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Removal of cyclops in pre-oxidizing cooperation water treatment process*

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Abstract: Zooplankton cyclops propagates profusely in waterbody, cannot be effectively inactivated by conventional disinfection process, and becomes a troublesome drinking water treatment problem. In this work, the qualitative and quantitative experimental studies were carried out on inactivation of zooplankton cyclops using oxidants, such as chlorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3), hydrogen peroxide (H_2O_2), ozone/hydrogen peroxide (O_3/H_2O_2), chloramines (Cl_2-NH_3) and potassium permanganate ($KMnO_4$). The influences of various factors include different oxidant dosages, organic substance contents and pH values. The results showed that currently available oxidants used all might inactivate cyclops in some extent. According to the experimental results, chlorine dioxide, ozone, ozone/hydrogen peroxide and chloramines can be selected as effective oxidants for inactivating cyclops because of their strong inactivation abilities. Then the synergic removal effects on cyclops with ozone, ozone/hydrogen peroxide pre-oxidation followed by conventional water treatment processes were investigated. The results showed that ozone and ozone/hydrogen peroxide pre-oxidation can inactivate cyclops effectively, which then can be removed thoroughly by conventional water treatment processes. Cyclops cannot appear in water after filtration with 1.65 mg/L of ozone and 6 mg/L of hydrogen peroxide, with the inactivation rate being 62% before conventional water treatment processes. Cyclops cannot appear in water after filtration with 1.8 mg/L of ozone, with the inactivation rate being 50% before conventional water treatment processes. For different oxidants, when removal rate was the best, the inactivation rate was not the same. These results may provide reference and model for actual waterworks.

Key words: Cyclops of zooplankton, Water treatment, Inactivation, O_3, O_3/H_2O_2 pre-oxidation
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INTRODUCTION

Eutrophication caused by water pollution results in excessive propagation of zooplankton cyclops in waterbodies, which are hard to be removed by the conventional disinfection processes like chlorination due to its strong resistance to oxidation. In addition, the motility of cyclops enables it to easily penetrate from sand filter into the clear water tank in waterworks, even municipal distribution network. It is a nuisance to water consumers and may become disease transmission medium as the host of pathogenic parasite, like schistosome or eelworm, to threaten human health (Cui *et al*., 2005; Lin *et al*., 2006; Liu *et al*., 2004a; 2004b).

The occurrence of cyclops which penetrates the filter tank in drinking water showed that it cannot be thoroughly removed from water by the conventional water treatment process of flocculation, sedimentation and filtration (Liu *et al*., 2004a; 2004b; 2005; 2006). Therefore the removal of cyclops with conventional water treatment process, and then, the fea-

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sibility to remove it by chemical pre-oxidation in cooperation with the conventional process are put forward in this paper. The following steps are considered: thorough inactivation of cyclops utilizing oxidants, inhibiting its activity by pre-oxidation and then removing it thoroughly by subsequent clarification process (Kanio and Kimata, 2000; Reckhow *et al.*, 1990; Fiessinger, 1991).

To inactivate or weaken cyclops with oxidants was believed to be the key to removing cyclops completely from water treatment system (Ruffell *et al.*, 2000; Gunter and Pinkernell, 2000; Driedger *et al.*, 2001). So its inactivation with currently available oxidants such as chlorine, chlorine dioxide, ozone, hydrogen peroxide, ozone/hydrogen peroxide, chloramines and potassium permanganate was researched experimentally. By comparison, chlorine dioxide, ozone, ozone/hydrogen peroxide and chloramines pre-oxidation were practicable methods to inactivate cyclops in water. Then the synergic removal effects on cyclops with ozone or ozone/hydrogen peroxide pre-oxidation followed by conventional water treatment processes were investigated. The conclusions gained could be used for reference for waterworks.

EXPERIMENTAL MATERIALS AND METHODS

The experiments were carried out in two phases: First, the cyclops inactivation with seven oxidants was studied in the laboratory; then, further study of its removal by oxidants pre-oxidation in cooperation with clarification process was conducted.

We first investigated distilled water solution. Cyclops was sampled from a reservoir in Harbin, and cultured in laboratory. In the experiment, the number of cyclops was controlled to 10 ind./L, the pH value of water sample was regulated with diluted acetic acid solution or sodium hydroxide solution with the organic substance in water sample being composed of humic acid, which was added according to the experimental demand. All analytical methods were conducted according to the Manual of Standard Examination Methods.

Chlorine dioxide, ozone, ozone/hydrogen peroxide and chloramines were selected as preferable oxidants for comparison. Then the inactivation effects on cyclops by conventional process alone and in cooperation with oxidants pre-oxidation and conventional process were further experimented on.

RESULTS AND DISCUSSION

Comparison of inactivation effects of different oxidants on cyclops

The experiment was conducted in a given volume of distilled water solution free of other extraneous oxidant-demand substances but cyclops. The inactivation of cyclops with seven oxidants was investigated under various working conditions of different oxidant dosage, organic substance content and pH value. In the experiment, the number of cyclops was controlled to 10 ind./L, and the oxidants dose ranged from 0.5 mg/L to 2.0 mg/L (the dose of chlorine for chloramines, and the dose of ozone for ozone/hydrogen peroxide).

1. Influence of dose of oxidants on the inactivation of cyclops

A series of experiments revealed that the cyclops inactivation with seven oxidants was strengthened gradually as the dose was increased. At pH value of 7.0, after reaction at 20 °C for 30 min, the inactivation rates with oxidant dose of 1.0 mg/L were observed and the results are shown in Table 1, showing that 100% of cyclops may be inactivated by lower dose of oxidants in the case of chlorine, ozone, ozone/hydrogen peroxide and chlorine dioxide. The inactivation capacities of these seven methods may be ranked as follows: $O_3/H_2O_2 \approx ClO_2 > O_3 > Cl_2 > Cl_2\text{-}NH_3 > KMnO_4 > H_2O_2$.

Table 1 Comparison analysis of inactivation effects of seven oxidants on cyclops

Oxidants	Inactivation effect on cyclops (%)*	Dose of oxidants (mg/L)**
Cl_2	70	2.0
ClO_2	100	1.0
O_3	75	1.8
H_2O_2	0	600 (reacting 6 h)
O_3/H_2O_2	100	O_3 1.0, H_2O_2 4
Cl_2-NH_3	30	Cl_2 available 3.0 (90% only)
$KMnO_4$	10	2.0 (75% only)

*with dose of 1 mg/L; **with 100% of inactivation effect

Single hydrogen peroxide had only little potential to inactivate cyclops, so that it was not studied in the following experiment.

2. Influence of pH value on the inactivation of cyclops

The inactivation effect of potassium permanganate on cyclops was affected by pH value to a certain extent; the efficiency of it was the lowest compared with other oxidants. With continually increasing pH, its inactivation rate trended to drop. As for ozone/hydrogen peroxide, there was no large change of the inactivation effect at certain rang of pH value. The effects of chlorine dioxide and ozone on cyclops inactivation were affected by pH value to the same extent; 100% of cyclops may be inactivated by them after reaction at 20 °C for 30 min at different pH values. The effect of chloramines on cyclops inactivation was affected by pH value sensitively, because HOCl plays the main role in inactivating cyclops using chloramines, just as chlorine. At the pH value ranged from 4.5 to 9.0, the adaptability of these methods for pH value may be ranked as follows: $ClO_2 \approx O_3/H_2O_2 \approx O_3 > Cl_2 > Cl_2\text{-}NH_3 > KMnO_4$.

3. Influence of organic content on the inactivation of cyclops

The inactivation efficiency of each oxidant declined with increasing organic content, because the reductive organic substances in water cause the extra depletion of oxidants. Especially, the influence of organic content on the inactivation effects of ozone was the most visible, with the inactivation rate decreasing from 100% to 40% in the range of organic content from 0 to 8.8 mg/L with the ozone dose of 1.8 mg/L and reacting for 30 min. The influence of organic content on the inactivation effects of ozone/hydrogen peroxide is also visible. While the more ozone added, the less the influence of organics on the inactivation is. With the dose of 3 mg/L of ozone and 10 mg/L of hydrogen peroxide, the influence of organic content on the inactivation effects was quite invisible. The inactivation of cyclops with potassium permanganate was also greatly influenced by the changes of organic content. For each 2.5 mg/L of organic content added, inactivation of cyclops would be decreased by 10%~20% for potassium permanganate. But the inactivation efficiency of chlorine dioxide was less influenced which still kept at about 80% under the organic content of 10 mg/L condition. For each 2.5 mg/L of organic content added, inactivation of cyclops would be decreased by 10%~20% for chloramines. When the proportion of chlorine and ammonia was changed from 1:1 to 3:1, with 2.0~3.0 mg/L of chlorine available, the inactivation of cyclops all could be more than 50%.

According to the result above, the adaptability of these methods for organic content may be ranked as follows: $ClO_2 > O_3/H_2O_2 > Cl_2\text{-}NH_3 > Cl_2 > KMnO_4 > O_3$.

Full-scale study of removing cyclops by pre-oxidation

1. Results of removal of cyclops by conventional water treatment processes

In the experiment, three parallel samples which were assembled in the lab were used for each group of test, with the water quality indexes being as follows: average water temperature: 24 °C; turbidity: 16 NTU; COD_{Mn}: 3.86 mg/L; pH: 7.1 and cyclops were added according to the experiment demand. 35 mg/L of $AlCl_3$ were added into each sample as coagulant. After 30 min's reacting in six couplet timing stirrer, the number of cyclops was investigated, and then the supernatant water after jar test was filtrated. The filtration velocity was 9 m/h, the time was 8 h, and the results are shown in Table 2, showing that the filtration process had much more visible removal effect than coagulation and sedimentation. Its removal rate was 50% which was quite close to 56.7% for combination processes, so in conventional water treatment processes, filtration plays the main role in removing cyclops.

Table 2 Removal results of cyclops by conventional water treatment processes

Water treatment processes		Original number of cyclops (ind./L)	Rudimental number of cyclops (ind./L)	Removal rate of cyclops (%)	Average removal rate of cyclops (%)
Coagulation and sedimentation	Group 1	10	8	20	13.3
	Group 2	10	9	10	
	Group 3	10	9	10	
Filtration	Group 1	8	4	50	50.0
	Group 2	9	4	55.6	
	Group 3	9	5	44.4	
Combination	Group 1	10	4	60	56.7
	Group 2	10	4	60	
	Group 3	10	5	50	

2. Removal effect on cyclops by ozone and ozone/hydrogen peroxide pre-oxidation cooperating with conventional processes

In the experiment of ozone/hydrogen peroxide pre-oxidation cooperating with conventional processes, the samples were also assembled in the lab and the water quality was the same as before. Two oxidants (ozone and hydrogen peroxide) were added sequentially, ozone first. In the experiment, the dose of hydrogen peroxide was 10 mg/L, while ozone dose was changed. Coagulation, sedimentation and filtration experiments were conducted after 30 min's pre-oxidation. The experimental method was the same as before with the results being shown in Fig.1a. As can be seen, the removal rate of cyclops is quite similar when the dose of ozone is more than 1.4 mg/L. The removal rate reaches 100% with 1.65 mg/L of ozone.

Then ozone dose was adjusted to 1.65 mg/L with the hydrogen peroxide dose ranging from 0 to 10 mg/L during the full-scale study. The results are shown in Fig.1b. As can be seen from Fig.1b, the influence of hydrogen peroxide dose on the removal of cyclops is evident in certain range. Considering economical factor, it is better to choose the lowest amount in the feasible dose range. So 6 mg/L of hydrogen peroxide is suggested, correspondingly, the inactivation rate is 62%. Although the cyclops was not inactivated absolutely under that condition, the activity of some cyclops was greatly weakened by inactivation of oxidants, and may deposit together with the flocs formed in the flocculation process. So they are effectively removed supernatant upper water by the clarification process.

In experiment of ozone peroxide pre-oxidation cooperating with conventional processes (Fig.1c), the removal rate can be 100% with 1.8 mg/L of ozone, correspondingly, the inactivation rate was only 50%.

The two methods of ozone and ozone/hydrogen peroxide pre-oxidation cooperating with conventional treatment processes, both had perfect effect on removal of cyclops, and both could remove cyclops thoroughly with relatively low dose of oxidant. The inactivation capacities of ozone were lower than that of ozone/hydrogen peroxide, but ozone could weaken the activity of cyclops, so that they were effectively removed from supernatant water by clarification process. In the process of ozone/hydrogen peroxide pre-oxidation, ozone played the more important role, while hydrogen peroxide played the role of catalyst during the whole reaction including inactivation and cooperation. So the inactivation rate was not in direct ratio to removal rate. For different oxidants, when removal rate was the best, the inactivation rate was not the same. These results could be used for reference, and different waterworks could choose the feasible water treatment processes according to the actual condition and water quality demand. Considering the practical differences in application, ozone pre-oxidation and ozone/hydrogen peroxide pre-oxidation were both put forward as feasible methods for removing cyclops, and can be selected in practice according to the practicality.

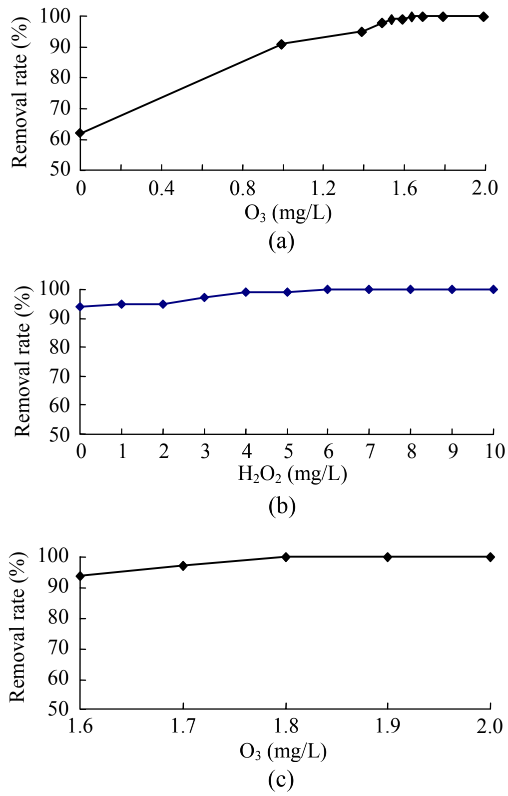

Fig.1 Removal effects on cyclops of O_3/H_2O_2 peroxide pre-oxidation cooperating with conventional water treatment processes (a) at various O_3 doses and (b) at various H_2O_2 doses, and (c) on cyclops of ozone peroxide pre-oxidation cooperating with conventional processes

CONCLUSION

Current available oxidants used might all inactivate cyclops in some extent. According to inactivation effect and external conditions influence, chlorine dioxide, ozone, ozone/hydrogen peroxide and chloramines all have relatively high inactivation effect, and can be selected as effective oxidant for inactivating cyclops.

The combination of pre-oxidation and conventional water treatment processes had perfect removal effect and cyclops can be removed thoroughly at lower dose of oxidants.

The inactivation rate was not in direct ratio to removal rate. For different oxidants, when removal rate was the best, the inactivation rate was not the same.

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