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Membrane cleaning assisted by high shear stress for restoring ultrafiltration membranes fouled by dairy wastewater

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HIGHLIGHTS

- The effect of shear stress on the permeability recovery was investigated.
- Shear stress could improve foulants removal by forming foam cleaning agent.
- Water rinsing and chemical cleaning process were studied.
- Membrane cleaning process was optimized by response surface methodology.

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ABSTRACT

High shear stress is a promising new approach with high potential to assist membrane cleaning. In this study, the effect of shear stress on the permeability recovery of ultrafiltration (UF) membranes fouled by dairy wastewater was investigated. Water rinsing and chemical cleaning are two main cleaning methods. With respect to water rinsing, the effect of shear stress, temperature and cleaning time on cleaning efficiency were studied. Results revealed that shear stress could effectively remove casein micelles and whey protein layer on membrane surface. As for chemical cleaning, the effect of shear stress, temperature, the type of cleaning agent, concentration and cleaning time on cleaning efficiency were studied. Due to the effect of shear stress, the convection diffusivity was enhanced and foam cleaning agent was produced, thus can remove foulants on membrane surface or ones in internal greatly. Response surface methodology was utilized to explain the significance of various operation conditions and optimize the water rinsing and chemical cleaning process. After that, with the optimum results, two long time industrial cleaning processes were conducted and compared. In general, the high shear stress shows high potential for improving membrane cleaning operation and exerting a relevant influence on the overall process efficiency.

1. Introduction

Advancements of membrane technology in the past decade have resulted in the extensive application of UF in wastewater treatment for removal of macromolecular pollutants, such as recycling protein in dairy wastewater [1–3]. At the present time, as an effective method for control flux decline, dynamic filtration has attracted considerable attention owing to its decisive advantages of high speed shear effect on membrane surface in comparison with conventional treatment processes [4,5]. Therefore, it has been widely researched in laboratory test or at pilot scale for wastewater treatment and food liquid concentration [6]. Despite the benefits of high shear effect on dynamic filtration, both concentration polarization and membrane fouling are impossible to be completely eliminated, accordingly, it still suffers from flux decline during long-term filtration [7]. To date, investigations [8–10] showed that inorganic and organic compounds which are deposited on the membrane surface or entered membrane pores in feed solutions, caused pore clogging, adsorption, gel and cake layer. Due to the accumulation of rejected solutes on membrane surface, concentration polarization forms, affecting membrane fouling [11]. Besides, membrane fouling refers to both reversible and irreversible deposition of solutes on the membrane surface or into its pores [12]. These phenomena account for flux decline and pro-

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cess efficiency. As for the dairy wastewater pre-treatment with shear-enhanced UF, membrane fouling is mainly composed of casein micelle and whey proteins on the membrane surface or internal membrane pores [4,13].

In order to overcome this challenge and maintain the sustainable operation, membrane cleaning as a crucial step of global process are widely applied to wash the equipment and restore the membrane permeability [14,15]. However, this process is expensive and may cost up to 80% of the total production expense for wastewater treatment in the dairy industry [16]. For that reason, it is significant to choose efficient cleaning agents and optimize the procedure.

The general approach to clean fouled membrane can be divided into physical, chemical and biological methods [17]. As for the food industry, chemical method are the most commonly used to remove the protein foulants [18]. However, frequent chemical cleaning not only causes the shortness of membrane life-time, but also increases additional energy cost and produces cleaning wastewater, thus reducing sustainability of filtration [15]. In addition, the extensive use of cleaning agent containing chlorine has brought about many environmental and health problems, for example, by-products like trihalomethanes (THMs), organic halogen compounds come into being in presence of organic matters in natural water bodies [19]. To our knowledge, some areas and countries control the use of chlorine strictly.

Although there are numerous studies [20–22] on flux decline control, systematic investigation about cleaning is rare. Most cleaning technologies [16,19] are largely based on empirical knowledge of conventional filtration system. They require a considerable volume of cleaning agents [19], but a major part of them cannot contact fouled membrane and foulants sufficiently, due to the lack of stirring force and low diffusion rate. As for shear-enhanced filtration system, an intriguing method to overcome the above-mentioned problems and to enhance the cleaning efficiency is the application of high speed rotating disk. During the cleaning process, the high shear stress produced by rotating disk can help to spread cleaning agents, increase the contact between cleaning agents and fouled membrane, thus improving the use efficiency and minimizing the volume of cleaning agents required. An extra advantage is that, under the high speed rotating circumstance, cleaning agent containing surfactants can produce plenty of foam, which has a higher concentration than liquid cleaning agent and the amount of active cleaning composition directly contacting the fouled membrane surface is notably greater. Therefore, shortening cleaning and down time, removing foulants and reducing the usage amount of cleaning agent efficiently, which are especially significant for industrial-scale processes, can be achieved with the help of high shear stress. To date, however, no studies of the application of high shear stress to enhance membrane cleaning efficiency have been reported.

In this study, we demonstrate, for the first time, high shear stress functions as an assisting method for improving membrane cleaning process including water rinsing and chemical cleaning. The effect of high shear stress on the cleaning of UF membranes fouled by dairy wastewater with various cleaning operating conditions was investigated. First, water rinsing tests under different shear stress and various temperature was conducted; then the effect of cleaning agents (NaOH, HCl, SDS and P3-ultrasil 10), shear stress, concentration of cleaning agent and temperature on permeability recovery was studied respectively; after that, response surface methodology was employed to explicate the significance of various operation conditions and to optimize the water rinsing and chemical cleaning processes; at last, two kinds of industrial cleaning operations were conducted and compared. The result of this study is helpful to find out the operational effect and to evaluate the value of high shear stress on membrane cleaning. At the same time, it is of importance for providing support for exploring new and efficient membrane cleaning modes for dynamic shear-enhanced filtration in wastewater treatment.

2. Materials and methods

2.1. Experimental apparatus and membranes

The rotating dick module (RDM), which consists of one disk mounted on a single shaft and rotating near a fixed circular membranes, has been designed and built in our laboratory. A flat membrane, with an effective area of 176 cm^2 (out radius R = 7.72 cm, inner radius r = 1.88 cm), was fixed on the cover of the cylindrical housing in front of the disk. The disk equipped with 6 mm-high vanes can generate very high shear stress on the membrane. The shear stress could be adjusted by modifying rotating speed of the disk.

Three commercial UF membranes fabricated by MICRODYN-NADIR Membrane Corporation, Germany were selected in this investigation owing to its strong antifouling performance and high retention permeability property, and their properties [6] are summarized in Table 1.

2.2. Fouling solution

Model dairy wastewater was prepared from commercial UHT skim (Carrefour, France), diluted 1:2 to one-third of normal concentration with deionized water (Aquadem E300, Veolia Water, France). The main compositions and characteristics of model effluents are described in Table 2. According to the previous studies [6,23], the effluent compositions and filtration behaviors for this model dairy effluent and the real dairy wastewater are very similar.

2.3. Experiments and procedure

2.3.1. Filtration procedure

A new membrane was used for each series of experiments to ensure the same initial membrane conditions for the entire study. The membranes were soaked in deionized water for at least 24 h prior to use, and pre-pressured with deionized water for 1 h under a pressure of 0.2 MPa. After stabilization, the pure water flux of membranes was measured at four pressures of 0.8, 0.6, 0.4 and 0.2 MPa to calculate water permeability (L_p). Before the experiments started, the feed was heated to 35 °C, and was fully recycled in the system at zero TMP, and this process lasted about 10 min for each test. The fouling experiments were carried out at 20 °C and 0.6 MPa for 2 h. The rotating speed throughout the experiment was maintained at 500 rpm. The permeate solution was not return to feed tank.

2.3.2. Cleaning procedure

The cleaning method included two types: water rinsing with distilled water and chemical cleaning with cleaning agent solution [24]. After that, a final water rinsing step until neutral pH was reached. A rotating disk was used in some tests. The water rinsing

Table 1
Properties of MICRODYN-NADIR UF membranes tested.

Membrane	Surface material	Molecular weight cut-off (kDa)	Water permeability ($L\ m^{-2}\ h^{-1}\ 0.1\ MPa^{-1}$)[a]
UH030P	PESH	30	33

PESH, Permanently hydrophilic polyethersulphone.
[a] Own measurement at 25 °C and 0.1–0.8 MPa.

Table 2
Main characteristics of model dairy wastewater.

Index	Model diary wastewater
Casein (g L^{-1})	8.5
Whey protein (g L^{-1})	2.1
Lactose (g L^{-1})	15.3
Calcium (g L^{-1})	0.40
Sodium (g L^{-1})	0.17
Lipid (g L^{-1})	<0.33
COD (g O_2 L^{-1})	36
Conductivity (μs cm^{-1})	1500–1600
pH	~6.7
Dry mass (g L^{-1})	32

was carried out at TMP of 0.02 MPa for 130 min. Rinsing was stopped and permeability was measured at 10, 50, 90 and 130 min. The chemical cleaning was carried out at TMP of 0.02 MPa for 130 min. Permeate and retentate cleaning solutions were returned to feed tank. Four cleaning agents (HCl, NaOH, SDS and P3-ultrasil 10) were evaluated. Shear stress, temperature and cleaning agent concentration of the solution were varied between 500 and 2500 rpm, 20 °C and 50 °C and 0.05% and 0.45%, respectively.

2.4. Evaluation of flux recovery

The cleaning efficiency was determined by following the method proposed by Astudillo et al. [25]. They investigated and compared the flux and membrane resistance in all ranges of TMP, then proposed the term "membrane performance recovery (MPR)", which use average water permeability achieved after cleaning and the average water permeability of the original membrane, to evaluate the efficiency of water rinsing or chemical cleaning to restore the membrane permeability. The MPR is given as follows:

$$MPR\ (\%) = \frac{\int_{TMP_1}^{TMP_2} L_{pa} \cdot d(\Delta TMP)}{\int_{TMP_1}^{TMP_2} L_{pi} \cdot d(\Delta TMP)} \times 100 \tag{1}$$

where L_{pa} and L_{pi} are the membrane water permeability after cleaning and initial membrane water permeability. (TMP_1, TMP_2) are the TMP study ranges. A graphical interpretation of MPR is shown in Fig. 1. MPR represents the areas ratio under the L_p vs. TMP curves in the TMP study range. Normally, this value is lower than 100% and the cleaning is incomplete. If MPR > 100%, it can lead to membrane physical damage.

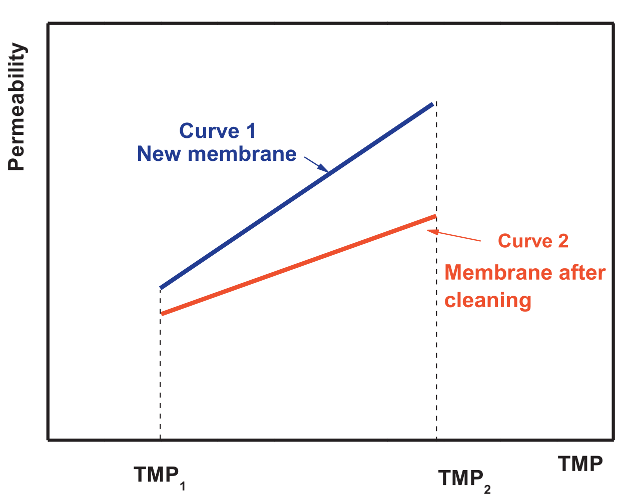

Fig. 1. MPR geometric interpretation presents the ratio of areas under the curves permeability vs. TMP, between the lowest TMP_1 to the highest one TMP_2.

2.5. Response surface methodology (RSM) analysis and optimization method

After the cleaning processes, a RSM analysis was applied to estimate the significance of operation conditions on the MPR. The RMS analysis was conducted with design expert 7.0 using historical model [26]. Experimental data of RSM are derived from in s 3.2 and 3.3.

Historical model of RSM is totally different from the RSM experimental design. For RSM experimental design, the experimental number and repetition are generated by RSM according to the factors and levels of experimental conditions. But for historical model of RSM, the obtained experimental results are inputted into RSM. Both of them can be used to analyze the effect and interaction for various experimental conditions and the optimal experimental conditions. Their difference lies in: RSM experimental design is used for experimental design before experiments with preset factors and levels, and historical model of RSM is utilized for experimental analysis after experiments without preset factors and levels. Historical model of RSM, not RSM experiment design, was employed in this study, therefore, there was not information about number of experiments, repetitions factors and levels. Besides, all the experimental conditions and results of historical model were shown in the figure of s 3.2 and 3.3, which included the factors, levels and responses for the historical model of RSM.

A relationship between the variables (shear stress, concentration, cleaning time and temperature) and the response variable (MPR) was achieved. A multiple linear regression analysis was used to seek a model equation for MPR as a function of operating conditions [27]. All independent variables and their interactions were taken into consideration. In addition, not significant regression coefficients (p-values higher than 0.05) were neglected.

Based on the RSM analysis, an optimization algorithm was used to optimize the operating conditions and maximize the MPR with some weights and restrictions (seen in Supplementary information). The optimization method performed with the "process optimization" function of design expert 7.0. This method used the pattern search to find out the maximum value of MPR with some weights and restrictions, while optimum operation conditions were obtained [28].

2.6. Analytical method

Turbidities of permeate were measured with a Ratio Turbidimeter (Hach, USA). COD was measured using Nanocolor Kits (Machery-Nagel, Hoerdl, France) in order to quantify organic matter concentration. Conductivity was measured with a Multi-Range Conductivity Meter (HI 9033, Hanna, Italy) and pH was measured with pH Meter (MP 125, Mettler Toledo, Switzerland). Dry mass was determined by measuring the weight loss after drying samples at 105 ± 2 °C for 5 h in an oven. Powers of feed pump under different pressures were measured with Power & Energy Monitors (Metric MX240, Chauvin Arnoux, France) and the overall measurement accuracy was estimated to be 8%, including experimental error.

2.7. Calculated parameters

The permeate flux (J) was calculated by:

$$J = \frac{1}{A}\frac{dV_p}{dt} \tag{2}$$

where A is the effective membrane area, V_p is the total volume of permeate, and t is the filtration time.

The pure water permeability (L_p) was calculated from the water flux as follows:

$$L_p = \frac{J_w}{TMP} \quad (3)$$

where TMP is the mean transmembrane pressure and J_w is the permeate flux using pure water as feeding solution.

The COD rejection could be determined by:

$$R(\%) = \left(1 - \frac{X_f}{X_p}\right) \times 100 \quad (4)$$

where X_p and X_f are the COD in permeate and feed, respectively.

The average membrane shear stress [29] was calculated by:

$$Shear\ stress\ (pa) = 0.0164\rho\upsilon^{0.2}(\kappa\omega)^{1.8}\left(\frac{R_m^{3.6} - R_{in}^{3.6}}{R_m^2 - R_{in}^2}\right) \times 100 \quad (5)$$

where ω is the disk angular velocity, $\kappa\omega$ is the fluid angular velocity in the gap between membrane and disk, $\kappa = 0.42$ [30] for a smooth flat disk and m and in subscripts are referred to outer and inner radius of the membrane, respectively.

P_d is the power of rotating disk (kW) and could be determined by the fitting formula proposed by Luo et al. [31]:

$$P_d = 0.141e^{0.000756N} \quad (6)$$

where N is the rotating speed of disk motor (rpm).

Total energy consumption (E_c, kW) [31] for the entire filtration process was represented by:

$$E_C = (P_f + P_d) \times t \quad (7)$$

where P_f is the power of feed pump (0.08 kW in this study), and t is the filtration time (h).

3. Results and discussion

3.1. Filtration experiments

Fig. 2 presents the evolution of permeate flux with time for 30 kDa UF tested at a TMP of 0.6 MPa, a shear stress of 4.6 Pa and a temperature of 20 °C. The sharp flux decline occurred at first 30 min. After that, it decreased slightly to 45.93 L m^{-2} h^{-1}. The flux of 50.37 L m^{-2} h^{-1}after 30 min, could be seen as the threshold value for distinguishing the decay rate of flux: before that, protein foulants deposited and attached to membrane surface promptly, so membrane fouling formed rapidly and the flux decreased markedly; after that, the shear stress created a self-cleaning capacity [6] which decreased concentration polarization, thus the flux reduced slightly and the rate of membrane fouling weakened, which corresponded to an equilibrium between shear rate and TMP. Although the flux decline (13.3 L m^{-2} h^{-1} 0.1 MPa^{-1}, 22.5%) was not significant, but the permeability reduced greatly (25.1 L m^{-2} h^{-1} 0.1 MPa^{-1}, 76.06%), implying that the reduction of permeability was not necessarily to decrease flux and the serious pore blocking may exist.

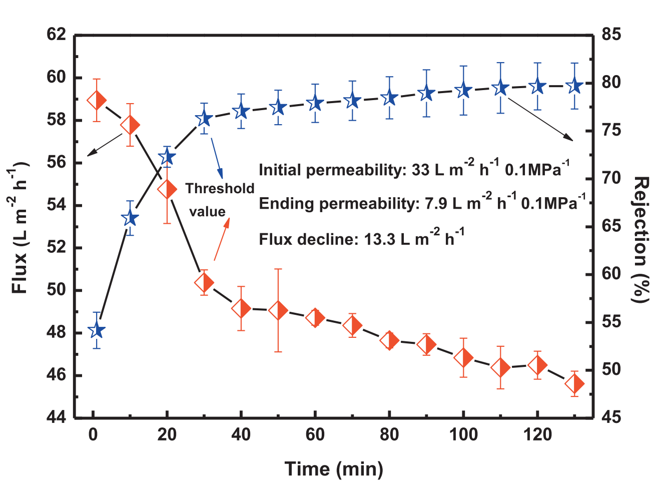

Fig. 2. The permeate flux and COD rejection vs. time during fouling experiments.

The evolution of COD rejection as time goes by during filtration experiment is shown in Fig. 2. It was evident that rejection increased rapidly from 54.17% to 76.3% with time before threshold time (30 min), and achieved stable final value (about 80%). This was due to that, before 30 min, the pore blocking and fouling layer were at a low level, so some small proteins and particles passed easily; after 30 min, the pore blocking and fouling layer formed and played a role in "second filter" [32], therefore, the COD rejection improved.

3.2. Water rinsing

Water rinsing operations are applied to remove the target fouling on membrane surface [33] and reduce the subsequent advanced membrane cleaning loading. In industrial operation, water rinsing precedes chemical cleaning, so optimization of water rinsing was beneficial for decreasing the usage amount of cleaning agent and the frequency of chemical cleaning [34], thus reducing operation cost and preventing excessive membrane damage caused by use of chemical cleaning.

3.2.1. Effect of shear stress

Fig. 3 shows the effect of shear stress on MPR with time at TMP of 0.12 MPa and temperature of 20 °C. It was clear that shear stress enhanced MPR, which was reasonable. According to the previous study [18] of our laboratory, the whey protein layer and casein micelles were the main compositions of membrane fouling. The shear stress improved the efficiency of removing casein micelles and whey protein layer on membrane surface, therefore, MPR increased continuously with time at all shear stresses. As we know, the extending of cleaning time can lead more foulants into dissolving on rinsing water [35]. However, excessive rinsing times may decrease production efficiency per unit time, therefore, a balance between rinsing efficiency and system productivity needs be taken into consideration. This study illustrates the significance of taking

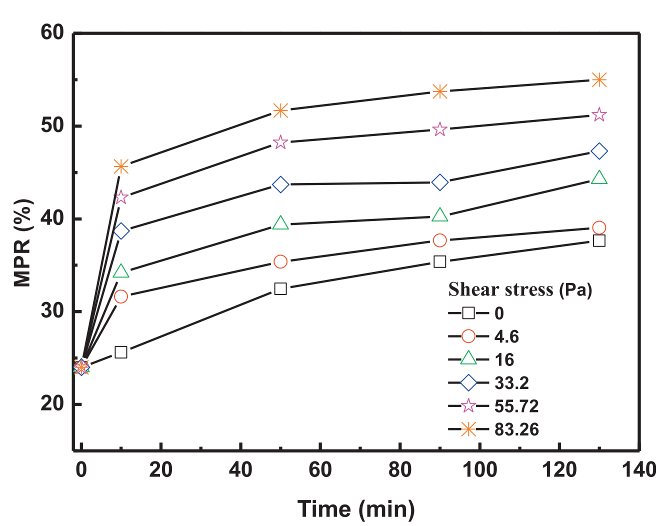

Fig. 3. The MPR vs. time at various shear stress.

both water rinsing and chemical cleaning times into consideration when optimizing the cleaning operation in Section 3.4.

3.2.2. Effect of temperature

The effect of temperature on MPR during water rinsing process is presented in Fig. 4. It could be observed that when temperature was elevated from 20 °C to 35 °C, MPR was increased. However, this effect was not obvious at 50 °C. This was because: high (50 °C) and moderate (35 °C) rinsing temperatures could enlarge pore size [36], loosen the protein compositions (casein micelles and whey protein layers) depositing on membrane surface or blocking pores and decompose them into amino acids, which were soluble in water. Moreover, the loosening effect was reinforced at high shear stress, because the high shear stress could take away the loosened foulants quickly. In the industrialized operation, raising water rinsing temperature needs much energy and time to heat waster [37], which increases the economic burden for enterprises. So considering the rinsing efficiency and operation cost, a moderate (35 °C) rinsing temperature should be adopted.

3.3. Chemical cleaning

Chemical cleaning can be employed to remove stubborn fouling that strongly adheres to the membrane surface or into the membrane pores with various chemical agents [18]. In comparison with water rinsing, chemical cleaning is able to recover a greater permeability and more important in the entire membrane cleaning process [14]. At the same time, the selection of suitable and effective cleaning agent, as well as how to optimize operation conditions are the crucial problems for industrial productivity.

3.3.1. Effect of the cleaning agent type

MPRs of four different cleaning agents were illustrated in Fig. 4. It was clearly observed that P3-ultrasil 10 had the best MPR, the next was NaOH and SDS, and the lowest value was HCl, which could be explained as follow. HCl could dissolve the inorganic salt foulants [24] which were partly adsorbed in pores or deposited on membrane surface. SDS had an ability to decrease the surface tension of foulants and increased their solubility, and, at the same time, enhanced the hydrophilic of membrane [24], thus it dissolved organic matters, such as proteins and fats. However, some adsorption between membrane pores and SDS occurring in this process may lead to new membrane fouling. As for the alkaline solution-NaOH, the cleaning effect could be explained as follow: first, alkaline solution caused membrane swelling [18], penetrated the deep fouling position and took away the stubborn foulants; secondly, the proteins containing excess carboxyl could react with alkaline solution and become negatively charged state, meanwhile weakening the binding force between proteins and membrane materials [36], thus their molecular repulsion and solubility increased. In this study, protein was the main foulant [38], the content of fat and inorganic salts in foulants was low, and so NaOH and SDS had better cleaning effect. P3-ultrasil 10 is a multi-component detergent including EDTA, gluconate, phosphate, sulfate, NaOH and surfactant [18]. It has the comprehensive effects of NaOH and SDS, while EDTA could remove calcium salt foulants [24], therefore, owning the most complete foulants removal ability and the best MPR.

From Fig. 4, all of MPRs with shear stress of 16 Pa are higher than that of 0 Pa, because cleaning solution can spread sufficiently in the module and contact with fouled membrane fully at higher shear stress on membrane surface. Especially for SDS and P3-ultrasil 10, they could produce a mass of foam by the mean of shear stress, and foam was able to enhance foulants removal ability greatly which was explained in detail at Section 3.3.2. In general, the cleaning effect reinforced with cleaning time. However, different cleaning agents had different growth trends. For NaOH and HCl at shear stress = 0 Pa, the stability time was 50 min, while the stability times of P3-ultrasil 10 and SDS were 90 min. This suggested that their reactions between surfactant composition and foulants were relatively slow. When the shear stress was 16 Pa, the cleaning process was significantly “accelerated”, and all of the four cleaning agents almost reached the highest MPR at 50 min. Unexpectedly, there were different degrees of MPR decline exceeding 90 min, which may be due to the occurrence adsorption between cleaning agent and pores [18] and reduction of hydrophilicity of membrane caused by excessive cleaning under shear stress effect.

3.3.2. Effect of shear stress

Fig. 5 shows the values of MPR at different shear stresses. In the experiments, shear stress varied from 0 Pa to 83.26 Pa. The increase of MPR with shear stress was also clearly observable. The reasons had three facts, firstly, the increased shear stress on membrane surface created by rotating disk near membrane [29,39,40] could cause the erosion and removal of the whey protein and casein micelles layers from the membrane surface; secondly, the shear stress enhanced the diffusivity coefficient of mass transfer process remarkably [41], facilitating the interaction

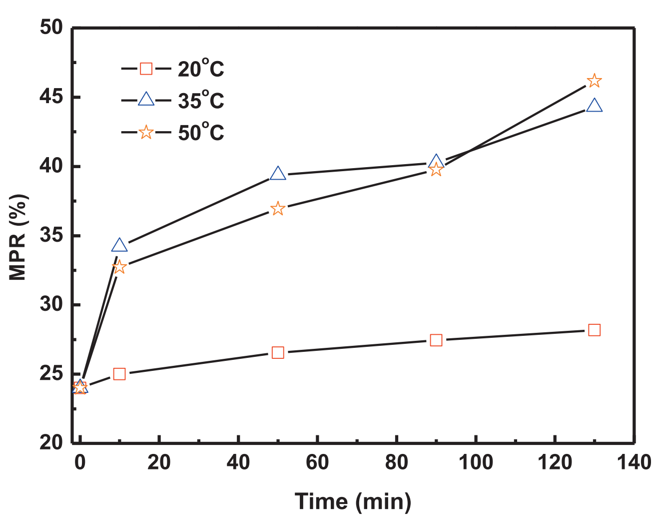

Fig. 4. The MPR vs. time at various temperature (TMP = 0.12 MPa and shear stress = 16 Pa).

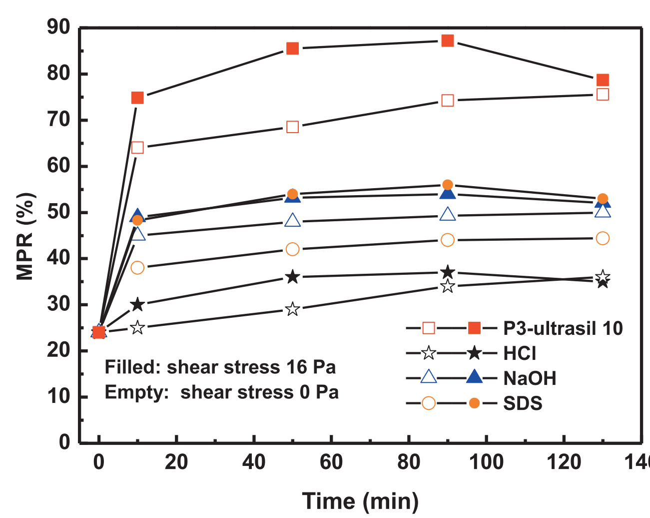

Fig. 5. The MPR vs. time at various cleaning agents (Concentration = 0.25%, TMP = 0.12 MPa and temperature 35 °C).

between foulants on membrane surface and cleaning agents in bulk solution; the most important was the foam, which was produced from P3-ultrasil 10 under shear stress condition, and contained sufficient levels of active cleaning composition, and kept the chemical agents on membrane surface long enough for the active compositions to penetrate the membrane pores and remove the foulants. This was in agreement with the studies of Gahleitner et al. [16,19]: cleaning agent with foam had a more excellent cleaning efficiency and results. As we can see from Fig. 6, higher shear stress generated more forms, thus leading to higher MPR. In addition, all of MPR had the similar change trends with time except 0 Pa and MPR decreased from 90 min. This was due to the adsorption behavior exceeding the cleaning effect [42], which was explicated in detail at Section 3.3.3. As for shear stress 0 Pa, it did not "accelerated" the phenomenon and the cleaning effect was greater than adsorption behavior.

3.3.3. Effect of cleaning agent concentration

Fig. 7 shows that the values of MPR obtained when P3-ultrasil 10 solutions at various concentration were employed to clean 30 kDa membranes. It could be observed that the MPR of 0.05% and 0.25% were significantly higher than that of 0.45%. Normally, the increase of cleaning agent concentration should enhance MPR [43], but at the same time, the exceeding cleaning agent in solution caused a large number of adsorption between membrane and cleaning agents [44], especially for the surfactant composition, when the adsorption behavior were greater than cleaning effect, the MPR decreased. For the same result, the extending of cleaning time not only promoted the cleaning effect, but also facilitated the adsorption behavior. When cleaning time exceeded 90 min, adsorption behavior dominated, therefore MPR reduced and 0.45% was the largest decrement. In another aspect, the higher concentration of alkaline composition and longer cleaning time could deteriorate the membrane hydrophilic [42] and damage membrane permeability. In addition, salt concentrations reduced at lower concentration of P3-ultrasil 10. According to the study of Álvarez-Blanco et al. [14], the decrement of salt concentrations can reduce the surface tension and the salting-in effects enhance at low surface tension. So, lower concentration of P3-ultrasil 10 resulted in more protein foulants removal.

3.3.4. Effect of cleaning solution temperature

Fig. 8 shows the values of MPR for the 30 kDa membranes when the cleaning step was performed at different temperatures and a

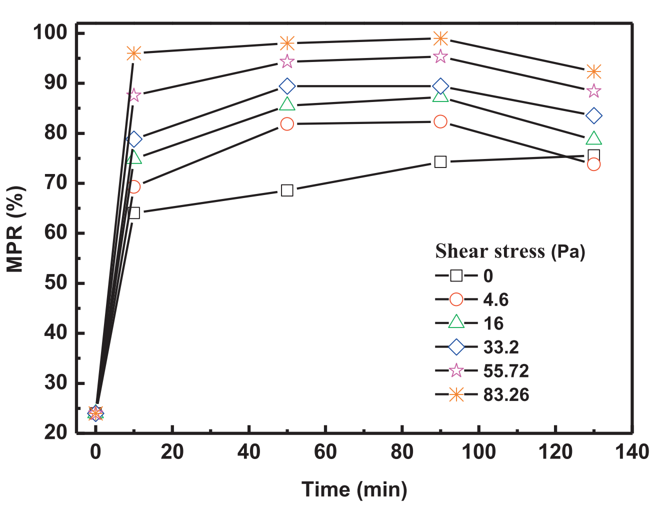

Fig. 6. The MPR vs. time at various shear stress for P3-ultrasil 10 (Concentration = 0.25%, TMP = 0.12 MPa and temperature 35 °C).

Fig. 7. The P3-ultrasil 10 solution before (left) and after (right) cleaning (shear stress = 16 Pa and time = 50 min).

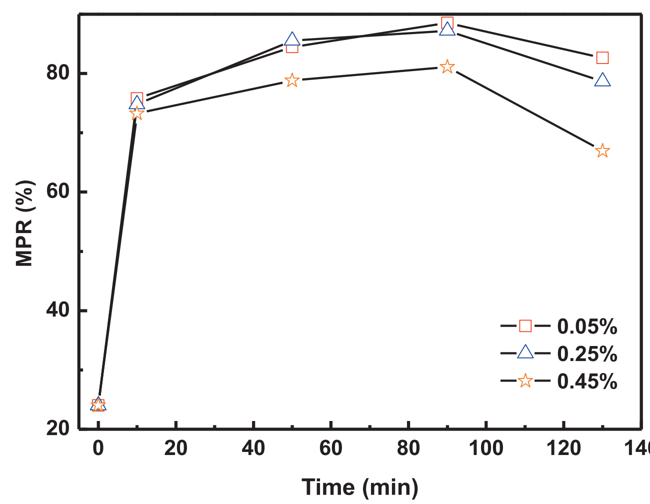

Fig. 8. The MPR vs. time at various concentration of P3-ultrasil 10 (Temperature = 35 °C, TMP = 0.12 MPa and shear stress = 16 Pa).

P3-ultrasil concentration of 0.25%. As could be observed, the higher the temperature of the cleaning process, the better the MPR was, reaching an efficiency of 98% when the cleaning process was carried out at 50 °C. The increment of MPR when temperature elevated from 25 to 35 °C was greater than the increment of MPR when temperature elevated from 35 to 50 °C (about 28% in the first case and 20% in the second case). The similar influence can also be seen in Fig. 4. Due to the adsorption of hydrophilic ions from the air/water surface, the surface tension reduced with the increase of solution temperature [45], thus the salting-out effects of the P3-ultrasil 10 enhanced and organic foulants removal improved. Besides, higher temperature had a positive influence on protein solubility [46]. Therefore, the highest protein solubility was achieved at 50 °C. But the effect was not unlimited and protein solubility may decrease below a certain temperature, because the protein was denatured due to the breaking of non-covalent bonds involved in the stabilization of secondary and tertiary structure [14]. Furthermore, the raise of temperature elevated the diffusivity coefficient in mass transfer processes [47] and improved the rate of foulants from the membrane surface to the bulk solution. In addition, high temperature could weaken the structure of membrane fouling layer [18], expand the membrane pores and facilitate foulants removal. The increase of temperature also enhanced the salting-in effects between the inorganic salts (gluconate, phosphate and sulfate of P3-ultrasil 10) and the protein foulants [18]. What's more, the PESH membrane may be destroyed exceeding 50 °C. For all these reasons [38], the most appropriate temperature to clean the fouled membrane with dairy wastewater was about 50 °C.

3.4. Statistical and optimization analysis

MPR is influenced by various operation conditions such as shear stress, temperature, TMP, cleaning time, the type of cleaning agent and its concentration. In this study, response surface methodology was adopted to investigate the significance of various operation conditions and optimize the water rinsing and chemical cleaning processes. For the water rinsing, shear stress, temperature and rinsing time were chosen as variables of model, while shear stress, temperature, concentration of cleaning agent and cleaning time were selected as variables of chemical cleaning.

The mathematical relationships between values of MPR and the operating conditions were obtained for the water rinsing and chemical cleaning (Eqs. (8) and (9), respectively). The related ANOVA results were shown in Support Information. With high multiple regression coefficient values (R^2, 0.9821 and 0.9832 for water rinsing and chemical cleaning) and sufficient p-value analysis [48], most of the estimated coefficients were significant. It is clearly observed that the optimal MPR increases in the order as follows: time < temperature < shear stress for water rinsing, while time < concentration of cleaning agent < shear stress < temperature for chemical cleaning. This means that both shear stress and temperature have a strong positive impact on the MPR, but the effect of shear stress is greater in water rinsing and that of temperature is better in chemical cleaning. In addition, the concentration of cleaning agent has a negative effect on MPR.

Fig. 9 presents the surface contours for the response variable-MPR as a function of the operating conditions of shear stress and temperature for water rinsing and chemical cleaning. Time was set at 70 min and concentration was 0.25%. The blue part in the lower left corner represents the most unfavorable operation conditions, because lower MPR was achieved (lower than 28% for water rinsing and 63% for chemical cleaning). On the other hand, the red part in the upper right corner shows the highest MPR obtained (greater than 48 % for water rinsing and 95% for chemical cleaning). It is important to note that the shear stress and temperature can enhance MPR evidently. Moreover, from the Supplementary material Figs. S1 and S2, the sustained increasing of time can't lead to the elevation of MPR.

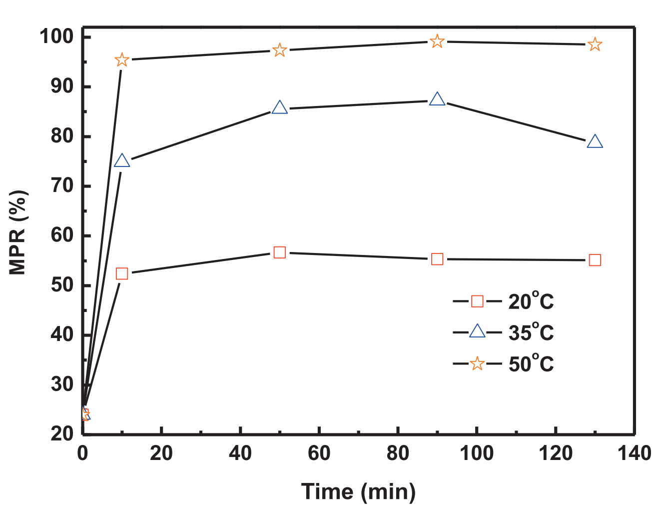

Fig. 9. The MPR vs. time at various temperature for P3-ultrasil 10 (Concentration = 0.25%, TMP = 0.12 MPa and shear stress = 16 Pa).

Although the shear stress improves membrane cleaning, the high total energy consumption is a disadvantage for this cleaning process [44]. In order to balance the enhancing of MPR and conserving the energy, the optimization for the maximum MPR and the minimum total energy consumption in water rinsing and chemical cleaning process was conducted. According to Table 3, their optimum temperatures were similar, but the shear stress and time values varied widely, which is due to the different importance of shear stress and time in water rinsing and chemical cleaning processes. In the Section 3.5, we adopte these optimization results to perform the membrane cleaning processes.

$$\begin{aligned}\mathrm{MPR}\ (\%) = {} & 46.23 + 8.55 \times \text{shear stress} + 6.05 \times \text{temperature} \\ & + 4.32 \times \text{time} - 0.14 \times \text{shear stress} \times \text{time} \\ & + 2.45 \times \text{temperature} \times \text{time} - 3.05 \times \text{shear stress}^2 \\ & - 6.09 \times \text{temperature}^2 - 1.23 \times \text{time}^2\end{aligned} \tag{8}$$

$$\begin{aligned}\mathrm{MPR}\ (\%) = {} & 92.51 + 11.55 \times \text{shear stress} + 21.36 \times \text{temperature} \\ & + 0.67 \times \text{time} - 3.91 \times \text{concentration} \\ & - 2.2 \times \text{shear stress} \times \text{time} + 0.33 \times \text{temperature} \\ & \times \text{time} - 3.08 \times \text{time} \times \text{concentration} \\ & - 4.21 \times \text{shear stress}^2 - 3.7 \times \text{temperature}^2 \\ & - 6.96 \times \text{time}^2 - \text{concentration}^2\end{aligned} \tag{9}$$

3.5. Comparison of two industrial cleaning processes

In industrial membrane cleaning operation, waster rinsing and chemical cleaning are two common cleaning modes. Water rinsing is simple, fast and cheap, but with low efficiency. Chemical cleaning is efficient, but complex, multi-step, high cost and produces secondary effluent. In this study, we attempted to select a suitable timing (30 min, threshold value in Fig 2) of the filtration process to interrupt filtration and used "water rinsing" with the optimum condition to clean the membrane with the fouled level, thus increase the cleaning frequency and strengthen its cleaning result. As for chemical cleaning, we conducted the cleaning operation with the optimum condition after the entire filtration (120 min). All of these cleaning membranes were reused for multiple filtrations. All these cyclic operations continued five times.

Fig 10 shows the permeate flux and MPR for 5 times cycle operation with water rinsing (a) and chemical cleaning (b). For water rinsing, it was conducted after 30 min filtration. As shown in Fig 2, at the threshold point, flux is about 50.37 L m^{-2} h^{-1} and flux decline and membrane fouling are in a threshold state. With the effect of water rinsing, the permeate fluxes in these cycle operations are similar and keep at a high level, but the MPR is very low and water rinsing cannot elevate permeate recovery much. This was because water rinsing could remove most foulants on membrane surface which was a small part of reverse fouling, and it was helpless for the removal of internal foulants which was the most reverse fouling. With respect to chemical cleaning, it was conducted after 2 h filtration, during which the flux behavior

Table 3
Optimum values of the process parameters for maximum MPR and minimum E_c.

	Shear stress (Pa)	Temperature (°C)	Time (min)	Concentration (%)
Water rinsing	83.26	42.04	67.36	
Chemical cleaning	35.74	49.79	10	0.24

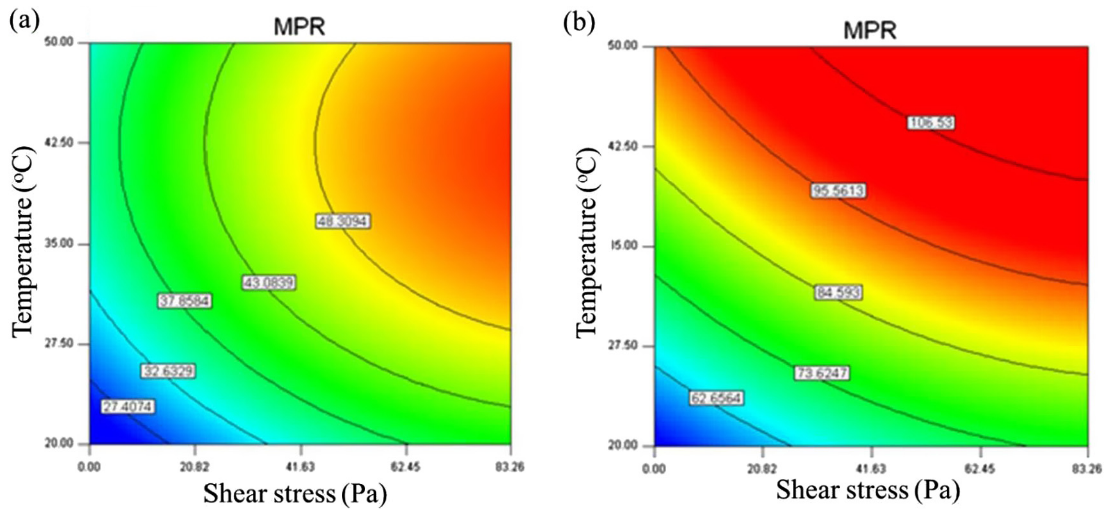

Fig. 10. Contour plot for MPR as a function of shear stress (Pa) and temperature (°C) for water rinsing (a) and chemical cleaning (b).

was presented in Fig 2. Average flux of 5 times cycle for chemical cleaning is 48 L m^{-2} h^{-1}, which is a litter smaller than that of water rinsing (52.5 L m^{-2} h^{-1}). This is due to the longer filtration, more serious fouling and the flux decline. The MPR before chemical cleaning (average 23%) is lower than the MPR before water rinsing (24%), which proves that conclusion. However, after chemical cleaning, the average MPR raises to 88%, which is much higher than water rinsing of 50% average value implying that even in the case of much more serious fouling, chemical cleaning assisted by high shear stress can still remove most of reverse fouling and possess excellent permeability recovery capacity. Moreover, after repeated high shear stress chemical cleaning (5 times cycle), membrane permeability can still keep at a high level.Fig. 11

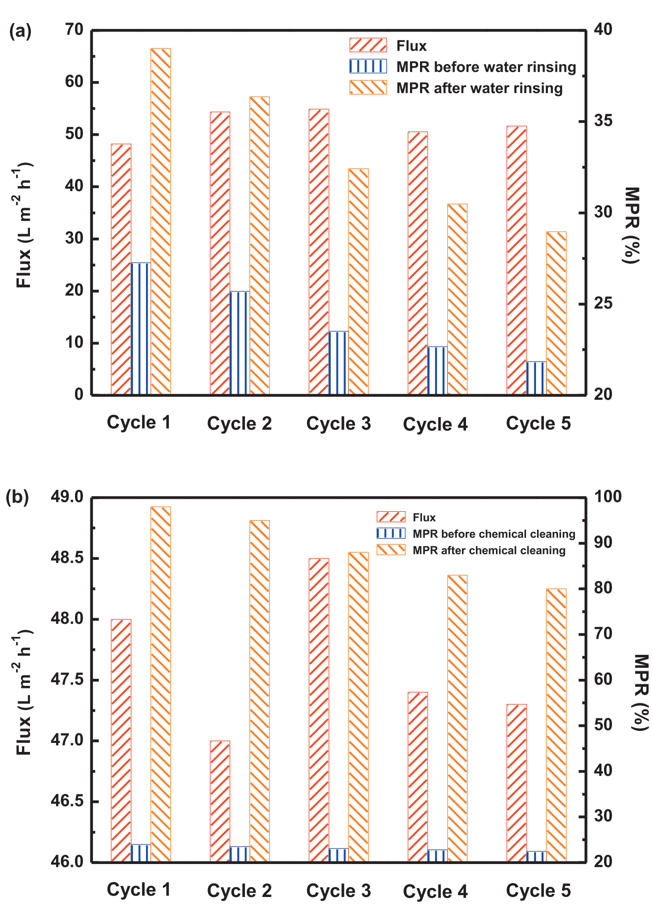

Fig. 11. The flux and MPR for 5 times cycle operation with (a) water rinsing and (b) chemical cleaning.

4. Conclusion

In this study, a novelty membrane cleaning method for restoring UF membrane in dairy wastewater pre-treatment was investigated. Membrane cleaning assisted by high shear stress is a widely unexplored field. The cleaning of dairy wastewater fouled membranes has been estimated with water rinsing and chemical cleaning. The role of high shear stress for enhancing membrane cleaning was studied.

For physical cleaning-water rinsing, shear stress and cleaning time continued prove to fortify cleaning efficiency. High shear stress improved the efficiency of removing casein micelles and whey protein layer on membrane surface. The cleaning temperatures of 35 and 50 °C had a much greater cleaning capacity than that of 20 °C. High temperature facilitated the solubility of foulants in the solution.

As for chemical cleaning, in comparison with other cleaning agents, due to the comprehensive compositions, P3-ultrasil 10 had better cleaning efficiency. Shear stress could reinforce the convection diffusivity and form foam on membrane surface, excessively promoting the cleaning effect. Owing to the adsorption effect, MPR decreased, when cleaning time exceeded 90 min.

Response surface methodology was adopted to investigate the significance of various operation conditions and to optimize the water rinsing and chemical cleaning process. In water rinsing, shear stress was the most important condition factor, while for chemical cleaning, shear stress was second only to temperature. For both, cleaning time was the least important condition factor.

Finally, with the optimum results, two long time industrial cleaning processes were carried out. The cleaning operation conditions were the optimum condition obtained by response surface methodology in Section 3.4. Water rinsing kept operation flux at a high level, if the cleaning timing before the threshold value, but it just removed a small part of reverse fouling and MPR was only 50%. Chemical cleaning assisted by high shear stress displayed excellent flux behavior in long time filtration and average 88% MPR, because it could remove most reversible fouling accumulated by long time filtration.

This study suggests that high shear stress is an effective and promising mean to enhance the cleaning process and minimize the environmental impact of chemical cleaning and chemical costs in diverse UF applications such as treatment of dairy wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.05.076.

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