Prediction of the Optimum Conditions for Hydraulic Cleaning Process of Typical Organic Foulants on the Membrane Surface

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Abstract. In order to systematically analyse the impacts of stirring speed, temperature and cleaning duration on the membrane flux during hydraulic cleaning, a series of experiments were carried out with the PAN MF membrane and SA solution. Through comparative analysis, it is found that the membrane flux increases with the increase of temperature and stirring speed, but there is a critical value for cleaning duration. Considering the swelling, dissolution and redeposition of foulants, a formula to predict the instantaneous membrane flux during hydraulic cleaning is proposed. This method was used to successfully predict the instantaneous permeate flux of the membrane during the hydraulic cleaning process on the membrane fouled with different foulants. This method can be embedded into the automatic cleaning program and will greatly save cleaning time and improve production efficiency.

1. Introduction
In recent years, membrane bioreactor (MBR) developed rapidly in municipal sewage and industrial wastewater treatment due to its advantages such as high product water quality and small footprint [1,2]. However, the membrane fouling is still one of the great challenges faced by MBR, because the membrane fouling will reduce its filtration efficiency, increase power consumption and affect service life [3, 4]. Among the foulants on MBR, natural organic matter (NOM) accounts for a large part, which mainly consists of polysaccharides, proteins, humic substances [5,6].

In order to alleviate membrane fouling, many physical, chemical and even biochemical cleaning methods have been developed. Among them, hydraulic cleaning is the most widely used physical approach for removing reversible fouling from the membrane surface [2]. The main factors affecting the efficiency of the hydraulic cleaning process include surface shear force and liquid temperature and many researchers have conducted in-depth studies on the influencing mechanism of these parameters. For example, Zhang [7] found that the increasing of cleaning liquid temperature and shear stress could affect the convection diffusivity coefficient and improve the removal rate of foulants. Our research group systematically studied the impacts of temperature and shear force on swelling, dissolution and redeposition processes of the foulants on the membrane surface during hydraulic cleaning process and proposed a model which could accurately predict the instantaneous membrane resistance [3]. Wang [8]
and Kong [9] respectively demonstrated in the laboratory that the removal rate of foulants can increased significantly in the initial cleaning stage.

It is worth noting that although extending hydraulic cleaning duration could theoretically improve foulants removal rate and approach the virgin membrane indefinitely, there is an extreme value of hydraulic cleaning, and sometimes the flux will decrease due to the foulants entering the membrane pores. In addition, unnecessarily extend the cleaning duration also means increasing of power consumption and decreasing of water production efficiency of the MBR. Therefore, the optimization of hydraulic cleaning procedure has important practical significance for the improving running efficiency for MBR. In this study, considering the characteristics of organic foulants and their swelling, dissolution and redeposition in the process of hydraulic cleaning, a method to select the optimum cleaning conditions is proposed. This method can also be embedded into the automatic membrane cleaning program, which can greatly improve the hydraulic cleaning efficiency. We hope that this method can help promote the development of membrane cleaning towards a more efficient and sustainable direction.

2. Materials and methods

2.1 Chemical agents and solutions/suspensions
NaCl, NaOH, HCl, KCl, KH2PO4, Na2HPO4 and CaCl2 were provided by the Beijing Chemical Works. Unless otherwise stated, all of the chemical agents used in the experiment were analytical grade and all solutions were prepared with DI-water supplied by the ultrapure water system (Millipore, France). The activated sludge (AS) was obtained from a lab-scale sequencing batch reactor (SBR) which was kept running for over three years. Sodium alginate (SA), bovine serum albumin (BSA) and humic acid (HA) were respectively employed as representative of polysaccharides, proteins and humic substances in this experiment. Their suppliers and the process of preparing stock solutions can be found in the published literatures of our research group [3,8,10].

2.2 Membrane type and experimental procedures
Four types of commercially available microfiltration (MF)/ultrafiltration (UF) flat-sheet membranes (ANDÉ, Beijing, China) were used in this study. The material and pore size/molecular weight cut-off of the membranes respectively were polyacrylonitrile (PAN, 0.1 μm), polyvinylidene fluoride (PVDF, 0.1 μm), PAN (200 kDa) and polyethersulfone (PES, 200 kDa). Before used, the virgin membranes need to be immersed in DI-water for 12 hours at the temperature of 4 °C to remove the protective layer on the membrane surface. All the experiments were carried out on a dead-end filtration cell (effective filtration area was 37.39 cm²) coupled with a magnetic stirrer and follow these steps: I) compress the virgin membranes with DI-water at 0.1/0.2MPa, II) measure the pure water flux of the virgin membranes at 0.05/0.1MPa, III) filtrate the fouling solutions at 0.05/0.1MPa with a stirring speed of 200 rpm, IV) clean the fouled membrane with DI-water at different stirring speeds, temperatures and durations, V) measure the pure water flux of the cleaned membranes at 0.05/0.1MPa.

2.3 Analytical Method
The instantaneous flux of the membrane during hydraulic cleaning process can be calculated by the following formulas.

\[
J_c(t) = \frac{\Delta P}{\mu \times R_f(t)} = \frac{\Delta P}{\mu \times (R_f(t) + R_m)}
\]

\[
R_f(t) = R_f(0) \left(1 - \frac{k_y - k_x}{k_y - k_R - k_x} \right) e^{-k_x t} + \left( \frac{R_f(0)(k_y - k_x)}{k_y - k_R - k_x} - R_f \right) e^{-(k_y + k_x) t} + R_f
\]

where \(J_c(t)\) is the membrane permeate flux at cleaning time \(t\) (m³/(m²·h)), \(\Delta P\) is transmembrane pressure (TMP) (Pa), \(\mu\) is the viscosity of DI-water (Pa·s), \(R_f(t), R_f(0)\) and \(R_m\) respectively represent the total resistance at time \(t\), the fouling resistance of membrane at time \(t\) and the resistance of the membrane.
itself \( (m^{-1}) \), \( k_w \), \( k_D \) and \( k_R \) respectively represent the first-order kinetics constants of swelling, dissolution and redeposition of foulants.

### 3. Results and Discussion

#### 3.1 The impacts of stirring speed and temperature

Figure 1(a) and (b) respectively exhibited the impacts of stirring speed and DI-water temperature on the process of hydraulic cleaning PAN membrane (0.1 μm) fouled with SA solution. When the stirring speed goes from 200 rpm to 500 rpm, the flux of membrane after cleaning increases rapidly (Figure 1 (a)). The main reason is that the increase of stirring speed directly leads to the increase of Reynolds number near the membrane surface, which overcomes the adhesion of the foulants to the membrane surface and accelerates the separation of the foulants [3]. The increasing of the temperature of the cleaning solution (DI-water, from 20℃ to 50℃) will also increase the membrane flux after the hydraulic cleaning (Figure 1 (b)). For example, at 50℃, the membrane flux can be restored to 468.76 L/(m²•h), while at 20 ℃, the value was only 242.81 L/(m²•h). The main mechanism for this phenomenon is that the increase of temperature not only increases the solubility of the foulants, but also expands the membrane pores due to thermal barrier shrinkage, which resulted parts of foulants in the pores swell, dissolve and eventually diffuse into the cleaning solution.

![Figure 1](image.png)

**Figure 1.** The impacts of cleaning conditions on the membrane permeate flux after cleaning:(a) stirring speeds and (b) DI-water temperatures.

#### 3.2 The impact of cleaning duration and critical point

Regarding for the impact of hydraulic cleaning duration (Figure 2(a)), the permeate flux of the PAN MF membrane fouled with AS suspension after hydraulic cleaning can be obviously divided into two stages under three cleaning conditions. In the first stage, the membrane flux increases rapidly with the increase of the cleaning duration, but in the second stage, the membrane flux reaches an extreme value at different stirring rates and temperatures, and the membrane flux will not increase if the cleaning duration is prolonged. Such trend was also verified by using PVDF MF membrane (Figure 2(b)). There is a critical point during the hydraulic cleaning process, at which the swelling, dissolution rate and redeposition rate of foulants reach an equilibrium state, and unnecessarily prolonged cleaning time will only cause energy loss and water production efficiency reduction. Therefore, how to predict this critical point in advance is of great significance in practical engineering applications.
Figure 2. The effects of cleaning duration on the permeate flux after cleaning: (a) the PAN MF membrane fouled with AS suspension and (b) the PVDF MF membrane fouled with AS suspension.

3.3 Verification of instantaneous flux prediction method

In order to verify the application and validity of the predicted flux method, the cleaning data of different MF membranes (PAN and PVDF) and two UF membranes (PAN and PES) respectively fouled with four different organic matters (SA, HA, BSA and AS) were compared with the predicted values. The predicted values were very similar to the experimental data at any stirring speeds and temperatures (Figure 3(a)-(f)). For example, during the hydraulic cleaning process for the PAN UF membrane fouled with SA solution, R² respectively was 0.998 (5℃ and 200rpm) and 0.986 (25℃ and 400rpm) (Figure 3(a)). The critical point of cleaning efficiency appeared at 4 minutes, and the membrane flux would not increase after prolonged cleaning duration. Similarly, the critical point occurred at 2 min when cleaning the PES UF membrane fouled with SA solution (Figure 3(b)). For the PAN UF membrane (Figure 3(c)) and MF membrane (Figure 3(d)) fouled with AS suspension, the optimum cleaning duration respectively were 5 minutes and 6 minutes. For the PAN MF membrane respectively fouled with HA and BSA solution, the respond effective cleaning time respectively was 4 minutes and 12 minutes.
Figure 3. Comparison of the instantaneous membrane flux (experimental data) and predicted flux in hydraulic cleaning process of different membranes and different organic foulants ((a) - (f)) and particle size distribution of BSA, SA and HA solutions and AS suspension (g).

For different membranes and different foulants, the critical point of cleaning efficiency is different, which is mainly due to three reasons: (1) the first major reason is the characteristics and fouling mechanisms of the foulants. As showed in Figure 3(g), the particle size distribution of BSA, SA and HA solutions respectively is 1.5 nm, 965 nm, 1970 nm and 38.87 μm and they played an important role in the membrane fouling process (complete blocking, intermediate blocking, standard blocking and cake filtration) [10]. For example, in the initial stage of filtration, HA first adsorbs rapidly in the membrane pore, then gradually transforms into pore blocking, and finally starts to form fouling...
layer on the membrane surface, while for SA, the fouling mechanism is first to shrink pores and then to be dominated by cake filtration [11]. (2) The nature of the membrane surface. Because the membrane material is different, the surface energy of the membrane will be different, and also lead to the fact that the adhesion between the foulants and the membrane surface is different [12]. (3) The hydraulic cleaning mainly removes reversible fouling from the membrane surface, and the removal effect on the foulants in the membrane pores and those closely bonded to the membrane surface is limited [4,9].

4. Conclusion
In this study, the impacts of stirring speed temperature and duration of cleaning on membrane flux after cleaning were systematically analysed with the PAN MF membrane and SA solution. The results showed that the membrane flux increased rapidly with the increase of stirring speed and cleaning temperature, which was mainly attributed to their promoting effect on the swelling and dissolution process of foulants. There is a critical point in the process of hydraulic cleaning, after which the membrane flux will not increase if the cleaning duration was extended. Based on this finding, a method is proposed to determine the optimal cleaning conditions during the cleaning process. During the cleaning process of the MF/UF PAN, MF PVDF and UF PES membranes fouled with SA, AS, HA and BSA solutions/suspensions, the predicted values were in good agreement with the actual experimental data. Finally, the phenomenon of critical point appearing at different time in the process of cleaning different foulants and membranes was analysed.

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