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Performance and mechanism of phycocyanin removal from water by low-frequency ultrasound treatment

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ABSTRACT

Ultrasonication pretreatment of raw water with high content of algal cells might cause an increase in dissolved organic nitrogen (DON) and proteins, which must be removed effectively before coagulation. In this study, the efficiency of sonication treatment in removing typical proteins derived from algal cells was investigated by applying ultrasonic waves at 20, 40, 60, 80, and 100 kHz, and the influencing factors and removal mechanism were discussed. The results showed that low-frequency sonication could degrade phycocyanin to some extent, achieving about 95% removal rate after 150 min of sonication. However, excitation emission matrix analysis indicated that ultrasonication could not entirely degrade phycocyanin into inorganic nitrogen, and many proteins and nitrogen-containing organics were found in the samples after sonication. While the total nitrogen concentration remained consistent during the entire sonication process (240 min), the total inorganic nitrogen concentration increased from 0.6 to 1.3 mg/L, indicating that only 33.3% of DON was oxidized into inorganic nitrogen. Nevertheless, sonication could significantly attenuate the interference of phycocyanin in coagulation and enhance coagulation. The mechanical effects and free-radical oxidation resulting from cavitation collapse could be responsible for the degradation of phycocyanin and proteins following sonication. In all, the use of ultrasonic treatment as a posttreatment following sonication to remove algal cells from raw water may not be beneficial.

1. Introduction

Algal bloom is one of the problems faced by some water plants, especially those that use eutrophic water as the water source, such as the water from Taihu Lake. The excessive algal cells in raw water not only seriously influence the normal operation of the water treatment process, but also deteriorate the water quality [1]. Moreover, algal cells, algogenic organic matter (AOM), and their metabolites cannot be removed efficiently by conventional water treatment technology [2], which may result in microcystins, odor-causing substances, and disinfection byproducts (DBPs) [3,4]. Recently, dissolved organic nitrogen (DON), which produces nitrogenous disinfection byproducts (N-DBPs), has been reported to be a crucial problem in drinking water [5]. Although several methods have been developed to control the excessive proliferation of algae, including chemical pre-oxidation, flotation, advanced oxidation technology, etc., they are complicated, expensive, and may cause secondary pollution [6,7].

As a pollution-free technology and an advanced oxidation process (AOP), ultrasonic irradiation has received increasing attention for the degradation of various micropollutants, including parathion [8], 5-methylbenzotrizole [9], ibuprofen [10], ethyl paraben [11], etc. In addition, ultrasonic treatment at several tens to hundreds of kHz has been found to effectively remove algal cells directly and enhance removal performance of coagulation [12–17]. Ultrasound irradiation can produce several different effects that can be divided into three types in general [18,19]. Although chemical effects, shock waves, and shear stress of microstream have always been considered as the main inactivation mechanisms for algal cells, in a recent study, physical effects have been deemed as the primary mechanism for algal cell disruption [19]. When compared with its application to eutrophic water body, the use of ultrasonication as a pretreatment to conventional drinking water treatment technology is more attractive because of its convenience, effectiveness, and low cost. The main purpose of ultrasonication treatment is to enhance coagulation effects [12,17], and the ultrasonic condition should be strictly restricted to prevent negative effects.

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The results of our previous study showed that excessive sonication may deteriorate the subsequent coagulation effects and increase the concentration of DON, microcystins, and odor-causing substances [20]. Moreover, the main categories of the protein in the intracellular organic matters (IOM) were phycocyanin and its derivations [21]. As the increase in DON, especially proteins, is considered to be one of the important problems interfering with coagulation as well as producing N-DBPs [22], there has been increasing attention in recent years on the development of new effective technology to remove DON and proteins derived from algal cells from drinking water.

Besides its ability to remove organic pollutants from water, ultrasonication may also remove proteins to some extent. However, studies on the direct removal of proteins using ultrasound treatment are limited, whereas numerous studies have focused on the removal of other biological macromolecules, such as polysaccharides [23,24], chitosan [25], pullulan [26], pectin [27], etc., and achieved better removal rates. Although the results of these studies may provide the basis for sonication of proteins derived from algal cells, the removal effect, underlying mechanism, and influencing factors need to be examined in detail. Therefore, the main objective of the present study was to assess the potential of ultrasound treatment to remove proteins from water by examining the removal performance and influencing factors of ultrasonication, as well as by analyzing the effects of sonication on coagulation and its underlying mechanism. In addition, the possibility of application of ultrasonication as a posttreatment following sonication to remove algal cells from raw water was also discussed. Phycocyanin was chosen as the removing target proteins according to former study [21,28].

2. Materials and methods

2.1. Materials

Phycocyanin was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the other chemicals employed were of analytical grade and used without further purification, unless stated otherwise. Commercial polymeric aluminum chloride (PACl) powder was obtained from Nanning Chemical Engineering Co. Ltd. (Nanning, China) with basicity (OH/Al) of 1.35 and Al_2O_3 content of 30% (mass fraction).

2.2. Ultrasonic and coagulation devices

Low-frequency ultrasounds (20–100 kHz) were used because they can be applied in practice. The effect of ultrasound on the removal of phycocyanin was assessed using an ultrasonic device (Huaneng Ultrasonic Co., Ltd., Wuxi, China) with a power of 1.2 kW (adjustable) and frequency of 20, 40, 60, 80, and 100 kHz, respectively [20] (Fig. 1). The containers used to hold the solutions were cylindrical beaker with a volume of 1000 mL. To test the effect sonication on the coagulation performance, a jar tester (ZR4-6, Zhong-run Water Co., Ltd.) was employed.

2.3. Experimental methods

The experimental methods were similar to those employed in our previous study, except for the parameters, which were adjusted according to the requirements of the present study [20].

2.3.1. Ultrasonication pretreatment

Certain volumes of standard suspension of phycocyanin were sonicated for a specific period of time at various frequencies and powers. Samples were collected after 15, 30, 45, 60, 90, 120, 180, 210, and 240 min of ultrasonication, respectively, and the main parameters (phycocyanin, total dissolved protein, DON, NH_4^+, NO_3^-, and NO_2^-) were assayed. In addition, samples collected before and after sonication were added into the raw water to investigate the influence of ultrasonication pretreatment on coagulation. Furthermore, the influence of power intensity was determined by changing the volume of the samples and was calculated as the average power per volume of the water samples (W/cm^3).

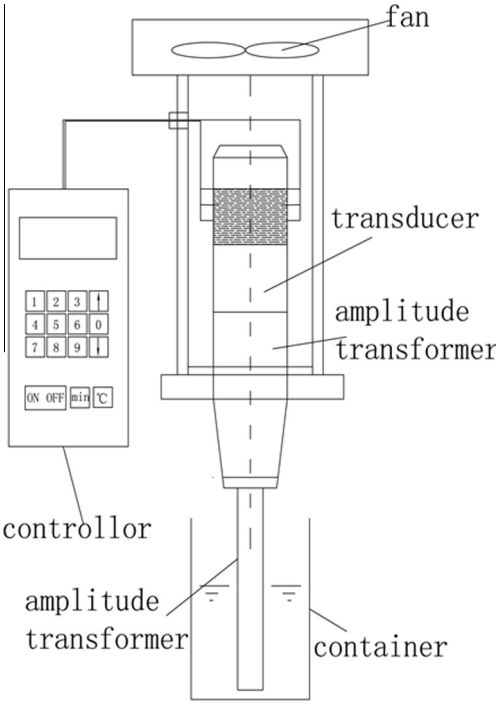

Fig. 1. The diagram of ultrasonic device.

2.3.2. Coagulation treatment

Certain doses of PACl at specific concentrations were added to 1000-mL circular jars containing 1000 mL of each sample collected before and after ultrasonication pretreatment, and mixed at 100 rpm for 20 min, followed by 60 rpm for 15 min. Subsequently, the samples were left for 20 min, and the supernatants (100 mL) were collected using a U-shaped pipette to avoid suction of the precipitated solids.

2.4. Analytical methods

All the samples were filtered using 0.45-μm filters prior to chemical analysis. The DON was determined from the difference between the measured total dissolved nitrogen (TDN) and the sum of measured dissolved inorganic nitrogen (DIN) species as follows:

$$\mathrm{DON\ (mg/L)} = \mathrm{TDN} - \left(\mathrm{NH_4^+\text{-}N} + \mathrm{NO_2^-N} + \mathrm{NO_3^-\text{-}N}\right) \quad (1)$$

Therein, TDN was measured with a TOC analyzer equipped with a TNM total nitrogen detection unit (Shimadzu TOC-VCPH, Japan). DIN species (ammonia, nitrate, and nitrite) were measured with an ICS-2100 ion chromatograph (Dionex™, USA) [29].

Coomassie brilliant blue method was used to determine the concentration of total soluble proteins (TDP), and three-dimensional excitation emission matrix (3D-EEM) fluorescence spectrophotometer (Hitachi F-4500 fluorescence spectrometer, Japan) was employed to ascertain the composition of algal cells (intracellular organic matter, IOM), following the procedures