Ultrasonics Sonochemistry 28 (2016) 376–381

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Influence of ultrasound enhancement on chlorine dioxide consumption and disinfection by-products formation for secondary effluents disinfection

Xiaoqin Zhou, Junyuan Zhao, Zifu Li *, Juanru Lan, Yajie Li, Xin Yang, Dongling Wang

School of Civil and Environmental Engineering, Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, University of Science and Technology Beijing, Beijing 100083, PR China

ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form 25 August 2015
Accepted 25 August 2015
Available online 28 August 2015

Keywords:
Wastewater disinfection
Ultrasound
Chlorine dioxide
Disinfection by-products

ABSTRACT

Chlorine dioxide (ClO_2) has been promoted as an alternative disinfectant because of its high disinfection efficiency and less formation of organic disinfection by-products (DBPs). However, particle-associated microorganisms could be protected during the disinfection process, which decreases the disinfection efficiency or increases the required dosage. Besides, the formation of inorganic disinfection by-products is a significant concern in environment health. Ultrasound (US)-combined disinfection methods are becoming increasingly attractive because they are efficient and environmentally friendly. In this study, US was introduced as an enhancement method to identify its influence on ClO_2 demand reduction and to minimize the production of potential DBPs for secondary effluents disinfection. Fecal coliform was used as an indicator, and DBPs, including trichloromethane (TCM), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), chlorite (ClO_2^-), and chlorate (ClO_3^-), were analyzed to observe the potential DBPs formation. Results show that US pretreatment could reduce half of ClO_2 dosage compared with ClO_2 disinfection alone for the same disinfection efficiency, and that an input power density of 2.64 kJ/L pretreatment with the 1.5 mg/L ClO_2 was enough to meet the discharge requirement in China (i.e., fecal coliform below 1000 CFU/L for Class 1A) for secondary effluent disinfection, and the ClO_2^- concentration in the disinfection effluent was only 1.37 mg/L at the same time. Furthermore, the different effects of US on the two processes (US as pretreatment and simultaneous US/ClO_2 disinfection) were also analyzed, including deagglomerating, cell damage, and synergistic disinfection as well as degasing/sonolysis. It was proved that the production of TCM, DCAA, and TCAA was insignificantly influenced with the introduction of US, but US pretreatment did reduce the production of ClO_2^- and ClO_3^- effectually. In general, US pretreatment could be a better option for disinfection enhancement methods combined with ClO_2 in terms of both disinfection efficiency and disinfection by-product formation.

1. Introduction

Chlorine dioxide (ClO_2) was thought to be one of the most ideal disinfectants for water disinfection because of its broad-spectrum inactivation to pathogenic bacteria, such as bacteria, viruses, algae, and animal planktons [1,2]. Over the years, major factors that influence the disinfection process, such as organic substances and suspended particles, have been investigated. Particles in water could protect bacteria from irradiating by disinfectants; thus, microorganisms entrapped in suspended solids would survive after disinfection [3–5]. To solve the problem, sonication-combined technology has been highly recommended recently, and a number of studies have reported the combination of ultrasound (US) with ultraviolet (UV), chlorine, or ozone (O_3) [6–11]. In these hybrid systems, the mechanical shear force produced by US helped break larger particles into small ones and deagglomerated flocs, exposing particle-associated bacteria to disinfectants, and therefore improving the disinfection efficiency [12]. Torben Blume demonstrated that even low US energy (30 W/L, 20 s) was sufficient to provoke a satisfactory change in the particle distribution. Thus, sonication combined disinfection was suspected to be more energy-efficient than US disinfection alone [13,14]. Previously, research was conducted on the effect of ultrasonic pretreatment with ClO_2, and a 10-min sonication with US input power densities of 75, 150, and 300 W/L were conducted, respectively, which led to a significant enhancement in *Escherichia coli* elimination [15]. However, the sonication time and US input power density applied in the

* Corresponding author.
E-mail address: zifulee@aliyun.com (Z. Li).

http://dx.doi.org/10.1016/j.ultsonch.2015.08.017
1350-4177/

aforementioned research led to high energy consumption, which was equal to the lowest specific energy consumption of 45 kJ/L, and therefore was not economical. Moreover, ultrasonic simultaneous disinfection was not conducted in this study.

Meanwhile, ClO_2 disinfection is proven to be an alternative disinfectant to chlorine because it forms a significantly smaller amount of harmful organic disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs). Thus, ClO_2 has taken the place of hypochlorite in some newly built or retrofitted wastewater treatment plants (WWTPs) in China. To the best of our knowledge, past studies have reported the formation of DBPs with ClO_2 disinfection of drinking water [16,17] and seawater [18], while only a few studies have addressed the formation of DBPs when treating wastewater with ClO_2. Moreover, wastewater is more complex than drinking water because the former contains various matter, such as natural organic elements, synthetic organic compounds, and soluble microbial products [19]. Besides, chlorine dioxide can react with both organic and inorganic compounds, thus forming inorganic by-products, such as chlorite (ClO_2^-) and chlorate (ClO_3^-) ions, which are also suspected to pose potential risks to human health [20]. Although DBPs concentrations are not currently regulated in China for wastewater discharge, they do contain a substantial amount of toxicologically important compounds and pose health risks to human beings and the environment. Thus, investigating the production of DBPs during the secondary effluent disinfection by ClO_2 is necessary. According to this requirement, clarifying the potential DBPs for ClO_2 disinfection and developing US as both enhancement of ClO_2 reduction demand and measure to minimize or eliminate the disinfection by-products might be effective for further optimum application of ClO_2.

In this study, secondary effluents from a municipal WWTP in Beijing were used. The research objectives are (1) to investigate the potential enhancement effect of US as pretreatment and simultaneous disinfection with ClO_2; (2) to study the possible effect of US in the two disinfection processes; and (3) to evaluate the impact of potential DBPs production by US, including trichloromethane (TCM), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), chlorite (ClO_2^-), and chlorate (ClO_3^-).

2. Material and methods

2.1. Wastewater samples

Water samples were collected from the outlet of a C-TECH sedimentation tank of a municipal WWTPs in Beijing, which utilized activated sludge technology (CAST), a commonly activated sludge process used as a type of sequencing batch reactor (SBR). The main parameters of the secondary effluent are shown in Table 1.

Table 1
Main parameters of water sample.

Parameters	Value
pH	6–9
Suspended solids, SS (mg/L)	<5
Color	4
Chemical oxygen demand, COD (mg/L)	30.6
Total nitrogen, TN (mg/L)	20.8
Ammonia, NH_4^+ (mg/L)	8.80
Total organic carbon, TOC (mg/L)	6.5
UV_{254} (cm^{-1})	0.116–0.229
Fecal coliform (CFU/L)	3×10^4–5.15×10^6

2.2. Experimental procedures

2.2.1. Ultrasound and ClO_2

Ultrasound was used as pretreatment or simultaneous disinfection in combination with ClO_2. Low-frequency US was recommended to be effective in wastewater treatment [21]. Thus, the present study employed a low US frequency (33 kHz) with adjustable power from 0 W to 200 W (Hainertec Ultrasonic Technology Co. Ltd., Suzhou, Jiangsu Province, China). US was employed at a constant specific energy consumption of 2.64 kJ/L (66 W/L with 40 s sonication time) with various ClO_2 dosages in this study for the purpose of evaluating the possible enhancement effect of US on ClO_2 disinfection, and the sonication parameter was selected from our previous researches because it performed good enhancement effect on UV disinfection [22]. The real US input power was measured by using a power meter (LCDG-ZJ1-62010) for each unit. The disinfection processes with or without sonication were tested separately.

ClO_2 liquid solution was produced by slowly adding diluted HCl (9%) to sodium chlorite ($NClO_2$) in a small batch reactor in which ClO_2 was produced in a gaseous form and then absorbed in distilled water. ClO_2 stock solution was prepared daily before the experiment and constantly sealed in a dark glass bottle at 4 °C to prevent decomposition to ClO_2^- and ClO_3^-. All reactors used in the experiments were made of dark-colored amber glass with a total volume of 2.5 L.

2.2.2. Disinfection process

2.2.2.1. ClO_2 disinfection. At the beginning of the experiment, eight concentrations of liquid ClO_2 (0.5, 1, 1.5, 2, 3, 4, 5, and 6 mg/L) were tested to identify the most appropriate dosage for the experimental scope. Thus, six liquid ClO_2 dosages (0.5, 1, 1.5, 2, 2.5, and 3 mg/L) were used for further investigation based on the experimental results.

2.2.2.2. US pretreatment disinfection (US + ClO_2). For US pretreatment, 2 L of water sample was added into the reactor, and the water sample was then irradiated with US for 40 s. Once US sonication was completed, an objective amount of liquid ClO_2 was added to the sonicated water and stirred gently for another 3 min for good distribution of disinfectants. The water samples were then kept silent.

2.2.2.3. Simultaneous US/ClO_2 disinfection (US/ClO_2). For simultaneous US/ClO_2 disinfection, 2 L of water sample was added into the reactor, and sonication was turned on for 40 s once an objective amount of liquid ClO_2 was added to the water samples. Gentle stirring was maintained for 3 min for good distribution of disinfectants. Water samples were then kept undisturbed for the rest of the 30 min reaction time.

All disinfection processes with different liquid ClO_2 dosages (0.5, 1, 1.5, 2, 2.5, and 3 mg/L) were carried out respectively, and a series of experiments using ClO_2 disinfection alone were carried out as control group. When each disinfection scenario was finished, a water sample was taken to test for residual ClO_2 immediately. Sodium thiosulfate ($Na_2S_2O_3$, 0.1 M) was then substantially added to the water to prevent further inactivation by residual ClO_2, and then another water sample was withdrawn from the reactor for bacteriological test. All disinfection process tests were run in duplicate, one with high initial microorganism and another with low initial microorganism.

Further experiments were performed for DBPs analysis (one US and ClO_2-combined disinfection process and three ClO_2-alone disinfection processes). The applied ClO_2 doses were related to the aforementioned disinfection conditions and design standard to evaluate the potential formation of TCM, DCAA, TCAA, ClO_2^-, and ClO_3^-. Water samples were withdrawn after 30 min disinfection time, and analysis of ClO_2^- and ClO_3^- were conducted before the formation of potential DBPs tests.