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Inactivation of Chironomid larvae with chlorine dioxide

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Abstract

In this paper, comparative experiments on the inactivation of Chironomid larvae by chlorine dioxide and chlorine were conducted. In addition, batch experiments were performed in order to analyze the influence of pH value, organic precursor concentration and temperature on the inactivation efficiency of Chironomid larvae with chlorine dioxide. Based on it, removal effect of different pre-oxidation followed by coagulation process on Chironomid larvae in raw water was evaluated. The results showed that chlorine dioxide possessed better inactivation performance than chlorine, and complete inactivation of Chironomid larvae was obtained at *CT* value of 37.5 mg min/L (dose of 1.5 mg/L and exposure time of 25 min). The pH in the range of 6–8 did not affect the inactivation efficiency of chlorine dioxide, whereas pH 10 resulted in around 10% decrease in inactivation rate. Meanwhile, the organic precursor had negative effects on inactivation, indicated by the decreased inactivation rate from 100% at TOC concentration of 0 mg/L to 62.2% at 8 mg/L when the *CT* value was 45 mg min/L. With regard to the temperature, the inactivation efficiency of Chironomid larvae was significantly improved with the temperature increasing within the range investigated of 10–25 °C. The inactivation rate was reduced by 68.9% when temperature reduced from 25 °C to 10 °C. The coagulation jar test showed that Chironomid larvae in the raw water could be completely removed by chlorine dioxide pre-oxidation in combination with the coagulation process at *CT* value of 24.8 mg min/L.
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1. Introduction

Chironomid, from the dipteran family Chironomidae, is widely distributed in the northern hemisphere at temperate latitudes. Chironomid have four life stages: egg, larva, pupa and adult. The larval stage consists of four instars (juvenile stages), and the larvae shed their exoskeleton and increase in size to the next instar. The first instar larvae are plankton, while older instars (second, third and fourth larval stages) in most species migrate to the sediment and build tubes constructed from detritus, algae and sediment particles [1]. Chironomid larvae can be found both in lentic and lotic environments, usually in organically enriched waters. Chironomid larval densities rapidly increased in water source such as reservoir or fresh lake due to eutrophication [2], which induced first instar larvae in source water to enter drinking water treatment system. There are many serious accidents of Chironomid larvae pollution in the water treatment system in the Britain, USA and China [3–5]. Although there are no indications that these organisms pose a threat to public health, their presence is still not appreciated because most people associate the organisms with low hygiene [6].

The first instar larvae can easily penetrate sand filter and then goes into waterworks reservoir and municipal service pipe due to its motility [6,7]. Several researchers have investigated that Chironomid larvae is difficult to inactivate using free chlorine at concentrations commonly used by drinking water utilities [7]. As a powerful substitute or a supplemental disinfectant for chlorination, chlorine dioxide can eliminate bad odor and oxidize ferrous, manganous ions in underground water. Moreover, chlorine dioxide has been reported to be effective in the inactivation of pathogenic organisms including *Cryptosporidium parvum* oocysts [8,9]. Further, the oxidation of natural organic matter (NOM) with chlorine dioxide does not form halogenated disinfection by-products (DBPs) such as dissolved organic halides, trihalomethanes, and haloacetic acids [10,11].

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Previous studies on chlorine dioxide focused on the disinfection efficiency for harmful microorganism [8,9,12–16]. However, information regarding chlorine dioxide inactivation Chironomid larvae is not found. Experiments were conducted at bench-scale to evaluate the inactivation of Chironomid larvae by chlorine dioxide and compared with that of liquid chlorine. Two specific objectives were discussed here as follows: one was to determine the usefulness of chlorine dioxide pre-oxidation followed by coagulation process to remove Chironomid larvae in raw water and the other was to examine influence of organic precursor concentration, temperature and pH value on inactivation of Chironomid larvae with chlorine dioxide.

2. Materials and methods

2.1. The preparation of chlorine and chlorine dioxide

The stock solution of chlorine was prepared by diluting commercial solution of sodium hypochlorite (NaOCl, 9% active chlorine). Chlorine dioxide stock solution with purity of 99% was made using the method described by Ruffell et al. [8]. The stock chlorine dioxide solution was usually diluted to obtain a concentration of about 1 g/L in order to facilitate the addition of low concentration to the water samples. Diluted chlorine dioxide stock solutions were stored in the head-free 50 mL amber vials at 4 °C in the dark. The concentration was measured with the *N*,*N*-diethyl-*p*-phenylenediamine (DPD) methods [17].

2.2. Buffer solutions

Experiments were performed in 0.01 M buffer solutions prepared by adding reagent grade phosphates, borate or carbonates to DDI water. Phosphates were used for experiments performed at pH 6 and 8, and borate or carbonates were selected for buffering solutions at pH 10.

2.3. Culturing of Chironomid larvae

Egg masses of *Chironomus riparius* were initially obtained from a population collected in the Shenzhen reservoir (Guangdong, China) and maintained in the laboratory for several generations. Chironomid larvae were cultured in aerated 25 L glass aquaria filled with aerated tap water. A 5 cm thick artificial sediment layer consisting of washed siliceous sand and cellulose was introduced at the bottom of the aquarium. Adult midges were confined using wooden cages covered with 1 mm mesh size metal net. Aquaria were placed under constant temperature (20 °C) and photoperiod (14 h light/10 h dark). In order to obtain homogenous samples (size and age), egg masses were transferred from rearing aquaria into 2 L glass experimental tanks filled with aerated tap water. Egg masses were left 24 h in these tanks and non-hatched eggs were then removed. All bioassays were conducted using first instar larvae.

Table 1
Water quality characteristics of raw water during the experiment

Water quality parameter	Value
Temperature (°C)	23.2–25.7
TOC (mg/L)	2.13–2.51
UV_{254} (cm^{-1})	0.387–0.419
Turbidity (NTU)	4.91–6.2
pH	6.7–7.1

2.4. Organic precursors

Humic acid was used as the source of organic carbons in the artificial water samples to mimic the organic precursors found in aquatic environments. One gram of humic acid was dissolved in distilled water to produce a liter solution. The pH value was adjusted to 12.0 by adding 6N NaOH. It was then filtered using 0.45 μm filter paper (MFS, membrane filters cellulose acetate) and stored in brown glass bottles. The concentration was measured for total organic carbon (TOC) just before application to ensure the accuracy.

2.5. Experimental procedures

In order to investigate the effect of several important factors, such as pH value, organic precursor concentration and temperature on the inactivation of chlorine dioxide, the experiment was firstly undertaken in distilled water solution. Furthermore, the inactivation efficiency of chlorine dioxide was studied in the actual raw water taken from the Shenzhen Water Treatment Plant (WTP). The characteristics of the raw water are shown in Table 1.

One liter jar was used as the test reactor. The first larval stage organisms used in each experiment were obtained by transferring egg ropes from the culture to glass vessels containing culture water. The time required to hatch the first instar larvae was about 3 days at 20 °C. The hatched animals were then transferred randomly to each test jar with a glass pipette until each jar contained 15 larvae. Larvae were regarded as dead if unable to make a sustained and coordinated response (at least two consecutive sinuate movements involving 25% or more of total body length) when grasped with a pair of fine forceps. Mortality data were pooled and corrected against the mean control mortality using Abbott's formula. For each treatment group, four replicates were undertaken and no oxidant was added to the control jar. The differences in mortality for each treatment were statistically compared using Fisher's least significant difference (LSD) multiple comparison test.

The coagulation jar test was carried out to evaluate removal efficiency of different pre-oxidation followed by coagulation process on Chironomid larvae in raw water. A standard jar test apparatus was used in the coagulation tests. The oxidants, chlorine and chlorine dioxide, were added into water together with coagulant, 2 mg/L of $AlCl_3$. After 1 min of rapid mix at 200 rpm, 10 min of slow mixing at 50 rpm was provided, followed by at 20 min of settling. The removal effect on first instar larvae was studied by observing the supernatant fluid.

Table 2
CT values generated by the different oxidant doses (*C*) and exposure 30 min (*T*) combinations

Chlorine		Chlorine dioxide	
Dose (mg/L)	*CT* (mg min/L)	Dose (mg/L)	*CT* (mg min/L)
0.5	15	2	30
1.0	30	4	120
1.5	45	6	180
2.0	60	8	240

3. Results and discussion

3.1. The inactivation effect of chlorine dioxide and chlorine in distilled water

Various dosages of oxidants were added into a given volume of distilled water solution and exposure time was 30 min. Chlorine dioxide dosages ranged from 0 to 1.5 mg/L and chlorine from 0 to 8.0 mg/L. The *CT* values (product of disinfectant concentration and exposure time) generated by the different oxidant dosages (*C*) and exposure 30 min (*T*) combinations are presented in Table 2. Experimental results for the inactivation of Chironomid larvae with chlorine dioxide and chlorine at 25 °C and pH 7 are presented in Fig. 1. The data show that there was a significant difference in the inactivation rate between chlorine dioxide and chlorine ($P < 0.05$). As a whole, the inactivation efficiency of chlorine dioxide was obviously better than that of chlorine. When 100% inactivation of Chironomid larvae was obtained, the required chlorine dioxide *CT* values were 45 mg min/L, while 240 mg min/L was required for chlorine due to high resistance of Chironomid larvae to free chlorine.

3.2. The effects of pH value on the inactivation of chlorine dioxide

Bench scale experiments were conducted to evaluate the impact of pH, in the range of 6–10, on the chlorine dioxide inactivation. The dosage of chlorine dioxide was 1.5 mg/L according

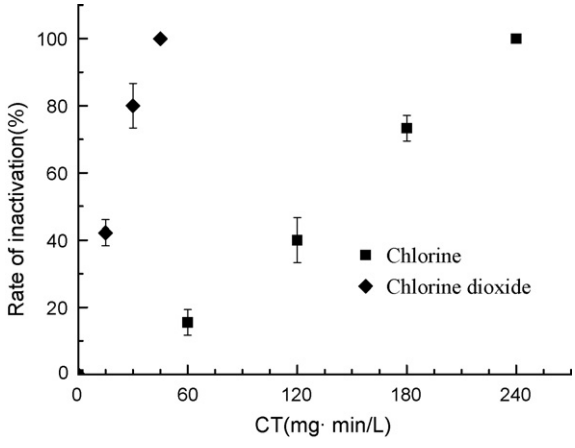

Fig. 1. Inactivation effect of chlorine and chlorine dioxide on Chironomid larvae at pH 7.0 and 25 °C.

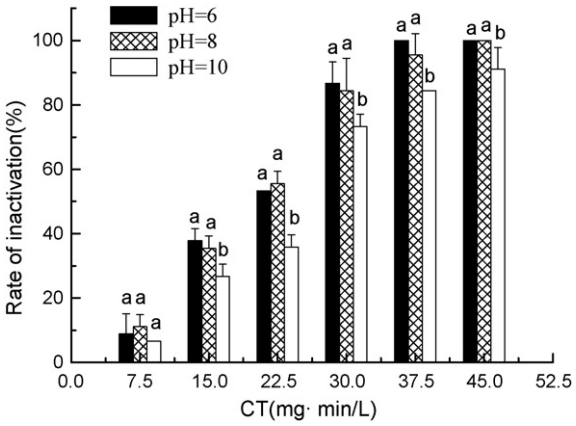

Fig. 2. Effect of pH value on inactivation of Chironomid larvae with chlorine dioxide at 25 °C. Vertical bars indicate standard errors of the mean ($n = 4$). Different letters on the bars indicate that the mean are significantly different among the treatments ($P < 0.05$) in least significant difference multiple comparison tests.

to the required chlorine dioxide *CT* values at neutral condition while 100% of inactivation was attained (see Fig. 1 and Table 2). The inactivation effects at 25 °C were observed and the results are shown in Fig. 2. As depicted in Fig. 2, all treatments provided high and statistically similar levels of inactivation rate at *CT* value of 7.5 mg min/L ($P > 0.05$). However, for other *CT* values, inactivation rate at pH 10 was significantly lower than that at pH 6 and 8 ($P < 0.05$). Generally, the pH in the range of 6–8 did not affect the inactivation efficiency of chlorine dioxide, whereas pH 10 resulted in around 10% decrease in inactivation rate. Liyanage et al. [18] examined the chlorine dioxide inactivation of *C. parvum* oocysts and presented evidence that chlorine dioxide, and not its disproportionation products such as chlorite and chlorate, was the active disinfecting species. Further, In contrast to aqueous chlorine ($HOCl/OCl^-$), the chemical structure of aqueous chlorine dioxide does not change with pH [19]. However, the literature contains conflicting reports on the effects of pH on chlorine dioxide efficiency. Huang et al. [13,14] reported that the six kinds of virus and *Staphylococcus aureus* were more rapidly inactivated by chlorine dioxide at pH 3.0, 5.0, 7.0 than at pH 9.0. The authors speculated that the decreased efficiency of chlorine dioxide at pH 9.0 might be due to the disproportionate reaction of chlorine dioxide occurring under the basic condition (Eq. (1)). Similarly, lower inactivation rate of Chironomid larvae was presented under higher pH value in this study:

$$2ClO_2 + 2OH^- = ClO_2^- + ClO_3^- + H_2O \quad (1)$$

3.3. The effects of organic matters on the inactivation of chlorine dioxide

Various experiments were performed to investigate the inactivation effect of chlorine dioxide at different organic precursor concentration. The dosage of chlorine dioxide was also 1.5 mg/L. It was found from Fig. 3 that the organic precursor significantly affected inactivation of Chironomid larvae with chlorine dioxide ($P < 0.05$). At *CT* value of 45 mg min/L, the inactivation rate significantly reduced from 100% at TOC concentration of 0 mg/L to 62.2% at 8 mg/L ($P < 0.05$). The

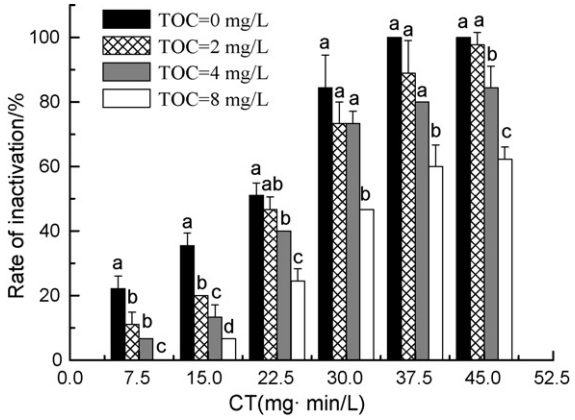

Fig. 3. Effect of organic matters on inactivation of Chironomid larvae with chlorine dioxide at 25 °C and pH 7.0. Vertical bars indicate standard errors of the mean ($n = 4$). Different letters on the bars indicate that the mean are significantly different among the treatments ($P < 0.05$) in least significant difference multiple comparison tests.

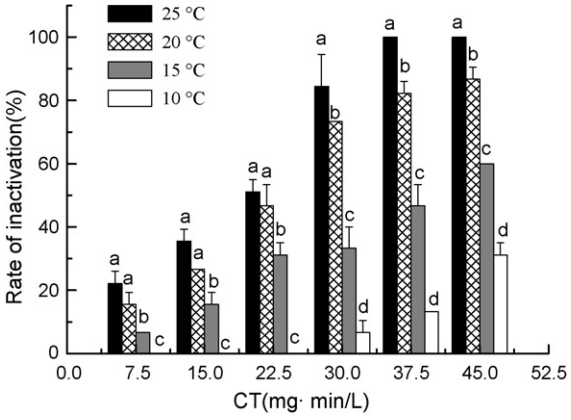

Fig. 4. Effect of temperature on inactivation of Chironomid larvae with chlorine dioxide at pH 7.0. Vertical bars indicate standard errors of the mean ($n = 4$). Different letters on the bars indicate that the mean are significantly different among the treatments ($P < 0.05$) in least significant difference multiple comparison tests.

suggested reason was that when the concentration of organic precursor was raised, it would react with more functional groups. This decreased the possibility of chlorine dioxide destroying Chironomid larvae and dropped the inactivation efficiency.

3.4. The effects of temperature on the inactivation of chlorine dioxide

At the same dosage of chlorine dioxide as mentioned above, the inactivation of Chironomid larvae over the temperature range of 10–25 °C was also conducted. Experimental results obtained for tests performed to assess the role of temperature in the inactivation of Chironomid larvae with chlorine dioxide are shown in Fig. 4. As depicted in the figure, the inactivation rate of Chironomid larvae was significantly increased as the temperature increased ($P < 0.05$). At *CT* value of 45 mg min/L, the inactivation rate of Chironomid larvae at 25 °C was approximately three times higher than that at 10 °C, and their rates were 100% and 31.1%, respectively. Ruffell et al. [8] reported that the rate of inactivation on *C. parvum* oocysts decreased with decreasing temperature. *CT* values requirements for *C. parvum* oocysts inactivation were found to increase by an average factor of approximately 3.4 for every 10 °C decrease in temperature.

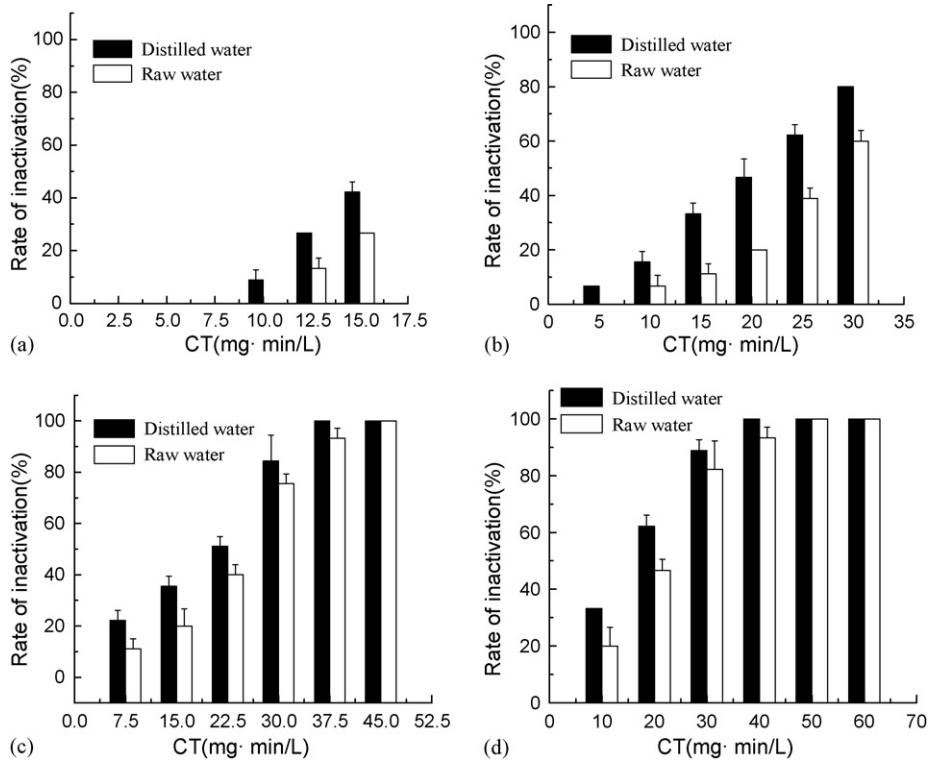

Fig. 5. Inactivation effect on Chironomid larvae at 25 °C with different doses of chlorine dioxide: (a) 0.5 mg/L, (b) 1.0 mg/L, (c) 1.5 mg/L, and (d) 2.0 mg/L.

Similarly, Corona-Vasquez et al. [9] suggested that chlorine dioxide disinfection of *C. parvum* oocysts improved as the temperature increased, and demonstrated that the increased efficiency of chlorine dioxide at a higher temperature may be due to the activation energy of chlorine dioxide for killing *C. parvum* oocysts became lower than that at a lower temperature. Commenting on these results, inactivation effects of chlorine dioxide on Chironomid larvae were much lower at the lower water temperature since inactivation kinetics is slower in cold water.

3.5. The inactivation effects of chlorine dioxide in actual raw water

To better understand the behavior of inactivation process, actual raw water taken from the Shenzhen WTP was also used as the test samples in addition to the distilled water. The comparative experiments were carried out at various dosages of chlorine dioxide, and the results are shown in Fig. 5. Compared with that in distilled water experiment, the chlorine dioxide inactivation efficiency of Chironomid larvae in raw water assumed in a different manner (Fig. 5): at the lower dosage (Fig. 5a and b), the inactivation rate of Chironomid larvae was significantly lower than that occurred in distilled water experiment ($P < 0.05$), but the gap in inactivation efficiency was gradually lessened as the dose of chlorine dioxide was increased. Similar to distilled water experiment, complete inactivation of Chironomid larvae was also attained at *CT* value 45 mg min/L (Fig. 5c).

In contrast to distilled water, many extraneous oxidant-demand substances exist in raw water including organic compounds, algae, bacteria, etc. Since most of them can be oxidized more easily than Chironomid larvae, the reaction between chlorine dioxide and organic compounds always proceeds prior to that with Chironomid larvae. The superiority of extraneous substances in competition for oxidant results in greatly weakening the inactivation of Chironomid larvae especially under lower dose conditions (0.5 and 1.0 mg/L). But as the dose is increased, there will be much more chlorine dioxide residual after its reaction with the extraneous oxidant-demand substances, where the remaining oxidant was preferably used for killing Chironomid larvae rather than for further degrading hard-to-oxidize product of oxidizable substances. Thus, the inactivation of Chironomid larvae in raw water is greatly enhanced at higher level of dose, and minor difference in inactivation efficiency between both test samples is presented.

In theory, if the disinfectant concentration is doubled but the exposure time reduced by half, the same inactivation will be obtained. However, the data in Fig. 5 does not demonstrate this relationship. For example, for a chlorine dioxide dose of 2.0 mg/L and *CT* value of 20 mg min/L in the raw water, 46.7% inactivation of larvae was achieved (Fig. 5d). However, for a chlorine dioxide dose of 1.0 mg/L and *CT* value of 20 mg min/L in the raw water, only 20% inactivation was achieved (Fig. 5b). Therefore, the larvae were more sensitive to being exposed to high concentrations of chlorine dioxide for short time than to low concentrations of chlorine dioxide for longer time. This result can be explained from the point of the body structure of Chironomid larvae. Contrasted to common bacteria or virus, Chironomid larvae have a special surface structure consisting of seven layers cell tissue, such as bottom membrane, epithelium, calcific layer, etc. The body surface provides Chironomid larvae stronger protection against oxidation. Chironomid larvae cannot be effectively inactivated unless the oxidant destroys its surface structure by oxidation or directly penetrates through it into the body as to oxidize inner protein to lose the enzyme activity. So penetration of chlorine dioxide on surface structure of Chironomid larvae is key to thoroughly inactivate Chironomid larvae. At lower dose conditions, chlorine dioxide cannot effectively penetrate surface structure of Chironomid larvae even if exposure time was longer.

3.6. The removal effect of pre-oxidation followed by coagulation process

To evaluate removal efficiency of different pre-oxidation followed by coagulation process on Chironomid larva in raw water, the coagulation jar test was carried out using different dosages of oxidants for pre-oxidation. Chlorine dioxide dosage ranged from 0 to 0.9 mg/L and chlorine dosage ranged from 0 to 6.0 mg/L during the study. As shown in Fig. 6, the removal rate of Chironomid larvae was 75.5% by coagulation process with no pre-oxidation dosing, which illustrated that Chironomid larvae could be partially removed from water by single coagulation process. As motility of Chironomid larvae was found to be different, some Chironomid larvae, which finished planktonic stage, may be more easily deposit together with the floc formed in coagulation process.

The removal efficiencies of Chironomid larvae were strengthened gradually with the increase of the *CT* value regardless the oxidant type. However, chlorine dioxide proved more efficiency for Chironomid larvae removal than chlorine. When 100% removal rate of Chironomid larvae was achieved, the *CT* value of chlorine dioxide was only 24.8 mg min/L, whereas 186 mg min/L was required for chlorine. Thus, the removal of 24.5% was due to inactivation of chlorine dioxide. Based on the results mentioned above, Chironomid larvae with stronger vitality could not be completely removed at the lower *CT* values (<24.8 mg min/L), so that the coagulation process still could not

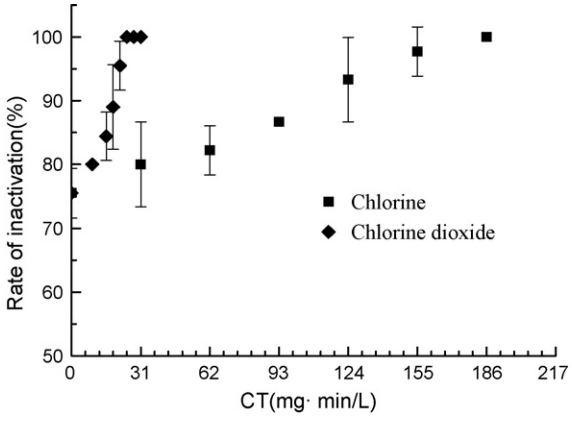

Fig. 6. Removal effect of pre-oxidation followed by coagulation process on the first instar larvae under the conditions of 25 °C, pH 7.1 and TOC = 2.47 mg/L.

capture this part of Chironomid larvae. Therefore, it was important to inactivate or weaken Chironomid larvae with adequate available chlorine dioxide in order to remove it completely from water treatment system. In viewpoint of the security of drinking water, it is necessary to combine chlorine dioxide inactivation with coagulation process for removing Chironomid larvae from raw water, which on the other hand also reduce the dosage of the oxidant.

4. Conclusion

The extensive studies were conducted to evaluate the inactivation efficiency on Chironomid larvae with chlorine dioxide in bench-scale experiments. The results of the study demonstrated that chlorine dioxide had better inactivation efficiency than chlorine from the point of *CT* value.

The chlorine dioxide inactivation efficiency of Chironomid larvae was not affected at pH 6–8, and decreased at pH 10. The higher the organic matters concentration was, the lower inactivation rate was achieved. Inactivation efficiency improved with the increase in temperature from 10 to 25 °C.

To assure the security of drinking water, as well as to reduce the dosage of oxidant, it is necessary to combine chlorine dioxide inactivation and coagulation process when removing Chironomid larvae from raw water.

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