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Ultrasound-membrane hybrid processes for enhancement of filtration properties

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Abstract

Enhancing permeation in microfiltration (MF) hollow fiber membrane process was studied under ultrasound (US) by means of reflection technique. The US effect on the enhanced membrane process depended on the position of membrane module with or without a semi-cylindrical shaped reflection plate placed behind the membrane module. Evidence was presented that the membrane process influenced the detected sonic pressure distribution in the US bath. The correlation of sound pressure intensity and luminol fluorescence intensity suggested that violent collapse of cavity bubbles supported the enhanced membrane permeability of MF module in the US bath.
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Keywords: Ultrasonic membrane cleaning; Reflection; Sonoluminescence; Sonic pressure

1. Introduction

Ultrasound (US) has been interested to chemists as a processing aid in a wide variety of industrial application for chemical processing of filtration, precipitation and crystallization, atomization, and electroplating, etc. For accelerating these events, it has been known that US promotes both physical and chemical processes. As well known, in chemical processing US influences chemical reactivity in order to enhance the formation of radical species through the cavitation effects [1,2]. Such multi-bubble phenomenon generates the violent collapse of cavitation bubbles physically in acoustical liquid. Therefore, in the fields of organic synthesis, polymer chemistry, and catalytic preparation, US has been applied as an interesting technique. Among them, membrane separation processes have focused the uses of US in order to enhance permeability of solvent and permeate through membrane. In 1995, Li et al. applied US technique to enhance electrolyte diffusion through dialysis membranes [3,4]. The diffusion rate of an electrolyte through membrane was significant as US was operated. In recent work for membrane technology, US process has been focused in cleaning the membrane surface and reduce fouling [5–7]. Membrane fouling is characterized by the significant decline of the permeate flux, since the flux decline is due to plugging and adsorption of rejected macro-molecules solute in micro-pores of membrane surface. Therefore, such fouling is very serious problem in filtration process [8,9]. Relative to the membrane cleaning techniques by hydraulic, mechanical, and chemical methods, US cleaning is impressed to remove fouling condition and highly recover the declined permeate flux in membrane treatment [10]. In these processes, for instance, the US manner causes breakage of the strong interaction between foulant and the membrane within short operation time. In order to reduce the fouling behavior of polysulfone and polyacrylonitrile membrane processes, Chai et al. overcame the problems by use of US operation [7] in ultrafiltration

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(UF) and microfiltration (MF). The US effects at frequencies of 28 kHz, 45 kHz and 100 kHz were well studied to decrease fouling [6,11]. It was found that permeated rates of solute solution were effectively increased, when 28 kHz frequency was applied [10]. More recently, Li et al. reported practical application of US for cleaning of nylon MF membrane fouled by paper mill effluent [12]. Muthukumaran et al. also indicated the importance of cleaning parameters effect such as pH, surfactant concentration on ultrasonic cleaning of the fouled membranes [13]. However, still few evidence is only known concerning about the US effect on the decline of fouling condition. We would like to emphasize that more attractive approach is needed in order to be clear the interesting phenomenon of US in membrane processes. For one of such approach, the power of ultrasound was controlled near the fouled membrane by means of reflection technique [14]. In the preliminary work, we introduced different shaped reflection plates in the MF membrane process and led to high enhancement of the resultant permeation rate in the process. However, we only reported US effect on enhancement of membrane permeability without details evaluation of US condition.

In the present study, US effect of membrane cleaning was investigated in detail, when both of sonic pressure and sonoluminescence correlated with the enhancement of membrane process. Cleaning the polyethylene hollow fiber membrane fouled by aqueous milk solution was carried out under the US with 28 kHz frequency. As concentrated the US onto vicinity of fouled membrane by placing semi-cylindrically shaped reflection plate, the US effect on the membrane process was discussed on the basis characterization of sonic pressure distribution in the US bath. We also considered results of sonoluminescence, which is caused by collapse of cavitation bubbles for the enhanced permeability of the membrane process [15–17].

2. Experiments

2.1. Materials and instruments

Polyethylene (PE) hollow fiber MF membrane used in this experiment was the product of Mitsubishi Rayon. The membrane module contained a bundle of 240 numbers of PE MF fibers having 0.8 mm diameter and 8 cm in length and the bundle of the fiber made 6 cm module in the width. The total surface area of the membrane was 0.05 m^2 and average pore size of the MF membrane module was 0.4 μm diameter. For membrane filtration process, 1 wt% aqueous milk solution was used as an effluent solution. Filtration process was done in a stainless steel US bath (20 length × 20 width × 25 height cm^3) for 8 l of milk solution, which contained 1 wt% of solid content. The side wall of the US bath had seven numbers of piezo electric ultrasonic transducers having 3 cm diameter, which were connected with ultrasonic multi-cleaner having 300 W output for emission of 28 kHz frequency ultrasound (WN-600-NWS, Honda Electronics Co., Ltd). The US intensity in the US bath was estimated by using immersion transducer probe (Panametrics V301) that was connected to the pulse receiver (Model 5058PR). The received US intensity (mV) was displayed as a function of time on oscilloscope.

When the filtration was carried out, the aqueous milk solution was circularly pumped by Model XXX80 (Millipore Company) with 54 ml/min feed rate and 60 kPa in the US bath. The performance of the filtration of the membrane module was evaluated by volume flow of the solution through the membrane [8]. The permeation rate was defined as the volume flowing through the membrane per unit area and time. Using a volume flow meter (OVALM-III, OVAL), the permeated volume was measured. Then, the resultant flow rate of permeate solution was converted to volume flux (m^3/m^2s).

2.2. Experimental procedure of hybrid ultrasound-membrane system

Filtration process was carried out in the absence and presence of US field. The schematic flow diagram of hybrid US membrane process is shown in Fig. 1. The PE module was immersed in the 8 l volume of milk solution with 1 wt% concentration. We examined the effect of ultrasonic cleaning on the volume flux of the MF membrane as followed; firstly, milk solution was pumped through MF membrane to foul it in the absence of US for 30 min. In the filtration of the milk solution, the permeate solution was recycled to the feed tank, as

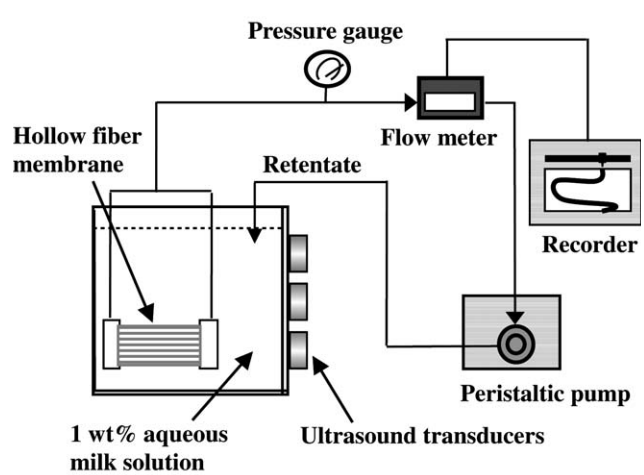

Fig. 1. Schematic flow diagram for permeation of 1 wt% aqueous milk solution through MF hollow fiber membrane under ultrasound irradiation.

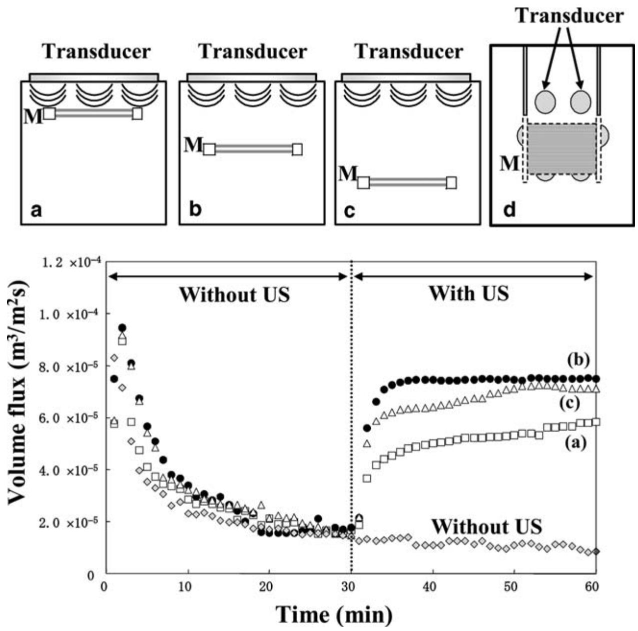

Fig. 2. Volume flux changes of 1 wt% aqueous milk solution at various filtration times. The MF membrane was positioned at (a) 4 cm, (b) 8 cm and (c) 12 cm distance from US transducers. The top views of US bath with different membrane position are shown in the inserted figures. Also the side view for all experiments was illustrated in (d) as the membrane was set at 15 cm depth from water surface level. M: membrane.

indicated by retentate in the figure. After fouling, cleaning the fouled membrane was done by the continuous milk permeation under US irradiation with 28 kHz frequency for additional 30 min. The cleaning operation was carried out at different positions of the membrane in the US bath, i.e., milk filtration processes were done by placing the membrane at 4 cm, 8 cm and 12 cm distance from transducers.

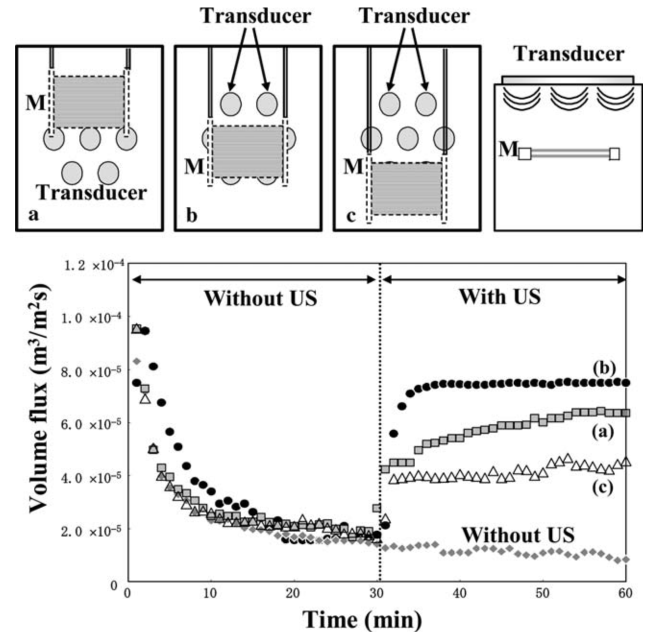

Fig. 4. Volume flux changes of 1 wt% aqueous milk solution at various filtration times. The MF membrane was positioned at 8 cm distance from US transducers in each depth of (a) 7 cm, (b) 15 cm and (c) 19 cm from water surface level in the US bath. The inserted figure (d) expressed the top view of US bath for all experiments. M: membrane.

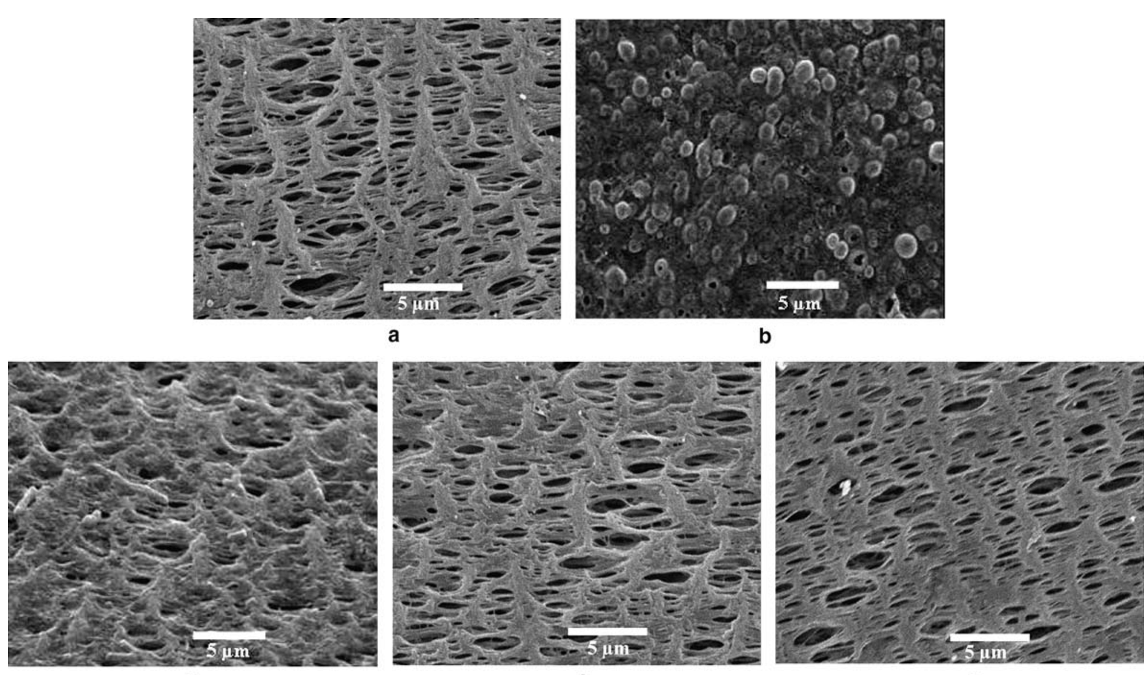

Fig. 3. SEM photographs of PE hollow fiber membrane surface for (a) new membrane, (b) fouled membrane, (c) cleaned membrane under US irradiation at 4 cm, (d) at 8 cm, and (e) at 12 cm distance from transducers.

Furthermore, to concentrate US intensity on the membrane module, a semi-cylindrical reflection plate ($15 \times 20\ cm^2$) with 12.5 cm diameter was placed at 6 cm behind the membrane module. Then, pressure distribution in the US bath was measured by detecting the sound intensity emitted from transducers at different points. The immersion transducer probe was set at the different positions in US bath in order to view the mapping of the sound pressure intensity.

For morphology of the fouled membrane and US treated membranes, scanning electron micrographs (SEM) were taken with JSM-5310 LVB scanning microscope. The wet samples of the membranes were dried under vacuum condition for 6 h. Then, gold sputter on

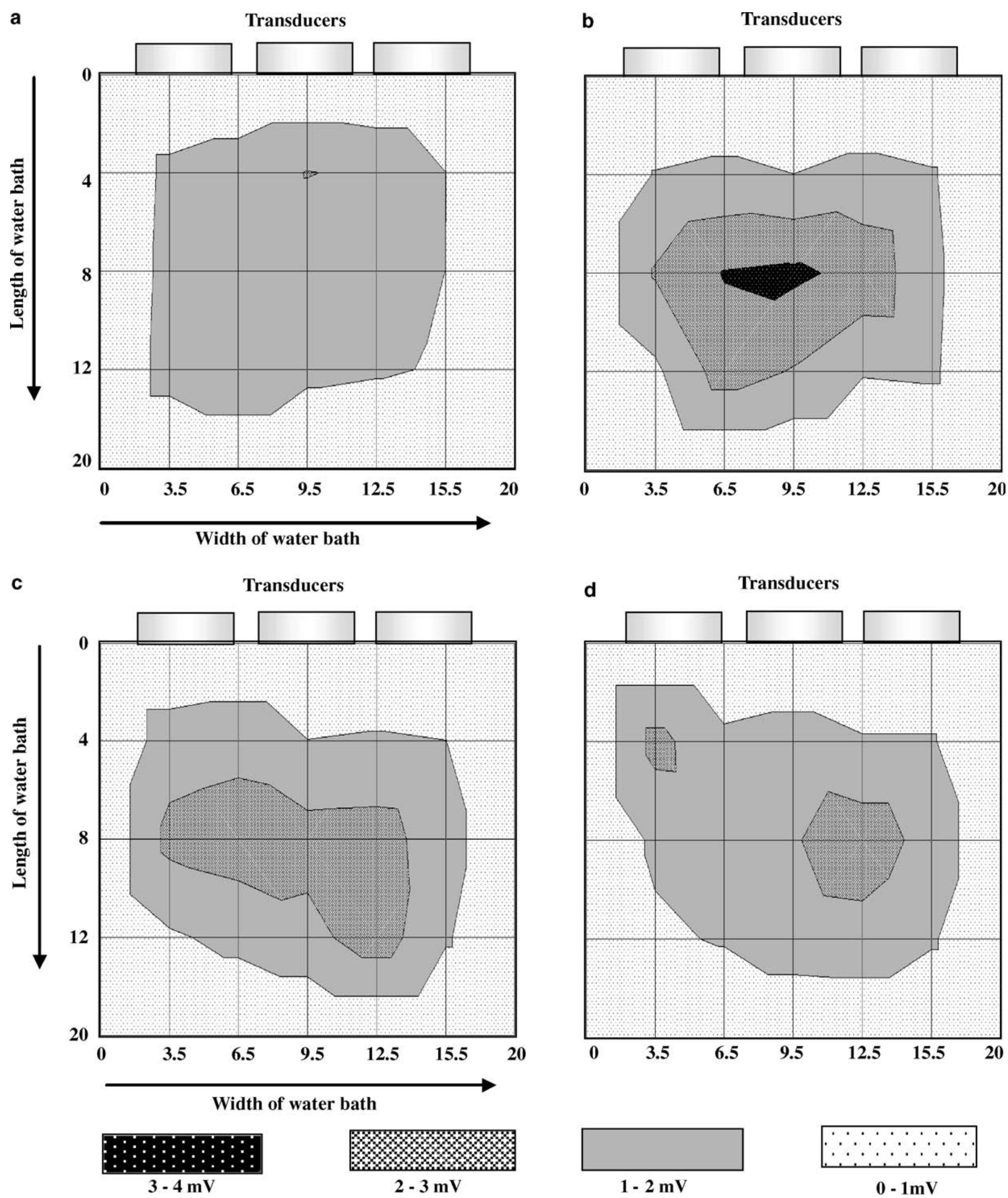

Fig. 5. Pressure distribution for top view of the US bath under US irradiation. The detection was performed at the depth of (a) 6 cm, (b) 12 cm, (c) 15 cm and (d) 21 cm from water surface level in the US bath.

the sample membranes was carried out using SPM-112 (Anelva) sputter gun.

Sonoluminescence of luminol was also evaluated to confirm the improvement of cavitation by reflection technique. In the present study, using 0.23 mM of luminol solution, sonoluminescence image was observed photographically by taking pictures of the surface of the US bath. The luminol solution was prepared by distilled water of 8 l with 0.04 g (0.23 mM) of luminol containing 4.0 g (0.04 M) of Na_2CO_3 to be pH 10. In the dark room, the luminol luminescence pictures of US bath were taken with 5–8 min exposure time for the cases of with and without reflection plate behind the membrane module.

3. Results and discussion

3.1. Effect of US irradiation on the MF membrane performance

When the MF membrane filtrated 1 wt% milk solution, the volume flux was measured in the absence and presence of US operation. Fig. 2 shows changes of the volume flux on various filtration time in membrane filtration process. As illustrated by the inserted figures, the membrane module was placed at different three membrane positions from US transducers namely, (a) 4 cm, (b) 8 cm and (c) 12 cm were on the distance with 15 cm depth from the water surface level of the US bath. Herein, the depth was to center of the membrane module having 8 cm length and 6 cm width size as presented by the right side illustration. For first 30 min, only filtration was carried out without US for all experimental sets. During this period, the value of volume flux was declined from about 8×10^{-5} m^3/m^{2}s to about 1.8×10^{-5} m^3/m^{2}s. Then, we operated the ultrasonic cleaner for additional 30 min. Under the 28 kHz US operation, it was observed that the value of volume flux increased to 5.8×10^{-5} m^3/m^{2}s for (a), 7.5×10^{-5} m^3/m^{2}s for (b) and 7.1×10^{-5} m^3/m^{2}s for (c) within few minutes. As noticed, the US irradiation was more effective on the recovery of the volume flux at the 8 cm distance.

To investigate membrane morphology operated at different positions in the US bath, SEM pictures of the membrane surface before (a) and after (b) the 30 min fouling were measured (Fig. 3). It was clear that (b) surface was completely covered with milk layer. Pictures (c), (d) and (e) present the cleaned membranes by US irradiation at 4 cm, 8 cm and 12 cm, respectively. It was observed that the porous surface of the MF membrane treated at 8 cm appeared during the 30 min operation. In the 4 cm distance, only some larger pores were present and others are still remained as blocked by the fouled milk. Although most of milk particles were removed from the surface of treated membrane at 12 cm (e), some are still remained on the surface. These results

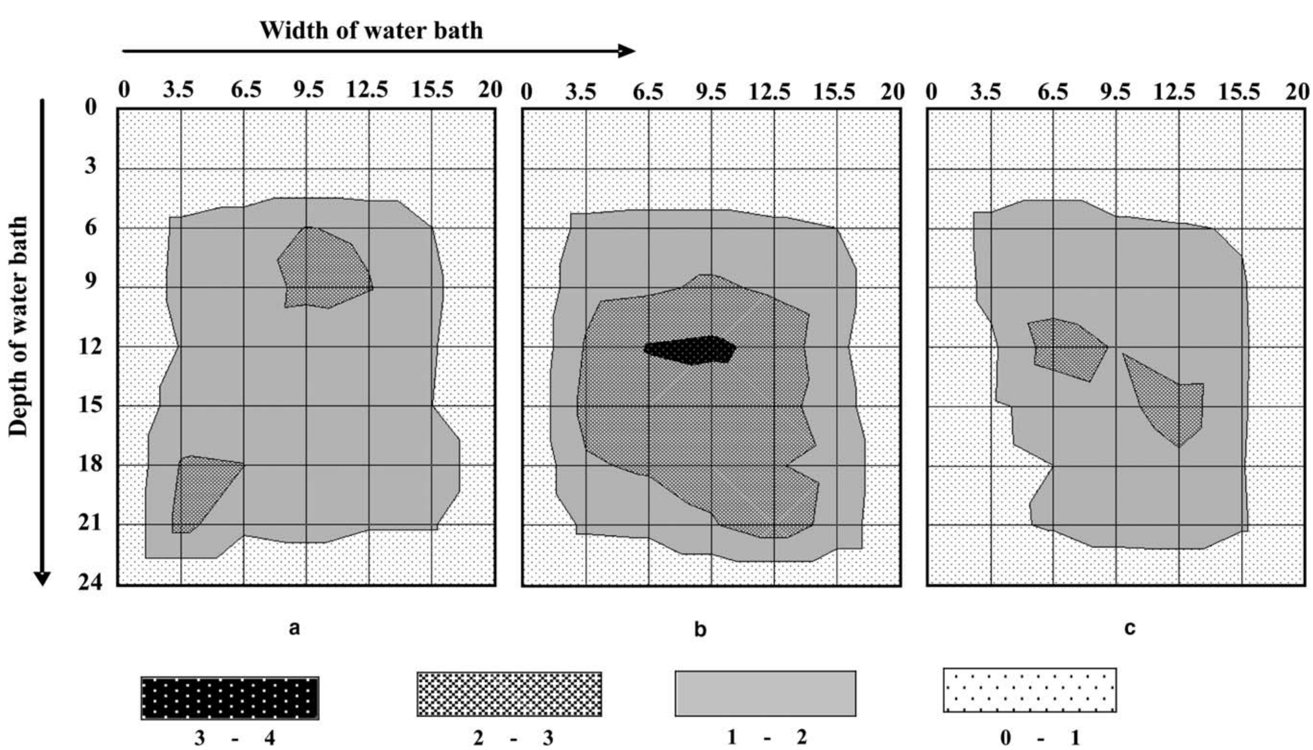

Fig. 6. Pressure distribution for side view of the US bath under US irradiation at position area of (a) 4 cm, (b) 8 cm and (c) 12 cm from US transducers.

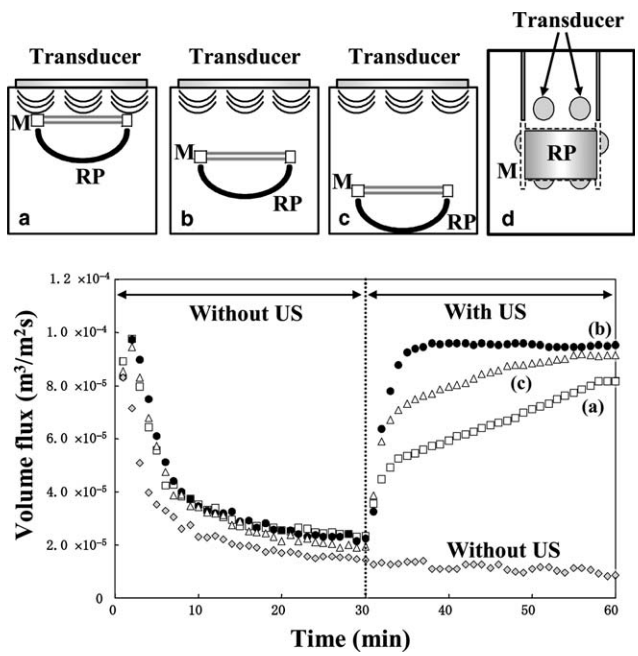

Fig. 7. Volume flux changes of 1 wt% aqueous milk solution measured with rounded shaped reflection plate. The MF membrane was positioned at (a) 4 cm, (b) 8 cm and (c) 12 cm distance from US transducers. The top views of US bath with different membrane position are shown in the inserted figures. Also the side view for all experiments was illustrated in (d), as both of membrane module and reflection plate were set at 15 cm depth from water surface level. M: membrane; RP: reflection plate.

of morphology suggested that the US irradiation was effective at the 8 cm distance for the membrane cleaning.

Because the fouled condition was successfully cleaned at 8 cm distance with 15 cm depth, we also changed the depth position of membrane module as illustrated in Fig. 4 (a) 7 cm and (c) 19 cm. Relative to 15 cm depth (b) from water surface level, the value of volume flux operated at 7 cm depth became low. In the (a) configuration, the value of volume flux was about $6.4 \times 10^{-5}\ m^3/m^2s$ in about 24 min under the US field. For the 19 cm depth of (c), the values of volume flux were no more recovered than $4.0 \times 10^{-5}\ m^3/m^2s$. These comparisons indicated that there was optimum position of the membrane module in the US bath.

In order to clearly understand such position effect of the membrane module on the US cleaning, sound pressure distribution was measured. We moved the immersion transducer probe at each 3 cm distance from left side to right side in the US bath. Fig. 5 shows resultant pressure distribution measured at each depth of (a) 6 cm, (b) 12 cm, (c) 15 cm and (d) 21 cm from water surface level of the bath. Herein, the intensity of the detected sonic pressure intensity was expressed by electrical current I (mV). In the time profile intensity of wave form observed with 28 kHz frequency, the values were grouped as 0–1 mV, 1–2 mV, 2–3 mV and 3–4 mV.

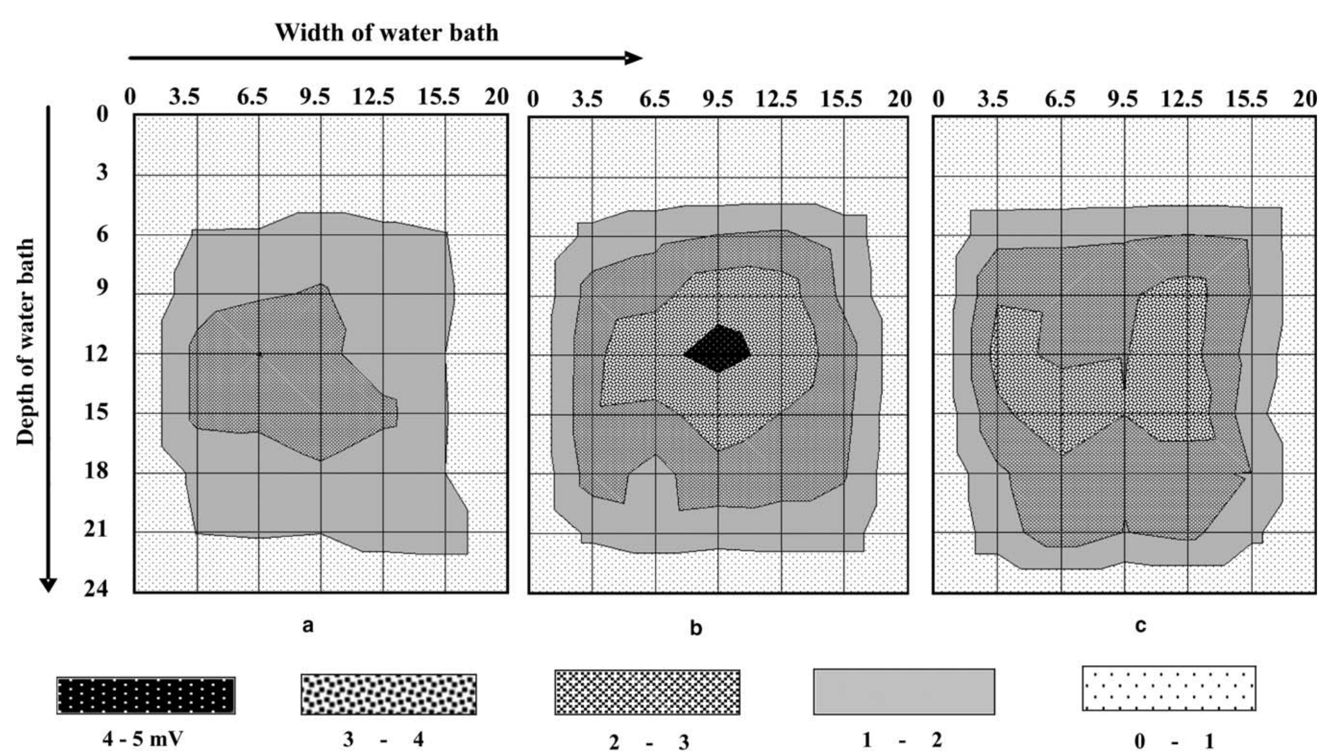

Fig. 8. Pressure distribution for side view of the US bath for the semi-cylindrical reflection plate system. The reflection plate was positioned at (a) 4 cm, (b) 8 cm and (c) 12 cm from US transducers.

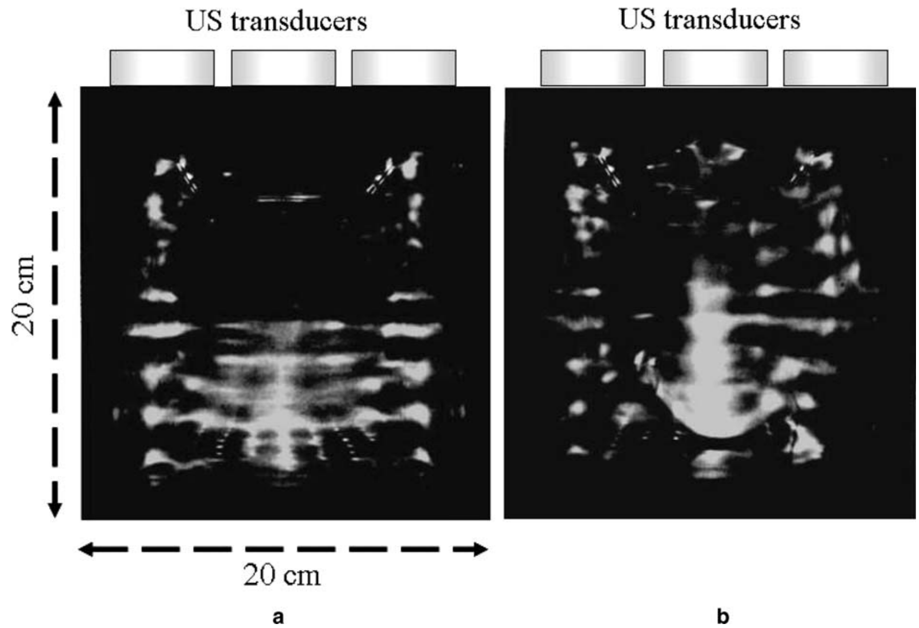

Fig. 9. Luminol luminescence observed from top view of US bath containing 0.23 mM luminol solution at pH 10. The pictures of (a) and (b) are measured without and with rounded reflection plate, respectively.

In Fig. 5(a) for the 6 cm depth, the range of maximum intensity was almost equivalent to 1–2 mV in the center of the US bath. In cases of (c) 15 cm and (d) 21 cm, the observed maximum intensity was in the range of 2–3 mV. But, this comparison indicated that the sonic pressure intensity near the center of the former was stronger than that of the latter. When the intensity was detected at (b) 12 cm depth, the 3–4 mV area was distributed at the center of the US bath. Similar monitoring of the sound pressure intensity was also shown as side view of the US bath. Fig. 6 presents the US intensity mapped at (a) 4 cm, (b) 8 cm and (c) 12 cm from the US transducers. It was noted at (b) 8 cm distance that the US intensity was high in the center of the sonic bath relative to other (a) and (c). Based on these results of Figs. 5 and 6, it is reasonable that the enhanced recovery of volume flux was significant in the area of high US intensity.

3.2. Enhanced membrane treatments under reflection US field

As preliminary reported [14], the membrane filtration properties were highly enhanced by use of reflection plates. Only comparison of shape of the reflection plates was made without systematic examination while these experiments indicated that semi-cylindrical shaped reflection plate was effective. Therefore, detail experiments were carried out by using a semi-cylindrical shape placed behind the membrane module at different distance. As illustrated in Fig. 7, the inserted figures (a), (b) and (c) are for top views of the membrane position in US bath with 4 cm, 8 cm and 12 cm distance from US transducers, respectively. The right side figure is illustration of depth view of the US bath containing both the module and the reflection plate at 15 cm depth. In these experiments, the similar filtration and US treatment were conducted for 1 wt% of milk solution.

As shown in the plots of the figure, the resultant values of the volume flux of the MF membrane were measured at 60 min operation as $8.2 \times 10^{-5}\ m^3/m^2s$, $9.5 \times 10^{-5}\ m^3/m^2s$ and $9.2 \times 10^{-5}\ m^3/m^2s$ for (a), (b) and (c), respectively. Especially in the 8 cm case, the volume flux of $9.5 \times 10^{-5}\ m^3/m^2s$ was reached within approximately 5 min. On the other hand, other two cases showed that the US effect was gradually happened within 35–57 min. Therefore, when the reflection plate was placed behind the membrane, the enhanced permeability was remarkable.

Fig. 8 shows perpendicular description of the US intensity distribution when the reflection plate was at (a) 4 cm, (b) 8 cm and (c) 12 cm distance from the US transducers. Based on these resultants, the intense strength area with 4–5 mV was detected at the center potion of the 8 cm position in the US bath. In order to be clear the evidence of the focused US intensity at the center portion of US bath, we tried to take overview photographs of luminol luminescence. Fig. 9 shows the resultant pictures of US bath, which contained the luminol solution without (a) and with (b) the reflection plate. Evidently, both lightened and darkened patterns are observed in the pictures. The picture (a) represents that luminescence pattern of luminol without reflection plate was distributed behind the membrane module located at the center of US bath. The pattern of the standing wave observed in the range of about 10–18 cm regions behind

the module with about 2.5 cm interval. In the presence of semi-cylindrical plate (b), the concentrated US intensity onto the membrane module was observed in the center of the US bath. Relative to the resultant US intensity distribution of Fig. 8(b), the picture view of the luminol suggested that the intense portion of the luminescence reached to the behind of the membrane module from the inside center of the semi-cylindrical plate. As a result, in the filtration process with the semi-cylindrical plate system, the increase of the volume flux was due to the sonic pressure around the membrane module. In addition, it is very interesting to note that the intense luminescence area focused in the behind potion of the US bath. This strongly suggested that US cavitation effect was more strongly appeared in the behind region. Namely, the small cavity bubbles were generated by high sound intensity in this portion. This was also one of reasons for the enhanced US effect on the membrane process.

4. Conclusion

In ultrasound-membrane system, 28 kHz US frequency was irradiated onto the MF membrane module to successfully remove the milk fouling layer from membrane surface. The resultant US effect of the membrane process obviously corrected with the US intensity, which was intense by the reflection plate. Namely, the concentrated sonic power on the vicinity of the behind membrane module prohibited the fouled condition. It was found that generated violence collapse of the cavitation bubbles caused intense luminol luminescence, especially for the position between the module and reflection plate.

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References

[1] T.J. Mason, Sonochemistry: The Uses of Ultrasound in Chemistry, The Royal Society of Chemistry, 1990, p. 132.
[2] S. Leeman, P.W. Vaughan (Eds.), Cavitation PhenomenaG.J. Price (Ed.), Current Trends in Sonochemistry, The Royal Society of Chemistry, Thomas Graham House, Science Park, Cambridge CB4 4WF, 1992, p. 26.
[3] H. Li, E. Ohdaria, M. Ide, Jpn. J. Appl. Phys. 34 (5B) (1995) 2725.
[4] H. Li, E. Ohdaria, M. Ide, Jpn. J. Appl. Phys. 35 (5B) (1996) 3255.
[5] X. Chai, T. Kobayashi, N. Fujii, J. Membr. Sci. 148 (1998) 129.
[6] X. Chai, T. Kobayashi, N. Fujii, Sep. Purif. Tech. 17 (1999) 31.
[7] X. Chai, T. Kobayashi, N. Fujii, Sep. Purif. Tech. 15 (1999) 139.
[8] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, 1996, p. 154.
[9] R.D. Noble, S.A. Stern, Membrane Separation Technology Principles and Applications, Elsevier, Amsterdam, 1995, p. 70.
[10] T. Kobayashi, T. Kobayashi, N. Fujii, Jpn. J. Appl. Phys. 39 (2000) 2980.
[11] T. Kobayashi, T. Kobayashi, Y. Hosaka, N. Fujii, Ultrasonics 41 (2003) 185.
[12] J. Li, R.D. Sanderson, E.P. Jacobs, J. Membr. Sci. 205 (2002) 247.
[13] S. Muthukumaran, S. Kentih, S. Lalchandani, M. Ashokkumar, R. Mawson, G.W. Steven, F. Grieser, Ultrasonics Sonochem. 12 (2005) 29.
[14] T. Kobayashi, Y. Hosaka, Jpn. J. Appl. Phys. 42 (2003) 2954.
[15] M.C. Smythe, R.J. Wakeman, Ultrasonics 38 (2000) 657.
[16] T. Tuziuti, S. Hatanaka, K. Yasui, T. Kozuka, H. Mitome, Ultrasonics 40 (2002) 651.
[17] H.N. McMurray, B.P. Wilson, J. Phys. Chem. A 103 (1999) 3955.