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Short Communication

The effect of solids retention times on the characterization of extracellular polymeric substances and soluble microbial products in a submerged membrane bioreactor

Liang Duan [a,b], Yonghui Song [a,*], Huibin Yu [a], Siqing Xia [c], Slawomir W. Hermanowicz [b,d]

[a] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, PR China
[b] Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720-1710, USA
[c] State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, 1239 Siping Rd., Shanghai 200092, PR China
[d] National High-End Foreign Experts of China Program, Tongji University, 1239 Siping Rd., Shanghai 200092, PR China

HIGHLIGHTS

- More carbohydrates and proteins in shorter SRT were due to higher biomass activity.
- Macromolecules and small molecules were the main fraction of EPS and SMP.
- Other organic moieties were exuded by microbes into the solution.
- The shorter SRT had more small molecules and less macromolecules.
- The shorter SRT had different O—H bonds in hydroxyl functional groups.

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ABSTRACT

In this study, the effect of solids retention times (SRTs) on extracellular polymeric substances (EPS) and soluble microbial products (SMPs) were investigated in a membrane bioreactor (MBR) at SRTs of 10, 5 and 3 days. The results showed that more carbohydrates and proteins were accumulated at short SRT, which can due to the higher biomass activity in the reactor. The molecular weight (MW) distribution analysis suggested that macromolecules (MW > 30 kDa) and small molecules (MW < 1 kDa) were the dominant fraction of EPS and SMP, respectively. The reactor at shorter SRT had more small molecules and less macromolecules of carbohydrates. The MW distribution of total organic carbon (TOC) suggested that other organic moieties were exuded by microbes into the solution. The shorter SRT had more undefined microbial by-product-like substances and different O—H bonds in hydroxyl functional groups.

1. Introduction

Membrane bioreactors (MBRs) have been used as an innovative and promising option for wastewater treatment and reuse. However, membrane fouling and its consequences in terms of plant maintenance and operating costs limit widespread application of MBRs. Extracellular polymeric substances (EPS) and soluble microbial product (SMP) contain carbohydrates, proteins, humic substances and nucleic acids and are considered as major causes of membrane fouling in MBRs. Solids retention time (SRT) is an important factor influencing the membrane fouling. MBRs tend to be operated with long SRT to maintain high biomass concentrations, reduce solids production and minimize reactor volume. The higher MLSS concentration at higher SRT creates serious problems, such as high aeration rates are required to provide adequate oxygen supply and effective membrane scouring is difficult to achieve due to increased mixed liquor viscosity. Some MBR try to operate at shorter SRT to reduce external energy usage and even to become energy self-sufficient in recent years. Currently, there have not theoretical conclusions about the impact of SRT on the membrane fouling. Several researchers had reported that the membrane fouling increased as SRT increased (Chuang et al., 2011). In contrast, other researchers indicated that enhanced fouling occurs at low SRT due to increased concentration of EPS and worse activated sludge bioflocculation (Trussell et al., 2006). Some researchers suggested that no significant change of fouling under certain conditions (Villain and Marrot, 2013). These conflicts imply

* Corresponding author. Tel./fax: +86 10 84915308.
E-mail address: songyh@craes.org.cn (Y. Song).

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that membrane fouling is not only related to the concentration of EPS and SMP but also be influenced by various constituent organic fractions of EPS and SMP.

Therefore, the objective of this study is to investigate the effect of short SRT on the characterization of EPS and SMP in the MBRs. Organic fractions of EPS and SMP were analyzed to develop detailed molecular weight (MW) distributions. Composition and functional group of EPS and SMP were analyzed with three-dimensional excitation emission matrix (EEM) fluorescence spectroscopy and Fourier transform infrared (FTIR) spectroscopy.

2. Methods

Three laboratory-scale MBRs each with working volume of 4 L were operated in parallel at SRT of 3 days (reactor S3), 5 days (reactor S5) and 10 days (reactor S10), respectively. Hollow-fiber membranes were made of polyethylene (Mitsubishi Corporation, Japan) with a surface area of 300 cm^2 and with a nominal pore size of 0.4 μm. The reactor was fed with synthetic wastewater (Table S1), and the concentration of chemical oxygen demand (COD) and ammonia-nitrogen (NH_4^+-N) were approximately 200 mg/L and 40 mg/L, respectively. All MBRs were operated at the same HRT of 6 h. In order to control membrane fouling by hydraulic shear force and agitation, the aeration rate for each MBR was maintained at 27.6 L/min, resulting in the dissolved oxygen concentration close to the saturation. The reactors were inoculated with activated sludge from the San Jose/Santa Clara Water Pollution Control Plant (San Jose, CA). The activated sludge was used as an inoculum to achieve initial mixed liquor suspended solids (MLSS) concentration of 2000 mg/L. All MBRs were operated at continuous model for about 40 days.

MLSS and mixed liquor volatile suspended solids (MLVSS) were measured using standard methods (APHA et al., 1998). COD and NH_4^+-N were measured according to Hach Method 8000 and 8008, respectively. The non-flocculating microorganisms were quantified by measuring the turbidity of the supernatant after centrifuging for 2 min at 1300*g* (Duan et al., 2013). The activities of biomass were assessed through quantification of dehydrogenase activity using the 2-(*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyltetrazolium chloride (INT) method (Maurines-Carboneill et al., 1998). Extraction of total EPS (TEPS) was based on a cation exchange resin method (Frolund et al., 1996). Briefly, 50 mL of untreated mixed liquid samples from each reactor were centrifuged for 15 min at 12,000*g* and SMP was measured in the supernatant. The difference between TEPS and SMP concentrations was taken as the EPS concentration. Carbohydrate and protein concentrations were quantified using the anthrone method and modification of the Lowry method, respectively (Lowry et al., 1951; Morris, 1948). Total organic carbon (TOC) and DNA concentrations were measured with TOC analyzer (Shimadzu, Japan) and ultraviolet spectrophotometer (Shimadzu, Japan), respectively. Molecular weight distribution tests were carried out using the ultrafiltration method (with Millipore membranes of the nominal MW cutoff of 1, 5, 10, 20, 30, 50 and 100 kDa) (Duan et al., 2013). Dead-end filtration experiments with the UF membranes of 100 kDa were used to determine filterability of mixed liquor, SMP and suspended solids. The FTIR spectrometer (Equinox 55, Bruker, Germany) and fluorescence spectrometry system (F-4500, Hitachi, Japan) were used to characterize composition of TEPS and SMP.

3. Results and discussion

3.1. MBR performance

As shown in Table 1, all MBRs can remove more than 94% of COD and 87% of NH_4^+-N, regardless of the SRT values. This can be due to complete suspended solid retention, higher content of non-flocculating microorganisms and smaller sized flocs in the MBR. The MLSS and MLVSS concentrations were lower than traditional MBR, since more sludge were wasted daily in three MBRs at short SRT. Non-flocculating bacteria content in the reactors increased at longer SRT. Ammonia degradation rate, dehydrogenase activity and VSS/SS ratio all increased as SRT decreased as expected since biomass at shorter SRT is growing faster and is more active. For the shortest SRT (reactor S3) high food to microorganism (F/M, 2.93 gCOD/gVSS d) lead to high sludge volumetric index (SVI = 212 mL/g), indicating poorer floc stability.

SRT times also affected filterability of mixed liquor and its SMP and suspended solids fractions. In the dead-end filtration experiments, filtration flux for all three components declined faster for the shortest SRT (Fig. S1). These findings are similar to those reported in the literature (Masse et al., 2006). The changes of mixed liquor characteristics were attributed to smaller biopolymer production by non-flocculating bacteria and better degradation and hydrolysis of macromolecules at high SRT.

3.2. Molecular weight distributions of EPS and SMP

As shown in Fig. S2, the EPS and SMP concentrations (protein, carbohydrates, DNA and TOC) in reactor S3 were higher than in two other reactors. These results indicated that carbohydrates and proteins were accumulated in the MBR at short SRT, possibly due to higher biomass activity associated with higher F/M in the S3 reactor. Furthermore, the increase of EPS and SMP with decreasing SRT follows two broad trends. For EPS, the increase is attributed to a significant increase of 30–50 kDa fraction and a moderate increase of the smallest molecules (MW < 1 kDa). For SMP, the increase is primarily due to a very large accumulation of the smallest fraction (MW < 1 kDa) with a minor increase of very large molecules (MW > 100 kDa).

The MW distributions of EPS and SMP are shown in Fig. 1. The fraction of MW > 30 kDa (macromolecules) was dominant for EPS_P, accounting for 56–74%. This can due to superior rejection of proteins in the supernatant by membrane separation. Small molecules with MW < 1 kDa composed the second dominant fraction, accounting for 19–36%. The MW distribution of EPS_D followed similar trends as protein. The fractions with MW > 30 kDa (46–60%) and MW < 1 kDa (28–47%) were the dominant components. However, the MW distribution of EPS_C presented different features than EPS_P and EPS_D. The dominant fraction of EPS_C was composed of small molecules with MW < 1 kDa (61–80%). It is interesting that the midrange fractions of EPS with MW between 1 and 30 kDa (1–5 kDa, 5–10 kDa, 10–20 kDa and 20–30 kDa) only represented a very small amount in all MBRs. They contributed only about 8–10% of EPS_P, 11–14% of EPS_C and 7–18% of EPS_D at all operating conditions. The trend of decreasing content of macromolecules (MW > 100 kDa) is also seen for all EPS components with the lowest fraction of these macromolecules in reactor S3 and the highest in S10. A reverse trend is seen for the smallest molecules (MW < 1 kDa). The fraction of MW > 100 kDa of EPS_C decreased from 21% to 1%, but the MW < 1 kDa of EPS_C increased from 61% to 80% as SRT reduced from 10 days to 3 days. For SMP, as shown in Fig. 1B, the fraction of MW < 1 kDa was dominant. These small molecules constituted 71–83% of protein, 51–85% of carbohydrate and 43–70% of DNA. The result is consistent with previous research. Jang found that small molecules with MW < 1 kDa constituted more than 86% of carbohydrate SMP (Jang et al., 2007).

While conventionally EPS and SMP are defined as a sum of proteins and carbohydrates (and sometimes also DNA), there are also other compounds present in the flocs and as soluble organics. We measured all organics in EPS and SMP as total organic carbon and the results are shown in Fig. 1. For SMP, the MW distribution