅰ. Introduction

Hazardous wastewater have potential to impact on environmental quality and on human health (Park, *et. al.*, 2016). Oil wastewater is an industrial waste that is inevitably generated along with industrial development. Oil wastewater is non biodegradation. It must not be discharged to the receiving stream due to the adverse effects to the environments. Oil wasterwater forms a foam film on the water surface which also has potential for burning and creating a safety hazard. It also gives toxicity to aquatic life. Also Oil wastewater interfere with municipal wastewater treatment or water purification operation (Wang, *et. al.*, 2015).

Several emerging technologies are currently available for separating oil from wastewater (Hlavacek, 1995). The filtration method is widely used as a treatment technique, which has a simple treatment process, a relatively low energy consumption and a low production of byproducts (Palacios-Jaimes, *et. al.*, 2011). It is a physical separation for removing free oil and emulsified oil and finely dispersed solids from wastestream by

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forcing the water through a membrane under low pressure (Ichikawa, 2007). Microfiltration membranes have been extensively used in various industries such as separation and concentration in various processes, industrial water purification and water treatment, and medical industry (Pihlajamaski, 1994). The biggest problem in the application of microfiltration membrane process is the gradual decrease of permeation flux with the passage of time (Yang, *et. al.*, 2005). The separation process is difficult for continuing to proceed if the fouling is occurred (Yang, *et. al.*, 2005). The hydrophobic membranes are characterized by a flux decline that is caused by fouling due to solute adsorption and pore blocking. In order to reduce the fouling of membranes, various studies(Rana & Matsuura, 2010) have been carried out to study the properties of membranes and to change the physico chemical properties of polymers by introducing functional monomers onto the membrane surface. The zeta potential may be an important tool for identifying the physicochemical properties between oil and membrane interface and reducing fouling phenomena.

The investigation in this paper was to focus the fouling characterization in the oil and membrane interface. In order to improve the permeation flux and improve the separation efficiency, the hydrophobicity of the membrane was chemically reacted to make the surface hydrophilic. The flux and zeta potential measurements were mostly made at different pH, concentration of the oil emulsions, and operating time with original and the surface modified membrane.

II. Materials and Methods

The microfiltration membrane used in this experiment was a disc type manufactured by Amicon of USA and a membrane having a diameter of 43 mm and an effective area of 21.24㎠ was used. The surface modification by HCHO were affected by reaction time, reaction temperature and concentration. The highest permeation flux and removal efficiency were obtained at 80℃ and 30% concentration for 2 hours(Kim, 1997). A variety of oil/water mixtures was prepared with different SDS (sodium dodecyl sulfate) concentrations. Dodecane was selected as oil due to a pure compound. The SDS was supplied by Junsei Chemical Co. The demineralized water was filtered again by a UF membrane prior to the experiments. The KCl was used for adjusting ionic strength. The solution pH was adjusted by adding HCl or NaOH.

A variety of oil/water mixtures are tested with different concentration of oil and surfactants for the flux and zeta potential measurements. The oil emulsion was prepared by an ultrasonic homogenizer for 150 seconds prior to the experiment.

The detailed preparation of membranes for the measurements of fluxes and zeta potentials can be shown in 〈Figure 1〉. 〈Figure 1〉 shows a schematic diagram of the experimental apparatus used in this study.

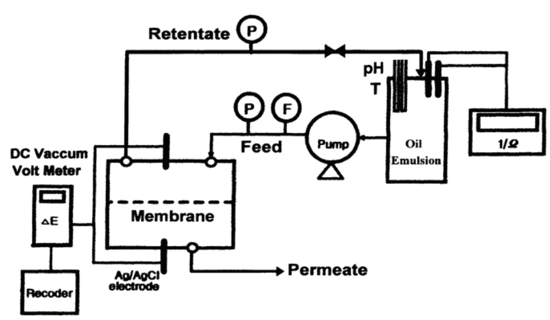

Figure 1. Schematic diagram of the micro filtration apparatus

The modified disc type flux housing consists of membrane module and two Ag/AgCl electrodes. A diagram of the zeta potential in membrane system is shown in 〈Figure 2〉. The flux and zeta potential measurements were performed to evaluate the operating characteristics of the continuous membrane setup.

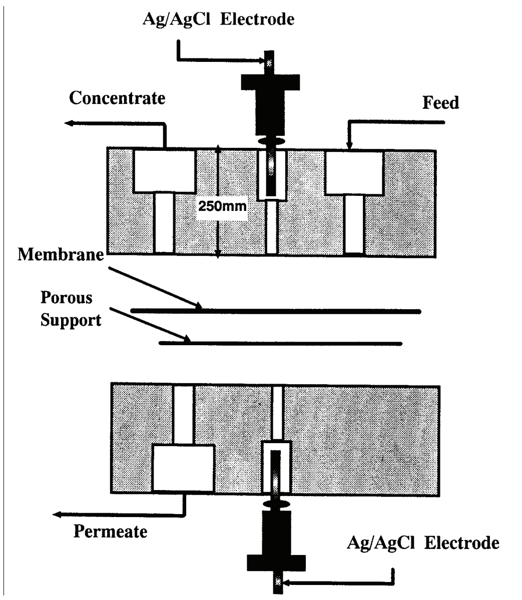

Figure 2. Module for flux and zeta potential measurements

Ⅲ. Results and Discussion

The most important index in the microfiltration membrane process is the flux rate. The optimized condition for surface modified membrane was obtained in the elsewhere (Kim, 1997). The conditions were chemically grafted in the original film at 50° C for 2 hours with 30% HCHO.

〈Figure 3〉 compares the fluxes of surface modified membrane and original membrane as the function of operating time. In this figure, fluxes of both membranes were decreased as the operating time was increased. Fouling occurred as the operating time was increased. The modified membrane showed much more flux than the original membrane. The steep decline for modified membrane can be observed until 50minutes and was reached constant to 100minutes. In contrast, the original membrane was fouling more rapidly. The modified membrane was changed from hydrophobic to hydrophillic. It increases the absorptivity and surface tension of the modified membrane, thereby minimizing the contamination of the membrane.

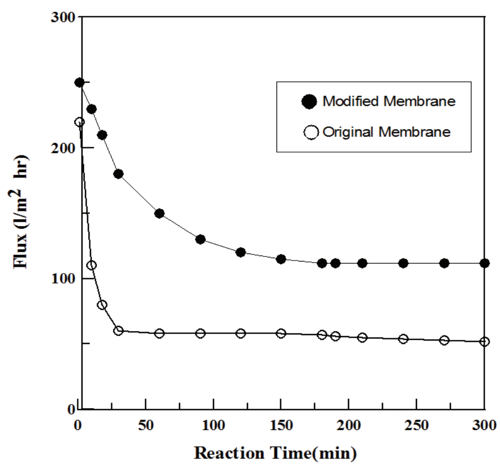

Figure 3. Fluxes of the modified and original membranes in terms of time

〈Figure 4〉 shows flux results in terms of HCHO concentration as a function of time. The membrane modified with 30% HCHO showed the higher than flux compared to membrane modified to 20% HCHO concentration. The HCHO concentration increased to 40% indicated that the fluxes had almost no difference compared to the 30% modified membrane. This may be due to the chemical stability.

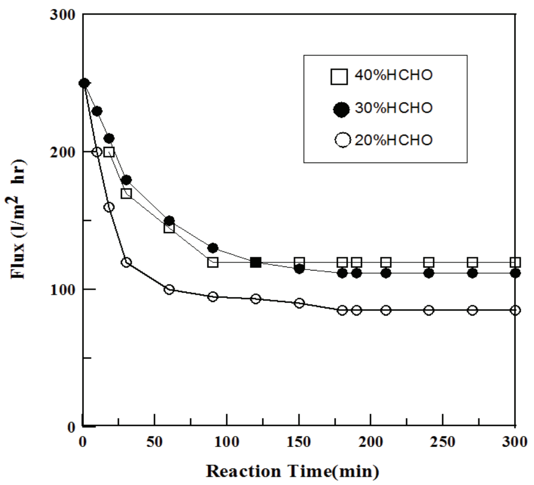

Figure 4. Fluxes of the different concentrations of modified membrane in terms of time

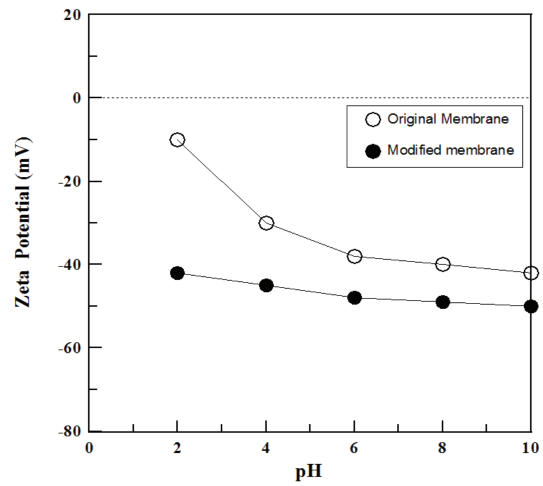

Figure 5. Zeta potentials of the chemically modified membrane as a function of pH

Zeta potentials have been reported to understand not only the electrokinetic properties between the oil and the membrane interface (Ichikawa, 2007). A series of zeta potential measurements was performed to determine the electrokinetic characteristics of the chemically modified membranes. 〈Figure 5〉 shows the zeta potentials of membrane in oil emulsions as a function of pH. The zeta potentials of both original membranes were affected by pH. The zeta potential results were located in the negative ranges. The zeta potentials of original membrane at pH 2 were almost −10mV which indicates the iso electric point(i.e.p) of the membrane was close. When pH of the oil emulsion was raised to 10, the potentials were more negative values to almost -40mV. The zeta potential results of the modified membrane were almost constant over the entire pH. There was no significant difference of zeta potentials of both membranes in the alkaline region above pH 7.

When pretreating with anionic surfactant, SDS, the fouling of membrane was minimized in the treatment of oil solution (Sanchez & Valle, 2001). It gives a strong electrostatic potential on the surface of the membrane, so that it has full electrical repulsion. Initially, membrane flux decreased but overall flux increased. 〈Figure 6〉 showed the results of the zeta potential values for both original and the modified membranes in oil emulsion The zeta potential results were affected by the increasing SDS concentrations. The zeta potential of the

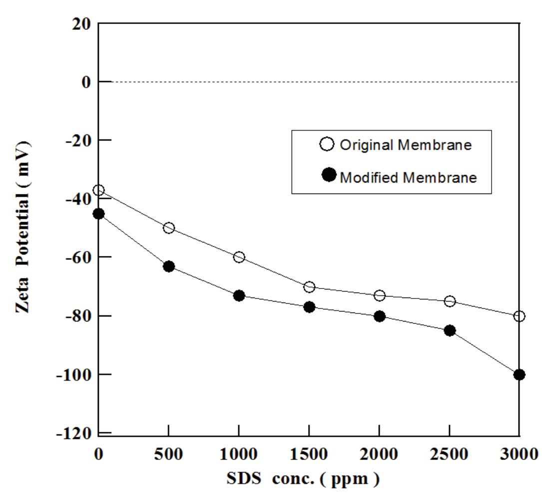

Figure 6. Zeta potentials of the chemically modified membrane as a function of SDS concentration

modified membrane was remained −100mV at 3000ppm SDS concentrations. The SDS may affect the attachment of oil droplets by lowering the interfacial tension which the oil droplets.

The electrostatic interaction between oil droplets, surfactants, and the membrane surface was significant. The both original and the modified membranes had a negative zeta potentials over the SDS concentrations,

The chemical modification of the membrane modifies the surface by introducing several functional groups such as SO_3H, COOH and enzymes(Athens, *et. al.*, 2009). The introduction of a hydrophilic group on the surface of the hydrophobic membrane increases the flux efficiency of the operation. The surface modification by using a plasma gamma ray was reported (Kim & Anthony, 1995; Pihlajamaski & Neda, 1994). The fouled membrane by UV also shift i.e.p to the more positive values. It may be disadvantageous, however, the equipment is expensive and the high energy is required.

Ⅳ. Conclusion

The following conclusions were drawn from this study on the characterization of the separation oily wastes.

1. The polypropylene membranes were modified by formaldehyde and made the surface hydrophilic in order to reduce fouling of flux in the oil wastewater.

2. Both the original membrane and the surface modified membrane showed the fouling phenomena during the flux tests in the separation of oil emulsion. The surface modified hydrophilic membrane had a high selectivity for the oil emulsion separation compared to original membrane. The fluxes surface modified membrane were significantly higher than the original uncoated membrane.

3. The zeta potential measurements were carried out with original and surface modified membrane. Repulsive electrostatic interactions between the negatively charged oil droplets and the membrane, which is also negatively charged, hinder droplet approach and attachment. The zeta potential of the modified membrane was remained −100mV at 3000ppm SDS concentrations. The anionic surfactant may affect the attachment of oil droplets by lowering the interfacial tension which the oil droplets.

감사의 글

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오일분리에 따른 표면 개질 막의 특성

국문초록 본 연구에서는 오일 폐수의 처리과정에서 여과 막의 오염을 최소화하기 위하여 폴리프로필렌 정밀여과 막을 화학적으로 표면개질 하였으며, 이 개질된 막의 성능을 측정하기 위하여 플럭스 실험 및 막의 동 전위를 측정하였다. 파울링을 개선하기 위하여, 폴리프로필렌 정밀여과 막을 화학적으로 개질 하였으며, 표면개질은 포름알데히드 및 수산화나트륨을 촉매로 하여 일정한 pH와 온도 하에서 행 하였다. 표면개질을 통해 소수성 정밀여과 막은 친수성 막으로 변했다. 실험 결과에 따르면 개질된 폴리프로필렌 여과 막은 원래의 여과 막보다 훨씬 높은 투과 flux를 보였다. 표면개질 막의 제타전위 값은 pH가 증가할수록 더욱 음으로 하전되었다. 실험결과 표면개질 막의 제타전위 값은 pH 뿐만 아니라, 이온 강도 및 계면 활성제의 농도에 따라 변하였다. 개질 막의 제타 전위가 음의 값이 높을수록, 막의 투과율도 향상 되었다. SDS 농도가 증가함에 따라 제타전위의 값도 음의 값으로 증가하였다. SDS가 막의 표면장력을 낮춤으로써 오일의 부착에 영향을 주었다.

주제어 : 폴리프로필렌 정밀여과 막, 오일폐수, 플럭스, 제타전위, 표면개질

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