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Static adsorptive fouling of extracellular polymeric substances with different membrane materials

Xinying Su [b,c], Yu Tian [a,c,*], Wei Zuo [c], Jun Zhang [c], Hui Li [c], Xiaoyue Pan [c]

[a] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (SKLUWRE, HIT), Harbin 150090, China

[b] Department of Environmental Engineering, School of Food Engineering, Harbin University of Commerce, Harbin 150076, China

[c] School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

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ABSTRACT

Adsorptive fouling of microbial extracellular polymeric substances (EPS) greatly influences the fouling behavior and membrane characteristics in a membrane bioreactor (MBR). In this study, adsorptive fouling of the EPS on different membrane materials was compared and adsorptive mechanism between membranes and EPS was investigated by thermodynamic analysis. The results suggested that both the absolute and relative changes of hydraulic resistances should be considered to evaluate fouling of membranes with different materials, and Sips isotherm was the most suitable model to describe the EPS carbohydrate and protein adsorptions on membranes. Thermodynamic analysis showed that both EPS carbohydrate and protein adsorptions were spontaneous ($\Delta_r G^\theta < 0$), endothermic ($\Delta_r H^\theta > 0$), and entropy driven ($\Delta_r S^\theta > 0$). Decreasing $\Delta_r G^\theta$ values with temperature suggested that EPS adsorptive fouling can be limited by reducing temperature. In addition, physisorption processes and hydrogen bonding interactions between EPS and membranes might play a relatively major role in the adsorption mechanism of EPS on the membrane surface. Atomic force microscopy (AFM) and contact angle analysis confirmed that the adsorptive fouling modified the membrane surface, making the membrane surface more heterogeneous and more hydrophobic.

1. Introduction

Membrane fouling, which directly leads to the increase in maintenance and operating costs, has been considered to be the major drawback to limit the widespread application of membrane bioreactors (MBRs) (Zhang et al., 2011). The fouling behavior over time in MBRs is generally characterized by a three-phase evolution: conditioning fouling (adsorptive fouling), slow transmembrane pressure (TMP) rise, and sudden TMP rise (TMP jump) (Zhang et al., 2006). Conditioning fouling, not observed or described until recently, may be a key aspect of fouling creation in MBRs (Le-Clech et al., 2006). Considering relative hydraulic resistance contribution, the initial adsorption has been reported to account for 20–2000% of the clean membrane resistance (Ognier et al., 2002).

* *Corresponding author*. State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (SKLUWRE, HIT), Harbin 150090, China. Tel./fax: +86 451 8628 3077.
E-mail address: hittianyu@163.com (Y. Tian).

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Furthermore, the interaction between organic foulants and membrane surface may modify the surface characteristics of membranes, eventually provide conditions suitable for biomass attachment and cake deposition (Zhang et al., 2008). Thus, it is important to fundamentally investigate adsorptive fouling for a better understanding of fouling phenomena.

Extracellular polymeric substances (EPS), which surround the microorganisms, are usually considered as the major cause of membrane fouling in MBRs. In addition, different polymeric membranes exhibit different fouling behavior of EPS. A direct comparison between polyethylene (PE) and polyvinylidene fluoride (PVDF) membranes clearly indicated that PVDF is superior to PE in terms of prevention of irreversible fouling in MBRs used for treatment of municipal wastewater (Yamato et al., 2006). The affinity between foulants (e.g., EPS/SMP) and membrane determined the fouling behavior. Wang et al. (2013) assessed the membrane–foulant interaction between model foulant (alginate) and polymeric membranes and observed that the order of normalized flux reduction was PVDF > polyvinylchloride from Kubota (PVC–K) > polyvinylchloride (PVC) > polyacrylonitrile (PAN). Xiao et al. (2011) investigated the combined effect of membrane and foulant hydrophobicity and surface charge on adsorptive fouling during microfiltration. This study suggested that hydrophobic interaction, rather than electrostatic interaction, may be the predominant mechanism affecting adsorptive fouling. All these studies focused on the fouling behaviors of different membrane materials during filtration. However, few researchers have paid attention to the adsorptive interaction between EPS and different types of membrane. Zhang et al. (2008) investigated the adsorptive interaction between EPS and different membranes, suggesting that the adsorptive fouling of polyethersulfone (PES) membranes were much more severe due to its relatively high roughness and hydrophobicity based on FR_{PWF} values (flux reduction of pure water). Nakamura and Matsumoto (2006) analyzed the effects of volumetric flow on the adsorption properties of bovine serum albumin (BSA) on the pore surface of sirasu porous glass (SPG) membrane and found that the static adsorption was a Langmuir type while that for the dynamic adsorption was a multilayer type. Susanto et al. (2008) investigated the adsorptive fouling behavior of polysaccharide-protein mixture solutions and observed significant water flux reductions and changes in membrane surface property after static adsorption for PES membranes. It was also verified in this study that synergistic effects between polysaccharide and protein can form a mixed fouling layer with stronger reduction of flux than for the individual solutes under the same conditions (Susanto et al., 2008).

It is essential to use real EPS solution extracted from an MBR in experiments. However, no research has been conducted on the adsorptive interaction between sludge EPS and different types of membrane into adsorption isotherm and thermodynamic. To completely characterize the adsorption performance of different membranes by EPS, the adsorption behaviors of membranes by EPS should be examined. A detailed comparison of the adsorption performance will help us understanding membrane fouling better.

Therefore, the objectives of the present research were to investigate the adsorption behaviors of EPS for three types of commercial membranes. Static adsorption experiments were carried out to study the adsorption capacities of different membranes. The adsorption isotherms were identified to understand the adsorption mechanism of EPS onto membranes. Furthermore, some important thermodynamic parameters were evaluated to understand the nature of adsorption process for different membranes.

2. Materials and methods

2.1. Set up and operation of MBR

A lab-scale 8 L MBR was operated in this study at room temperature (Su et al., 2013). The MBR was installed with a submerged hollow fibre microfiltration (MF) membrane module. The membrane module was made of PVDF with a nominal pore size of 0.1 μm and an effective surface area of 0.1 m^2 (Motian, China). The MBR was fed with synthetic municipal wastewater (glucose 227 mg L^{-1}; starch 227 mg L^{-1}; $NaHCO_3$ 254 mg L^{-1}; urea 33 mg·L^{-1}; $(NH_4)_2SO_4$ 121 mg L^{-1}; KH_2PO_4 15.4 mg L^{-1}; K_2HPO_4 19.6 mg L^{-1}; $MgSO_4 \cdot 7H_2O$ 51 mg L^{-1}; $CaCl_2$ 12 mg L^{-1}; $FeSO_4 \cdot 7H_2O$ 17.48 mg L^{-1}; $ZnCl_2$ 0.13 mg L^{-1}; $Pb(NO_3)_2$ 0.27 mg L^{-1} and $MnSO_4 \cdot 4H_2O$ 0.13 mg L^{-1}). A liquid level control system was used to control the water level in the bioreactor. The effluent was collected directly from the membrane module by a peristaltic pump. A vacuum gauge was fixed between the membrane module and the peristaltic pump to monitor the TMP. Aeration was provided continuously underneath the membrane module so as to control membrane fouling and supply air for the biomass. The dissolved oxygen (DO) was monitored with a portable on-line DO meter (WTW inoLab Oxi level 2) and aeration rate was adjusted through the air flow meter. The membrane flux was set at 10 L m^{-2} h^{-1} with an intermittent suction of 8-min on and 2-min off. The hydraulic retention time (HRT) was 10 h and the mixed liquid suspended solids (MLSS) was maintained at 9000 ± 500 mg L^{-1} by sludge discharge. Prior to the experiments, the MBR was operated for over 5 months.

2.2. Extraction and properties of EPS

The total EPS of sludge was extracted using the heating method (Morgan et al., 1990). The mixed liquor of activated sludge was centrifuged at 5000 g for 5 min in order to remove bulk solution. After discarding the supernatant, the remaining pellet was washed and resuspended with distilled water. The mixed liquor was then subjected to heat treatment (80 °C, 30 min) and centrifuged at 5000 g for 5 min again. The centrifuged supernatant was filtered through a 0.45-μm membrane filter and the filtrate was defined as the EPS solution. The extracted solution was analyzed for total carbohydrates and proteins contents.

The concentrations of carbohydrates and proteins in the extracted EPS were 700 ± 35 mg L^{-1} and 1700 ± 55 mg L^{-1}, respectively. Accordingly ratio of proteins/carbohydrates was 2.4. The sample solutions were prepared with fresh distilled water containing the same ion concentration as the synthetic municipal wastewater and the pH was adjusted to 7.0 with HCl/NaOH. Carbohydrates and proteins have been identified as the