Chemical Cleaning of Ultrafiltration Membranes
Fouled by Whey

Sayyed Siavash Madaeni* and Shahram Sharifnia
Chemical Engineering Department, Razi University, Kermanshah, I.R. Iran

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ABSTRACT

A hydrophobic polysulphone ultrafiltration membrane was used for whey processing. Fouled membranes were cleaned with acids (HCl and H₂SO₄), alkali (NaOH) and surfactant. The latter resulted in maximum flux recovery and resistance removal. Sodium hydroxide had moderate effect and hydrochloric acid was the weakest cleaning agent. This is due to the cleaning strength of emulsifiers compared to acid or alkali. However alkaline solutions are more efficient than acids for removal of organic compounds such as proteins. Cleaning efficiency depends on the concentration of cleaning agent being higher for higher surfactant concentration. For acids and alkali, the efficiency increases with increasing the concentration of the reagent reaches to a maximum (optimum concentration) and then decreases. Operating conditions affect the cleaning process. At higher stirring speeds (turbulent flow) or longer cleaning time better removal of deposits and higher cleaning efficiency were observed. The sequential cleaning process may or may not improve the cleaning efficiency. When alkaline cleaning was followed by acidic washing no improvement was achieved. This can be attributed to the removal of most of the reversible deposits by alkali. If the sequence is in the opposite direction an improvement in cleaning efficiency is obtained.

Key Words: membrane, ultrafiltration, whey, chemical cleaning, fouling

INTRODUCTION

Membrane technology is attracting more attention for treatment of different feeds. A major membrane process i.e., ultrafiltration is widely used for treatment of water, wastewater and microorganisms suspensions including: fermentation broths, organic solutions, proteins, paint and pulp effluents.

The membranes, depending on the type, materials in the feed and process conditions, lose their performance after sometime. Flux, a measure for membrane performance is controlled by two phenomena, concentration polarizations and fouling [1].

Based on the terminology introduced by
IUPAC, fouling is "a process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings or within its pores" [2]. Fouling not only reduces the flux but also changes the retention. Numerous researches are carried out around the world for fouling reduction and cleaning of the fouled membranes. However, it is unlikely to eliminate fouling completely [3].

Control of fouling is of utmost importance. Techniques involved are firstly pretreatment of feed, which can reduce the particulate density onto the membranes and therefore reduce fouling. Secondly, by operating conditions, e.g. moderate pressure, crossbow and backwashing, fouling can be controlled. Thirdly, the membrane regeneration and its performance may be restored, at least partially, by cleaning the membranes with chemicals to remove deposited substances.

An important technique for membrane regeneration is chemical cleaning of fouled membranes. The technique involves washing the membrane with a suitable cleaning agent. Cleaning is defined as "a process where material is relieved of a substance which is not an integral part of the material" [4]. Many substances mostly chemicals and different procedures are used for cleaning of membranes.

Chemical cleaning means removing impurities by means of chemical agents. However cleaning consumes time and money. In general around 5–20% of the operating cost is the cost of cleaning [5]. This shows the importance of the continued research in this field.

Up to now there are some problems associated with membrane cleaning. Cleaning procedures need long operation time [6], consume chemicals [7], degrade some membranes [8] and may cause corrosion in the system [9].

For higher cleaning efficiency, hybrid processes i.e., chemical materials plus physical techniques are widely used. These procedures include pretreatment, pulsating gas, back washing, addition of chemicals in opposite direction, flushing the feed at high pressure and combination of mechanical devices with chemical cleaners.

A dominant application of ultrafiltration membrane is whey processing. Whey, a by-product from cheese manufacturing companies, contains valuable constituents including proteins. However, fouling is a serious problem in whey filtration and cleaning is a vital step in maintaining membrane performance.

In this work ultrafiltration membranes were fouled with whey. The fouled membranes were washed with chemical agents such as acid, alkali and surfactant. The type of chemical agent and process conditions i.e., concentration of the cleaning solution, stirring speed during cleaning process and cleaning time affect cleaning efficiency. The effects of these parameters on cleaning efficiency as well as sequential cleaning are discussed.

Investigation of the mechanism of membrane cleaning results in better understanding of the process and may results in introducing the tailor-made chemicals and procedures. Fouling and cleaning mechanisms for whey processing using ultrafiltration membranes are described.

**EXPERIMENTAL**

**Materials and Methods**

**Membrane**

Amicon hydrophobic polysulphone PM30 (molecular weight cut off=30 kDalton) membrane was used as ultrafilter. Membranes were prepared for use according to the information provided by the manufacturer i.e., prior to the experiments the membrane was soaked face down in distilled water for at least 1 h.

**Feed**

Whey was obtained from West Cheese Factory (Kermanshah, Iran) and used as feed during all experiments. Whey is produced as a by-product in the cheese manufacturing companies and consisted of various proteins, fat, lactose, lactic acid and minerals. The characteristics of the whey used was as follows: 5.5 ≤ pH ≤ 6.5, 1.023 ≤ density ≤ 1.024, 6.0 % ≤ total solids ≤ 6.5 % and 0.2 % ≤ fat ≤ 0.3 %.

For experiments the received whey was diluted to obtain a feed with the total solid concentration of
1%. The feed was used immediately after the preparation. For comparison of the results each set of the experiments was carried out in the same day using the same feed.

Cleaning Agents
In this work, acids (HCl and H$_2$SO$_4$), alkali (NaOH) and surfactant (Triton-X100) supplied by Merck were used as cleaning agents.

Fouling Procedure
All experiments were carried out in a 110 mL capacity batch cell, with a membrane area of 15.2 cm$^2$. The cell consisted of a cylindrical vessel containing the feed solution, two circular end pieces all of which were made from Perspex and a porous medium to support the membrane. The top end piece of the cell contained a feed and a gas inlet and a pressure relief valve. Stirring was achieved by an internal magnetic bar (25.4 mm long, 6.4 mm diameter) suspended 2 mm above the membrane. The magnetic stirrer was started with a specified stirring speed prior to the filtration. Nitrogen gas was used to pressurize the cell to the operating pressure.

The filtration started after 100 mL of whey (total solid concentration 1%) was poured into the cell, which was quickly pressurized by nitrogen gas. The feed solution was fed continually from a feed reservoir connected to the cell to replenish the permeate. The flux was measured gravimetrically with a Mettler PJ 6000 electronic balance by continuously weighing the permeate. For each experiment whey solution was ultrafiltered at ambient temperature, 400 rpm stirring speed and 100 kPa applied pressure until 50 mL of permeate was collected. Passage of this amount of whey causes formation of a steady deposit, which is necessary for cleaning investigation.

Cleaning Protocol
Prior to the cleaning, ultrafiltration membrane was fouled as described above. The fouled membranes were cleaned according to the protocol suggested by Fane and colleagues [10]. Before and after fouling the water flux of the membrane was measured by passing 10 mL of distilled water through the membrane at 100 kPa and 400 rpm (initial water flux=J$_{wi}$, water flux after fouling=J$_{wd}$). The fouled membrane was washed with 100 mL of distilled water at 400 rpm for 30 min to remove unbound substances from the membrane surface. The water flux was measured after washing (J$_{we}$). This was followed by washing the membrane with a cleaning agent for a specific time (30 min) and at a specific stirring speed (400 rpm) without applying pressure. The water flux was determined (J$_{we}$) after chemical cleaning.

RESULTS AND DISCUSSION

Fouling and Cleaning Quantification
Fouling can be quantified by the resistance appearing during the filtration and cleaning can be specified by the removal of this resistance. The resistance is due to the formation of a cake or gel layer on the membrane surface or in the membrane matrix. The latter results in plugging or narrowing of the membrane pores. The flux ($J$), through the cake and the membrane, may be described by Darcy's law:

$$J = \frac{\Delta P}{\mu \Sigma R}$$

in which $\Delta P$ is transmembrane pressure (driving force), $\mu$ is viscosity of the fluid and $\Sigma R$ is sum of the resistances. Membrane resistance ($R_m$) can be estimated from the initial water flux:

$$R_m = \frac{\Delta P}{\mu J_{wi}}$$

The resistance, which is appeared after fouling ($R_f$), can be calculated from the water flux after washing with water:

$$R_f = \left(\frac{\Delta P}{\mu J_{wd}}\right) - R_m$$

The resistance, which is remained after cleaning ($R_c$), can be calculated from the water flux after chemical cleaning:

$$R_c = \left(\frac{\Delta P}{\mu J_{we}}\right) - R_m$$
Resistance removal (RR), which is a tool for cleaning quantification, can be estimated from:

\[
RR (%) = \frac{\left(R_\text{t} - R_\text{c}\right)}{R_\text{t}} \times 100
\]  

(5)

Flux recovery (FR) is another method for quantification of cleaning efficiency:

\[
FR (%) = \frac{J_\text{w}}{J_\text{w}} \times 100
\]  

(6)

Both of the parameters i.e., resistance removal and flux recovery have been used for demonstrating the cleaning efficiency [3, 10].

Membrane Fouling
Flux declines during ultrafiltration of whey due to deposition of materials on the membrane surface or in the membrane pores. Figure 1 shows a typical flux history for ultrafiltration of whey. As it is expected the permeate flux is much lower than the pure water flux. At the beginning, flux is high but it drops quickly and then decreases gradually. This behaviour is a typical trend shows membrane fouling during whey processing.

Membrane Cleaning
The cleaning process carried out in two steps, washing with water and cleaning with a chemical agent. In the first step unbound proteins and other foulants in the vicinity of the membrane are washed away. This simple procedure results in partial flux recovery or resistance removal due to the low solubility of proteins and other whey components in water. For the experimental conditions i.e., washing the membrane with distilled water for 1/2 h after ultrafiltration of whey (around 1 h filtration or collection of 50 mL permeate) resistance removal and flux recovery were 45% and 15%, respectively.

In the second step, the fouled membrane was washed with chemical agent without applying pressure (no permeation). The cleaning depends on the type of chemical agent, concentration of the cleaning solution, stirring speed during cleaning process and cleaning time.

Comparison of Cleaning Agents
To compare the cleaning agents (acid, alkali and surfactant) three similar membranes were fouled with the same feed in the same day and the fouled membranes were cleaned with HCl, NaOH and Triton-X100. The concentrations of all the cleaning solutions were 0.5%. Figure 2 shows that for polysulphone 30 kD, (PM30) membrane fouled with 1% whey, Triton-X100 results in maximum resistance removal (96%) and flux recovery (84%). Sodium hydroxide had moderate effect and hydrochloric acid was the weakest cleaning agent for the experimental conditions. The effect of surfactant can be attributed to the cleaning strength of emulsifiers, which is being higher than acid or alkali. Meanwhile the ability of
sodium hydroxide for dissolving and removing the proteins and other constituents in whey is higher than the influence of hydrochloric acid.

This is in agreement with the general observation i.e., organic compounds are removed by alkaline solution and mineral deposits by acidic solution [11].

Effect of Cleaner Concentration
The cleaning efficiency depends on the cleaner concentration (see Figures 3 to 6 for surfactant, acids and alkali). Using surfactant higher concentration causes higher resistance removal or flux recovery. However the effect is insignificant at high concentration. This is due to the limited ability of cake removal by any agent. The adsorbed layers or irreversible fouling materials cannot be removed.

For acid and alkali the cleaning efficiency increases with the cleaner concentration, passes a maximum and decreases afterwards. This trend has been observed by other researchers [3, 10, 12]. The concentration, which provides maximum efficiency, is the optimum concentration.

The first part of the curves (increasing efficiency with concentration) is anticipated. The cleaning agent

Figure 3. Effect of Triton-X100 concentration on cleaning efficiency for PM30 ultrafiltration membrane fouled by 1% whey solution.

Figure 4. Effect of NaOH concentration on cleaning efficiency for PM30 ultrafiltration membrane fouled by 1% whey solution.

Figure 5. Effect of H2SO4 concentration on cleaning efficiency for PM30 ultrafiltration membrane fouled by 1% whey solution.

Figure 6. Effect of HCl concentration on cleaning efficiency for PM30 ultrafiltration membrane fouled by 1% whey solution.
dissolves the foulants, which are deposited on the membrane surface as a cake or a gel and it removes them. More chemical results in more removal of the foulants.

The second part of the graphs (decreasing efficiency with concentration) needs more attention. This effect can be explained due to the permeability of the cake layer. In general cleaning may remove the deposit layer or alter its permeability [13]. Chemicals can cause swelling of the deposit, which results in an increase in the cake voidage [3]. Increasing the concentration of cleaning agent up to the optimum concentration provides maximum voidage and highest cleaning efficiency. The cake voidage may decrease with further increase in chemical concentration as it results in lower cleaning efficiency.

Another explanation is the fragile nature of proteins and other materials in whey. At high concentrations, acid or alkali may destroy a part of the proteins. The breakage expels fouling materials from the inside of the proteins. Chemical agents can also attack the membrane during cleaning process causing swelling of the membrane [5]. Both phenomena would result in less cleaning efficiency.

**Effect of Stirring Speed**

Cleaning process was carried out in different stirring speeds. Figure 7 shows that cleaning efficiency increases by increasing the stirring speeds. Lower speed (200 rpm) results in laminar flow and higher speed (800 rpm) provides turbulent. In turbulent flow a better removal of the foulants from membrane surface is anticipated. However it should be noticed that the higher speed means more energy consumption. The speed may be optimized according to the cleaning efficiency and energy requirements.

**Effect of Cleaning Time**

The time required for cleaning the fouled membrane is a crucial parameter affecting the cleaning efficiency. Generally longer time provides higher resistance removal. However the results (Figure 8) show that after a while longer time does not have a significant effect on cleaning performance. This is due to the removal of loose deposits in a certain time. Continuation of cleaning process cannot significantly remove the strongly adsorbed fouling materials.

**Effect of Acid/Alkali Sequence**

The effect of acid/alkali sequence on the cleaning efficiency was elucidated by cleaning the membrane with different combinations of cleaning agents. In the first set of the experiments the fouled membrane was cleaned with NaOH and resistance removal was measured (91%). This was followed by cleaning with HCl and determination of resistance removal (92%). This indicates that the cleaning efficiency remained...
almost the same after the second treatment. This is due to the removal of most of the reversible deposits by alkali. In this case usage of acid has no benefit. It was shown that for the experimental conditions NaOH is a stronger cleaning agent compared to the hydrochloric acid. If the sequence changes to acid/alkali the cleaning efficiency should increase because acid cannot remove all deposits and the remaining substances may be removed by alkali. The results confirm this trend. Resistance removal increased from 83% after washing with HCl to 94%, when the cleaning process was continued by washing the membrane with NaOH.

Similar results were obtained when the sequence was alkali/acid/alkali or acid/alkali/acid. For the first sequence the resistance removals were 90%, 91% and 91% after cleaning with NaOH followed by HCl and NaOH. It means that there is no improvement in cleaning efficiency after the cleaning with alkali, which is able to remove loose matters. For the second sequence the resistance removals were 85%, 95% and 94% after cleaning with HCl followed by NaOH and HCl. In other words the alkali can dissolve the foulants, which have been remained after cleaning with acid. The extra cleaning with acid after alkali does not have any benefit.

Fouling and Cleaning Mechanisms

Fouling mechanism can be investigated using the blocking laws [14]. In this procedure the unstirred data (permeate volume V, and time t) are compared. For a mechanism of pore blocking the plot of \( \exp(t) \) versus V should be linear, for cake deposition control \( t/V \) versus V should be linear and for internal pore closure \( t/V \) versus t should be linear.

For ultrafiltration of whey, the plot of \( \exp(t) \) versus V is completely non-linear. The plots of \( t/V \) versus permeate volume and time (Figure 9) show that none of the pore closure or cake formation is the dominant mechanism during the course of ultrafiltration. However it is possible to divide the graphs into two parts. In the first part (up to the filtration of 20 mL) no cake formation or internal closure is anticipated. If filtration progresses the adsorption sites in the membrane matrix may be filled.

Meanwhile the accumulation of constituents on the membrane surface is started. Figure 10 shows the results for progressive filtration (both graphs are linear).

A technique was employed to investigate the internal deposition of whey in PM30 membrane pores. The method is based on the passage of cleaning agent through the membrane [15]. For this purpose membrane was fouled and then cleaned with no passage of the cleaning agent through the membrane. This technique partially removes the external deposition of the foulants from membrane surface. The cleaning procedure was followed by passage of cleaning agent (NaOH 0.5%) through the membrane.

![Figure 9](image_url)

**Figure 9.** Mechanism determination for ultrafiltration of 1% whey solution using PM30 membrane. (a) \( t/V \) versus V; (b) \( t/V \) versus t.
under low pressure. If there is some deposition of fouling materials in the membrane matrix the cleaning agent may remove a part of the deposits. In this case the passage of cleaning agent should improve water flux. The results show that there is no improvement in either resistance removal or flux recovery after the passage of the cleaning agent through the membrane. This indicates no significant internal deposition in the case of whey ultrafiltration using PM30 membrane.

Combination of these data indicates that fouling occurs by deposition of foulants on the membrane surface. It seems that in whey processing most of the foulants are large size proteins and macromolecules, as they cannot penetrate into the membrane pores.

During ultrafiltration of whey, large substances (compared to the membrane pores) settle on the membrane surface and the small species pass through the membrane without significant adsorption in the membrane pores. Cleaning dissolves and removes large size proteins and other constituents, which remain on the membrane surface.

**CONCLUSION**

Fouling, which is the most important problem associated with the application of membrane, reduces the flux and changes the retention. A solution for fouling reduction is cleaning the membrane with suitable materials mostly chemicals. The selection of a substance as a cleaning agent depends on many factors including the feed and the membrane. Up to now this selection is mainly based on trial and error due to the lack of knowledge in the field of fouling and cleaning mechanisms. The understanding of the cleaning process needs to be improved.

Ultrafiltration is used for the treatment of various feeds. The cleaning agent depends on the feed and the membrane material. In general, ultrafiltration membranes may be cleaned by acids, bases, detergents, surfactants, enzymes, oxidizing agents and other chemicals.

Complex proteins such as whey may be concentrated using ultrafiltration membranes. In this work, the whey was processed using hydrophobic polysulphone membrane. Various chemicals such as acid, alkali and surfactant can be used for membrane cleaning. The surfactant (Triton-X100) resulted in maximum flux recovery and resistance removal. Sodium hydroxide had moderate effect and hydrochloric acid was the weakest cleaning agent. For all chemicals an optimum concentration exists above which the cleaning efficiency remains mainly stable or decreases. It means that there is no benefit to use concentrated chemicals.

Cleaning process may be carried out using chemical agents in sequence. This procedure may or may not improve the cleaning efficiency depending on feed, membrane and chemical agent.
Processing of whey causes deposition of large size proteins and other foulants on the membrane surface. The small species may pass through the membrane without significant adsorption on the membrane matrix. Cleaning dissolves and removes large size proteins and other constituents from the membrane surface.

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REFERENCES