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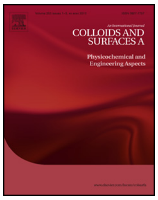

Enhancing integrated removal of *Microcystis aeruginosa* and adsorption of microcystins using chitosan-aluminum chloride combined coagulants: Effect of chemical dosing orders and coagulation mechanisms

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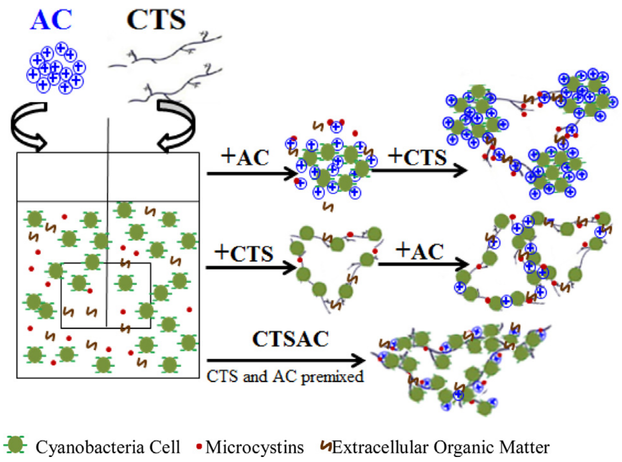
HIGHLIGHTS

- Two dual-coagulants and a novel composite were prepared using CTS and AC.
- CTS combined AC dual/composite coagulants caused no damage to *M. aeruginosa* cells.
- CTSAC obtained best cell removal for stronger entrapment and bridging ability.
- The first addition of AC aids the MCs adsorption of CTS.
- CTSAC (2.6 mg/L CTS and 7.5 mg/L AC) has desired EOM removal ability.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of two chitosan (CTS)-aluminum chloride (AC) dual-coagulants with different dosing orders and a composite coagulant CTSAC (CTS and AC premixed) on removal of *Microcystis aeruginosa* (*M. aeruginosa*) cells and second metabolites in cyanobacteria-laden drinking water treatment were investigated, and in comparison with AC and CTS. Response surface methodology (RSM) was used to model and optimize the coagulation processes. The coagulation mechanisms were investigated via zeta potential, scanning electron microscope (SEM), and three-dimensional excitation-emission matrix spectra (EEM) analyses. The investigated dual/composite coagulants caused no evident damage to *M. aeruginosa* cells, and achieved better removal effects than coagulant individually applied. The CTSAC removed cells was the most effective for stronger entrapment and bridging ability. While the highest adsorption of extracellular microcystins (MCs) was obtained through AC–CTS (AC added firstly). CTS–AC (CTS added firstly) provided slight higher extracellular organic matter (EOM) removal. The optimal coagulation performance was obtained when CTSAC was set as 2.6 mg/L CTS plus 7.5 mg/L AC, under which 97.8% of intact cells, 53.08% of extracellular MCs and almost all EOM were simultaneously removed. Overall, the combination of CTS and AC coagulation process has proven to be a better substitute for conventional coagulation in cyanobacteria-laden drinking water treatment.

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1. Introduction

The proliferation of harmful cyanobacteria is considered as a serious environmental issue since its ability to produce toxins as well as taste and odor compounds which adversely affect aquatic ecosystems and human [1,2]. *Microcystis aeruginosa* is one of typical toxin-producing cyanobacteria found in highly eutrophic water bodies [2]. Microcystins (MCs) produced by *M. aeruginosa* are hepato-toxins which pose a health threat on humans [3,4]. Other algal organic matters (AOM) could also compromise the safety of drinking water since they are precursors leading to the development of disinfection by-products (DBPs) during chlorination [2]. Generally, most AOM including MCs are contained within cells which are classified as intracellular organic matters (IOM), and those releasing metabolites deriving from cyanobacterial cells are categorized as extracellular organic matters (EOM) [2]. The cell contained IOM can also be released into the environment once cell integrity is damaged [1]. The removal of dissolved AOM (including MCs) is more difficult than those in the cells of *M. aeruginosa* [5]. Therefore, an efficient method to remove *M. aeruginosa* cells without damaging the membrane is significant in preventing dissolved MCs and DBPs precursors from increasing into the treated water.

Coagulation is considered as the most important process for algal removal in conventional drinking water treatment. However, the chemical stress exerted onto the cell membrane may disturb the cell stability during the coagulation process [5,6]. It has been reported that the application of some copper sulphate and potassium permanganate chemicals in cyanobacteria removal could cause cell damage [3]. However, the appropriate usage of ferric chloride and aluminum sulphate could avoid cell lysis [1,6]. Study showed the aluminum chloride (AC) coagulation would effectively remove the *M. aeruginosa* cells without causing cell lysis, but it was ineffective at the removal of extracellular MCs [5].

Bioflocculants have attracted much attention in the field of coagulation research since they are environmental friendly and exert less health concern. Chitosan (CTS), a biodegradable and nontoxic bioflocculant, has been proposed as a substitute for conventional coagulants in water treatment [7]. It is obtained by the deacetylation of the chitin, which is an abundant polysaccharide in nature [8]. The intrinsic characteristics of CTS, especially the presence of primary amino groups, render their effectiveness in removing various contaminants [7,9]. Previous study showed that not only 99% of *M. aeruginosa* cells were integrally removed by CTS, but also a significant amount of extracellular MCs were adsorbed by CTS polymers [10]. Actually, there is a need for the treatment of total EOM for they are also water quality issues and make subsequent water treatment processes difficult [2]. However, information about the influence of coagulation on EOM removal was limited and the effectiveness of CTS coagulation on EOM was still unknown as well. Despite there are many desired properties of the CTS as a coagulant, the formation of DBPs has been reported for chitosan is an organic compound [7]. In addition, high cost of CTS due to its low production yield has hindered its application as a sole coagulant in practice [7]. One solution is to prepare a coagulant combining the advantages of bioflocculant with inorganic coagulant in water treatment [11–13]. Simultaneous removal of intact *M. aeruginosa* cells, dissolved MCs and DBPs precursors can safeguard drinking water quality and effectively facilitate water treatment. However, previous study found that chitosan modified kaolinite (CMK) could cause the damage of *M. aeruginosa* cell membranes and the release of intracellular substances [14]. Pan et al. [13] found chitosan-modified local soils could effectively remove harmful cyanobacterial in Taihu Lake. But the effect of chitosan-modified local soils on MCs removal and cell integrity was unknown. Furthermore, the chemical modification may alter CS properties, making it toxic and reducing its unique properties [15]. And the chemicals used to modify and the high amount of solvent applied are the main drawbacks for commercialization. Studies found that the application of the organic and inorganic combined coagulants by dosing chemicals at different sequence achieved better coagulation efficiency with lower coagulants used [11,12,16]. Bo et al. [11] found the floc properties was significantly enhanced when a bioflocculant was added before/after aluminum sulfate with lower coagulants consumed in kaolin-humic acid solution treatment. Wei et al. [12] reported premixing of polyferric chloride and organic polymer gave higher color removal efficiency than polyferric chloride and organic polymer used individually. Zhao et al. [17] observed compared to aluminum sulfate applied individually, coagulation efficiency of dye was greatly improved when Enteromorpha polysaccharides-aluminum sulfate dual-coagulants were used. However, for the specific purpose of examining the effect of chemical addition sequence of inorganic–organic dual/composite coagulants on the simultaneous removal of intact *M. aeruginosa* cells, extracellular MCs and EOM, there has been no published. If the dual/composite coagulant performed well in the treatment of cyanobacteria-laden drinking water resource, it will be a novel and preferable choice in practical application for it could reduce the cost of organic coagulant without the needs of chemical modification.

In this study, AC and CTS were further investigated for above mentioned effects based on previous results [5,10]. Two dual-coagulants, CTS–AC (CTS dosed firstly) and AC–CTS (AC dosed firstly) were prepared by dosing CTS and AC in different orders, and a novel composite CTSAC coagulant was obtained by premixed AC and CTS. The goal was to compare these coagulants in terms of the removal of *M. aeruginosa* cells, extracellular MCs and EOM during the coagulation processes. The study also made a comparison between these dual/composite coagulants and the traditional coagulants based on their effectiveness on *M. aeruginosa* removal and coagulation mechanisms. Response surface methodology (RSM) was applied to model and predict the coagulation processes.

2. Experimental procedures

2.1. Materials

2.1.1. Algal culturing

M. aeruginosa FACHB-905, provided by the Institute of Hydrobiology, Chinese Academy of Sciences, was used as a model algal strain in this study. It was cultivated in BG11 media (pH 7.5) at 25 °C with a light/dark cycle (14/10) in conical flasks [5]. Algae solution was harvested at the late exponential growth phase for all experiments.

2.1.2. Natural water

The natural water from the intake of the Queshan Reservoir (a drinking water source, Jinan, Shandong province) was filtered through a 0.45 μm glass fiber membrane. The main characteristics of raw water were as follows: Temperature 18.5 °C, pH 8.4, turbidity 4.7 NTU, DO 9.13 mg/L.

2.1.3. Coagulants

CTS (Mw = 50000, D.D. = 95%) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). CTS was dissolved in 1.0% acetic acid solution and stirred overnight at 100 rpm to obtain 1.0% (w/w) stock solution. Aluminum chloride (AC) stock solution (3 g/L) was prepared by dissolving AC in ultrapure water. Two CTS and AC dual-coagulants were prepared as following: The first dual-coagulant was achieved by adding CTS at the beginning of the 2 min rapid mixing process, followed by adding AC 1 min later. This way of dosing dual-coagulant was referred as CTS–AC. When the sequence of adding CTS and AC was reversed, it is denoted as AC–CTS. A composite coagulant, referred as CTSAC, was prepared by adding CTS