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Prediction of the instantaneous fouling resistance of sodium alginate during water rinsing

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ABSTRACT

Based on swelling and dissolution mechanism, a model describing first-order parallel-reversible process was developed to predict the fouling resistance of 0.1 μm polyacrylonitrile (PAN) membrane fouled with sodium alginate (SA) during water rinsing. The results showed that there were good agreements between model predictions and experimental values ($R^2 > 0.9$). Especially in the situation when the impact of water rinsing condition on model parameter was considered. Moreover, the applicability of the proposed model was validated by a series of rinsing experiments with 0.1 μm polyvinylidene fluoride (PVDF) membrane or active sludge suspension. In addition, feed concentration had a great role in the fouling process while temperature impact on the cleaning process was also very appreciable. And the reversibility of SA fouling was well explained by the electrostatic and hydrophilic repulsions between PAN membrane and SA.

1. Introduction

Microfiltration has been widely applied in the wastewater treatment (He and Vidic, 2016; Lee et al., 2013), especially for membrane bioreactors (MBR) (Masao et al., 2016; Amarasiri et al., 2016). One of the major drawbacks to limit the widespread of MBR is membrane fouling, which makes a rapid decay of flux, increases operating cost and shortens the lifetime of the membrane. Extracellular polymeric substances (EPS), which are mainly composed of polysaccharide, protein, humic substances and uronic acid was proved to be as the main substance that causes membrane fouling in MBR (Chang et al., 2001; Cho et al., 2001, 2004; Ye et al., 2005). Sodium alginate (SA) has been frequently used, as one popular model substance of polysaccharide in EPS, to study its membrane fouling behavior (Nataraj et al., 2008; Van de Ven et al., 2008; Listiarini et al., 2009; Arndt et al., 2016).

Hydraulic cleaning is a popular approach for alleviating membrane fouling due to the environment-friendly character of no chemical reagents and the advantage of less membrane degradation/damage (Qi et al., 2016; Li et al., 2016; Chang et al., 2016). The fouling layer of forward osmosis membrane fouled with SA was easy to be removed by water rinsing (Mi and Elimelech, 2010). The flux recovery of polyvinylchloride UF membrane fouled with SA can achieve 92% for hydraulic flushing (Guo et al., 2009). Water rinsing could remove 80% protein from the UF inorganic membrane (Matzinos and Álvarez, 2002) and dissolve most of the deposits on the surface of PVDF MF membranes fouled with α-lactalbumin (Bansal et al., 2006). SA fouling on the UF membrane was highly reversible with backwashing (Katsoufidou et al., 2008). The flux recovery could reach 80% for UF membrane fouled by algae when backwashing followed by forward flushing were used (Liang et al., 2008). Moreover, the maximum cleaning efficiency of 90% was obtained for UF ceramic membrane fouled with whey protein when water rinsing was conducted under optimized conditions (Cabero et al., 1999).

Kinetic models provide basis and guide for industrial process control, process optimization, and automation (Fan et al., 2015). Some cleaning model has been developed. A sum model of two first-order models for water rinsing was developed to predict the fouling resistance decay for UF membrane fouled with whey proteins (Matzinos and Álvarez, 2002; Cabero et al., 1999). A first-order kinetic model was developed to describe the fouling resistance of commercial beer (Gan et al., 1999) and the cleaning ability of four cleaning agents in chemical

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cleaning was compared (Li et al., 2005). A first-order model of cleaning rates was also established to depict alkaline cleaning process (Xin et al., 2004). In addition, a first-order model containing three parameters (transmembrane pressure, pH, and turbidity) was used to predict the variation of the irreversible fouling state (Zondervan et al., 2007). A first-order kinetic model of cake resistance with a second-order swelled kinetics for in-pore fouling was proposed to predict the total resistance variation for alkali cleaning process (Popović et al., 2009a,b). A second order model for cake resistance was combined with a second-order model for resistance due to in-pore swelling to describe the cleaning process of the inorganic MF membrane fouled with whey protein concentrate (Bird and Bartlett, 2002). A second order model for fouling resistance was developed for the NaOH cleaning process of UF membrane fouled with dairy (Alvarez et al., 2007). A cleaning model was hypothesized with 3 removal characteristics of protein during the rinsing and chemical cleaning process (Bartlett et al., 1995).

However, water rinsing of 0.1 μm PAN microfiltration membrane fouled with SA solution and the modeling of the fouling resistance of SA during water rinsing has not been reported. Therefore, the aim of this work is to establish a model considering swelled and solving mechanisms to predict the instantaneous fouling resistance of SA for 0.1 μm PAN MF membrane during water rinsing.

2. Materials and methods

2.1. *Chemicals and membranes*

All chemicals of analytical grade including sodium alginate, sodium bicarbonate, glycerol, and diiodomethane were provided by Beijing Chemical Engineering Factory. DI-water was produced by a Milli-Q water system (Millipore, France). PAN and PVDF MF membranes with mean pore size of 0.1 μm were purchased from ANDE Membrane Separation Technology & Engineering, Beijing CO., Ltd. Before being used, the virgin membrane samples with an effective filtration area of 37.39 cm^2 were soaked in the DI-water at 4 °C for 12 h to remove glycerin.

2.2. *Experiments*

The experiments were performed in a dead-end cell with magnetic stirring. And the SA solution, which consists of given concentration and 0.5 mM sodium bicarbonate (buffer) (Hashino et al., 2011) was kept for 12 h to completely dissolve. Then the permeate weight was recorded by electronic balance and counting software with the time interval of 30 s.

2.2.1. *The pure water flux (PWF) of the membrane*

The PWF of the membrane was measured in 5 min before fouling and after rinsing. About 300 mL DI-water at 20 °C was filtrated through the membrane at 0.05 MPa. To reduce the experimental error caused by the membrane, the membranes used in the following experiments were selected by the error of pure water flux (PWF) was less than 10%.

2.2.2. *Membrane fouling*

The membranes were compacted before carrying out fouling experiments at 0.025 MPa for 20 min. 250 mL SA solution (20 °C) was used to carry out the fouling tests at fixed stirring speed and under constant transmembrane pressure (TMP) for 1 h. When the fouling process was finished, the cell was empty by pouring out the residual SA solution. Then the fouling conditions (SA concentration, stirring speed and TMP) were altered to conduct the fouling experiments with other virgin membranes. Each operation was repeated three times to obtain a convincing result.

2.2.3. *Rinsing experiments*

100 mL DI-water was poured into the cell to clean the fouled membrane at constant stirring speed and temperature. The temperature was kept by a thermostatic water bath. When the rinsing process was finished, the cell was emptied by pouring out the water and the PWF of the cleaned membrane was measured (see Section 2.2.1). Subsequently, the rinsing conditions (time, stirring speed and temperature) were changed to conduct the rinsing experiments with the fouled membrane at the same fouling condition. Each operation was repeated three times to obtain a convincing result.

2.3. *Analysis method of membrane process*

The permeate flux of the membrane (*J*) could be calculated as following (Steinhauer et al., 2015):

$$J = \frac{\Delta m}{\rho \cdot A \cdot \Delta t} = \frac{\Delta P}{\mu \left(R_m + R_f \right)} \quad (1)$$

where *m* is the permeate mass at the time *t*, kg; ρ is the permeate density, kg/m^3; *A* is the effective area of the membrane, m^2; *t* is the filtration time, s; *TMP* is transmembrane pressure, Pa; μ is the viscosity of the permeate, Pa s; R_m is the resistance due to the membrane itself, which is usually regarded as a constant, m^{-1} and R_f is the fouling resistance due to fouling, m^{-1}.

The average shear stress in a dead-end cell was obtained by integrating the shear stresses, which was reported by Shamsuddin et al. (2015), over radical distance and then averaging the sum of the shear stresses in the inner and outer region.

$$\bar{\tau} = \frac{0.825 \times \frac{\mu\omega}{\delta} \left(\int_0^{r_c} r dr + {r_c}^2 \int_{r_c}^{D_c/2} \frac{1}{r} dr \right)}{D_c/2} \quad (2)$$

where μ is the dynamic viscosity of fluid, Pa s; ω is the angular velocity, rad/s; δ is the thickness of momentum boundary layer, m; r_c is the critical radius where the shear stress is maximum, m; *r* is the radial distance to the center point in the stirred cell, m and D_c is the diameter of stirred cell, m.

Temperature is an important factor for the diffusion of SA particle and the diffusion coefficient (*D*) at different temperatures could be roughly evaluated by Stokes–Einstein equation (Garcia-Ivars et al., 2015):

$$D = \frac{k_B T}{6\pi\mu r_a} \quad (3)$$

where k_B is the Boltzmann constant (1.38×10^{-23} J/K), *T* is the operating temperature, K; r_a is the average radius of SA particle, m. The particle size distribution of 100 mg/L SA solution was measured by the Malvern laser particle diameter distribution instrument (MAF-5001, Malvern CO., England). The pH and temperature of the feed solution was 7.8 and 25 °C, respectively. The background electrolyte salt was 0.05 mM sodium bicarbonate.

The interaction energy could be used to determine the interactions between the foulant and membrane for aqueous system as following (Zhao et al., 2016):

$$\Delta G_{d_0}^{LW} = 2 \left(\sqrt{\gamma_w^{LW}} - \sqrt{\gamma_m^{LW}} \right) \left(\sqrt{\gamma_f^{LW}} - \sqrt{\gamma_w^{LW}} \right) \quad (4)$$