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Chemical cleaning of ultrafiltration membranes in the milk industry

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Abstract

Ultrafiltration (UF) is one of the membrane processes has the most applications in dairy industries such as milk dehydration and whey concentration. Fouling of UF membranes in the milk industry is mostly due to precipitation of microorganisms, proteins, fats and minerals on the membrane surfaces. Thus, chemical cleaning of the membranes is essential. Results from investigations on a polysulfone UF membrane fouled by precipitation of milk components are presented. The effect of different cleaning agents on recovery of the fouled membrane was studied. Results showed that a combination of sodium dodecyl sulfate, EDTA and sodium hydroxide could be used as a cleaning material to reach an optimum recovery of the membrane used for milk dehydration. It seems that the results obtained on an experimental scale can be applied to an industrial scale, and the method is able to overcome fouling on any scale.

Keywords: Membrane; Ultrafiltration; Milk; Fouling; Chemical cleaning

1. Introduction

Separation technology using membranes has shown considerable progress in recent years. Ultrafiltration (UF) is one of the processes of this technology which has the most applications in dairy industries such as milk dehydration and whey concentration. The membrane fouling phenomenon is an important limitation of the technology to be generally employed. Fouling is

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defined as existence and growth of micro-organisms and irreversible collection of materials on the membrane surface, which results in a flux decline. To overcome the problem, a cleaning process must be carried out. Cleaning is usually performed in three forms: physical, chemical and biological [1]. Chemical methods are used most often. The first step of chemical washing is finding appropriate materials as cleaning agents. Choosing the best materials depends on feed composition and precipitated layers on the membrane surface and in most cases is performed using a trial-and-error method [2]. The selected materials should have some characteristics such as chemical stability, safety, low cost and ability to wash with water [3]. These materials also must be able to dissolve most of the precipitated materials and take them away from the surface while they should not damage the membrane surface [4].

Some of these cleaning agents are acids, alkalis, surfactants, disinfectants and combined cleaning materials [1,5]. While using these materials as cleaner, the effect of some parameters such as pH, concentration and washing time [4] and operating conditions like crossflow velocity, pressure and temperature [6,7] must be considered. In order to clean the membranes fouled with milk and whey, one alkali washing step followed by an acid washing step has been suggested [6], and to get better results one enzyme washing step could be used before chemical washing [2]. Thus, to reach the optimum conditions for cleaning processes, having enough information about operating conditions and effects of cleaning materials is necessary [3,8].

In this research, effects of different washing materials and cleaning process conditions on the performance of the membrane recovery were investigated. Results of the investigations on a polysulfone membrane used in milk dehydration industry are presented.

2. Materials and methods

In all experiments, a polysulfone membrane with a molecular weight cutoff (MWCO) of 30 kD produced by Dow (Denmark) was used. The feed was milk with the following composition supplied from the Tehran pasteurized milk factory.

- Water: 88%
- Protein: 3.4%
- Fat: 3%
- Lactose: 4.9%
- Other: 0.7%

Various chemicals were used as cleaning agents as presented in Table 1.

Table 1
Chemical cleaning agents

Material	Company
Sodium hydroxide	Panreac
Sodium hypocholorite	Fluka
Hydrochloric acid	Merck
Sulfuric acid	Merck
Nitric acid	Merck
Ethylene domain tetra acetic acid (EDTA)	Merck
Sodium dodecyle sulfate (SDS)	Merck

3. Fouling and cleaning processes

All of the UF experiments were performed in a cell in the form of crossflow on the membranes having a surface of 29.24 cm^2 as shown in Fig. 1. The membrane was placed in a special location and the permeation flux of distilled water at a temperature of $30 \pm 1\,^{\circ}$C and a pressure of 3 bar was measured in 10 min. This flux is named J_{wi}.

In the second step, which is fouling, milk at a temperature of $50 \pm 1\,^{\circ}$C and a pressure of 3 bar was fed into the system. The fouling operation was performed for all samples in 30 min to make similar fouling conditions and particle precipi-

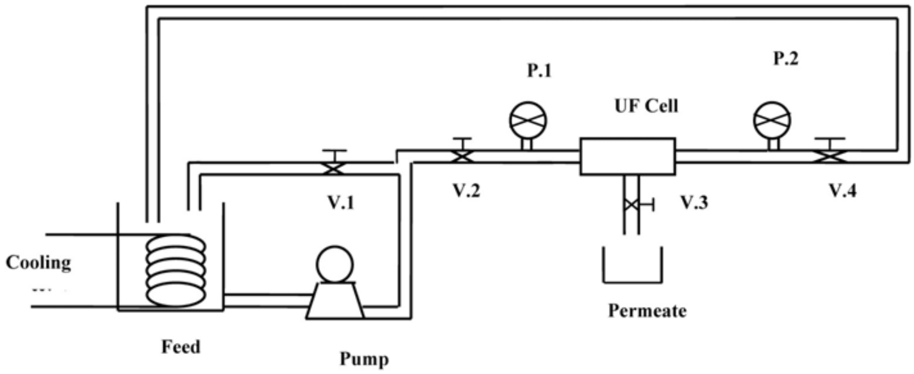

Fig. 1. Scheme of UF crossflow system.

tation on the membrane surface in all samples. Feed was passed across the membrane surface continuously with a linear crossflow velocity of 1 m/s. The flux of this step is introduced as J_{uf}.

In the next step, the fouled membrane was washed with distilled water and then permeation flux of distilled water was measured. The flux of this step is named J_{ww}. Then, chemical washing at a temperature of $30 \pm 1\,^{\circ}$C and with no pressure was performed within 30 min and then the final flux of distilled water was measured. This flux is named J_{wc}.

Therefore, in all the experiments, distilled water flux was measured three times: (J_{wi}, J_{ww} and J_{wc}). Formation of cake or gel on the membrane surface or into the membrane pores increases fouling due to the fact that present pores are (partially) blocked or become narrow and this finally reduces the permeation flux. Fouling was evaluated using resistance removal (RR) and flux recovery (FR) [9]:

$$\text{RR}\ (\%) = [(R_f - R_c) / R_f] \times 100$$

$$\text{FR}\ (\%) = [(J_{wc} - J_{ww}) / (J_{wi} - J_{ww})] \times 100$$

where R_f is the resistance after fouling and R_c is the resistance after cleaning. Therefore, using these two parameters, the effectiveness of various chemicals with different concentrations and at different operating conditions can be compared.

4. Results and discussion

4.1. Comparison of cleaning agents

After analyzing the feed and also the cake formed on the membrane surface, different cleaning agents were selected. A preliminary understanding about the nature of precipitated layers indicated that acids are less capable than alkalis for cleaning of membranes.

To compare the cleaning agents, similar membranes were fouled with the feed and the fouled membranes were cleaned with different chemicals. Concentrations of all the cleaning solutions were the same. Table 2 shows the cleaning efficiency of FR and RR for various cleaning agents.

As expected, acids were the weakest cleaning agents for the experimental conditions. Results showed that alkaline solutions have a moderate effect, but combinations of chelating agent, surfactant and alkali provide the best cleaning efficiency. EDTA as a chelating agent has a good ability to combine with metals. It is used in special soaps to remove metallic contaminations. The effect of SDS as a surfactant can be

Table 2
Cleaning efficiency of different chemicals

Chemical agents	FR (%)	RR (%)
HCl	9	14
HNO_3	2	5
NaOH	10	30
NaClO	40	58
EDTA	8	13
SDS	27	35
EDTA+NaOH	52	89
EDTA+SDS+NaOH	100	100

attributed to cleaning strength of emulsifiers due to altering interfacial tension of water. This results in better separation of deposited materials from the membrane surface. NaOH changes pH of the solution and provides a better condition for the highest removal of foulants using EDTA and SDS [11,12].

4.2. Cleaning mechanism

Investigation of fouling and cleaning mechanisms leads to better understanding of the cleaning process and provides a basis for tailor-made chemicals and procedures. It seems that the cleaning agent diffuses into the deposited cake layer on the membrane surface. Diffusion rate depends on different factors including turbulency. A chemical reaction occurs between the cleaning agent and the deposited materials at the membrane surface. The reaction may be hydrolysis, dissolution or dispersion. This results in removal of fouling materials from the membrane surface.

4.3. Effect of cleaning conditions

After feed filtration, some materials which are not chemically adsorbed on the membrane surface can be washed with distilled water. This causes fewer chemicals to be used for cleaning

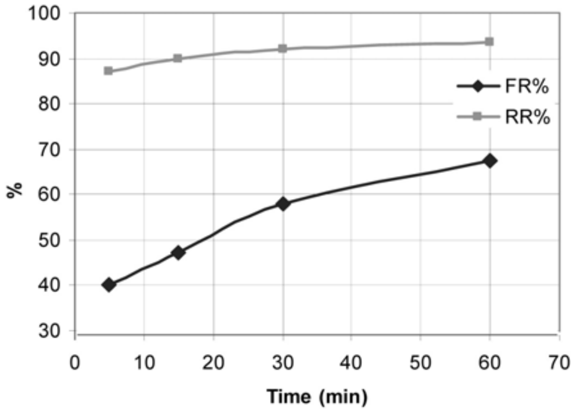

Fig. 2. Effect of cleaning time on RR and FR.

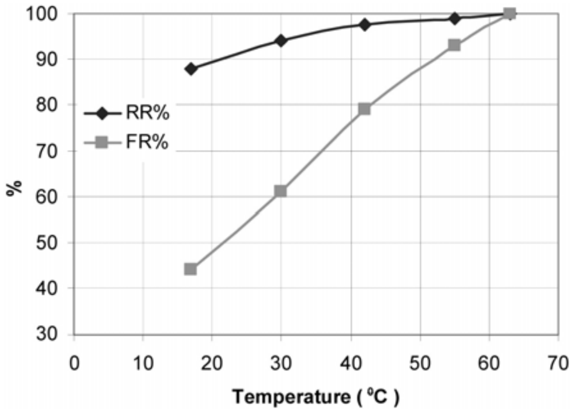

Fig. 3. Effect of cleaning temperature on RR and FR.

[9]. As shown in Fig. 2, FR increases within 50 min and then it remains almost constant. So, it seems that 50 min washing time with water before chemical cleaning must be enough and quite effective.

To study the effect of cleaning temperature on FR (and RR), some experiments were carried out within a temperature range of 17–63°C. As seen in Fig. 3, the results show that the optimum temperature is about 60°C.

To study the effect of cleaning pH on FR (and RR), some experiments were carried out within a pH range of 9.2–12.7. As seen in Fig. 4, the results show that the optimum value of pH is 12.

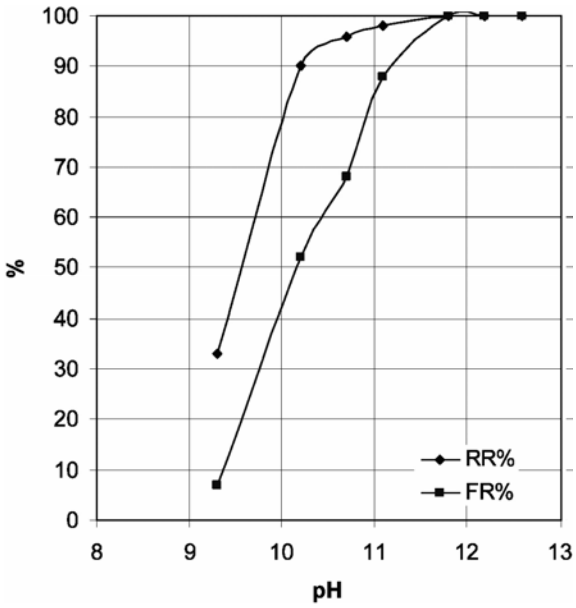

Fig. 4. Effect of pH on RR and FR.

4.4. Cleaning in industry

Pegah Milk Industries includes eight plants in different cities in Iran. The capacity of these plants is 100 tons of milk (20 tons of produced cheese) daily and each of them has 50 polysulfone UF membrane modules. Membranes are cleaned twice a day. Each cleaning procedure consists of three stages: alkali, acid and alkali. Various commercial chemical materials which are licensed by the supplier are used in the plants. Cleaning efficiency was 40–60% in all the plants. Water consumption was 40 m^3/d.

The chemical combination developed in this study was tested in the plants. A significant cleaning result of once a day, 5 m^3/d water consumption and 100% cleaning efficiency was obtained.

5. Conclusions

The best composition of the cleaning agents to enhance FR (and RR) of the UF fouled membrane (in milk industries) was found. A combination of SDS as a surfactant, EDTA as a chelating agent and NaOH as a powerful cleaning agent had good cleaning results. EDTA is able to combine with metals. The effect of SDS can be attributed to the cleaning strength of emulsifiers due to the altering interfacial tension of water. NaOH changes pH of the solution and provides a better condition for the highest removal of foulants using EDTA and SDS.

The best cleaning temperature, cleaning time and pH were found to be 60°C, 50 min and 12, respectively.

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References

[1] T. Gun, Membrane cleaning, Desalination, 71 (1989) 325–335.
[2] M.J. Munoz-Aguado, D.E. Wiely and A.G. Fane, Enzymatic detergent cleaning of polysulphone membrane fouled with BSA and whey, J. Membr. Sci., 117(1–2) (1996) 175–187.
[3] K.J. Kim, P. Sun, V. Chen, D.E Wiely and A.G. Fane, The cleaning of ultrafiltration membrane fouled by protein, J. Membr. Sci., 80 (1993) 241–249.
[4] J. Lindau and A.S. Jonsson, Cleaning of ultrafiltration membrane after treatment of oily waste water, J. Membr. Sci., 87 (1994) 71–78.
[5] M. Moro, Y. Yamaday, S. Izumi and J. Soeda, Chemical cleaning of membrane cartridges, JP 0952,026, 1997.
[6] G. Daufin, U. Merin and J.P. Labbe, Cleaning of inorganic membranes after whey and milk ultrafiltration, Biotechnol. Bioeng., 38(1) (1991) 82– 89.
[7] H.F. Bohner and R.L. Bardley, Effective cleaning of polysulphone ultrafiltration system, J. Dairy Sci., (1992) 718–724.

[8] S. Ishimura, Cleaning of ultrafiltration membranes, JP 60,220,108, 1985.
[9] S.S. Madaeni, T. Mohammadi and M.K. Moghadam, Chemical cleaning of reverse osmosis membranes, Desalination, 134 (2001) 77–82.
[10] C. Schwab, U. Kulozik and H.G. Kessler, Effect of structure controlled deposited layers on the retention of flavour compounds in reverse osmosis, Desalination, 90 (1993) 173–182.
[11] D. Wu and M.R. Bird, The fouling of ultrafiltration membranes using model tea component solutions, Fouling, Cleaning and Disinfection in Food Processing, Cambridge, UK, 2006.
[12] M.F.A. Goosen, S.S. Sablani, H. Al-Hinai, S. Al-Obeidani, R. Al-Belushi and and D. Jackson, Fouling of reverse osmosis and ultrafiltration membranes: a critical review, Sep. Sci. Technol., 39(10) (2004) 2261–2298.