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Application of response surface methodology to the chemical cleaning process of ultrafiltration membrane☆

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ABSTRACT

A numerical model was established to predict and optimise the chemical cleaning process of Polyvinylidene Fluoride (PVDF) Ultrafiltration (UF) membranes with the results from the experiment that applied the Response Surface Method (RSM) and Central Composite Design (CCD). The factors considered in the experimental design were sodium hydroxide (NaOH) concentration, sodium hypochlorite concentration (NaClO), citric acid concentration and cleaning duration. The interactions between the factors were investigated with the numerical model. Humic acid (20 mg·L^{-1}) was used as the model foulant, and chemical enhanced backflush (CEB) was employed to simulate the chemical cleaning process. The concentrations of sodium hydroxide, sodium hypochlorite, citric acid and cleaning duration tested during the experiments were in the range of 0.1%–0.3%, 100–300 mg·L^{-1}, 1%–3% and 0.5–1.5 h, respectively. Among the variables, the sodium hypochlorite concentration and the cleaning duration showed a positive relationship involving the increased efficiency of the chemical cleaning. The chemical cleaning efficiency was hardly improved with increasing concentrations of sodium hydroxide. However, the data was sharply decreased when at a low level of sodium hydroxide concentration. In total, 54 sets of cleaning schemes with 80% to 100% cleaning efficiency were observed with the RSM model after calibration.

1. Introduction

Low-pressure hollow membrane filtration is considered to be one of the most promising technologies in drinking water production [1]. Although MF and UF technologies have been widely studied and implemented, membrane fouling is still the technical bottleneck of these technologies [2,3]. Recently in China, due to the gradual degradation of source water quality, the upgrades of water treatment processes have become the top priority for water supply companies. UF technology, which is recognised as an efficient process with great effluent qualities, has become one of the preferred drinking water treatment technologies for upgrading and expanding existing facilities. Since 2009, a large number of water treatment plants (WTPs) using membrane filtration technology have been constructed, such as the Dongying Nanjiao WTP (50000 t·d^{-1}), the Beijing No. 9 WTP (90000 t·d^{-1}), the Shanghai Qingpu No. 3 WTP (100000 t·d^{-1}) and the Wuxi Zhongqiao WTP (150000 t·d^{-1}). With the application of the membrane filtration process in a large number of WTP upgrade projects, the development of effective chemical cleaning processes with fewer experiments has become a challenging day-to-day topic. However, the work on the membrane cleaning was much less than the work on understanding the membrane fouling mechanism [4]. Moreover, a majority of the research on membrane cleaning focused on physical cleaning [5].

Currently, a model developed by Feng *et al.* for cleaning of fouled membranes has been widely recognised. The model suggested that membrane fouling was governed mainly by the electrostatic interaction and the hydrophobic/hydrophilic interaction between the membranes and foulants. Electrostatic repulsion majorly enhances the cleaning efficiency [6]. The membrane cleaning options can be categorised as chemically enhanced backwashing (CEB) and cleaning in place (CIP), or as regeneration cleaning and maintenance cleaning, according to its purpose. Caustics (NaOH), oxidants (H_2O_2 and NaClO), acids (weak HCl, citric acid, *etc.*) and surfactants were widely used chemical cleaning agents. Recently, studies suggested that combination cleaning (the sequential use of caustics, oxidants and acids) could obtain a relatively high cleaning efficiency, due to the electrostatic interactions between foulants and membrane surfaces [7–11].

Membrane chemical cleaning can be illustrated in 6 steps [5,12,13]: 1) the introduction of the cleaning agent to the filter feed; 2) the cleaning agent makes contact with the foulant layers; 3) the cleaning

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agent travels through the foulant layers to the membrane surface; 4) the cleaning agent dissolves and detaches the foulant; 5) the reacted cleaning agent and suspended foulants are transported to the interface; and 6) the waste matter (used cleaning agent and detached foulants) is transported to the feed.

It is difficult to develop models from these complex factors to precisely evaluate the effects of chemical cleaning to the efficiency [5]. Therefore, current studies on chemical cleaning have been limited to a small number of selected schemes [14,15]. Bartlett *et al.* attempted to use the recovery rate of membrane flux as the indicator to quantitatively evaluate the impact of various cleaning factors on cleaning efficiency and suggested that it was possible to optimise the chemical cleaning process by using appropriate modelling methodology [16]. Chen *et al.* introduced factorial study in the testing of chemical cleaning processes and used the analysis of variance (ANOVA) to assess the impact of each factor [17]. Tian *et al.* considered that the chemical cleaning efficiency of the UF membranes could be indicated by the removal rate of the irreversible resistance of membrane [18].

In this study, software Design Expert Version 8.0 was used to develop the experimental plan and to response surface model within the limits of the experiment. The significance of the model was analysed by performing an analysis of variance (ANOVA). The interactions of the four factors, *i.e.*, sodium hydroxide concentration, sodium hypochlorite concentration, citric acid concentration and cleaning duration, affecting the chemical cleaning efficiency were assessed. The objective was to demonstrate that fitted response surface model could serve as a tool to perform and optimise control factors in the chemical cleaning process of a UF membrane.

2. Materials and Methods

2.1. Materials

The PVDF UF membrane, produced by the Suzhou Litree Ultrafiltration Membrane Technology Co. Ltd., was used in the experiment. According to the membrane producer, the average pore size of the given UF membrane was approximately 0.01 μm. The effective surface area of the membrane module was 0.003 m^2. Detailed information on the PVDF membrane module used in the experiment can be found in a previous paper [18]. The humic acids, bought from Sigma-Aldrich Co., were used as the foulant in the modelling. The sodium hydroxide (NaOH), NaClO and citric acid were of analytical purity. Milli-Q water was used to prepare the feed water and the cleaning solution.

2.2. Contamination and cleaning experiments

The resistance-in-series model [2] is widely used to describe the fouling properties of membranes and can be expressed as the formula below [19,20]:

$$R_{\mathrm{m}}+R_{\mathrm{f}}=R_{\mathrm{m}}+R_{\mathrm{rev}}+R_{\mathrm{irr}}=\frac{\Delta P}{\eta J} \tag{1}$$

where R_{m} is the intrinsic membrane resistance(m^{-1}); R_{f} is the total foulant resistance, including reversible (R_{rev}) and irreversible (R_{irr}) fouling resistance; ΔP is the transmembrane pressure (TMP, Pa); η is the dynamic coefficient of viscosity(Pa·s); and J is the filtrate flux($\mathrm{m}^3\cdot\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}$).

Prior to the experiments, the virgin membranes were placed into the filtering vessel after soaking in demineralised water for 30 min. To accelerate the fouling process, a relatively high membrane flux of 40 $\mathrm{L}\cdot\mathrm{m}^{-2}$ was applied. First, the membrane was used to filter the demineralised water for 1 h to reach a stable transmembrane pressure, which was used to calculate the intrinsic membrane resistance [21]. Then, a 20 $\mathrm{mg}\cdot\mathrm{L}^{-1}$ humic acid solution at pH 7 was fed to the membrane for a 12-hour fouling test. After the fouling test, the residual foulants on the surface of the membrane were wiped off by a sponge to physically eliminate the reversible fouling resistance before the chemical cleaning test. It was followed by another 1 h of filtration of demineralised water to measure the irreversible fouling resistance prior to the chemical cleaning. The chemical cleaning process was then conducted according to the central composite experimental design. Finally, the irreversible fouling resistance was measured again by filtering demineralised water for 1 h. Each experiment set was applied to 4 sets of new membrane modules in parallel.

2.3. Experiment design

Central composite design (CCD) is a method that can be efficiently applied to develop second-order response models with limited numbers of factors n ($2 < n < 6$). Based on the CCD, the experimental design was used to develop a response surface model by quadratic approximation. In this experiment, the central composite design (CCD) together with the response surface methodology was used to simulate the PVDF membrane cleaning process. Four independent variables were considered (NaOH concentration, NaClO concentration, citric acid concentration and the cleaning duration). According to existing studies on chemical cleaning of membranes, the operating ranges and the levels of the considered variables were chosen and are given in Table 1 [17,18]. The experimental design is shown in Table 2. The design involved 30 runs. The removal rate of the irreversible membrane resistance [as described by Eq. (2)] was the response variable. The chemical cleaning efficiency of the UF membranes could be indicated by the removal rate of the irreversible resistance of membrane [18].

$$R_{\mathrm{irr}}R=\frac{R^{\mathrm{b}}_{\mathrm{irr}}-R^{\mathrm{a}}_{\mathrm{irr}}}{R^{\mathrm{b}}_{\mathrm{irr}}}\times 100\% \tag{2}$$

where $R_{\mathrm{irr}}R$ is the removal rate of the irreversible resistance of membrane, $R^{\mathrm{b}}{}_{\mathrm{irr}}$ is the irreversible fouling resistance before chemical cleaning (m^{-1}), and $R^{\mathrm{a}}{}_{\mathrm{irr}}$ is the irreversible fouling resistance after chemical cleaning (m^{-1}).

3. Results and Discussion

3.1. Model establishment and sensitivity analysis

As shown in Table 2, the influence of the four variables [NaOH concentration (X_1), NaClO concentration (X_2), citric acid concentration (X_3) and cleaning duration (X_4)] on chemical cleaning process was evaluated in terms of cleaning efficiency ($R_{\mathrm{irr}}R$) of the UF membrane. When a statistical analysis using the Design Expert Version 8.0 was performed on the four factors of study, the interactions among the factors could be determined. The regression equation for the response variables (in coded terms) obtained from the experimental data based on the interaction effects between the factors was as follows:

$$\begin{aligned}R_{\mathrm{irr}}R=&\,97.27+6.39X_1+14.60X_2+0.59X_3+16.47X_4-6.43X_1X_2\\&+2.75X_1X_2-4.15X_1X_3-1.70X_2X_3+8.73X_2X_4-3.24X_3X_4\\&-7.09X_1^2-4.87X_2^2-10.48X_3^2-6.48X_4^2\end{aligned} \tag{3}$$

An ANOVA was applied to the regression model. The ANOVA result, with $F = 2.44$ and the p-value < 0.05, showed that the fitting equation was significant, which indicated that the four factors had an effect on the cleaning efficiency. The NaClO concentration and the cleaning duration were the significant factors. As shown in Fig. 1, the residuals generally falling on a straight line were distributed normally. The predicted value was close to the actual one. This observation implies