Journal of Industrial and Engineering Chemistry 24 (2015) 153–160

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Ultrasound-chitosan enhanced flocculation of low algal turbid waters

Sara Ann Fast, Veera Gnaneswar Gude *

Department of Civil and Environmental Engineering, Mississippi State University, Mississippi State, MS 39762, USA

ARTICLE INFO

Article history:
Received 15 February 2014
Received in revised form 18 September 2014
Accepted 19 September 2014
Available online 27 September 2014

Keywords:
Algae
Chitosan
Ultrasound
Flocculation
Sedimentation

ABSTRACT

In this study, we evaluated the effect of ultrasound-chitosan enhanced flocculation process for efficient removal of algal cells from low algal turbid waters comparing with the conventional rapid mix process. The results show that the turbidity removal efficiencies for ultrasound-enhanced coagulation (97.8–99% removal) were comparable to the conventional rapid mix coagulation (96.8–99% removal) for alum and for chitosan (84.1–90.5% for RM and 84–97% for US). This study confers that ultrasound mixing can be performed instead of conventional rapid mixing to improve the algal cell removal efficacies from the low algal turbid waters.

Introduction

Algae growth is a common problem in water treatment plants and water reservoirs. Algae are aquatic organisms classified separately from plants. Algae are a large and diverse group of simple, typically autotrophic organisms, ranging from unicellular to multicellular forms. Algae blooms are a seasonal problem in many surface waters worldwide both in natural and engineered/industrial systems. Many rivers and streams which serve as drinking water sources are contaminated by algal growth and are considered nuisance [1,2]. For example, cooling towers in power plants also provide ideal conditions for algal growth, offsetting the heat transfer capacity of the cooling surfaces and eventually reducing the process performance [3]. The presence of algae is often associated with production of phthalate esters and polychlorinated biphenyls (PCBs) [4,5]. Algae are of particular concern to water companies with respect to the provision of drinking water to a satisfactory standard. Cell populations can vary widely in terms of cell count and diversity, and this can impact the treatability of the algae. Algae can also affect the color, taste and odor of drinking water, and a limited number of species also excrete toxic metabolites which, if consumed in insufficient quantities, can cause health problems [1,6,7]. Many freshwater blue-green algae can produce toxins, i.e., cyanotoxins (classified based on their toxin group as heptotoxins, neurotoxins, cytotoxins and dermatoxins) which can result in liver hemorrhage, muscular paralysis, respiratory effects and can cause headache, anorexia, vomiting and damage to organs [8]. Algae presence can also increase the coagulant demand and treatability issues including filter blockage [1]. A survey on 76 water supply utilities in the USA by EPA has recommended many alternatives to control the algal growth in the water treatment plants by chlorination for disinfection, use of an occasional shock treatment, and addition of algaecides in-situ in reservoirs [8,9].

Algae can be removed by using techniques such as centrifugation, air floatation, coagulation, flocculation, electro-coagulation–flocculation and hydrodynamic cavitation [10,11]. Among these, flocculation is the most widely practiced technique for simplicity and economic feasibility. Commonly used flocculants are aluminum and ferric based salts which form precipitates to agglomerate the microalgae. Despite the high efficiency of these flocculants, the abundant sludge that is generated in the process is difficult to dehydrate, its efficiency is entirely dependent on the pH, and when formed in cold water, alum flocs are not very mechanically resistant. In addition, the use of alum is a source of concern, and the debate about its possible toxicity is still open. Since high aluminum concentrations in water may have human health implications, environmentally friendly coagulants will present an interesting alternative for water purification [12]. Chitosan, a naturally occurring organic biopolymer, seems to be a promising alternative to address the aforementioned issues. Chitosan is a linear poly-amino-saccharide, which is produced by alkaline deacetylation of chitin [13]. Chitin is the second most abundant biopolymer in the world, after cellulose. The main sources exploited are two marine

* Corresponding author. +1 662 325 0345.
E-mail addresses: gude@cee.msstate.edu, gudevg@gmail.com (V.G. Gude).

http://dx.doi.org/10.1016/j.jiec.2014.09.023
1226-086X/

crustaceans, shrimps and crabs. It is insoluble in water and soluble in acids. Chitosan also possesses several intrinsic characteristics that make it an effective coagulant and/or flocculant for the removal of contaminants in the dissolved state. It has characteristics of both coagulants and flocculants, i.e., high cationic charge density, long polymer chains, bridging of aggregates and precipitation (in neutral or alkaline pH conditions). Its uses are justified by two important advantages: firstly, its non-toxicity and biodegradability [14,15]; secondly its outstanding chelation behavior. Its unique physico-chemical properties render it very efficient in interactions with various contaminants including both particulate and dissolved substances. These properties have been exploited for the design of coagulation/flocculation processes applied to the treatment of various effluents [16].

Harvesting highly concentrated algal suspensions does not appear to be a serious concern since it can be achieved by sweep flocculation, a widely practiced technique. On the other hand, removing low algal cell concentration from low turbid waters (especially in drinking water sources) can pose several process challenges. Thus, the aim of this research is to utilize the chitosan (a biopolymer coagulant/flocculant) and ultrasound (a non-conventional mixing and inactivation technique) simultaneously to enhance the algal cell removal efficiency from low algal turbid waters. Chitosan and ultrasound were individually evaluated for their effect and enhancement of coagulation and flocculation processes in the past, but their combined effect on these chemical/physical processes was not reported to date. In this study, the chitosan-ultrasound enhanced coagulation/flocculation method was compared with the conventional rapid mix/flocculation process to evaluate the performance of the proposed method. Another aim of this research is to investigate if the ultrasound effect can be used as a mechanism to distribute the chemical coagulant (rapid mix step) and promote pin-floc formation while simultaneously inactivating the algal cells by the shock treatment of the acoustic waves to facilitate easy flocculation/sedimentation process. The following sections will provide the details on the experimental procedures and the process optimization study for chitosan-ultrasound enhanced coagulation/flocculation process to treat the low algal turbid waters.

Materials and methods

Low algal turbid waters and coagulants

Concentrated *Chlorella sp.* paste was obtained from a commercial producer which was used to prepare a stable algal cell suspension of 10–40 NTU of measurable turbidity. The suspension was tested to ensure 99.9% of turbidity over a 24 h settling period. A 1% chitovan coagulant polymer was purchased from a commercial water chemicals company Dungeness Environmental Inc., Washington, USA. We also prepared a different chitosan solution by using dry chitosan powder purchased from Fisher Scientific (Acros-Organicas) with molecular weight in the range of 600,000–800,000. This chitosan aqueous solution was prepared by dissolving chitosan in a 1% dilute aqueous acetic acid solution (1% v/v) with a 90% degree of deacetylation and mixed with a magnetic stirrer at 100 rpm for over 24 h to obtain a 1% (w/w) stock solution. The aluminum sulfate ($Al_2(SO_4)_3nH_2O$; $n = 12–14$) coagulant was procured from Fisher Scientific™. 5.8 g of aluminum sulfate was added to 50 mL of DI water to form a concentrated solution of 100, 000 ppm, while the chitovan or chitosan concentrations were 10,000 ppm. Thus, for alum, 0.1 mL of dosage equals to an actual concentration of 10 mg/L whereas the dosage for chitovan and chitosan are 1 mg/L (for 0.1 mL dosage).

Coagulation/flocculation experiments

Several experiments were conducted to study the combined effect of alum, chitosan and ultrasound. The effects of chitosan dosage and ultrasound power were tested in low algal turbid waters with a turbidity ranging between 10 and 40 NTU at 10 NTU intervals. The ultrasound enhanced coagulation/flocculation was performed using a NO-MS100 ultrasonicator manufactured by Columbia International Technologies with 1000 W power output capacity. The ultrasonic frequency was 25 kHz. The horn is made of titanium alloy with 10 levels of amplitude to vary the effect of ultrasonic application. An ultrasound exposure time of 1 min was applied in lieu of rapid mixing process. After the simultaneous ultrasound exposure and coagulant addition (alum or chitovan), the algal suspension was subjected to slow mixing at 50 rpm for 20 min. For the tests which followed conventional rapid mixing, a 200 rpm mixing speed was applied for 2 min. For both methods (conventional rapid mix-flocculation–sedimentation vs. ultrasound-flocculation–sedimentation), the sedimentation time was 24 h. The turbidity was measured at 1 h of settling time and at 24 h settling time to capture the maximum removal efficiency.

The algal suspension test volumes were fixed at 1000 mL in a 1500 mL standard jar for both conventional rapid mix (RM) and non-conventional ultrasound (US) methods. This study consisted of batch experiments, using a Phipps and Bird jar tester unit (model 7790-400; 120 V, 60 Hz and 220 V, 50/60 Hz) which accommodates six 2-L jars/beakers. The beakers were filled with 1000 mL of the microalgae culture for each test run. Six stainless steel $1'' \times 3''$ paddles are spaced 6 in. apart and are adjustable to a maximum depth of 9 in. with a highly reliable electronic motor control system regulated at variable speeds (of all paddles simultaneously), from 1 to 200 rpm. The contents of each beaker were simultaneously stirred at the same speed with a six-spindle of steel paddles.

The experiments started with the effect of coagulant dosage for both alum and chitosan. For the coagulant dosage effect test the pH was maintained at 7. To measure the effect of optimum pH, the pH was varied between 5 and 9 units, i.e. at 5, 6, 7, 8, and 9 while fixing the coagulant dosage. The pH of the algal suspension was adjusted by adding either NaOH (base) or HCl (acid) prior to flocculation. Also, the effect of ultrasound power on the algal cell removal efficiency was tested at different power levels 100, 250, 500 and 1000 W which gives a power density of 0.1 W/mL, 0.25 W/mL, 0.5 W/mL and 1.0 W/mL respectively. All the experiments were conducted in triplicate, and the average of the three results were evaluated.

Flocculation removal efficiency

The samples were collected at the start of the experiments, after 1 h sedimentation time as well as 24 h sedimentation time. The turbidity of the water samples was measured at these specified steps and time intervals. The turbidity was measured using HACH 2100 N Turbitimeter®turbidity meter. The turbidity removal efficiency (RE) was calculated using the following equation [17]:

$$\mathrm{RE}(\%) = \left[1 - \frac{T_F}{T_I}\right] \times 100\% \quad (1)$$

where T_I is the initial turbidity and T_F is the final turbidity of the algal suspension.

The concentration factor (CF) was measured using the following equation [18]:

$$\mathrm{CF} = \frac{V \times \mathrm{OD}_I - V_S \times \mathrm{OD}_F}{(V - V_S) \times \mathrm{OD}_I} \quad (2)$$