



Calcium ion on membrane fouling reduction and biofloculation promotion in membrane bioreactor at high salt shock



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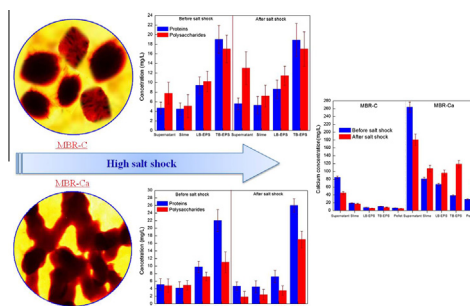
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HIGHLIGHTS

- Impact of calcium on membrane fouling and biofloculation at high salt shock.
- Distributions of calcium and EPS compositions affected biofloculation process.
- Calcium addition was an effective approach to remediate MBR at salt shock.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 August 2015
 Received in revised form 21 October 2015
 Accepted 23 October 2015
 Available online 28 October 2015

Keywords:

Membrane bioreactor
 Calcium ion
 Salt shock
 Biofloculation
 Membrane fouling rate

ABSTRACT

Fouling propensity of activated sludge in membrane bioreactor (MBR) is closely related to the disturbance of a salt shock. In this work, the characteristics of membrane fouling and biofloculation were compared in two laboratory-scale MBRs (one with calcium addition, MBR-Ca, the other without, MBR-C) with a transient salt shock. Particle size distributions, zeta potential, relative hydrophobicity, modified fouling index, the content of polysaccharides, proteins and calcium ions in different layers of sludge were monitored prior to, during and after the salt shock. Comparison with MBR-C showed that the recovery time and fouling rate of MBR-Ca were reduced by 50% and 34%, respectively. Remarkable variations of sludge properties in terms of biofloculation, such as larger particle sizes, higher relative hydrophobicity and zeta potential, lower polysaccharides in supernatant, higher proteins/polysaccharides ratio in slime and loose bound extracellular polymeric substances, were observed in MBR-Ca after the salt shock.

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1. Introduction

Membrane bioreactors (MBRs) are a well-established technology for wastewater treatment, water reclamation and reuse. However, membrane fouling is an unavoidable and probably the most serious challenge for the technology that increases operational cost and shortens membrane life in MBRs (Yang et al., 2006). Membrane fouling behavior and filtration performance are directly influenced

by the characteristics of the activated sludge, such as morphological properties, physical parameters and biochemical components governing filterability and fouling propensity of the sludge onto the membrane (Ji et al., 2010). Activated sludge is usually negatively charged due to the fact that microbial cells or flocs are embedded in a matrix of extracellular polymeric substances (EPS), which typically carry negatively charged functional groups including carboxyl, hydroxyl and phosphoric groups (Sobeck and Higgins, 2002). EPS can often be divided into two major fractions: soluble EPS (soluble microbial products, SMP) and bound EPS. The inner layer consists of tightly bound EPS (TB-EPS), whereas the

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outer layer contains loosely bound EPS (LB-EPS) (Sheng et al., 2010). Due to the high negative charge density of EPS, cations play an important role in bioflocculation. Bioflocculation could be closely related to filterability or membrane fouling propensity of sludge (Zhang et al., 2014a). Enhanced bioflocculation is known to result in larger and more permeable flocs and reduced fouling (Arabi and Nakhla, 2009). The theoretical support to the role of cations in sludge flocculation are divalent cation bridging (DCB) theory (include the alginate theory) and Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Sobeck and Higgins, 2002). It has been found that divalent cations promoted sludge flocculation according to DCB theory, but extended DLVO theory could account for the bioflocculation with trivalent cations (Li et al., 2012). Though monovalent cation concentrations are not high enough to form cationic bridges, a high concentration of monovalent cations is deemed undesirable for bioflocculation (Zhang et al., 2014a).

One significant challenge for both industrial and municipal wastewater treatment is the increase in the inflow concentration of monovalent salt (Temmerman et al., 2014), e.g., due to discharge of industrial effluents, road application for thawing snow and ice (Jang et al., 2013), or toilet flushing with seawater (Aslan and Simsek, 2012). High salt concentration in wastewater can cause cell plasmolysis due to the dramatic increase in osmotic pressure and changes on microbial metabolism (Bassin et al., 2011). Moreover, salinity may significantly affect the physical and biochemical properties of the biomass, leading to changes on surface charge, hydrophobicity, filterability and bioflocculation of biomass (Sun et al., 2010). A limited number of studies have been conducted on MBR operation for the high salt shock, which indicated that salinity not only exerted adverse impact on the pollutant removal, biomass activity and microbial diversity, but also significantly deteriorated sludge filterability and resulted in serious membrane fouling (Reid et al., 2006; Zhang et al., 2014b). Therefore, it is necessary to develop an effective method to reduce membrane fouling for MBR process at high salt shock.

Recently, application of calcium ions in MBR to modify the properties of mixed liquor artificially for fouling mitigation has been reported in several publications (Arabi and Nakhla, 2008; Chen et al., 2011). According to DCB model, calcium ion is able to form cationic bridge between negatively charged EPS constituents in sludge, hence promoting bioflocculation (Arabi and Nakhla, 2008). The enhanced sludge filterability in MBR with the addition of calcium ion was attributed to an increase in floc size and a decrease in concentration of soluble foulants in the supernatant (Chen et al., 2011). Considering the significant impact of calcium addition on the bioflocculation, it would be very interesting to study how calcium-induced activated sludge affects membrane fouling at high salt shock.

In the present study, calcium-induced activated sludge was carefully studied for its effectiveness on membrane fouling reduction in MBR at high salt shock. The sludge filterability and distributions of calcium ion in activated sludge were determined and correlated during and after the salt shock in two parallel lab-scale MBRs, one with calcium addition and the other without. The critical role of calcium ion on the fouling propensity of sludge in MBR at high salt shock was elaborated.

2. Methods

2.1. MBR systems

Two MBRs of identical working volume, MBR-C (the control reactor) and MBR-Ca (with calcium ion addition) were operated. CaCl₂ (HeBei Standard Chemicals Co., Ltd., Shijiazhuang, China) is used as the calcium ion source, which is provided in the form of

powder of purity 94%. A schematic experimental setup was shown in Fig. 1. The two MBRs were run in parallel under the same conditions, except that 100 mg/L of Ca²⁺ was added to the feed in MBR-Ca. Each MBR had a working volume of 8 L. The membrane module used in both systems was a bundle of U-shaped hollow fiber membranes (polyvinylidene fluoride, PVDF) with a pore size of 0.2 μm and total membrane area of 0.1 m². Air was supplied to both MBRs at 5 L/min. Permeate through the submerged membrane module was continuously withdrawn using a peristaltic pump (Model BT-300, Baoding Longer Precision Pump Co., Ltd., China) at a constant flux of 10 L/(m² h), which was operated for 13 min of production and paused for 2 min of relaxation. Transmembrane pressure (TMP) was continuously monitored and physical cleaning was performed when the TMP reached about 30 kPa. The hydraulic retention time (HRT) and sludge retention time (SRT) of the MBRs were maintained at 8 h and 30 days, respectively.

The seed sludge was taken from a lab-scale MBR that has been running for more than two years. Each MBR was seeded with 7.5 g/L of the acclimatized activated sludge. The synthetic wastewater with average concentrations of chemical oxygen demand (COD), total nitrogen (TN) and total phosphorous (TP) of about 310, 30 and 7 mg/L was prepared (Table 1) and used as nutrients for the MBRs biomass. After three times of their SRTs of operation under good conditions, both COD and NH₄⁺-N were being steadily removed in both MBRs regardless of the influent conditions, keeping an average removal rate over 94.5% and 95.2%, respectively. Before the salt shock, both MBRs had similar mixed liquor suspended solids (MLSS) concentrations and mixed liquor volatile suspended solids (MLVSS) concentrations typically in the range of 10–12 and 8–9.2 g/L, respectively. One simulation of salt shock was applied on day 10 in this experiment, 10 g/L of NaCl was added in the feed for a period of 6 h to simulate a shock salt loading for both MBRs.

2.2. Batch filtration test

The filterability of mixed liquid was investigated in batch tests using Amicon 8400 dead-end cells (Millipore, Billerica, MA). The cells had a volume of 350 mL and an effective membrane filtration area of 41.8 cm². All experiments were carried out at room temperature and under a pressure of 30 kPa. The permeation flux was determined by weighing permeates on an electronic top loading balance (XY500C, Xinyun Electronic Equipment Co., Ltd., Changzhou, China) connected to a personal computer with an auto-reading program. Prior to each test, a new PVDF membrane disc of pore size 0.2 μm (EMD Millipore, USA) was pre-compacted with Milli-Q water for 2 h at 30 kPa to ensure stable water flux.

Under unstirred conditions, modified fouling index (MFI) was obtained from the plot of t/V versus V using the filtration equation at constant pressure (Ognier et al., 2002). MFI parameter gives an idea of the fouling characteristics of the mixed liquor. A higher MFI results in a higher fouling rate for the mixed liquor. It is based on the cake filtration mechanism (Jang et al., 2006). MFI is defined as the gradient of the linear relationship between t/V and V .

$$\frac{t}{V} = \frac{\mu R_m}{\Delta P} + \frac{\mu \alpha C}{2 \Delta P} V \quad (1)$$

$$\text{MFI} = \frac{\mu \alpha C}{2 \Delta P} \quad (2)$$

where t is the filtration time (s), V the permeate volume per unit filtration area (m), μ the dynamic viscosity of permeate (Pa s), R_m the intrinsic membrane resistance (m⁻¹), ΔP the applied transmembrane pressure (kPa), α the specific resistance (m/kg) and C is macromolecules concentration in bulk solution (mg/L).

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