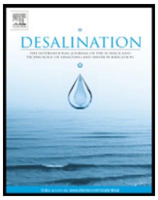
Desalination 331 (2013) 62–68

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Microfiltration (MF) membrane fouling potential evaluation of protein with different ion strengths and divalent cations based on extended DLVO theory

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HIGHLIGHTS

- Protein fouling potential of MF membrane was evaluated by extended DLVO theory.
- The measured interaction energies were related to fouling rate of MF membrane.
- The changed fouling potential of MF membrane was confirmed by interaction energy.
- The more attractive region surrounding each asperity enhanced the protein attachment.
- Fouling potential of MF membrane was predicated by interaction energy and roughness.

ARTICLE INFO

Article history:
Received 29 April 2013
Received in revised form 21 September 2013
Accepted 18 October 2013
Available online 8 November 2013

Keywords:
Microfiltration membrane fouling
Protein fouling
XDLVO approach
Foulant–MF membrane interaction energy
Foulant–foulant interaction energy

ABSTRACT

Membrane fouling is a major obstacle to the wide application of microfiltration membrane bioreactor (MF MBR). Protein-like substances have been known to contribute significantly to membrane fouling in MF MBRs. In this study, the effects of ionic strength and divalent cations on MF membrane fouling by protein were investigated. Fouling experiments showed that MF membrane fouling by protein was enhanced with increasing ionic strength and calcium ion addition. Measured interaction energies among protein molecules and between protein molecules and clean MF membrane confirmed the fouling trends of MF membrane. It was consistently shown that solution chemistries that induced higher fouling rates of MF membrane were associated with greater attractive and lower repulsive interaction energies among protein molecules and between protein molecules and clean MF membrane. Analysis of fouled MF membrane surface roughness further indicated that MF membrane fouled by protein with higher ion strength and calcium addition made attachment of foulant onto MF membrane surface easier.

1. Introduction

Microfiltration membrane bioreactor (MF MBR) as an efficient and compact treatment technology has been widely studied and increasingly applied in wastewater treatment [1,2]. However, membrane fouling which results in an increase of maintenance and operational costs is a major obstacle to the wide application of MF MBRs [3,4]. Studies had shown that extracellular polymeric substance (EPS) [5,6] and soluble microbial product (SMP) [1,7] played significant roles in MF membrane fouling. Protein was identified as one of the major components in EPS and SMP [8]. Analysis of fouling layer had shown high protein content in the organic fraction [9]. Therefore, understanding the mechanisms of protein fouling of MF membrane is important for successful and widespread application of MF MBR.

Protein fouling of MF membrane is a complicated process due to the complex interaction between protein and MF membrane and between protein molecules [10]. As we know, in the practical MBR, the protein fouling was influenced by many factors due to the existence of sludge flocs. Zhang et al. reported that calcium was effective in decreasing protein content to retard the membrane fouling by strengthening the neutralization and bridging of EPS with flocs [11]. Therefore, the interactions between protein and MF membrane surface and between protein molecules were not easily determined in the practical MBR. Thus, the experiments were performed in a model system using a batch filtration apparatus and simple solutions to contribute towards a better understanding of the protein fouling behaviors of MF membrane. Bovine serum albumin (BSA) has been used as a model foulant to study protein fouling processes of membrane in a few literatures [10,12,13].

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http://dx.doi.org/10.1016/j.desal.2013.10.017

Organic foulant deposition is usually interpreted through extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) models [14–16]. Recently, Xiao et al. applied XDLVO to describe the combined effect of membrane and foulant (dextran, bovine serum albumin and humic acid) hydrophobicity and surface charge on adsorptive fouling during microfiltration [17]. Subramani et al. utilized XDLVO to elucidate the impacts of adsorbed organics on membrane properties and on initial bacterial cell deposition rates [18]. The interaction energies between the BSA and the membrane surface might be predicted implementing the XDLVO theory.

The ionic strength and divalent cations played important roles in interaction between protein and membrane and between protein molecules. There were some other papers which had already addressed the fouling issues in different membranes caused by protein and its relation with the ionic strength and divalent cations. Nakamura and Matsumoto focused on the effects of the pH, ionic strength, and surface modification on the BSA adsorption properties during microfiltration [19]. Wang and Tang evaluated the effect of hydrodynamic conditions, membrane properties, and feed solution chemistry on BSA fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes [20]. Ang and Elimelech studied the effect of ionic strength and calcium concentration on BSA fouling of reverse osmosis (RO) membranes, meanwhile atomic force microscopy (AFM) is used to study the interaction forces between the foulant in the bulk solution and the foulant adsorbed on the membrane surface [21]. She et al. investigated the effect of hydrodynamic conditions and solution chemistry on protein fouling during ultrafiltration [13]. All the results obtained from these researches were to elucidate the BSA fouling mechanisms of different membranes with various conditions through different methods. However, in these researches, the XDLVO theory was not used to evaluate the protein fouling behaviors of MF membrane with different ion strengths and divalent cations.

Thus, the motivation of this research was to contribute towards a better understanding of the protein fouling behaviors of MF membrane with different ion strengths and divalent cations based on XDLVO theory. Firstly, the changed filtration characteristics of protein with different ion strengths and divalent cations were investigated by batch filtration experiments; secondly, the physicochemical interactions between protein and MF membrane surface, and between protein molecules were characterized through XDLVO models; and finally, the roughness of fouled MF membranes by protein with different ion strengths and divalent cations was detected using AFM. This study would provide a new method to investigate the protein fouling potential of different membranes based on XDLVO theory.

2. Materials and methods

2.1. Microfiltration membranes

Polyvinylidene fluoride (PVDF) membrane is advantageous over other membrane materials due to its high mechanical strength and excellent chemical resistance [22]. This relatively well-characterized membrane has been extensively applied in microfiltration for general separation purposes [22]. Therefore, the commercial PVDF membrane (Millipore) with a pore size of 0.22μm and an effective membrane area of 19.62cm^2 was selected for this study. The membrane characteristics are listed in Table 1. PVDF membranes were immersed in 75% (v/v) alcohol for ca. 2h, ensuring they were sufficiently wetted and degassed. Prior to fouling experiments, all membranes were soaked in deionized water for 24h with several intermediate water changes to remove impurities or additives.

2.2. Organic foulant

Commercially available biopolymer BSA (Sigma-Aldrich, Saint Louis, MO) was used as the model protein in this study. According to the manufacturer, the molecular weight of the BSA is about 66kDa. BSA was received in powder form, and stock solution (10g/L BSA) was prepared by dissolving the BSA in deionized (DI) water. Mixing of the stock solution was performed for over 24h to ensure complete dissolution of BSA, followed by filtration using a 0.45μm cellulose acetate membrane. The filtered stock solution was stored in sterilized glass bottles at 4°C. Then the stock BSA solution was diluted to desired concentration (BSA=20mg/L) before fouling experiments.

Table 1
Measured physicochemical properties and calculated surface energetic parameters of clean microfiltration (MF) membrane.

(a) Properties of membrane

	θ_{water} (°)	$\theta_{formamide}$ (°)	$\theta_{diiodomethane}$ (°)	Zeta (mv)	Pore size (μm)
PVDF	83.1	52.8	27.0	−15.5	0.22

(b) Surface energetic parameters (mJ/m^2)

	γ^{LW}	γ^{+}	γ^{-}	ΔG_{121}^{LW}	ΔG_{121}^{AB}	ΔG_{121}^{EL}	ΔG_{coh}
PVDF	45.4	0.12	2.23	−8.56	−66.9	0.055	−75.405

pH=6.8, temperature=20°C, ionic strength=10mM NaCl.

Reagent grade chloride salts of sodium, calcium and magnesium were used to adjust ionic strength of feed water. Solution chemistries investigated for fouling experiments and interaction energy calculations included variations in electrolyte concentrations (NaCl) and divalent cations (Mg^{2+} and Ca^{2+}). In all cases, identical solution chemistries were employed in both fouling experiments and interaction energy calculations. When investigating the effect of divalent cations (Mg^{2+} or Ca^{2+}), the feed solution was amended to desired value by adding 0.1M $MgCl_2$ or $CaCl_2$ stock solutions. Meanwhile, the total ionic strength was maintained constant by adjusting NaCl concentration.

2.3. Filtration apparatus

To investigate the influence of feed solution characteristics (ionic strength and divalent cations) on fouling of MF membrane, the fouling propensities of BSA with different ionic strengths and divalent cations were evaluated using a stirred dead-end cell (MSC300, Mosu Corp., China) at room temperature (20±1°C) and common pH (pH=6.8). The flat sheet PVDF membranes were employed for filtration with nominal pore size of 0.22μm and an effective membrane area of 19.62cm^2. Before each experiment, deionized (DI) water was filtered through the MF membrane for 1h to stabilize the filtration system. The permeate pressure was maintained constant at 10kPa and the stirring speed in cell was set at 250rpm throughout the experiments. Permeate flux data were continuously logged using a top-loading electronic balance (BL-1200S, Setra Systems, USA) connected to a personal computer.

2.4. Surface thermodynamics analysis

Surface tension components were determined from the extended Young equation using a contact angle approach [23].

$$(1+\cos\theta)\gamma_l^{TOT} = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}\right) \tag{1}$$

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}} \tag{2}$$

$$\gamma^{TOT} = \gamma^{LW} + \gamma^{AB} \tag{3}$$

where θ is the contact angle, γ^{TOT} is the total surface tension, γ^{LW} is the Lifshitz–van der Waals component, and γ^{+} and γ^{-} are the electron-acceptor and electron-donor components, respectively. The subscripts s and l represent the solid surface and the liquid, respectively.