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Control of ultrafiltration membrane fouling caused by *Microcystis* cells with permanganate preoxidation: Significance of *in situ* formed manganese dioxide

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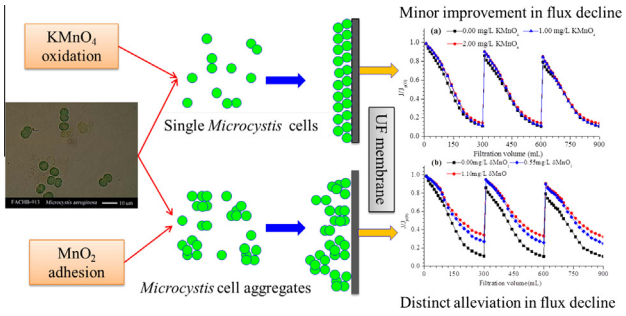
HIGHLIGHTS

- Algal cell-related UF membrane fouling control by $KMnO_4$ pretreatment was studied.
- Contributions of $KMnO_4$ oxidation and *in situ* formed MnO_2 adhesion were compared.
- $KMnO_4$ oxidation exhibited a minor effect on the characteristics of algal cells.
- MnO_2 adhesion promoted the aggregation of algal cells, improving their settleability.
- MnO_2 particles showed a superior ability in reducing cell-related fouling than $KMnO_4$.

GRAPHICAL ABSTRACT



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ABSTRACT

Control of the ultrafiltration (UF) membrane fouling caused by *Microcystis* cells using permanganate preoxidation was investigated with lab-cultured *Microcystis aeruginosa*. The contributions of two widely considered mechanisms, i.e. potassium permanganate ($KMnO_4$) oxidation and *in situ* formed manganese dioxide (MnO_2) adhesion, to the *Microcystis* cell fouling control were compared and discussed. Initially, effects of $KMnO_4$ oxidation and *in situ* formed MnO_2 adhesion on the characteristics of *Microcystis* cells, including viability, zeta potential, size distribution and settleability, were compared. Subsequently, filtration tests were undertaken to investigate the flux decline and fouling reversibility during UF of the untreated and treated cell solutions. The results indicated that $KMnO_4$ oxidation exhibited a minor effect on the characteristics of *Microcystis* cells as well as the cell integrity under the tested $KMnO_4$ exposure (1.0 and 2.0 mg/L). The adhesion of *in situ* formed MnO_2 particles could promote the aggregation of the cells, apparently improving their settleability. With regards to membrane fouling, the *in situ* formed MnO_2 particles displayed a superior capacity in alleviating both the flux decline and the irreversible fouling associated with *Microcystis* cells than $KMnO_4$ oxidation did, owing to the reinforced aggregation of the cells and the adsorption of released extracellular organic matter (EOM). Moreover, the effect of membrane precoating with *in situ* formed MnO_2 particles on the cell fouling was also studied. The precoating layer seldom reduced the flux decline by *Microcystis* cells, but improved the fouling reversibility probably by inhibiting the direct membrane-cell contact and retaining the released EOM.

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1. Introduction

How to guarantee the bio-safety of drinking water has become a worldwide concern since the discovery of the protozoa *Giardia* and *Cryptosporidium*, which have been the principal organisms controlling disinfection regulations [1]. Despite the removal efficiencies of the cysts of these protozoa up to 1.5–4.5 logs by traditional media filtration processes, the removal is not absolute [2]. In particular, *Cryptosporidium* is especially resistant to the commonly used disinfectant like chlorine. The deficiency of traditional water treatment processes in the bio-safety has promoted the application of low-pressure membrane filtration (i.e. ultrafiltration (UF) and microfiltration (MF)) in drinking water industry. The UF membrane, which has a pore size as small as 0.01 μm, can retain particles, colloids, protozoa (3–15 μm), bacteria (0.5–10 μm) as well as virus (0.02–0.08 μm) [2,3]. Till now, UF technology has been adopted in many waterworks; however, membrane fouling, which would increase energy consumption and shorten membrane life-span, hinders its further application [4,5].

As surface water is increasingly polluted by domestic sewage, *Microcystis* bloom frequently occurs in polluted reservoirs and lakes, bringing problems such as odors and toxins [6–9]. UF, which can completely retain *Microcystis* cells by size exclusion, becomes a promising technology to remove *Microcystis* cells from polluted water. Nevertheless, both *Microcystis* cells and their extracellular organic matter (EOM) proved to cause severe flux decline as well as irreversible fouling [10,11]. With regards to EOM, it was generally characterized and reported to have distinct features like high molecular weight and strong hydrophilicity [12]. Moreover, EOM fouling was also systematically investigated and was found to be closely related to both the organic content and the characteristics of EOM. As algal cell size is obviously larger than UF membrane pore size, *Microcystis* cells can only accumulated on the membrane surface, forming a cake layer [13]. Wicaksana et al. [14] studied the microfiltration membrane fouling by Chlorella cells using direct observation through the membrane technology (DOTM), and found that cell deposition started to occur even at a very low permeate flux. Babel et al. [15] reported that the cell layer formed by algal cell precipitation was compressible and that the fouling resistance would strongly aggravate when the cell layer was compressed. Qu et al. [11] compared the fouling potentials of *Microcystis* cells and their EOM, and concluded that the flux decline associated with the cells was even worse than that by EOM. Because cell fouling was usually considered to be less complicated than EOM fouling, the attention paid to the cell fouling was much less, leading to the lack of systematical understanding on the cell fouling mechanism and thus appropriate fouling control strategy.

To control the membrane fouling by algae, pretreatments with ozone and chlorine are widely adopted. Hung and Liu [16] reported that ozone preoxidation improved the performance of MF during the separation of green algae by reducing cake compressibility and biomass loading. However, the oxidation by strong oxidants often results in the release of intracellular organic matter as well as toxins [17,18]. Thus, a weaker oxidant, potassium permanganate ($KMnO_4$), is alternatively chosen for surface water treatment. Lin et al. [19] had demonstrated that permanganate preoxidation played a significant role in reducing the fouling during UF of surface water. There are two generally considered mechanisms for the algal fouling control by permanganate preoxidation. Liang et al. [20] put forwards that the weak oxidation provided by permanganate could inactivate the cells and make them easier separated. The other mechanism is associated with *in situ* formed manganese dioxide (MnO_2) particles which are found to coat the cell surface and to change the characteristics of the cells, i.e. increasing the zeta potential and gravity [21]. Among these two mechanisms, which makes a greater contribution is still under debate. The potential of permanganate pre-oxidation for *Microcystis* fouling control raises two critical questions: (1) can permanganate pre-oxidation lead to cell lysis? If so, to what extent? (2) which mechanism can be reinforced to maximize the fouling control performance.

The objective of this study was to verify the major mechanism of *Microcystis* cell fouling control by permanganate preoxidation, with $KMnO_4$ oxidation and MnO_2 adhesion compared. The effects of these two mechanisms on the characteristics of *Microcystis* cells, such as viability, zeta potential, size distribution and settleability, were investigated. Moreover, the flux decline and the fouling reversibility during UF of untreated and treated cell solutions were also compared and discussed.

2. Methods and materials

2.1. Algae culture and cell solution preparation

Microcystis aeruginosa was purchased from the Culture Collection of Algae at the Institute of Hydrobiology, Chinese Academy of Sciences, China. The detailed instruction for algae cultivation had been presented by Qu et al. [22]. Axenic cultures were conducted with BG11 medium in 1 L conical flasks. The conical flasks were placed in an incubator at 25 °C with an illumination of 5000 lx provided for 14 h every day. Cultures were harvested at the stationary phase with the culture time of 42 d. To reduce the interference of EOM in fouling study, the cells were extracted from the culture solution and resuspended by the simulated surface water which was Milli-Q water spiked with 0.5 mM $CaCl_2$, 1.0 mM $NaHCO_3$, and 15.0 mM $NaClO_4$ [23]. The chemicals were added to simulate the ionic strength of surface water and the pH was adjusted to 7.5 ± 0.1 with NaOH (0.1 M) and HCl (0.1 M) solutions. Specifically, the harvested algae solution was centrifuged at 4000*g* and 4 °C for 15 min, using a high speed refrigerated centrifuge (H2050R, Xiangyi, China). Subsequently, the supernatant was filtered through a 0.45 μm filter. The *Microcystis* cells remained in the centrifuge tube and those on the filter were collected and resuspended. Finally, the cell solution was diluted to the concentration of 1.0×10^6 cells/mL with the simulated surface water. The cell concentration was described by the optical density at the wavelength of 685 nm as demonstrated by Figs. S1 and S2 in the Supplementary information.

2.2. Membrane and experimental setup

Flat polyethersulfone UF membranes (OM100076, Pall, USA) were used in current study. The molecular weight cutoff and surface area of the membrane were 100 kDa and 4.5×10^{-3} m^2, respectively. A schematic diagram of UF system was illustrated by Qu et al. [22]. The system consisted of a stirred cell (Amicon 8400, Millipore, USA), a nitrogen gas cylinder, an electronic balance, a computer, gauges and pipes. UF experiments were performed in a dead-end filtration mode. The membrane was placed in the bottom of the stirred cell with its glossy side toward bulk solution. Nitrogen gas, at a constant pressure of 0.03 MPa, was utilized to drive feed solution across the membrane. Filtrate flowed into a beaker on an electronic balance connected to a personal computer and weighing data were automatically logged every five seconds. When the membrane was fouled, backwashing was conducted with Milli-Q water. The membrane was turned over and then the Milli-Q water (100 mL) was driven also by nitrogen gas through the membrane.

2.3. Experimental protocol

This study was to verify the contributions of the two mechanisms, permanganate oxidation and MnO_2 adhesion, to the control