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Influence of coagulation process on the ultrafiltration performance – The roles of Al species and characteristics of algae-laden water

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ABSTRACT

The aim of this study was to investigate the coagulation performances in different algal systems, and effects of algal morphology and composition of extracellular organic matter (EOM) on membrane flux were also investigated. The results indicated that Al_{13} generated the largest flocs, and strength factor and recovery factor were also largest. The results of ultrafiltration experiments also showed that the floc size and the concentration of Soluble Microbial Products (SMP) may be the main decision factors in the membrane fouling process. Al species distribution was important in removing EOM in the coagulation process. SMP in EOM could be effectively removed by Al_{13} and Al_{30}, so the membrane fouling could be alleviated due to the larger removal efficiency of SMP. The roughness of the sediment layer formed by Al_{13} was largest, and the sediment layer would adsorb and intercept more algae organic matter.

1. Introduction

Former studies had showed that the algal cells and pollutants caused by algae would affect the drinking water quality [1–4]. The production of unpleasant tastes and odors [5], formation of disinfection by products (DBP) [6], and toxins from cyanobacteria [7] were the most important problems. Membrane technology had gradually shown its important role and bright prospects in water treatment process, and ultrafiltration (UF) technology could remove a broad range of impurities almost completely [8,9]. Although the membrane technology had developed rapidly, membrane fouling was always a challenge for the development of membrane technology. Especially for the algae-laden source water, algal cells could secrete extracellular organic matter (EOM) and mucilaginous slime material, which could cement particulates on the membrane surface and increase the resistance to filtration [10,11]. Some researches had demonstrated the influence of different hydrophobic/hydrophilic fractions of EOM on ultrafiltration membrane fouling [12–14]. In the membrane fouling process, the deposited layer formation, pore plugging and hydrophobic adhesion were the main mechanisms for the membrane fouling caused by algal EOM [15]. In order to solve these problems, amounts of studies conducted on the removal of algae have been mainly concentrated on effects of organic matter of algae (AOM) and the disinfection by-products (DBPs) [16,17]. In different algal growth phases, the concentration and composition of EOM may be different [18]. Some researches investigated the flux decline and fouling potentials from different algal growth phases, with fouling for the stationary > late exponentially phase > early exponential phase [19]. However, few studies referred to the morphology of algal cells prior to entry into the UF system. It was therefore not clear whether the morphology of algal cells could influence membrane fouling of UF, particularly when the algae-laden water was treated using different Al-based coagulants.

Amount of pretreatment technologies had been conducted to improve the membrane performances, and the results showed that pretreatment technology could greatly expand the use of UF membrane system [20]. Although these pretreatment steps could improve the coagulation performances and decrease the amount of the algal cells, they could deteriorate disinfection process by changing the nature of the water and cause the formation of trihalomethanes (THMs) and haloacetic acids (HAAs). Coagulation, which is regarded as an economical and efficient pretreatment method, has been widely used in drinking water and wastewater treatment. The actual effect of pre-coagulation on the permeability

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of the membrane depends on coagulation conditions, including coagulant types, dosage and mixing condition [21]. The coagulant directly affected the coagulation performance, and the coagulation performance directly determined the efficiency of water treatment [22]. Aluminum salt is the most commonly used coagulant in water treatment plant, and a large amount of scientific researches and the applications results showed that the concentration of Al_{13} could reflect the coagulation behavior and performance of polyaluminum chloride (PACl) products. The Al_{13} structure is stable and carry large amounts of positive charges, so the Al_{13} molecules could directly been adsorbed on the surfaces of particles and a strong electrical neutralization process could be exerted [23]. Thus, production of PACl with a high concentration of Al_{13} has become the main target of the PACl research and production industry [24]. Al_{30} is another polycation with Keggin structure in hydrolysis polyaluminum solutions, and it is composed of two Al_{13} molecules connected by four Al monomers. Former studies showed that Al_{30} molecules performed better bridging effects in coagulation process [25]. Although the coagulation mechanisms for Al_{13} or Al_{30} had been investigated well, few researches focused on the treatment of different algae-laden water, and the membrane fouling process was also not investigated well. Thus, study focused on membrane fouling in treatment of different algae-laden water with Al-based coagulants is necessary.

The purpose of this study is to understand the role of Al species in membrane fouling when coagulation technology was used as pretreatment in treatment of algae-laden water. In this study, different algae-laden waters samples were generated by coagulated with different Al-based coagulants. The water samples were varied by an important operating conditions: with or without sedimentation after the coagulation process. Membrane fouling and flux decline associated with different algal systems, and the effects of Al species distribution on flux decline are described.

2. Materials and methods

2.1. Algae cultivation

The following freshwater algae cultures were obtained from the Institute of Hydrobiology, Chinese Academy of Sciences: *Microcystis aeruginosa* (cyanobacteria), *Chlorella* (green algae) and *Cyclotella* (diatoms). Axenic cultures were carried out in batch mode in 10 L and growth conditions have been described, regularly observed their growth and counting [26]. All algae were harvested for experiments in the early stationary phase.

2.2. Preparations of water samples and coagulant

The relationship between the density of algae cells and suspension absorbance will coincidence with linear relation. Thus, This study choose the algal cell suspension absorbance at 680 nm as a measure of algae cell density. The experimental water sample were prepared by algal cell suspension diluted with deionized water. To facilitate comparison between algae, adjusting the absorbance of the three algae was 0.300 under 680 nm. The reagents used in experiments were purchased from China National Pharmaceutical Group Corporation (Beijing). 5.0 mmol/L $NaNO_3$ and 4.0 mmol/L $NaHCO_3$ were added to provide a ionic strength and a contain buffer capacity. The pH of water sample was adjusted to 8.5 with NaOH (0.1 mmol/L) and HCl (0.1 mmol/L) solutions. Three Al-based coagulants were used in this study: $Al_2(SO_4)_3$, Al_{13} and Al_{30}. Their preparation methods as stated in the literature [25]. The total aluminum concentration in this paper was determined by titrimetric method according to National Standard of China. Al-species distributions of three coagulants were measured by Al-Ferron complexation timed spectrophotometry method [27], and the results are summarized in Table 1.

Results (Table 1) indicated that the Al species distributions of three coagulants used in this study were different, and these three coagulants could be used to investigate the effects of Al species distribution on the membrane fouling process in algal system.

2.3. Jar tests and UF membrane tests

A programmable Jar tests were performed on a Flocculator (MY3000-6F, Wuhan Meiyu, China), which enabled mixing speed and time to be preset. Coagulation test was be consisted of 4 steps: (1) Stirring the suspension at a speed of 250 rpm for 0.5 min to mix the solution evenly. (2) Adding certain amounts of coagulants and simultaneously stirring the solution at 200 rpm for 1.5 min to uniformly disperse the coagulant; (3) Stirring the solution at a reduced speed at 40 rpm for 10 min to allow floc growth to occur; (4) The coagulated water sample was sedimented for 30 min to measure the residual turbidity and the amount of residual algal cells. The coagulated water was treated with membrane without sedimentation, and the coagulated water which was sedimented for 30 min was used to be compared.

The previous series on algae removal by coagulation experiments had determined the optimum dosage of coagulant (Fig. S1), and results of optimum dosage of the coagulants were summarized in Table 2. With colony counting method, the residual cells in the treated water samples were calculated and summarized in Table 3, and the results indicated that the coagulation process could significantly decrease the amount of algal cells (cells/mL). After the coagulation process, the treated water samples were transported into filtration cells (without or after sedimentation) which was purchased from Millipore (Amicon 8400, USA). The flat sheet ultrafiltration membrane (100KDa) made of Polyvinylidene fluoride (PVDF) was purchased from Ande Membrane Separation Technology & Engineering Co., Ltd (Beijing). Under the process of ultrafiltration, the coagulation effluent always needs to provide in order to prevent membrane surface drying. Normalized flux J/J_0 as a function of time was shown for the flux decline results from the stirred cell experiments, and J_0 was the initial membrane flux. In order to facilitate the comparison, the fixed ultrafiltration time is 1800 s and the feed solution was driven to penetrate across the membrane by nitrogen gas at a constant pressure of 0.1 MPa. The membrane after filtration were taken out to be dried in natural conditions, and FE-SEM analysis (JEOL Ltd., Tokyo, Japan) and AFM analysis (Nanoscope, IIIa, Multimode) were used to investigate the mechanism for membrane fouling, respectively.

2.4. EOM analysis

The algae organic matter (AOM) comprises both extracellular organic matter (EOM) and intracellular organic matter (IOM). In order to study the effect of EOM on the fouling of ultrafiltration membrane, Fluorescence EEMs of EOM was measured on a Varian Eclipse fluorescence spectrophotometer (Hitachi F7000, Japan) in scan mode. The spectrums were gathered with scanning emission: Em spectra from 220 nm to 550 nm at 5 nm increments by varying the excitation; Ex wavelength from 200 nm to 400 nm at 5 nm increments. The spectra were recorded at a scan rate of 12,000 nm/min, using excitation and emission slit bandwidths of 5 nm. The voltage of the photomultiplier tube PMT was set to 500 V for low level light detection.

2.5. Characteristics of flocs formed in the coagulation process

Generally, floc size, strength factor (S_f), recovery factor (R_f) and fractal dimension (D_f) were some basic parameters to describe the