Chemical Engineering Journal 323 (2017) 233–242

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

# Fate of dissolved organic matter and byproducts generated from on-line chemical cleaning with sodium hypochlorite in MBR

Weiwei Cai [a,b], Jiaqi Liu [c], Xiaohu Zhu [c], Xiangru Zhang [c], Yu Liu [a,b,*]

[a] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore
[b] Advanced Environmental Biotechnology Centre, Nanyang Environment & Water Research Institute, Nanyang Technological University, Singapore
[c] Department of Civil and Environmental Engineering, Hong Kong University of Science and Technology, Hong Kong, China

## HIGHLIGHTS

- NaClO triggered bacterial lysis and DOM generation.
- Around 39% of generated DOM was eventually removed in an aerobic MBR.
- Protein-like substances were more readily biodegraded than humic-like substances.
- Up to 84.5% of overall halogenated byproducts ended up in MBR permeate.
- This study offers new insight on MBR cleaning and raises concern on permeate reuse.

## ARTICLE INFO

*Article history:*
Received 26 February 2017
Received in revised form 19 April 2017
Accepted 20 April 2017
Available online 22 April 2017

*Keywords:*
Membrane bioreactor
On-line chemical cleaning
Sodium hypochlorite
Dissolved organic matter
Byproducts

## ABSTRACT

On-line chemical cleaning with sodium hypochlorite (NaClO) has been extensively practiced for maintaining the stable permeability of membrane bioreactor (MBR), during which activated sludge is inevitably exposed to NaClO. The authors previously reported the NaClO-induced generation of dissolved organic matter (DOM) and halogenated byproducts, however their fate in terms of biodegradability and removability in MBR has been unknown. Therefore, this study investigated the removal mechanisms of generated DOM and byproducts in an aerobic MBR. It was found that about 39% of DOM produced was removed through biodegradation and membrane rejection. The fluorescence excitation-emission matrix (EEM) coupled with parallel factor analysis (PARAFAC) also revealed that protein-like substances were more readily biodegradable than humic-like substances. Moreover, 25 kinds of chlorinated and brominated byproducts were detected after the contact of biomass with NaClO by ultra performance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry, while nine of which were confirmed with standard compounds. 62.4–84.5% halogenated byproducts were ended up in permeate of MBR chemically cleaned with 5–20 mg/L of NaClO. This study raises a serious concern on reusing and recycling of such MBR permeate.



## 1. Introduction

In the operation of membrane bioreactor (MBR) for wastewater reclamation, membrane cleaning is essential for mitigating membrane fouling and maintaining membrane permeability [1]. Meanwhile, on-line chemical cleaning with sodium hypochlorite (NaClO), e.g. cleaning in-place (CIP) and chemical enhanced backwashing (CEB), has been widely practised in real-life MBR [2], during which activated sludge inevitably contacts with NaClO. It was found that NaClO had negative impacts on sludge floc formation and contaminants removal [3]. In addition, increasing evidence suggests that the exposure of biomass to NaClO may lead to enhanced membrane biofouling, inhibited enzymatic activity, and altered microbial community structure [4–7].

As a strong oxidant, NaClO can also trigger serious sludge foaming and concomitant release of dissolved organic matter (DOM) during on-line chemical cleaning of membranes in MBR [3–6,8]. For instance, the dissolved organic carbon (DOC) concentration was increased by 134% after 24 h exposure of activated sludge to 50 mg NaClO/g SS [6], and our previous study clearly showed the occurrence of bacterial lysis upon exposure of activated sludge to 0–20 mg/L NaClO, leading to 2.7–24.7 mg/L DOM release into liquid phase [9]. These suggest that DOM present in MBR may partially originate from biomass lysis triggered by NaClO instead of

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, Singapore.
*E-mail address:* cyliu@ntu.edu.sg (Y. Liu).

http://dx.doi.org/10.1016/j.cej.2017.04.099
1385-8947/

raw sewage. Therefore, there is an urgent need to systematically investigate the fate of these emerging micropollutants in MBR. Moreover, a broad spectrum of halogenated byproducts has been identified upon the exposure of microorganisms to NaClO, most of which were found to be haloaromatic compounds [9]. It should be noted that haloaromatic byproducts are substantially more toxic than haloaliphatic ones [10]. Obviously, the presence of such toxic byproducts in MBR may pose challenges on permeate reuse and recycle, but little information is available on the fate of these byproducts in MBR thus far.

Therefore, this study aimed to investigate the fate of the DOM and halogenated byproducts produced through exposure of activated sludge to NaClO in MBR. For this purpose, excitation emission matrix fluorescence with parallel factor analysis (EEM-PARAFAC) was employed to acquire the componential information of DOM. Total organic halogen (TOX) analysis was conducted for quantification of the overall halogenated byproducts, while ultra performance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry (UPLC/ESI-tqMS) was employed to identity and further quantify each individual byproduct. It is expected that this study offers in-depth insights into the generation and subsequent fate of chemical cleaning-associated DOM and byproducts in MBR.

## 2. Materials and methods

### 2.1. Chemical reagents

The stock solution of NaClO (4–4.99%) purchased from Sigma-Aldrich was standardized by N,N-diethyl-p-phenylenediamine (Hach, USA) before use. 4-bromo-2-chlorophenol (99%), 3,5-dibromo-4-hydroxybenzoic acid (98%) and 3,5-dibromo-4-hydroxy benzaldehyde (98%) were obtained from Acros Organics, Indofine, and Alfa Aesar, respectively. All the other standard compounds (e.g. chlorobromoacetic acid, dichloroacetic acid, trichloroacetic acid, dibromoacetic acid, 5-bromosalicylic acid, 5-chlorosalicylic acid, 2,4,6-trichlorophenol, 2,4,6-tribromophenol, iodoacetic acid) and organic solvents (HPLC grade) used in this study were all purchased from Sigma-Aldrich.

### 2.2. DOM generation

Activated sludge collected from a local wastewater treatment plant was acclimatized in lab for one month with synthetic wastewater, which mainly contained 690 mg/L $CH_3COONa$, 313 mg/L glucose, 200 mg/L $NH_4Cl$, 60 mg/L $K_2HPO_4$ and other trace minerals. Prior to use, the acclimated activated sludge was carefully washed three times with 10 mM phosphate buffered saline (PBS) solution. Standardized NaClO solution was then mixed with the harvest sludge for having initial NaClO dosages of 0, 5 and 20 mg/L, which were selected based on previous studies [4,9]. Dissolved oxygen was provided through aeration during a contact duration of 30 min, after which nearly all the chlorine was consumed. In fact, after 30-min exposure to 0–20 mg/L NaClO, the free chlorine residual was undetectable, while 0–0.7 mg/L of combined chlorine was found, which was further quenched with $Na_2S_2O_3$ based on stoichiometric reaction. Finally, DOM in the collected supernatant was determined.

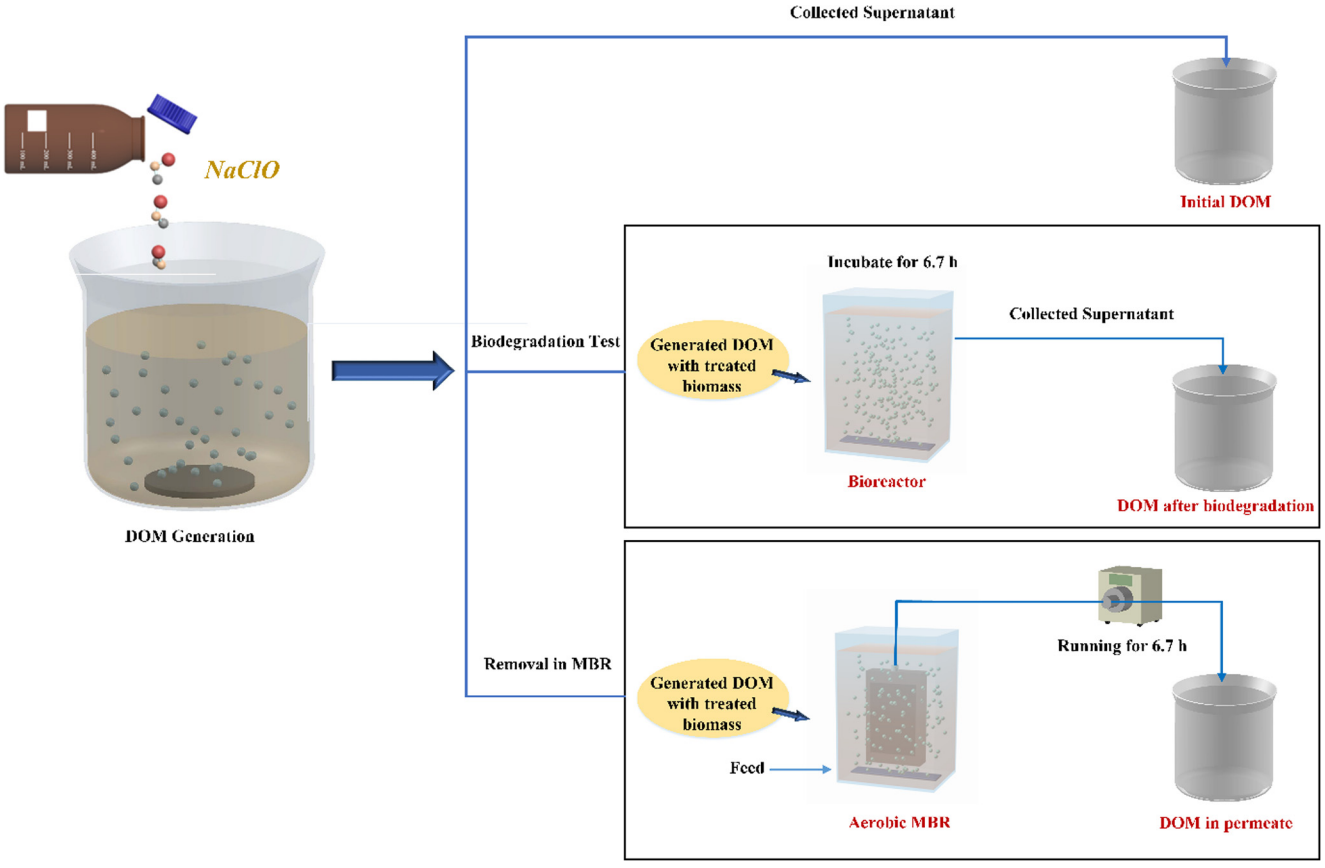


**Fig. 1.** Schematic illustration of experimental process.