Chemosphere 193 (2018) 295–303

Contents lists available at ScienceDirect

Chemosphere

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

Comparative study of dissolved organic matter generated from activated sludge during exposure to hypochlorite, hydrogen peroxide, acid and alkaline: Implications for on-line chemical cleaning of MBR

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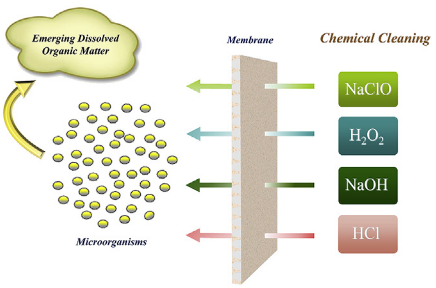
HIGHLIGHTS

- NaClO triggered substantial DOM release while no obvious DOM was found with H_2O_2.
- Compared with acid treatment, more DOM was generated under caustic condition.
- Principle components of generated DOM belonged to low-molecular-weight organics.
- This study offers insight into emerging DOM produced by various cleaning chemicals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 August 2017
Received in revised form
3 November 2017
Accepted 7 November 2017
Available online 8 November 2017

Handling Editor: A Adalberto Noyola

Keywords:
On-line chemical cleaning
Cleaning reagent
Dissolved organic matter
Membrane bioreactor

ABSTRACT

Although on-line chemical cleaning has been extensively employed for maintaining the MBR permeability, little attention has been given to the negative impacts of such prevalent membrane cleaning practice. This study thus comparatively investigated the potential release of dissolved organic matter (DOM) from activated sludge upon the exposure to different kinds of frequently-used cleaning reagents, i.e. NaClO, H_2O_2, HCl and NaOH. It was found that NaClO at 50 and 80 mg L^{-1} triggered significant release of DOM, while NaOH strongly promoted soluble nitrogen release. However, the DOM generation induced by H_2O_2 in the range of 0–80 mg L^{-1} was nearly negligible. The combined analysis by EEM-PARAFAC and LC-OCD-OND further revealed that NaClO-triggered DOM mainly originated from the breakdown of humic substances and other small humics with molecular weight (MW) less than 500 Da. In contrast, proteins and other biopolymers with higher MW highly contributed to DOM induced by NaOH. Most of DOM detected in this study belonged to low molecular weight (LMW) substances, which were not considered readily biodegradable or physically retainable by microfiltration membrane. It appears from this study that DOM generated from suspended activated sludge during membrane cleaning with different chemicals should be taken into serious consideration when water recycle and reuse are concerned.

1. Introduction

Membrane bioreactor (MBR) has been widely employed for wastewater reclamation due to its great advantages of superb

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https://doi.org/10.1016/j.chemosphere.2017.11.032
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permeate quality, small footprint, reduced sludge production etc (Le-Clech et al., 2006). However, membrane fouling is still of a perennial hurdle, resulting in reduced flux or increased *trans*-membrane pressure (TMP). To cope with such a challenge, regular on-line chemical cleaning is often conducted in the practical operation of large-scale MBR, which has been deemed to effectively alleviate both reversible and irreversible membrane fouling (Wei et al., 2011; Lee et al., 2016).

Chemical regents used for on-line chemical cleaning can be primarily classified into acids, bases and oxidants. In practice, several regents are often jointly or sequentially utilized to eliminate the complex fouling constituents of inorganics, organics and microorganisms (Wang et al., 2014). In general, acids are good for removing inorganic fouling caused by chemical precipitation of inorganic substances (e.g. multivalent cations) or biologically induced mineralization between biopolymer and salts through neutralization and double decomposition reactions (Meng et al., 2009; Wang et al., 2014). On the contrary, alkaline cleaning is mainly targeted for organic fouling. It had been reported that large-sized organic particles could be disintegrated into fine particles or soluble matter under alkaline conditions (Yu et al., 2013). Meanwhile, proteins and polysaccharides accumulated on the membrane surface could be hydrolysed and dissolved by alkali into small molecules like amides and monosaccharides, while oils and fats were saponified to soluble soap micelles (Liu et al., 2001). In addition, oxidants (e.g. NaClO and H_2O_2) are also commonly employed to eradicate organic and biological fouling. The dominating mechanisms for cleaning with oxidizing chemicals involve deactivation of microorganisms and conversion of functional groups of organic foulants into ketonic, aldehydic, and carboxylic groups with higher hydrophilicity, which in turn promote their subsequent removal from membrane surface (Wang et al., 2014). Especially, it is noteworthy that these oxidized functional groups can be further deprotonated and negatively charged at high pH conditions (Ang et al., 2011). Consequently, such repulsive forces between foulants are helpful for weakening fouling layer structure as well as facilitating foulants transportation from membrane surface into bulk suspension, suggesting the merits of combined or sequentially usage of chemical reagents.

In the course of on-line chemical cleaning, the cleaning reagents that pass through membranes eventually end up in the bulk suspension. Thus, the contact between microorganisms and cleaning chemicals is inevitable in MBR. Increasing evidences showed that on-line chemical cleaning may negatively impact on MBR performance in terms of membrane integrity, microbial properties, biomacromolecule structures and membrane biofouling redevelopment due to the contact between microorganisms/membranes and cleaning regents (Abdullah and Berube, 2013; Lee et al., 2013; Cai and Liu, 2016; Han et al., 2016; Navarro et al., 2016; Zhou et al., 2017). Moreover, our previous studies confirmed the generation of dissolved organic matter (DOM) and halogenated byproducts from activated sludge upon exposure to NaClO (Cai et al., 2016, 2017). These works implied that there would be a need to re-examine the origin of the emerging micropollutants present in MBR. However, except for NaClO, the possible DOM generation from other prevalent cleaning reagents has not been elucidated thus far, and there is a lack of comparative study among different kinds of chemicals for on-line membrane cleaning. Therefore, this study aimed to explore the potential generation of DOM from activated sludge upon exposure to different cleaning reagents, i.e. HCl, NaOH, NaClO, and H_2O_2, all of which are widely employed in chemical cleaning of large-scale MBR. The characterization of these DOM was conducted by multiple techniques, such as excitation emission matrix fluorescence with parallel factor analysis (EEM-PARAFAC) and size-exclusion chromatography coupled with organic carbon and organic nitrogen detection (LC-OCD-OND). It is expected that this study can provide new insights into the current practice of on-line membrane cleaning with different chemicals in MBR.

2. Materials and methods

2.1. Chemical exposure assays

Activated sludge collected from a local municipal wastewater treatment plant in Singapore was acclimatized in a chemostat reactor for three months with synthetic wastewater of 690 mg L^{-1} CH_3COONa, 313 mg L^{-1} glucose, 200 mg L^{-1} NH_4Cl, 60 mg L^{-1} K_2HPO_4 and other trace minerals. The organic loading rate was controlled at about 0.33 kg TOC m^{-3} d^{-1}, and hydraulic retention time was kept at 24 h in the chemostat reactor. Prior to experiments, suspended sludge was washed three times with 0.9% NaCl solution for thoroughly removing the remaining metabolites and contaminants. Thereafter, the washed sludge in dispersed form was resuspended in 0.9% NaCl solution and was made up to a MLSS concentration of 1000 mg L^{-1}. The original pH of the prepared sludge suspension was about 6.5.

The stock solution of 30% H_2O_2 from Merck was standardized by $KMnO_4$ titration, whereas NaClO solution with 4–4.99% effective chlorine (Sigma-Aldrich) was calibrated by N, N-diethyl-*p*-phenylenediamine colorimetric kit (Hach, USA). Afterwards, NaClO and H_2O_2 solutions were respectively dosed into a series of beakers containing 50 mL of dispersed sludge for having initial chemical concentrations of 0, 5, 10, 20, 50 and 80 mg L^{-1}. Meanwhile, another batch of sludge suspension with a pH range of 2–12 was prepared by using HCl and NaOH. The reaction period was set to be 1 h, after which nearly all the free chlorine and H_2O_2 residual were not detectable. For both chemical treatment and sludge acclimatization, aeration was provided during the entire process with dissolved oxygen concentration of 3–5 mg L^{-1}. After chemical treatment, the supernatant of each suspension was harvested through centrifugation at 3000 rpm for 5 min, and was further filtered through 0.45 μm PES membrane. The collected filtrates were used for determination.

2.2. EEM-PARAFAC analysis

Fluorescence EEMs were measured by a luminescence spectrometer (LS55, Perkin Elmer Company, USA). The excitation scanned from 200 to 500 nm with an increment of 5 nm, whereby for each excitation wavelength, emission was scanned in between 250 and 550 nm with 0.5 nm increment. The scanning speed was set at 1200 nm min^{-1}. To avoid the effect of inner filter, all samples were diluted to 254-nm UV absorbance of below 0.05 cm^{-1} (Phong and Hur, 2015). EEM spectra of Milli-Q water as blank was further subtracted from each sample to eliminate background influence. Thereafter, these Raman normalized and spectrally corrected EEMs were calibrated against the quinine sulfate (QS) dilution series (1, 5, 10, 20 μg L^{-1}) producing EEMs in the unit of quinine sulfate equivalent (QSE), and 1 QSE corresponds to the fluorescence intensity of 1 μg L^{-1} quinine sulfate in 0.1 N H_2SO_4 measured at Ex/Em of 350/450 nm.

Afterwards, the EEMs of 53 DOM samples were subject to PARAFAC modelling, which was conducted in MATLAB (R2013a) using the DOMFluor Toolbox according to the procedures proposed by Stedmon and Bro (2008). The number of components were validated via split-half analysis. The maximum fluorescence intensity (F_{max}) of each individual component was used to represent its relative concentration. In fact, EEM-PARAFAC models the three-way data with Eq. (1), fitting the equation by minimizing the sum of