Research Paper

Effect of Ultrasonication on the Membrane Structure and Flux Recovery for the Whey Ultrafiltration

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Abstract

In this study, the effect of ultrasound irradiation on the flux recovery and fouling mitigation for the membranes made of the polysulfone by the phase inversion method were investigated. Two ultrasound irradiation regimes, including inside and outside the module, were chosen for this study. The experiments were conducted to investigate the effect of ultrasound irradiation on the membrane structure and cleaning. The ultrasound was irradiated in the frequency of 20 kHz and at the intensity of 25.5-127.4 W/cm². When the membranes were irradiated directly out of the module, they may be damaged and the large holes were formed due to remaining in direct acoustic cavitation area. The flux recovery for the whey ultrafiltration process was increased with the increase of the irradiation time and the ultrasound intensity. The released energy which is the result of the cavitation threshold of bubbles indirectly may clean the foulant. During 60 min ultrasound irradiation, the flux recoveries were between 83-91% for membranes. At the probe distance of 1 cm from the module and after 20 min, the destruction or cracks in the membrane may be happened. The FE-SEM showed that the adjacent holes were connected and the crack was formed. The results for using the ultrasound for cleaning the fouled membranes showed that in the long distances, a large number of cavitation bubbles collapses before they reach to the membrane and in short distance, due to higher energy density, the produced acoustic and turbulence stream are increased and the membrane may be damaged.

1. Introduction

One of the main problems of the membrane filtration technology in the industry is the early fouling of polymeric membranes by deposition of organic and inorganic compounds on the surfaces or inside the pores of the membrane. The foulant compounds may be protein, mineral, microorganism, fat and suspended solid. This phenomenon is occurred in three steps. The first step is the concentration polarization (the concentration gradient of the accumulated compounds close to the membrane surface) and easily can be removed by water washing. By increasing the concentration and density of the deposited particles on the membrane surface, the second stage of fouling is occurred. At the third stage, by increasing the strength of the deposited...
particles, the flux decline continues with a very low flow rate [1].

Fouling phenomenon causes the flux decline leading to an increase in production cost due to increased energy demand, chemical cleaning, membrane lifetime reduction and additional labor for the maintenance. Fouling is affected by several reasons including [2]:

- Membrane properties (surface roughness, pore size distribution, thickness and charge of membrane)
- Feed properties (the concentration, the size, geometry and the charge of the solute, the solution and its interaction with membranes)
- The operation condition and the process environment (flowrate, hydrodynamics and pressure)

Membrane pretreatment including coagulation, filtration and sedimentation can mitigate the fouling. Chemical and biological methods use materials that may be more expensive or affect the membrane structure. Cleaning by chemical detergents may damage the membrane, which threatens the health of consumers arising from the remaining detergent in the product. The detergents consumption pollutes the environment and increases the product costs [3]. The used phosphates in detergents provide nutrients for marine plants, resulting in algae growth which they use the oxygen in the water, leading to a direct impact on the quality of local lakes and water supply. Nonylphenol ethoxylates and sodium perborate as the main constituent materials are toxic to marine life and pollutes the environment.

Several methods have been proposed for cleaning membranes via physical methods so far [4]. Ultrasound (US) waves, as a modern physical method, have great cleansing effects on the chemical solutions. When the ultrasonic wave passes through the solution, almost 20,000 microscopic bubbles per second are produced and then disappeared [5]. As a result of this phenomenon, local pressure about 680 atm and the high heat is produced. The local high pressure and heat produced clean the pores and surface of the membrane [6].

Recently, Qasim and co-workers [7] reviewed the use of ultrasound for enhancement of membrane flux and cleaning. They discussed the mechanisms of membrane fouling, theories related to ultrasonic waves, acoustic cavitation, cavitational collapse, and ultrasonic cavitation in improvements. Reuter and co-workers [8] constructed a laboratory filtration plant for drinking water treatment to study the conditions for ultrasound application for fouled polymeric membranes. They found that the short cleaning cycle including backwashing (the application of ultrasound and air flushing) could remove the cake layer from the membranes. Choi and co-workers [9] studied the effect of the ultrasound frequency and output power on the internal concentration polarization (ICP) coefficient in a flat-sheet forward osmosis (FO) membrane for NaCl rejection and proposed a modified solution-diffusion model based on film theory. Kobayashi and co-workers [10] used the ultrasound to remove the fouling of peptone ultrafiltration (UF) and milk solutions microfiltration (MF). They found that at 28 kHz frequency, cleaning is effective for the flux recovery. Lee and co-workers [11] used the ultrasound to improve the forward osmosis (FO) sludge dewatering process and control the fouling caused by organic aggregates flowing through the pores of the FO membranes. They reported that the application of continuous ultrasonic irradiation, unexpectedly serves the fouling due to the growth of organic aggregates and spreading them through the membrane pores. They combined the ultrasound and flushing and found that the flux recovery was reached to 70 %. Borea and co-workers [12] investigate the effect of two different membrane fluxes (75 and 150 L/m²h) and two different US frequencies (35 and 130 kHz) on treatment of municipal wastewater and fouling control in the UF process. Their results showed that the combination of UF with the US reduced the fouling rates especially at the higher flux and lower US frequency. Chanukya and Rastogi [13] investigated the effect of ultrasound on concentration polarization during forward osmosis concentration of different molecular weight compounds (sucrose and pectin). They found that application of ultrasound (30 kHz) significantly reduced the concentration polarization for sucrose concentration whereas, in case of pectin, the ultrasound was not able to effect on dislodging the gel layer formation and external concentration polarization. Yu and co-workers [14] considered the potential advantages of applying intermittent ultrasound for a long term UF operation (3 min/10 min every 3 days) to control membrane fouling. Their results showed that, compared to a control UF process, intermittent ultrasound reduces fouling with a 50% reduction in transmembrane pressure over 60 days of operation. Luján-Facundo and co-workers [15] investigated the effect of US on the membrane cleaning efficiency for four UF membranes with different molecular weight cut-offs (MWCOs) and materials (polyethersulfone and ceramics). Their membranes fouled with three different solutions (BSA, BSA + CaCl₂ and Renylat 45) using two membrane modules (flat sheet and tubular). Their results demonstrated that membrane cleaning with the US was effective and this effectiveness increased at the low frequencies. In another work [16], they studied the UF process in an integrated filtration and membrane cleaning. They carry out membrane cleaning experiments with and without US using Renylat whey protein concentrate solutions and CaCl₂ addition for increasing membrane fouling. Cleaning efficiency results demonstrated that ultrasounds application is an effective technique to clean UF membranes.

Cai and co-workers [17] studied the impacts of ultrasonic frequencies, power and irradiation mode on the flux and the resistance in the UF process. Their results showed that the ultrasonic irradiation had a strong effect on the UF process particularly in low-frequency and high output power. The intermittent irradiation was not important to increase the flux. Luján-Facundo and co-workers [18] studied the chemical cleaning with NaOH solution at different pHs and temperatures, and the impacts of repeated ultrasound at cleaning stage on the fouled membranes by the BSA. Their findings revealed that pH and temperature were not important factors in improvement of the flux. The ultrasound as an effective method had a significant impact on the efficiency of the process. Hashemi Shahraki and co-workers [19] investigated the flat membrane inside the cross-flow UF system with irradiation under different frequencies (37 kHz, 80 kHz) in the various modes of ultrasound (continuous and consecutive pulses). Their findings showed that the permeated flux increased with decrease in the ultrasonic frequency. Among used modes of irradiation, the continuous pulse mode had the greatest impact on increasing the permeated flux and decreasing the fouling percentage.

In this work, membrane samples were prepared by the polysulfone polymer. This polymer is the most widely used in manufacturing polymeric membranes for water and wastewater treatment [20-25] due to its excellent mechanical strength, chemical stability, film forming nature and thermal resistance. The novelty of this research with earlier works related to the US is that in this work, the membranes were prepared by the phase inversion method. The ultrasonic waves were used inside and outside the cell for the flux recovery and fouling reduction. The employed cell was the dead-end filtration and the feed was the whey and used as the fouling agent.

2. Materials and method

2.1. Materials

Polysolefonic (PS) (Mₙ = 35,000 g/mol) and polyvinylpyrrolidone (PVP) (Mₙ= 25,000 g/mol) were supplied from Merck (Germany). N-methylpyrrolidone (NMP) with the purity > 99.5% was purchased from DAEJUNG Company (Korea). The whey solution (including protein, fat, lactose and minerals with pH ~7) was obtained from Manizan Dairy Industries, Kermanshah, Iran.

2.2. Membrane preparation

The membrane was prepared by the phase inversion using the PS with different contents in the NMP as the solvent. PVP polymer (1 wt.%) was added to the solution as the pore former [26,27]. The solution was mixed at room temperature for 24 h. The composition of casting solution is shown in Table 1. This solution was cast on a clean glass plate by the film applicator. The prepared film was immersed in water basin as the non-solvent at 15±2 °C. By exchanging the solvent with the non-solvent the porous membrane was prepared. This membrane was peeled off from the glass plate. The prepared membrane was immersed in water bath for one day and finally, it was partially dried at room temperature for 24 h.

2.3. Ultrasonic system

The ultrasound system UP400S, made of Hielscher Company, Germany was used. The frequency of ultrasound was set at 20 kHz and its power could change from 80 to 400 W (with corresponding intensity of 25.5 to 127.4 W/cm²). The probe tip was circular with the diameter of 2 cm.

2.4. Microscopic images

The effect of ultrasound on the membrane surface was analyzed by field emission scanning electron microscope (FE-SEM), provided by TSCAN company (Czech). Before scanning, the membrane samples were washed, dried and broken in liquid nitrogen and sputtered by layer of gold.

2.5. Experimental set up

The experimental setup for measuring the flux is shown in Figure 1. The membrane was sandwiched between two cell plates. The cell was dead-end. During the experiment, the cell content stirred by the rate of 400 rpm to reduce the concentration polarization. The cell was cylinder shape with inside diameter of 4 cm and the capacity of 125 mL. The effective filtration area of the membrane was 12.56 cm². A tank was used and connected to the cell to measure the flux more precisely for a longer time. Nitrogen was used to push the feed and provide the pressure.

In all experiments, the membrane samples were immersed in the deionized water for 30 min before applying in the cell. At beginning, the feed pressure was set in 4 bar for 30 min and then it was fixed in 3 bar. The pure water flux (PWF) (kg/m²h) was measured using the following formula:

$$ J = \frac{W}{A t} $$

where, $W$ is the permeate (kg); $A$ is the membrane area (m²) and $t$ is the operating time (h). For each experiment, an unused membrane was used.

2.6. Physical properties

The thickness of membrane samples was measured by digital micrometer (MDC-25SB, China). The thickness was measured at different points of membrane samples and the average has been reported.

The porosity ($\varepsilon$) was calculated by measuring the dry and wet membranes weight. The membrane is first soaked in distilled water for 24 h. After removing the surface water, the wet weight ($w_{\text{wet}}$) was measured. Then, the membrane was dried at 50 °C for 2 h in vacuum oven and immediately, the dry membrane ($w_{\text{dry}}$) was measured. The porosity was calculated by following formula [28]:

$$ \varepsilon = \frac{W_{\text{wet}} - W_{\text{dry}}}{\rho_w A \delta} $$

where, $\rho_w$ (kg/m³), $A$ (m²), $\delta$ (m) are water density, membrane surface and the membrane thickness, respectively.

The mean radius pore of membrane ($r_m$) was calculated using the following formula [28]:

$$ r_m = \sqrt{\frac{2.9 - 1.75 \varepsilon \times 8 \eta Q}{\varepsilon \times A \times \Delta P}} $$

where, $\eta$, $Q$ and $\Delta P$ are water viscosity (Pa s), water volume flux (m³/s) and pressure drop (Pa) across the membrane, respectively.

2.7. Ultrasound irradiation regimes

Two irradiation regimes were chosen for this study: inside and outside the module. At outside the module, the membranes were fixed in a beaker full of distilled water. At inside the module, the cell turned upside down and immersed in water bath. After being fixed in the bathroom, the ultrasonic probe was used in constant frequency of 24 kHz (with different intensity) and at a distance of 2 cm from the bottom of the cell surface.

The experiments were conducted to investigate the effect of ultrasound irradiation on the membrane structure and cleaning. For investigation of the effect of ultrasound irradiation on the membrane structure, the clean membrane was used outside the module. The membrane samples were irradiated every 5 min at 24 kHz and the intensity of 63.7 W/cm² and the PWF was measured. By comparing PWF for the irradiated membrane samples with initial (without irradiation) flux, the effect of ultrasound potency on the membrane structure was studied. Furthermore, the surface structure of the irradiated membrane was observed by the FE-SEM micrograph.

For investigation of the ultrasound effect for membrane cleaning, firstly, the whey feed was passed through the membrane for 90 min. After this time, the flux rate reduced to less than 1 mL/min and the membrane was fully fouled. The fouled membrane brought out from the cell and then the deposited whey on its surface was washed by distilled water. After ultrasound irradiation, the PWF was measured. Again, by comparing the PWF amount, the effect of the ultrasound waves on the membrane cleaning and flux recovery was investigated. The flux recovery (FR, %) was measured by the following formula:

$$ FR (\%) = \frac{J_{\text{final}} - J_{\text{init}}}{J_{\text{init}}} \times 100 $$

where, $J_{\text{init}}$ and $J_{\text{final}}$ are the initial pure water flux at clean state and the final water flux after cleaning the fouled membrane by the US, respectively. If the FR is greater than 100%, it means that the US could cause the destruction in the membrane. The steady transmission flux was determined three times and the average value was considered.

3. Results and discussions

3.1. Physical properties and PWF

Table 1 shows the physical properties and the PWF for the prepared membranes. As it illustrated in Table 1, by increasing the polymer content, the thickness is increased but the porosity and mean pore radius are decreased. The reason is that, when the polymer content is increased, the viscosity of casting solution is increased and as a result, it leads to the delay in solvent and non-solvent and prevents the formation of large radius pores [5]. Table 1 also shows that by increasing the polysulfone content, the porosity of prepared membranes has been decreased. On the other hand, the PWF is inversely proportional to the polymer content. Therefore, $M_i$ and $M_f$ have been shown the maximum and minimum flux, respectively.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PS (wt. %)</th>
<th>PVP (wt. %)</th>
<th>NMP (wt. %)</th>
<th>thickness (μm)</th>
<th>$\varepsilon$</th>
<th>$r_m$ (nm)</th>
<th>PWF @ P = 3 bar (kg/m²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_i$</td>
<td>12</td>
<td>1</td>
<td>87</td>
<td>134</td>
<td>67.3</td>
<td>6.6</td>
<td>38.7</td>
</tr>
<tr>
<td>$M_f$</td>
<td>15</td>
<td>1</td>
<td>84</td>
<td>145</td>
<td>65.7</td>
<td>5.5</td>
<td>24.3</td>
</tr>
<tr>
<td>$M_1$</td>
<td>18</td>
<td>1</td>
<td>81</td>
<td>155</td>
<td>61.5</td>
<td>4.6</td>
<td>16.4</td>
</tr>
<tr>
<td>$M_2$</td>
<td>20</td>
<td>1</td>
<td>79</td>
<td>160</td>
<td>59.5</td>
<td>4.1</td>
<td>9.2</td>
</tr>
</tbody>
</table>

3.2. Effect of irradiation on the membrane structure

Figure 2 illustrates the changes of PWF with the irradiation time for the clean membranes out of the module. As this figure shows by increasing the irradiation time, the flux increased more vigorously. This behavior was true for membranes with different polysulfone content. Also, it can be inferred that after 20 min of irradiation, the flux of membranes has got more than its initial value. This result shows that the membrane may be damaged due to the
ultrasonic irradiation and the pores of membrane surface may become larger. It can be illustrated that the adjacent pores may be connected to each other and lead to large cracks and dehiscence in the membrane [29]. Shock waves or the micro jet caused by collapsing bubbles are the reason of surface damage [30]. So, when membranes are irradiated directly out of the module, due to remaining in the area of acoustic cavitations, the membrane was damaged and the large holes may be formed.

For micrograph analysis and in order to observe the effect of the ultrasound on the membrane, the FE-SEM was taken after ultrasound irradiation. Figure 3a-d shows the FE-SEM from the surface of M1 membrane (thickness of 134 μm) after 10 min ultrasound irradiation with the distance from the probe to the module of 1 cm and the intensity of 63.7 W/cm². After irradiation, as seen in Figure 3a-b, the adjacent holes were connected and the crack was formed. In some place (Figure 3c), the large cracks can be seen. The applied pressure during the permeability could enlarge the created cracks (Figure 3d) and develop the defect.

Generally, in a short distance, the ultrasonic waves create micro-cracks in the surface, and with increasing the intensity, the created micro-cracks can be converted to large cracks.

Figure 4 shows the PWF for different membranes at clean state inside the module versus operating pressures with and without ultrasound. The ultrasound frequency, the power and the time were 20 kHz, 200 W and 20 min, respectively. The distance between the ultrasonic probe and the module was 2 cm. The results indicate that the flux for the dead-end filtration for all membranes with and without ultrasonic irradiation is the same. Therefore, based on this figure, at the distance of 2 cm from the probe to the membrane (inside the module), the ultrasonic irradiation does not affect the membrane structure and this distance was selected for the next experiment.

![Image](image1.png)

**Fig. 2.** Changing the PWF versus the irradiation time for clean membranes irradiated outside the module (The membrane samples were irradiated every 5 min at 24 kHz and the intensity of 63.7 W/cm² and then the PWF was measured at P= 3 bar and T= 15±2 °C).

![Image](image2.png)

**Fig. 3.** FE-SEM micrograph of M1 membrane surface after 10 min ultrasonic irradiation inside the module (probe distance=1 cm; intensity=63.7 W/cm²).
3.3. Effect of irradiation time on water flux for fouled membrane

Figure 5 shows the changes of the water flux with ultrasonic irradiation time for the fouled membranes during 60 min irradiation. The diagrams indicate that the flux for all membranes with different polysulfone content under the influence of ultrasonic irradiation has been improved. The flux recovery was increased with the increase of the irradiation time. The released energy which is the result of cavitation threshold of bubbles may clean the foulant. The bursting bubbles collapse the whey parts attached to the surface and pores of the membrane. The flux recovery and membrane cleaning is significantly high due to the use of ultrasound in the frequency of 24 kHz [31]. The flux recoveries have been 83, 85, 89 and 91% for M1, M2, M3, and M4, respectively during 60 min ultrasound irradiation. This result indicates that by increasing the polysulfone content, the porosity and membrane mean radius have been decreased and the fouling pore blocking mechanisms may change from standard to complete, intermediate and cake filtration [32]. As a result, the flux recoveries have been increased from M1 to M4.

3.4. Effect of ultrasound intensity

The ultrasound intensity is the power per unit of transform area. The intensity has been calculated from the ultrasound input power and probe area (because of more than 95% of ultrasound waves emitted from this area) [33]. In order to study the intensity effect on the flux recovery, four different intensities including 31.8, 63.7, 95.5 and 127.24 W/cm² were selected under the same conditions (ultrasound time=40 min and membrane operating P=3 bar; T=15±2 °C). The results are presented in Figure 6. The results show that by increasing the power of ultrasound system and thus increasing the volume of the cavitation area [30], the flux was more recovered. By increasing the ultrasound intensity, higher numbers of bubbles were produced and more intense collapses cause the turbulence in the liquid environment of the module container [30]. This phenomenon improved the separation and movement of particles through the membrane pores.

3.5. Changing the probe and the module distance

In order to examine the effect of the probe distance from the module on the flux recovery, the distance was reduced to 1 cm. The results for probe distance are represented in Figure 7. This figure shows that after 15 min, the flux recoveries have increased 103 and 108% for M1 and M2, respectively. After 20 min, the flux recoveries have increased 109, 118 and 110% for M1, M2 and M3, respectively. The flux recovery cannot be higher than 100% unless that the destruction in the membrane has been happened. The main phenomena that are responsible for the destruction is not precisely known [34]; however, some researchers have reported that shock waves and smaller jets due to the domain pressure and high speed are the main reason for the destruction of membranes [35].
The cavitation, leads to phenomena such as macro flow, micro flow, micro-jet, acoustic stream and shock waves [36]. The best performance is achieved when the membrane placed in the cavitation region. When the membrane is away from the cavitation region, the only effect on the removal of particles is acoustic flow which cause increase in the turbulence [31]. Therefore, in the long distances, a large number of cavitation bubbles collapses before they reach to the membrane. In short distance, due to the higher energy density, the produced acoustic and the turbulence stream are increased and the membrane may be damaged.

For investigation of the ultrasound effect for membrane cleaning, the results showed that during 60 min ultrasound irradiation, the flux recoveries have been 83-91% for membranes. By increasing the intensity, the number of bubbles and the cavitation area may be increased and as a result, more intense collapses cause the turbulent flow in the liquid and the cake layer removal from the membrane surface was improved. The flux recoveries at the probe distance from the module 1 cm indicate that the destruction or cracks in the membrane may be happened.

**References**


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**Fig. 6.** The effect of changing ultrasound intensity (frequency = 24 kHz; N = 40 min; probe distance = 2 cm) on the PWF (P= 3 bar; T = 15±2 °C) for fouled membrane inside the module

**Fig. 7.** Flux recovery for membranes versus ultrasound irradiation time at a probe distance = 1 cm and membrane operating P = 3 bar and T = 15±2 °C.

**4. Conclusions**

In this study, the clean membrane was used outside the module and result showed that the ultrasound irradiation may cause destruction in the membranes due to shock waves or the micro jet caused by collapsing bubbles. The result showed that for all clean membranes inside the module, at the distance of 2 cm from the ultrasonic probe and the module, the ultrasonic irradiation did not affect the membrane structure.

For micrograph analysis, the FE-SEM was taken after 10 min ultrasound irradiation on the membrane surface with the distance of 1 cm and membrane operating P = 3 bar and T = 15±2 °C. The FE-SEM showed that the adjacent holes were collapsed before they reach to the membrane. In short distance, due to the higher energy density, the produced acoustic and the turbulence stream are increased and the membrane may be damaged.


