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Experimental evidence for osmotic pressure-induced fouling in a membrane bioreactor

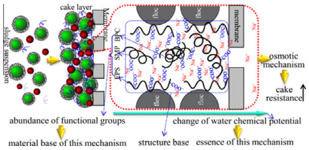
Hongjun Lin [a,*], Meijia Zhang [a], Fangyuan Wang [a], Yiming He [b], Jianrong Chen [a], Huachang Hong [a], Aijun Wang [a], Haiying Yu [a]

[a] *College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua 321004, PR China*
[b] *Department of Materials Physics, Zhejiang Normal University, Jinhua 321004, PR China*

HIGHLIGHTS

- A new fouling mechanism: osmotic pressure mechanism was identified in MBR.
- Functional groups were abundant in the surface of cake layer.
- SMP and BPC in supernatant played key roles in osmotic pressure mechanism.
- The formed cake layer was much hydrated and elastic.

GRAPHICAL ABSTRACT



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ABSTRACT

A lab-scale membrane bioreactor (MBR) was continuously operated to investigate the membrane fouling. A new membrane fouling mechanism: osmotic pressure mechanism in cake layer filtration process was identified. Osmotic pressure was proposed to stem from the retention of counter-ions in the matrix of biopolymers in cake layer. Through Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analyzes, it was found that functional groups were abundant in the surface of cake layer. Batch filtration tests showed that soluble microbial products (SMP) and biopolymer clusters (BPC) in the supernatant played key roles in osmotic pressure mechanism, and were thus largely responsible for the high cake resistance. The chemical potential of water varied along with cake depth. The formed cake layer was found to be much hydrated and elastic. These findings provided the direct evidence for the existence of osmotic pressure mechanism.

1. Introduction

While membrane bioreactors (MBRs) feature significant advantages over conventional activated sludge (CAS) systems, and have gained increasing popularity for wastewater treatment and reclaim in the past decades, membrane fouling problem still remains the biggest barrier to the universal application of MBRs. Investigation of the membrane fouling mechanism should enable such fouling to be more predictable, and also facilitate to develop membrane fouling control measures (Choi et al., 2006; Wang et al., 2007; Meng et al., 2009; Drews, 2010).

It generally believed that the deposition of a cake layer on the membrane surface is the major form of membrane fouling during operation of MBRs (Wang et al., 2007; Lin et al., 2009, 2013; Hwang et al., 2012). Many researchers have been concentrating on investigation of the foulants affecting cake layer formation. Biomass sludge was initially believed as the major factor affecting cake layer formation on membrane surface (Magara and Itoh, 1991). Thereafter, extracellular polymeric substances (EPS) surrounding sludge cells were considered to be mainly responsible for cake layer formation and its filtration resistance (Nagaoka et al., 1996;

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* Corresponding author. Tel.: +86 579 82282273.
E-mail address: hjlin@zjnu.cn (H. Lin).

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Wang et al., 2009; Herrera-Robledo et al., 2011). In the last decade, much attention has been paid on soluble microbial products (SMP) and other forms of organic matters in the liquid phase. Studies have indicated that these substances may be more crucial to membrane fouling (Defrance et al., 2000; Jarusutthirak and Amy, 2006; Farquharson and Zhou, 2010). In recent years, biopolymer clusters (BPC) were found to be largely responsible for the high filtration resistance of the cake layer (Wang et al., 2007, 2009, 2011). These studies definitely extended our understanding on membrane fouling. However, the underlying causes of these phenomena have not been well explored.

According to Darcy Law and dry cake mass determination, the specific filtration resistance of the formed cake layer has been determined to be around 10^{13}–10^{14} m/kg (Chu and Li, 2005; Wang et al., 2007; Lin et al., 2009, 2011a). On the other hand, Carman-Kozeny equation provides an alternative way to calculate the specific filtration resistance since cake layer was generally considered as a kind of porous media. Through this way, the specific filtration resistance was calculated to be varied from magnitude of 10^9 to 10^{11} m/kg (Zarragoitia-González et al., 2008; Gao et al., 2011), which is at least two orders of magnitude lower than the experimental value for the same cake layers. It is therefore believed that, other than hydrodynamic resistance, there is other force or mechanism regulating cake layer formation and its filtration resistance.

Recent studies have revealed an additional membrane fouling mechanism: osmotic pressure effect in cake layer filtration process (Chen et al., 2012; Zhang et al., 2013). Osmotic pressure was proposed to stem from the retention of counter-ions in the matrix of EPS in cake layer (Chen et al., 2012). The EPS in cake layer typically carry negatively charged functional groups, such as carboxyl, phosphoric and phenolic groups. For the reason of electro-neutrality, there should be a large amount of counter-ions present within cake layer (Keiding and Rasmussen, 2003). This means that the chemical potential of effluent is higher than that of water in cake layer. To drag the water from low chemical potential side (cake layer) to high chemical potential side (effluent), an additional force (energy) is needed. It has been suggested that most filtration resistance during cake layer filtration was contributed by osmotic pressure effect (Chen et al., 2012; Zhang et al., 2013). The osmotic pressure mechanism could be satisfactorily used to explain above mentioned phenomena if it really worked. For example, membrane fouling foulants, regardless of biomass, EPS, SMP or BPC, are mainly composed of proteins, polysaccharides, nucleic acids, and so on. Due to the presence of abundant negatively charged functional groups in these substances, filtration through cake layer containing these substances will induce osmotic pressure effect, and thus gives rise to the cake resistance. Existence of osmotic pressure effect also filled the great gap of the specific filtration resistance of cake layer between experimental results and calculation values. The identification of most cake layer filtration resistance stemming from osmotic pressure improved fundamental understanding of membrane fouling in MBRs. However, in previous studies (Chen et al., 2012; Zhang et al., 2013), this mechanism was deduced mainly based on mathematical models. It is a great concern whether there was significant experimental evidence for real existence of this mechanism. Meanwhile, factors affecting osmotic pressure have not well recognized. Since osmotic pressure effect may play a decisive role in cake resistance, it is of prime importance to further investigate this mechanism.

The objective of this study was therefore to provide direct experimental evidence to verify the real existence of this mechanism. The factors affecting osmotic pressure and its role in membrane fouling were further discussed. The results obtained in this study are expected to provide a sound understanding of membrane fouling mechanisms in MBRs.

2. Methods

2.1. Experimental setup and operation

Lab-scale installations are generally used to investigate membrane fouling issue in MBRs. In this study, a lab-scale submerged MBR (SMBR) was also used (illustrated in Fig. 1). The SMBR mainly consisted of a tank with 65 L effective volume (0.54 × 0.30 × 0.40 m height × length × width) where a flat sheet membrane module (Shanghai SINAP Co. Ltd., China) was submerged. The membrane was made of polyvinylidene fluoride (PVDF) with normalized pore size of 0.3 μm. The effective membrane area was 0.5 m^2. The membrane module was intermittently operated with a mode of 4-min-on and 1-min-off. The influent was synthetic municipal wastewater with following composition: 300 mg COD/L glucose plus the following mineral medium: $(NH_4)_2SO_4$ (27 mg N/L); KH_2PO_4 (7 mg P/L, 9 mg K/L); Na_2CO_3 (46 mg Na/L, 50 mg CO_3/L); $NaHCO_3$ (23 mg Na/L, 50 mg CO_3/L); $CaCl_2$ (6 mg Ca/L); $MgSO_4$ (7 mg Mg/L); $FeCl_3$ (4 mg Fe/L); $MnSO_4$ (0.04 mg Mn/L); $ZnCl_2$ (0.11 mg Zn/L); $CoCl_2$ (0.1 mg Co/L); $CuSO_4$ (0.03 mg Cu/L) and $NaMoO_4$ (0.02 mg Na/L, 0.07 mg Mo/L). Using glucose as organic source in synthetic wastewater is a general strategy to test new concepts or investigate membrane fouling issue for MBRs (Lin et al., 2013). Hydraulic retention time (HRT) of approximate 5.5 h was achieved by maintaining 30 $L\,m^{-2}\,h^{-1}$ membrane flux. Aeration was continuously supplied underneath the membrane module to provide shear force on the membrane surface and oxygen for the microorganisms. The specific aeration demand per permeate product (SADp) was approximate 180 $m^3_{air}/m^3_{permeate}$. The MBR set-up has been continuously operated for over 300 days. The sludge samples obtained in the last operation period (day 250–300) was used for the experiments. The sludge concentration indicated as mixed liquid suspended solids (MLSS) was maintained at 10–15 g MLSS/L during this period.

2.2. Analytical methods

Sludge samples were taken from the reactor operated in the stable operation period (day 250–300). The supernatant was obtained by centrifuging the sludge suspension for 5 min at 2500×g (GTR16-2 high-speed refrigerated centrifuge, Beijing Era Beili Centrifuge Co., Ltd., China). Considering the easy degradability of influent organics and the relatively low centrifugal force applied, the organics in the obtained supernatant was considered to mainly consist of SMP and BPC. EPS of bulk sludge and cake sludge were extracted according to cation exchange resin (CER) method. Proteins and polysaccharides were considered as the major components of EPS, SMP, and BPC. Proteins and polysaccharides were colorimetrically measured by using phenol/sulphuric acid method and Folin method, respectively. The operation details referred to Lin et al. (2009).

Water content was expressed as the ratio of the water mass to the total mass of the wet sample. The top, middle and bottom cake layers were firstly carefully scraped from the membrane surface one by one, and then collected in three alumina dishes. The water content of the sludge samples was measured by drying the samples in an oven at 105 °C for 2 h followed by weighing the wet samples and dry samples, respectively. To investigate the effect of centrifugal force on the water content of sludge, the sludge suspension samples in the reactor were centrifuged at different centrifugal forces. The water content of the sludge deposits was measured and compared. To investigate the effect of ion concentration on the water content of sludge, a cake layer with 37.58% water content was prepared by the dead-end batch filtration test. The cake layer was cut into several pieces, and then placed into a series of NaCl solutions with different concentration (0.00, 0.04, 0.08, 0.16,