

고분자형 계면활성제가 마이셀 촉진 한외여과법에 의한 1-나프틸 아민의 제거에 미치는 영향

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Effect of Polymeric Surfactant on the Separation of 1-Naphthylamine by Micellar Enhanced Ultrafiltration Membranes

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요 약 : 신규 고분자형 계면활성제(α -allyl- ω -methoxy polyoxyethylene and maleic anhydride block copolymer)를 사용하는 고분자형 마이셀 촉진 한외여과법을 제안하였다. 제거용질로서는 염료의 중간체이며 발암성 물질인 1-나프틸 아민을 사용하였다. 고분자형 마이셀의 촉진효과는 중공사형 폴리아크리로나이트릴 막(분획 분자량 6,000, 표면적 0.017m^2)을 사용하여 조사하였다. 플럭스의 선형의존성은 $0.6\text{kg}/\text{cm}^2$ 까지 유지되었고, 점차 압력증가에 따라 플럭스 증가율은 감소하였다. 고분자형 마이셀을 첨가하지 않은 상태에서의 제거율은 2mM의 용질에 대하여 0.19, 2wt.%의 고분자를 첨가한 상태에서의 제거율은 0.96이었다. 고분자형 마이셀 내부로의 가용화가 분리효율을 5배 촉진시킨 것을 확인하였다.

Abstract : Polymeric micellar enhanced ultrafiltration method using a new type of polymer, α -allyl- ω -methoxy polyoxyethylene and maleic anhydride copolymer (AKM-0531, Mw 15,000), has been proposed to separate 1-naphthylamine as a weak cationic toxic organic solubilizate. Enhancement effect of polymeric micelle was identified by the ultrafiltration runs using polyacrylonitrile(PAN) hollow fiber membrane with molecular weight cut off 6,000. The linear dependance of flux on the pressure difference is shown to be valid up to $0.6\text{kg}/\text{cm}^2$ and the rate of flux increase in response to change in the pressure is gradually reduced under the pressure difference. Rejection of 0.96 was observed for 2 mM of 1-naphthylamine with 2 wt.% polymer solution at the conditions of $0.4\text{kg}/\text{cm}^2$, natural pH, and 25°C . Solubilization of 1-naphthylamine into the polymeric micelle enhanced the separation efficiency.

1. Introduction

Researches have been made to find the effective ways to remove the trace contaminants such as dye stuff, phenol, polycyclic aromatic hydrocarbons and polychlorinated biphenyls from waste stream and contaminated sources. Pollution of the industrial waste, nations harbors, waterways, and ground water resources with these contaminants poses many serious environmental, health and economic problems owing to urban runoffs, waste disposal methods, and industrial and domestic effluents.[1-3] The awareness of these problems has focused attention on the need identifying the effective and energy efficient means for removing the toxic substances from waste water resources and industrial effluent.

Even though many methods have been developed to remove organic pollutants, including supercritical wet oxidation, ozonation, irradiation with UV light, and incineration, these methods are economically feasible only if they are applied to moderately concentrated solution. However the concentration of harmful organics in the water is in the ppm range. That is why new technologies for the concentration of trace organics in the aqueous stream are widely studied.

Micellar enhanced ultrafiltration (MEUF) method has been investigated since 1985.[4-7] MEUF is capable of removing dissolved organics and heavy metals in the ppm range from waste water with significantly less energy consumption than traditional process, and without introducing substantial toxicity from residual colloid and surfactants. Additionally, the final solutions produced are so concentrated that in many cases waste will be converted into new product streams because down stream process water often does not require further treatment. Also, MEUF can be used for the recycling of the value added materials included in the waste water or down stream.

MEUF, however, have some problems. Added colloids may leak and go through the membrane unless it is associated to micelle under the critical micelle concentration (cmc). It might make new pollution and should be separated again from the

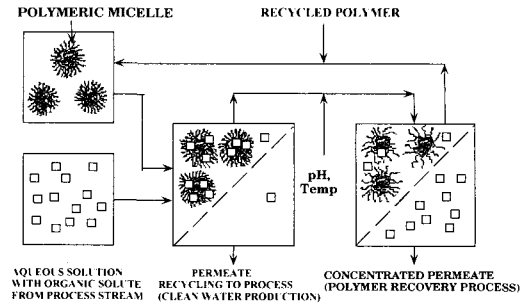


Fig. 1. Conceptual diagram of polymeric micellar enhanced ultrafiltration.

product stream if it could not reach safe level in concentration. Our group try to solve these problems. We proposed two methods. One is the application of biosurfactant from microbial origin which is mild and safe, and showed good biodegradability so that it does not make additional pollution problems.[9] It has peculiar and functional structure which has not been seen yet in the surfactants from chemically synthetic origin.[8-16, 20, 29] The other is the use of polymeric micelle which does not go through the membrane if it is unassociated as shown in Fig.1. In here, we will just mention the process using polymeric micelle. [17-19, 21-28]

One of the MEUF, polymeric micellar enhanced ultrafiltration (PMEUF) method using α -allyl- ω -methoxy polyoxyethylene and maleic acid copolymer (AKM-0531, Mw 15,000), which contains both nonionic and anionic surface active moieties, has been proposed to enhance the separation of 1-naphthylamine. 1-Naphthylamine was selected as a model solubilize of weak cationic toxic organic because 2-naphthylamine is well known as carcinogenic material and 1-naphthylamine is being used as the intermediate of the dye stuff. In the previous research, equilibrium dialysis have been applied to examine the adsorption and solubilization characteristics of the 1-naphthylamine toward the polymeric micelle.[18-19, 22-23] It was considered that 1-naphthylamine is solubilized into the polymeric micelle and stabilized because of not only the electrostatic attraction but also the shielding characteristics of polymer. From the

result of dialysis and short-cut ultrafiltration, 99% rejection of 1-naphthylamine was observed. In the present study, substantial effect of polymeric micelle on the rejection of 1-naphthylamine was investigated to develop a polymeric MEUF process.

2. Experimentals

2.1. Materials & Analysis

α -Allyl- ω -methoxy polyoxyethylene and maleic acid copolymer (AKM-0531, Mw 15,000) was selected as a polymeric micelle and 1-naphthylamine as a solubilize. AKM-0531 was obtained from kawasaki lab. of Japan Oil & Fats Co., Ltd. 1-Naphthylamine was purchased from Wako chemicals Co., Ltd. and used without any further purification. Molecular weight cut off (MWCO) 6,000 polyacrylonitrile (PAN) hollow fiber membrane (effective membrane surface area is 0.017 m²) from the Asahi Glass was used. Polymer and 1-naphthylamine were analyzed with UV spectrophotometer (Shimadzu UV-3500) at 234 and 310 nm, respectively.

2.2. Ultrafiltration Runs

AKM-0531 was pre-ultrafiltered in order to remove the molecules with low molecular weight. Pretreatment minimized the loss of AKM-0531 through the membrane. Prior to treatment of the AKM-0531, loss of polymers through the membrane was approximately 0.1-3.5 % of the feed. After treatment, AKM-0531 loss was reduced to 1 ppm. The continuous ultrafiltration system is composed of feed solution tank, pump, and hollow fiber membrane. As recommended by the manufacturer, ultrafiltration was carried out under pressure difference below 1.0 kg/cm², which was the critical operation pressure for the hollow fiber membrane. Transmembrane pressure difference was controlled by the back pressure valve. Flux measurements for the distilled water and the polymeric solution were carried out from low to high pressure difference and from low to high concentration. All measurements and samplings were delayed for 1 hour until the steady state was achieved. The observed rejection R_{obs} is defined by $R_{obs}=1-C_p/C_f$, where C_p and C_f are the concentration in the permeate and feed, respectively.

3. Results And Discussion

The change of the permeate fluxes was monitored as a function of time. As shown in Fig. 2, permeate fluxes in PMEUF were kept constant except those of the fluxes under the pressure difference 0.6 kg/cm². Decrease of flux with time in that condition indicates the formation of gel layer on the surface of the membrane.

Permeate fluxes of the distilled water and polymeric solutions were measured as the transmembrane pressure across the membrane was increased from 0 to 1.0 kg/cm² with the increment of 0.2 kg/cm². The feed solutions were composed of 1-naphthylamine and polymers at a fixed concentration ratio. We adopted five different polymer solutions to examine the effect of solute concentration. The fluxes are plotted in Fig. 3 for the membrane with MWCO of 6,000.

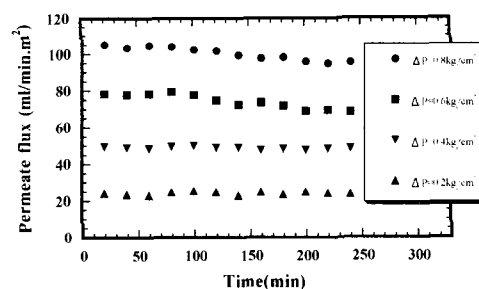


Fig. 2. Permeate flux of polymer solution (2 wt.% polymer and 2 mM 1-naphthylamine) as a function of time.

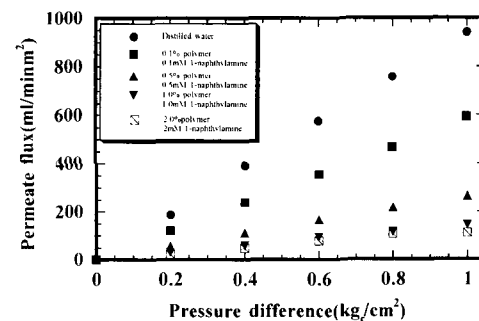


Fig. 3. Permeate flux as a function of the pressure difference across a MWCO 6,000 polyacrylonitrile membrane.

As expected, the flux of pure water increased in proportion to the pressure difference. For polymeric solutions, on the other hand, the linear dependence of flux on the pressure difference is shown to be valid only in the small pressure difference limit and the rate of increase of the flux in response to change in the pressure difference is gradually reduced in the region of large pressure difference. It is also noteworthy that the flux of the polymeric solutions exhibits a strong dependence on the feed.

As the feed concentration increases, the total permeate flux decreases. This can be simply explained by the fact that the formation of gel layer or plugging by the high concentration of the surfactant and solute adjacent to the membrane surface.

The minimum concentration of polymer that is necessary to attain a desired separation is important to the economics of the process. In Fig. 4, the rejection of 1-naphthylamine is plotted as a function of the initial concentration of AKM-0531 to 2 mM 1-naphthylamine for a membrane with MWCO 6,000. Increasing the polymer concentration causes a decrease in the permeate 1-naphthylamine concentration.

As noted from Fig. 4, the rejection of 1-naphthylamine was rapidly increased up to 0.68, as the polymer concentration reaches 0.5 wt.%. Beyond that concentration, the rate of increase in the rejection of 1-naphthylamine is gradually reduced. One effect that may occur at low polymer concentrations (near 0.2 wt.%) in the retentate is that a substantial fraction of the polymer can be present as unassociated instead of in micellar form. Observed rejection coefficient 0.96 was achieved for 2 mM 1-naphthylamine and 2 % polymer solution at 0.4 kg/cm^2 , natural pH, and $25 \text{ }^\circ\text{C}$. In comparison with the rejection coefficient 0.19 of blank system (without polymer addition), 5 times enhancement effect was observed. Solubilization of 1-naphthylamine into the polymeric micelle enhanced separation efficiency. Enhancement effect of polymeric surfactant was proved substantially in actual filtration runs.

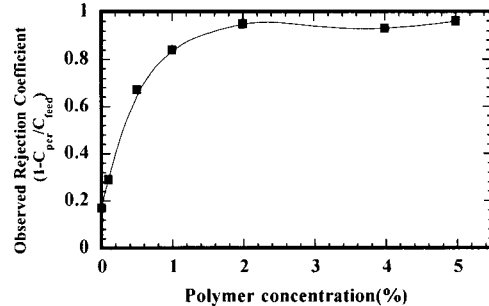


Fig. 4. Effect of initial polymer concentration on the rejection of 2mM 1-naphthylamine at 4 kg/cm^2 and natural pH.

4. Conclusion

Polymeric MEUF has been suggested. 1-Naphthylamine was rejected up to 96 % when 2 wt.% polymer and 2 mM 1-naphthylamine was used at $25 \text{ }^\circ\text{C}$. 5 Times enhancement effect of polymeric surfactant was achieved. Substantial effect of polymeric MEUF was proved.

Literature Cited

1. P. Alexandridis, J. F. Holzwarth, and T. A. Hatton, *Macromolecules*, **27**, 2417~2425 (1994).
2. P. Alexandridis, V. Athanassiou, S. Fukuda and T. A. Hatton, *Langmuir*, **10**, 2604~2612 (1994).
3. P. N. Hunter, and T. A. Hatton, *Langmuir*, **8**, 1291~1299 (1992).
4. J. F. Scamehorn, and S. D. Christian, "Surfactant Based Separation Process", Marcel Dekker, Inc., New York and Basel, U.S.A., pp. 3~51 (1989).
5. J. F. Scamehorn, and S. D. Christian, E. E. Tucker, and B. I. Tan, *Colloids Surf.*, **49**, 259~267 (1990).
6. M. Tuncay, S. D. Christian, E. E. Tucker, R. W. Taylor, and J. F. Scamehorn, *Langmuir*, **10**, 4688~4692 (1994).
7. M. Tuncay, S. D. Christian, E. E. Tucker, R. W. Taylor, and J. F. Scamehorn, *Langmuir*, **10**, 4693~4697 (1994).

8. Y. K. Choi, C. H. Lee, and Y. Ishigami, *Chem. Ind. and Tech. in Korea*, **11**, 1(37) (1994).
9. Y. K. Choi, C. H. Lee, Y. Takizawa, Y. Gama, and Y. Ishigami, *J. Jpn. Oil Chem. Soc. (YUKAGAKU)*, **42**, 2(95) (1993).
10. Y. Ishigami, Y. Gama, F. Ishi, and Y. K. Choi, *Langmuir*, **9**, 7(1634) (1993).
11. J. J. Hong, S. M. Yang, Y. K. Choi, and C. H. Lee, *J. of Colloids and Interface Science*, **173**, 92~103 (1995).
12. Y. Ishigami, F. Ishi, Y. K. Choi, and T. Kajiuchi, *Colloids and Surfaces B*, **7**, 215~220 (1996).
13. J. J. Hong, Y. K. Choi, T. Kajiuchi, C. H. Lee, and S. M. Yang, "Biosurfactant-Based Ultra-filtration of Heavy Metals from Aqueous Stream", *Colloids and Surfaces* (in preparation).
14. K. J. Hong, Y. K. Choi, T. Kajiuchi, and Y. Ishigami, "Effect of Ascin Biosurfactant on Removal of Cd and Pb", *JAACS* (J. of American Oil Chemists Society) (submitted).
15. Y. K. Choi, C. H. Lee, and S. H. Yuk, *The Ministry of Patents in Korea*, Registered Number 116724 (1997).
16. Y. Ishigami, T. Tokunaga, T. Kajiuchi, K. J. Hong, and Y. K. Choi, *The Ministry of Patents in Japan*, (pending, No. 96536, 1997).
17. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, *世界韓民族科學技術者綜合學術大會論文集*, 2896-2902 (1996. 8).
18. Y. K. Choi, O. Tomita, T. Kajiuchi, and Y. Ishigami, *Proceedings of the 60th Annual Meeting of the Chemical Engineering Society of Japan*, N.306 (p. 172), 1995. 3.
19. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, *Proceedings of the 29th Autumn Annual Meeting of the Chemical Engineering Society of Japan*, E115, p. 83 (1995).
20. Y. K. Choi, Y. Ishigami and T. Kajiuchi, *Proceedings of the 9th Annual Meeting of the Korean Scientist and Engineers Association in Japan (KSEAJ)*, PD-04 and PD-09 pp. 88~89 and pp. 98~99 (1995).
21. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, *Proceeding of the International Workshop on Chemical Safety Research (Chemical Reaction and Environmental Effect, IWCSR'96)*, Tsukuba, Japan, pp. 102~103 (1996).
22. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, "Solubilization Characteristics of 1-naphthylamine into the Polymeric Micelle and Concept of its Application", *J. Chem. Eng. Jpn.* (submitted).
23. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, *AIChE/Preprints Volume for 5th World Congress of Chemical Engineering (Advanced Fundamentals-Separation, technologies critical to changing world)*, 4s (1996).
24. Y. K. Choi, and T. Kajiuchi, "Evidence of Hydrophobic and Electrostatic Effects of Polymeric Micelle on the Solubilization of Weak Cationic Organics", *Colloids and Surfaces* (in preparation).
25. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, "Polymeric Micellar Enhanced Separation of 1-naphthol with PEO-PPO-PEO block Copolymer", *J. of Membrane Sci.* (in preparation).
26. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, *Proceedings of the 61th Annual Meeting of Chemical Engineering Society of Japan* J114, p. 165 (1996).
27. K. J. Hong, Y. K. Choi, T. Kajiuchi, S. Tokunaga, and Y. Ishigami, *Proceedings of the 35th Annual Meeting of Japan Oil Chemists Society* (2B20) (1996).
28. Y. K. Choi, Y. Ishigami, and T. Kajiuchi, *Proceedings of the 4th Korea-Japan Symposium on Separation Technology*, ME114 (P1097-1101) (1996).
29. K. J. Hong, Y. K. Choi, and T. Kajiuchi, "Removal of Heavy Metals from Soil by a Biosurfactant", *Proceedings of the 62th Annual Meeting of Chemical Engineering Society of Japan*, B103 (24p) (1997. 3).