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Reinvestigation of membrane cleaning mechanisms using NaOCl: Role of reagent diffusion

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ABSTRACT

Sodium hypochlorite (NaOCl) is a widely used cleaning reagent for membrane separation processes to recover membrane permeability; however, the competitive interactions of different chlorine species with fouling layers have not been adequately elucidated. In this work, we investigated the pH-dependent diffusion of the active chlorine species and reactions involved in the consequent dissociation and/or destruction of the fouling layers. The hypochlorite conductivity and dynamic diffusion tests showed that an increase in pH facilitated the uneven and fast diffusion of active chlorine via relaxing the matrix structure of the fouling layer. Under the synergetic effects of oxidation, hydrolysis and hydraulic shearing, the enhanced diffusion resulted in an uneven but massive removal of the foulants rather than a layer-by-layer dissociation, leading to a higher membrane cleaning efficiency. Sodium dodecyl sulfate (SDS), an anionic surfactant, was added into the cleaning solution to further validate the diffusion-dependent cleaning mechanisms. With a faster diffusion process aided by SDS, the cleaning efficiency was significantly improved. These findings provide new insight into the chemical cleaning mechanisms, which are of great importance to the optimisation of cleaning efficiency for various membrane-based processes.

1. Introduction

Membrane separation technologies including microfiltration/ultrafiltration, nanofiltration and reverse osmosis and their derivations (e.g., membrane bioreactors and membrane capacitive deionization), in the last few decades, have gained increasing popularity in advanced water and wastewater treatment due to the superior liquid-solid/-solute separation performance [1–4]. While substantial progress in the material preparation and process optimisation has made the use of membranes economical and practical, critical challenges remain with regard to the inevitable fouling/scaling resulting in the deterioration of membrane performance (i.e., higher resistance and lower flux), reduction of the membrane lifespan and, ultimately, increase in the operation cost [5–7]. As a consequence, chemical cleaning is of particular importance in the maintenance of membrane separation processes [7,8].

Sodium hypochlorite (NaOCl) is one of the most commonly used reagents in the maintenance and recovery cleaning of membranes to restore the permeability [8–10]. Generally, the cleaning and caustic effects of NaOCl are ascribed to the oxidation and hydrolysis (saponification) with the implementation of its protonated form, i.e., HOCl ($pK_a = 7.53$), initially expected to be more effective because of the stronger oxidation capacity of $HOCl/Cl^-$ ($E^\circ = 1.50$ V vs. SHE) compared to OCl^-/Cl^- ($E^\circ = 0.89$ V vs. SHE) [11,12]. However, numerous studies addressing the impacts of different operating parameters on the efficiency of NaOCl/HOCl have clearly shown that alkaline conditions are more favorable in the membrane cleaning protocols [11,13,14]. This phenonmenon is allegedly attributed to the competition of different active chlorine species interacting with the membrane surface; i.e., at $pH < 7$, chlorine is prone to incorporate into the membrane matrix with the chlorination causing the increase in membrane hydrophobility and decrease in permeability whilst OCl^--promoted saponification is dominant at $pH > 7$ with abundant hydroxyl groups generated on the membrane surface [11,14]. On the other hand, the cleaning efficiency of fouled membranes is also determined by the interaction between $HOCl/OCl^-$ and the foulants formed as a result of the precipitation of biopolymers and/or metal complexes [15,16]. However, there is surprisingly limited information on the competitive effects of different chlorine species involving the

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dissociation and/or destruction of the fouling layers.

Although the reaction of chlorine with the fouling layers (and membrane surface) has been emphasized above, consideration must be given to the diffusion process of the chlorine species as this step is precedent in the cleaning process where the following chlorination and/or hydrolysis in the fouling layers are kinetically dependent on the mass transfer of $HOCl/OCl^-$ [16]. In terms of the precipitation of biopolymers and/or metal complexes on the membrane surface, the dynamic identification of the occurrence and/or transformation of the foulants by fluorescence in situ hybridization-confocal laser scanning microscopy (FISH- CLSM) has been well addressed towards a better understanding of the fouling mechanism [6,17]. With regard to the mass transfer of chlorine in the cleaning process, while it has been implied that the mixture of oxidants and caustic could induce a synergy providing more access to chlorine to reach inner layers of the fouling substances, thus facilitating the mass transfer and reaction of the chlorine species [8,13,18], there is no detailed investigation on how the diffusion process occurs in the fouling layers. As such, quantitative understanding of the diffusion of chlorine and its influences on the following reactions in the fouling layer are of great importance for the optimisation of the cleaning tactics for membrane separation processes.

In this study, we elucidate the above issues by examination of the pH-dependent diffusion of the active chlorine species and, in parallel, reactions involving the consequent dissociation and/or destruction of the fouling layers by using CLSM techniques. Specific consideration has been given to: (i) How is the diffusion kinetics of the active chlorine species affected by the solution pH? (ii) How does the pH-dependent diffusion process influence the competitive interaction of $HOCl/OCl^-$ with the fouling layer? (iii) What is the relationship between the diffusion-dependent dissociation (and destruction) of the foulants and the chemical cleaning efficiency?

2. Materials and methods

2.1. Reagents

Unless specified otherwise, all chemicals used in this work were of analytical grade with purity over 99%. Bovine serum albumin (BSA) and sodium alginate (SA) were purchased from Aladdin (China). Sodium hypochlorite (~5% NaOCl, reagent grade), sodium dodecyl sulfate (SDS), sodium thiosulfate (NaS_2O_3), 2′,7′-dichlorofluorescein diacetate (DCF-DA) and calcium chloride were obtained from Sigma Aldrich (Sigma Inc., U.S). Solution pH was adjusted by 1 M NaOH or 1 M HCl when necessary. The ultrafiltration membranes (100 kDa) were purchased from Millipore (U.S.) and the membrane properties are presented in Table S1. Deionized (DI) water was used in all experiments.

NaOCl solutions at different pH were used as the cleaning agents. The total chlorine concentration (Cl_T) was defined as the sum of the active chlorine species, determined by the iodometric titration method in the unit of "ppm of Cl equivalent" [11,19]. pH of the cleaning solutions was maintained at 5, 7, 9 or 11 by adding HCl or NaOH respectively. According to the acidity constant of hypochlorous acid ($K_a = 2.9 \times 10^{-8}$), the concentrations of HOCl and OCl^- species were calculated according to Eqs. (1) and (2) [11,20]:

$$[\mathrm{HOCl}] = \frac{\mathrm{Cl_T}[\mathrm{H^+}]}{K_a + [\mathrm{H^+}]} \tag{1}$$

$$[\mathrm{OCl^-}] = \frac{\mathrm{Cl_T} K_a}{K_a + [\mathrm{H^+}]} \tag{2}$$

2.2. Preparation of the fouling layers

In this study, the fouling layers were prepared on the membranes in a bench-scale dead-end filtration cell (Millipore Cor., U.S.) (See Supporting Information (SI) Fig. S1). The cell has an effective volume of 400 mL and can house 76 mm diameter membrane samples. Pressure was provided by a compressed N_2 cylinder. Prior to tests, membrane samples were respectively compacted at 100 kPa with DI water until the permeate flux (J_0) became stable. A feed solution containing 1 g L^{-1} model foulant (BSA or SA) and 1 mM Ca(II) was then filtered through the membrane at 400 kPa with a constant stirring of the solution at 200 rpm. Experiments were stopped when the permeate flux (J_f) was declined to ~5% of the initial (J_0).

2.3. Evaluation of $OCl^-/HOCl$ diffusion

The diffusion behaviors of $OCl^-/HOCl$ in the fouling layer were evaluated in a self-made hydraulic conductivity measurement cell as shown in SI Fig. S2 with more details documented in SI Section S1. The permeate fluid used in all tests was NaOCl solutions with 100 ppm Cl_T at different pH. The specimens (i.e., membranes with fouling layers) were placed in the cell upon the backpressure saturated by the permeate fluid at a pressure of 0.1 kPa. Results of three consecutive measurements were provided with the deviations less than 25%. Confocal laser scanning microscopy (CLSM, Nikon A1, Japan) was further employed to investigate the dynamic diffusion process of $OCl^-/HOCl$ at different pH. The fouling layers were stained in 10 mM DCF-DA solution for 1 h and then washed with deionized water for three times. The reaction of active chlorine with DCF-DA generates fluorescence [21,22], which was recorded at excitation wavelength of 488 nm and emission wavelength of 510–560 nm at different diffusion time. The roughness coefficient (R_c) of the diffusion layer of the active chlorine species, an indicator between 0 and 1 with 1 representing the perfect evenness whilst 0 the highest unevenness, was calculated using the Nikon's NIS-Elements Advanced research software, version NIS 3 (updated to version 4.1) [23,24].

2.4. Batch-scale cleaning experiments

In all cleaning experiments, 40 mL of DI water was first added into the dead-end filtration cell following the preparation of the specimens, and stirred at 30 rpm for 30 s to remove the foulants loosely-bounded on the membrane surface. The subsequent cleaning process was carried out at 400 kPa with the use of 40 mL cleaning solutions containing different concentrations of $OCl^-/HOCl$. The flux recovery rates were calculated as follows: $R = J_t/J_0$, where J_t indicates the recovered flux in DI water following a period (t) of chemical cleaning.

Afterwards, the cleaning solution was collected for the characterization of the foulants in it. The size of the foulants was determined using dynamic light scattering (DLS) at 25 °C on a Zetasizer Nano-ZS system (Malvern Instruments, England). Total organic carbon (TOC) concentrations were determined using a TOC analyzer (Shimadzu Corporation, Kyoto, Japan) with Ca(II) concentrations measured by an inductive coupled plasma emission spectrometer (Agilent 720ES, USA) after the solution was filtered with 0.22-μm membranes. CLSM was introduced to visualize the structural changes of the fouling layers due to the interaction of $OCl^-/HOCl$. Specimens were withdrawn from the cell and soaked in 1 mM NaS_2O_3 solution to terminate the chlorine at pre-determined time (0, 15, 30 or 45 min). After that, Concavalin A (Con A, Molecular Probes, Inc.) and SYPRO Orange (SYPRO® Orange, Molecular Probes, Inc.) were used as fluorescent dyes to label α-glucopyranose polysaccharides and protein, respectively, according to the procedures described elsewhere [25–27].

To further validate the effect of diffusion on membrane cleaning, SDS was used as an anionic surfactant to enhance the diffusion of $OCl^-/HOCl$. 0.5 mM SDS, which alone has negligible cleaning efficiency [28], was added into the NaOCl solutions (Cl_T = 100 ppm, pH = 5 and 11) for batch cleaning tests. The hypochlorite diffusion was then evaluated following the protocols mentioned above. The digital image analysis program was also used for the fouling layer structure